# The Early Days of Quantum Monte Carlo

David Ceperley
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Thanks to the organizers for the opportunity to reminisce!

**Belval blast furnace**
**1965-1990**

# First VMC calculation

Simultaneous work of Levesque and Verlet in Orsay. France.

- Used "classic Metropolis" for energy, structure and condensate fraction of liquid $^4$He (bosons!)
- McMillan produced important physics! Verified that Jastrow wavefunction was in reasonable quantitative agreement with experiment.
- New methods:
  - Optimization of trial function
  - Expectations such as momentum distribution

PHYSICAL REVIEW VOLUME 138, NUMBER 2A 19 APRIL 1965

## Ground State of Liquid He$^4$†

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(Received 16 November 1964)

The properties of the ground state of liquid He$^4$ are studied using a variational wave function of the form $\Pi_{i<j} f(r_{ij})$. The Lennard-Jones 12-6 potential is used with parameters determined from the gas data by deBoer and Michiels. The configuration space integrals are performed by a Monte Carlo technique for 32 and 108 atoms in a cube with periodic boundary conditions. With $f(r)=\exp[-(2.6\text{ Å}/r)^5]$, the ground-state energy is found to be $-0.78\times10^{-15}$ ergs/atom, which is 20% above the experimental value. The liquid structure factor and the two-particle correlation function are in reasonably good agreement with the x-ray and neutron scattering experiments.

### INTRODUCTION

THE interacting Bose gas[1–5] has been the subject of intensive theoretical investigation as a microscopic model for the behavior of liquid He$^4$. Successful calculations have been performed for the Bose gas with weak repulsive interactions[1] and for the low-density Bose gas with short-range repulsive interactions.[2] This work provides a beautiful model of the superfluid behavior of the interacting Bose gas and of the existence of phonons and quantized vortices, but it does not permit one to perform quantitative calculations for liquid He$^4$.

A variational method[6–9] in which the trial wave function is expressed as a product of pair functions [see Eq. (3)] has been used extensively to describe the ground state of the interacting Bose system. This method can be applied directly to the intermediate density hard-sphere gas or to a realistic Hamiltonian for liquid He$^4$. In this paper we report the quantitative calculation of the properties of the ground state of liquid He$^4$ using this variational method.

### THEORY

We will consider $N$ helium atoms of mass $m$ in a cubic box of volume $\Omega$ interacting through the two-body potential $V(r)$.

$$H=-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2+\sum_{i<j=1}^{N}V(r_{ij}). \quad (1)$$

† This paper is based on a thesis submitted to the University of Illinois in partial fulfillment of the requirements of the Ph.D. degree and was supported in part by the National Science Foundation and by the U. S. Army Research Office (Durham) under Grant AR0-G340.

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Estimates of the potential have been made theoretically from the atomic structure of helium and empirically from the gas kinetic data. Theoretically, it consists of two parts: the attractive Van der Waals interaction at[10,11] large $r$ and the repulsive Coulomb and exchange interactions[12] for small $r$, where the wave functions of the two atoms overlap appreciably. deBoer and Michiels[13] have obtained an empirical interaction by fitting the parameters of the Lennard-Jones 12-6 potential to the experimental values of the second virial coefficient above 60°K. They found

$$V(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6],$$
$$\epsilon=10.22°\text{K},\quad \sigma=2.556\text{ Å}. \quad (2)$$

Using this potential, Kilpatrick *et al.*[14] calculated the second virial coefficient from 2 to 60°K and found a good fit to the experimental data in that temperature range. This form for the potential is convenient and it is used in the present calculation. More recent measurements at low temperatures by Keller[15] indicate that the potential should be somewhat more attractive.

The trial wave function may be formulated in the following way. In order to obtain a reasonable value for $\langle V\rangle$ in the many-body system, the wave function must be small whenever the potential is large, that is, whenever any two particles are less than 2.6 Å apart. This can be accomplished by choosing the trial wave function to be a product of pair functions, the product being taken over all pairs.

$$\psi=\prod_{i<j=1}^{N}f(r_{ij}),\quad r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|. \quad (3)$$

- The **ILLIAC II** was a revolutionary super-computer built by the University of Illinois that became operational in 1962.
- First computer to use transistors
- The concept, proposed in 1958, pioneered Emitter-coupled logic (ECL) circuitry, pipelining, and transistor memory
- ILLIAC II had 8192 words of core memory, backed up by 65,536 words of storage on magnetic drums. The core memory access time was 1.8 to 2 µs. The magnetic drum access time was 8.5ms.[1] A "fast buffer" was also provided for storage of short loops and intermediate results (similar in concept to what is now called cache). The "fast buffer" access time was 0.25 µs.

- McMillan did simulations of 32 and 108 atoms
- LJ potential
- $r^{-n}$ Jastrow factor
- 5000 steps, 41 different runs.

# Projector QMC: 50 years ago!

PHYSICAL REVIEW A VOLUME 9, NUMBER 5 MAY 1974

**Helium at zero temperature with hard-sphere and other forces**

M. H. Kalos*
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D. Levesque and L. Verlet
*Laboratoire de Physique Théorique et Hautes Energies, Orsay, France* †
(Received 22 August 1973)

- Mal Kalos and others had done preliminary calculations on bosonic systems including nuclear systems and helium
- Verlet generalized the work of Alder-Wainwright from hard-spheres to LJ with classical molecular dynamics
- Levesque had done the one of first large scale VMD calculations of helium 4, but McMillan published first.

- KLV did an exact calculation for the energy of 256 hard spheres! No other calculations at this scale until the electron gas 8 years later.
- Physical model for liquid and solid helium using a perturbation theory. The paper concerned this application, not the algorithm.

## KLV put together new QMC techniques

- Drifting, branching, diffusing random walk just like in the DMC algorithm. But an "**exact**" (no-time step error) algorithm
- Imaginary time was disguised in the inner workings of the code. Only the integral formulation is discussed
- Importance sampling, essential for N>>1.
- Discussed the **zero variance** principle of Projector MC
- Population control and bias estimates.
- Scaling addressed by using a cartesian product of spheres and neighbor tables.
- Forward walking used in companion papers.
- generalization from hard spheres to Yukawa (for neutron matter) and Lennard-Jones (for helium) potentials 1975-1980.

# My PhD project: Fermion QMC

Why the 12 year lag from McMillan's boson calculation for fermions?

**Antisymmetry required**!

- Slater-Jastrow for a fermion trial wavefunction.

$$\Psi_2(R) = Det\{e^{ik_i r_j}\} e^{-\sum_{i<j} u_{ij}(r_{ij})}$$

- We made the orbitals real to avoid complex arithmetic.
- Is there an ergodic problem? Since nodes divide space, will we get stuck?
  - No, we found that walks jump over nodes
  - No, all regions are the same. (I didn't know this until later)
- Too slow? Fermion determinants are $O(N^3)$ instead of $O(N)$.
  - Non-uniform transition probability improves convergence.
  - Update method for the determinants (the Sherman-Morrison formula) allow fast single particle moves.

PHYSICAL REVIEW B VOLUME 16, NUMBER 7 1 OCTOBER 1977

# Monte Carlo simulation of a many-fermion study*

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M. H. Kalos
*Courant Institute of Mathematical Sciences, New York University, 251 Mercer Street, New York, New York 10012*

(Received 15 December 1976)

The Metropolis Monte Carlo method is used to sample the square of an antisymmetric wave function composed of a product of a Jastrow wave function and a number of Slater determinants. We calculate variational energies for $^3$He and several models of neutron matter. The first-order Wu-Feenberg expansion is shown always to underestimate the energy, sometimes seriously. The phase diagram for ground-state Yukawa matter is determined. There is a class of Yukawa potentials which do not lead to a crystal phase at any density.

- CDC 6600
- Batch operating system
- Punch cards, overnight runs, paper output, no graphics, no remote access.
- 1200 sweeps/hour for 128 particles
- Saturdays we owned the computer, hands on!

We learned about:

- Determinant sampling
- Inverse updates
- Spins
- Local energy/zero variance
- Biased sampling

# Computer environment in 1975
# Courant Institute, New York University



TREX
Ceperley

# Electron gas enters QMC in Paris

**Ground state of the fermion one-component plasma: A Monte Carlo study in two and three dimensions**

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(Received 26 April 1978)

We have performed fermion Monte Carlo variational calculations to determine the equation of state of the uniform electron one-component plasma in two and three dimensions. The ground-state excess energies calculated by the Monte Carlo method are very precise and in agreement with those of other calculations in the metallic density range and in the very-low-density Wigner crystals. Three phases have been investigated: the Wigner crystal, the normal or unpolarized fluid, and the polarized fluid. The Wigner crystal has the lowest energy for $r_s > 67$ in three dimensions and $r_s > 33$ in two dimensions. The totally polarized quantum fluid is stable for $26 < r_s < 67$ in three dimensions and for $13 < r_s < 33$ in two dimensions, and the normal or unpolarized fluid is stable at higher densities, $r_s < 26$ in three dimensions and $r_s < 13$ in two dimensions. A

- UNIVAC 1108/1110 in Paris-Orsay
- Punch cards
- Overnight batch
- Print outs

- Ewald sums
- RPA trial function: no optimization necessary!
- Cusp condition, long range Jastrow

Ferromagnetism

Wigner crystal transitions

# Diffusion Monte Carlo (DMC)

## Berkeley 1978

$$-\frac{\partial \phi(R,t)}{\partial t} = H\phi(R,t) \qquad f(R,t) \equiv \psi_T(R)\phi(R,t)$$

$$-\frac{\partial f(R,t)}{\partial t} = -\lambda\nabla^2 f - \lambda\nabla\left(2 f \nabla \ln\psi_T(R)\right) + \left(\psi_T^{-1} H \psi_T\right) f(R,t)$$

**Evolution = diffusion + drift + branching**

- Invented a simplified projection approach for QMC based on the master eq. instead of integral approach in GFMC
- Rejection technique to minimize time step errors (from earlier work with Smoluchowski Eq. of polymers)
- Used months of CRAY 1 time ("free" standby time)
  - *E.g. after the Jan 24, 1980 Livermore earthquake*
- Working from Berkeley, I talked to MaryAnn Mansigh every day–she "vectorized" my new DMC code, ran production runs and mailed me output weekly.

MaryAnn Mansigh, Berni Alder
&Tom Wainwright 1962

Berni Alder & David Ceperley Jan. 1981

TREX Ceperley

# Fixed-node & release-node algorithm

## 1. Introduction

We describe here the methods we have been using to simulate the ground state of a quantum many body system. Our goals in this project are to construct an algorithm which will enable us to calculate the ground state energy of a many-body system (50-500 particles) in a reasonable amount of computer time (several hours on a CRAY) . We would like to eliminate all systematic errors and have the statistical error to be small (.1%) and unbiased.

## 2. The Bloch Equation

The basis for our Monte Carlo method is the Block equation.

$$\frac{\partial \Psi(R,t)}{\partial t} = [H(R) - E_T]\Psi(R,t) \qquad (2.1)$$

where H(R) is the Hamiltonian function, $E_T$ is a trial energy. Let $|a\rangle$ be a complete set of normalized states for H and let $\Psi_o(R)$ be $\Psi(R,0)$. Then

$$\Psi(R,t) = e^{-\Delta_a t}|a\rangle\langle a|\Psi_o\rangle \qquad (2.2)$$

where $[H-E_T]|a\rangle = \Delta_a|a\rangle$ For large time $\Psi$ will converge to the eigenvalue of H with the lowest energy and for which the overlap at zero time is nonzero. Interpreting this as a diffusion equation, we intially sample points R from the distribution $\Psi_o$ and then allow them to diffuse ,divide, and die off according to equation 2.1 For large time the distribution will be the ground state.

This equation is not suitable for a many particle system because the random walk will spend too much time in unfavorable regions of configuration space. The variance of the process can be made finite by multiplying equation 2.1 by a trial function, an analytic function which is a reasonable approximation to the ground state wave function. This trial function usually consists of an antisymmetric part times a correlation factor:

$$\Psi_T = \mathrm{Det}\|e^{ik_i r_j}\| \prod_{i<j} f(r_{ij}) \qquad (2.3)$$

## 3. The fixed node approximation

The fixed node approximation results when we allow the points to diffuse according to the Bloch equation but we prevent them from crossing the nodes of the trial function, in our present algorithm by making the pseudoforce infinite there. Hence we are solving the many body Schroedinger equation exactly within the volumes ( in 3N dimensional space) defined by the nodes of $\Psi_T$.

May 22, 1979



c) The total number of particles will grow asymptotically in time while the difference between the positive and negative particles at any point ( the signed distribution) will go to a constant. We need a way of cancelling the positive and negative points but leaving the difference unchanged.

d) The possible choices for S(R) are:

i) The boson ground state trial function. This is the simplest distribution to use but will lead to an inefficient use of the configurations since the weights will vary over an order of magnitude. In fact the efficency ( as measured by $\frac{\langle W\rangle^2}{\langle W^2\rangle}$ ) for 54 electrons is about 5%.

ii) If D(R) is the antisymmetric part of $\Psi_T$ ( the Slater determinant) let

$$S(R) = \sqrt{\epsilon^2 + D^2}\,\Psi_B$$

This function is like i) away from the nodes hence the variation of the weights will be much smaller. Unfortunately we seem to have runaway branching near the nodes of $\Psi_T$ ,if $\epsilon$ is made too small, because of the large curvature in S(R).

iii) Take the limit of $\epsilon$ goes to zero in ii) .

$$S(R) = |\Psi_T(R)|$$

This is the same as the fixnode importance function except that particles can tunnel through the nodes. The probability distribution should vanish only linearly near the nodes. The basis for this type of sampling is the exact relationship:

$$G_T(R,R',t) = G_B(R,R',t)\,|D(R')/D(R)|$$

where $G_B$ is the Greens function for the Boson diffusion and $G_T$ is the Greens function for the present case. This method has not yet been tried but I believe it to be more efficient than those above. because the weights will be plus and minus one only, and the excess branching is totally isolated at the nodal surface.

David Ceperley

May 22, 1979

# Electron Gas Standard for DFT

VOLUME 45, NUMBER 7 PHYSICAL REVIEW LETTERS 18 AUGUST 1980

**Ground State of the Electron Gas by a Stochastic Method**

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and
B. J. Alder
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(Received 16 April 1980)

An exact stochastic simulation of the Schroedinger equation for charged bosons and fermions has been used to calculate the correlation energies, to locate the transitions to their respective crystal phases at zero temperature within 10%, and to establish the stability at intermediate densities of a ferromagnetic fluid of electrons.

- Both fixed-node & release node in 2 & 3 dimensions, liquids and Wigner crystals
- Properties: energy, errors,1 body density matrix, pair correlation, structure function
- About 2K of vectorized FORTRAN lines
- Only about 50K words of ‘core’ memory
  - Dynamic memory management
  - Ensemble read/written to disk not held in “core”

# Research at the first QMC meeting
## Paris, Dec. 1982

- Helium droplets (nuclear physics model)
- Many fermion GFMC
- Electron gas and hydrogen
- Fock space QMC
- Chemistry
- PIMC for molecules
- F center in molten DCl
- PIMC of hard spheres
- Heisenberg model
- Quantum spin models
- Electron-phonon models
- Lattice Gauge Theory

# Applications of DMC followed in 1980's

Generalized to treat

- small molecules (Anderson) He-He interaction
- Molecular & atomic hydrogen
- Solid lithium
- Simulation of hydrogen without the BO approximation
- Muon-catalyzed fusion

*Physica 108B (1981) 875-876*
*North-Holland Publishing Company*

THE CALCULATION OF THE PROPERTIES OF METALLIC HYDROGEN USING MONTE CARLO*

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The application of Monte Carlo to hydrogen at zero temperature is discussed. The trial function is a generalization of the pair product type used for jellium. Preliminary results for the metallic phase are given.

**Fixed-node quantum Monte Carlo for molecules[a) b)]**

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(Received 3 May 1982; accepted 23 June 1982)

# Imaginary Time Path Integrals

PHYSICAL REVIEW

*A journal of experimental and theoretical physics established by E. L. Nichols in 1893*

SECOND SERIES, VOL. 91, NO. 6 SEPTEMBER 15, 1953

## Atomic Theory of the λ Transition in Helium

R. P. FEYNMAN
*California Institute of Technology, Pasadena, California*
(Received May 15, 1953)

It is shown from first principles that, in spite of the large interatomic forces, liquid $He^4$ should exhibit a transition analogous to the transition in an ideal Bose-Einstein gas. The exact partition function is written as an integral over trajectories, using the space-time approach to quantum mechanics. It is next argued that the motion of one atom through the others is not opposed by a potential barrier because the others may move out of the way. This just increases the effective inertia of the moving atom. This permits a simpler form to be written for the partition function. A rough analysis of this form shows the existence of a transition, but of the third order. It is possible that a more complete analysis would show that the transition implied by the simplified partition function is actually like the experimental one.

PHYSICAL REVIEW B VOLUME 30, NUMBER 5 1 SEPTEMBER 1984

## Simulation of quantum many-body systems by path-integral methods

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(Received 2 April 1984)

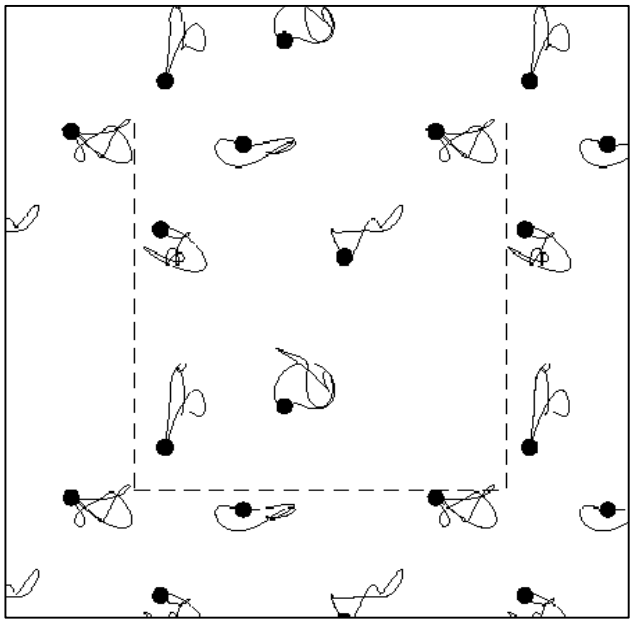
Computational techniques allowing path-integral calculations of quantum many-body systems are introduced and applied to liquid and solid helium. The computations presented in this paper do not include exchange effects. The range and limitations of the method are demonstrated by presenting thermodynamic properties, radial distribution functions, and, for the solid phase, the single-particle distribution and intermediate scattering function for imaginary times.

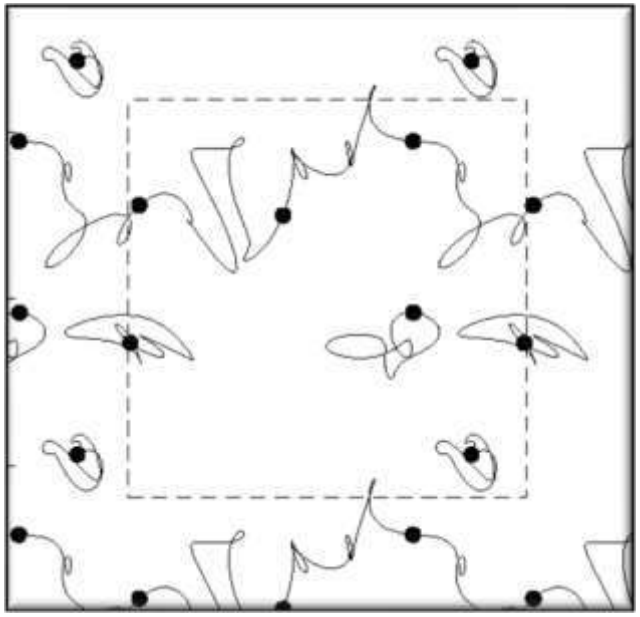
# Path Integral Picture

- Each atom is a ring polymer; an exact representation of a quantum wavepacket in imaginary time.
- Bose paths allow reconnecting differently.
- At the superfluid transition a "macroscopic" permutation appears.
- This is reflection of bose condensation within PIMC.

- NO trial function, only the Hamiltonian

- Fermion path integrals using restrictions followed in 1987.





# The Sign Problem

The expression for Fermi particles, such as $He^3$, is also easily written down. However, in the case of liquid $He^3$, the effect of the potential is very hard to evaluate quantitatively in an accurate manner. The reason for this is that the contribution of a cycle to the sum over permutations is either positive or negative depending on whether the cycle has an odd or even number of atoms in its length L. At very low temperature, the contributions of cycles such as L=51 and L=52 are very nearly equal but opposite in sign, and therefore they very nearly cancel. It is necessary to compute the difference between such terms, and this requires very careful calculation of each term separately. It is very difficult to sum an alternating series of large terms which are decreasing slowly in magnitude when a precise analytic formula for each term is not available. Progress could be made in this problem if it were possible to arrange the mathematics describing a Fermi system in a way that corresponds to a sum of positive terms. Some such schemes have been tried, but the resulting terms appear to be much too hard to evaluate even qualitatively.

The (explanation) of the superconducting state was first answered in a convincing way by Bardeen, Cooper, and Schrieffer. The path integral approach played no part in their analysis, and in fact has never proved useful for degenerate Fermi systems.

*Feynman and Hibbs,1965.*

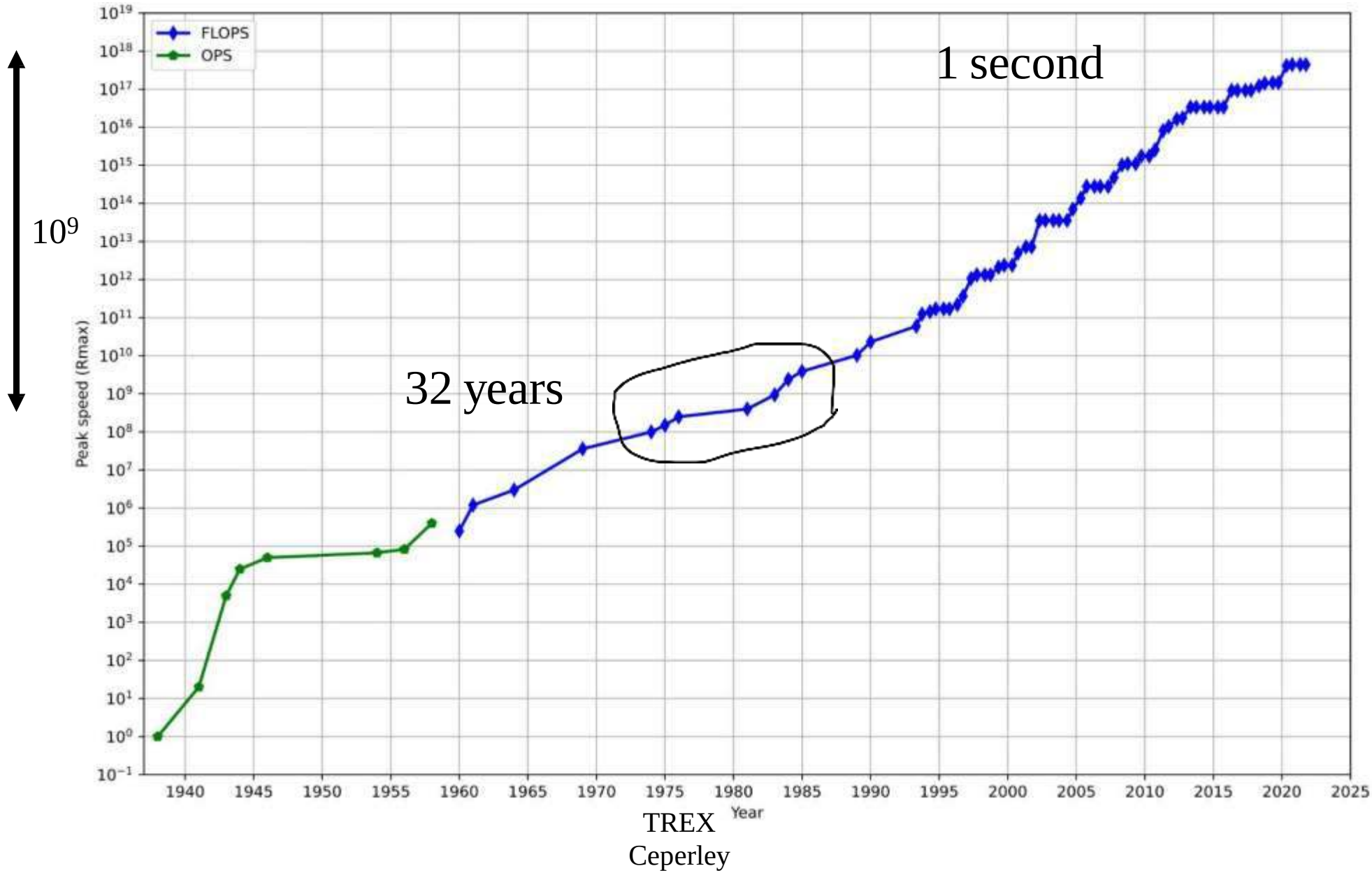
# Supercomputers

| | | |
|---|---|---|
| 1965-1969 | CDC 6600 | 10 MIPS 3 megaflops |
| 1969-1975 | CDC 7600 | 36 megaflops |
| 1974-1975 | CDC Star-100 | 100 megaflops (vector), ~2 megaflops (scalar) |
| 1975-1983 | Cray-1 | 80 megaflops (vector), 72 megaflops (scalar) |
| 1975-1982 | ILLIAC IV | 150 megaflops, <100 megaflops (average) |
| 1981-1983 | CDC Cyber-205 | 400 megaflops (vector), average much lower. |
| 1983-1985 | Cray X-MP | 500 megaflops (4 CPUs) |
| 1985-1990 | Cray-2 | 1.95 gigaflops (4 CPUs) 3.9 gigaflops (8 CPUs) |

During the 1970's and 1980's I used a variety of supercomputers in NYU, Berkeley, Livermore, Sandia, Los Alamos, Bochum Germany, NASAAmes; those with unused capacity.

Before 1986, supercomputers were primarily located at US government labs.

# Supercomputer peak performance



# Exact fermion calculations have a bad rep

## Errors grow exponentially in N

Release node calculations for the HEG.

Bottom line is NOT the asymptotic analysis but: can we do calculation with available resources?

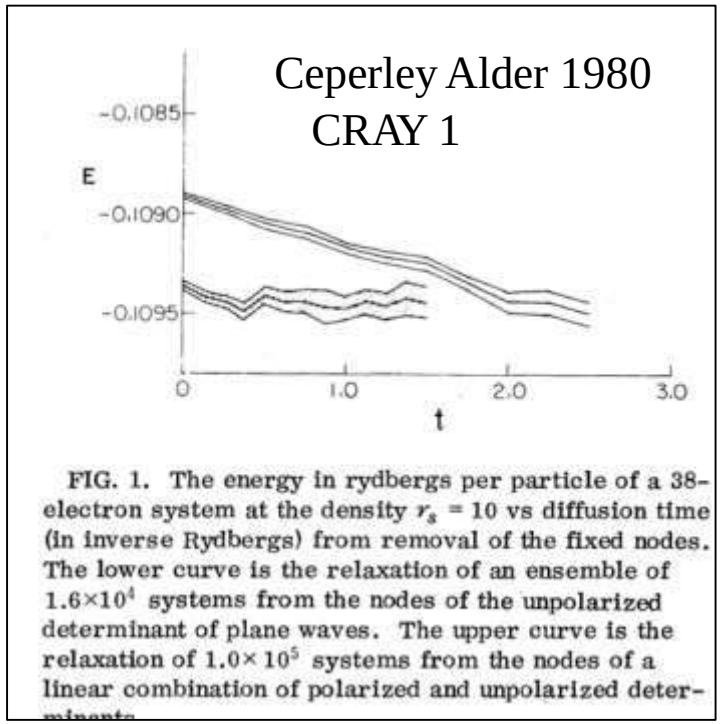
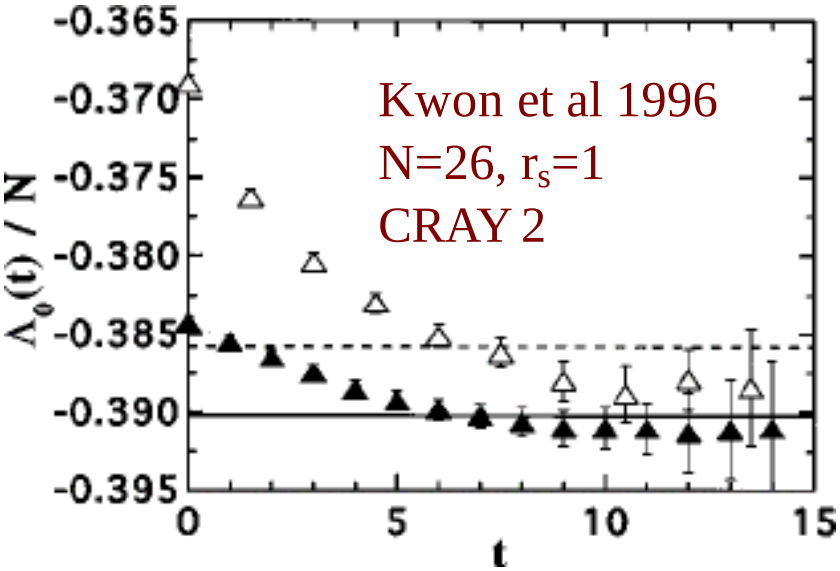
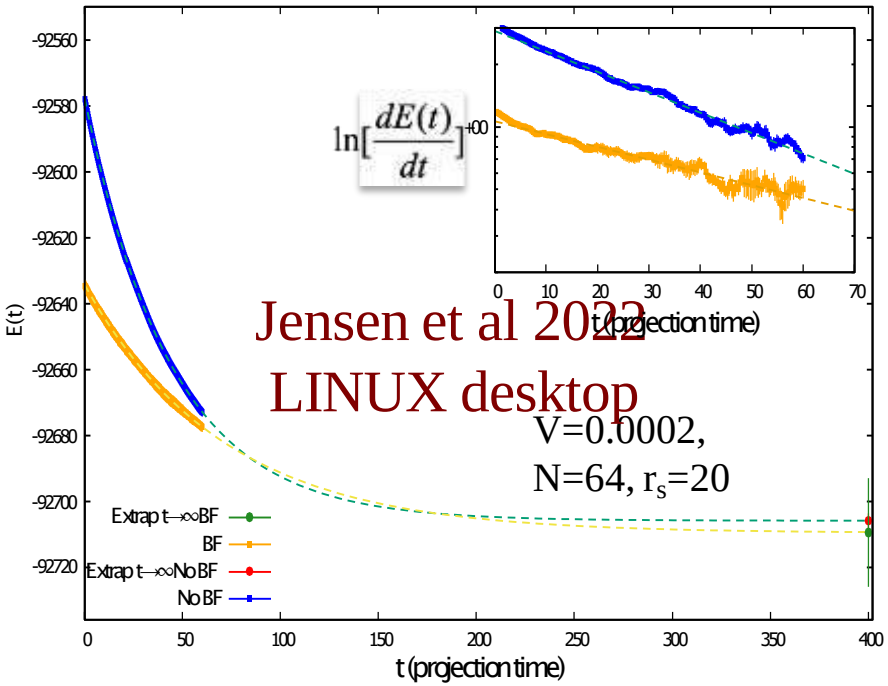



FIG. 1. The energy in rydbergs per particle of a 38-electron system at the density $r_s = 10$ vs diffusion time (in inverse Rydbergs) from removal of the fixed nodes. The lower curve is the relaxation of an ensemble of $1.6\times10^4$ systems from the nodes of the unpolarized determinant of plane waves. The upper curve is the relaxation of $1.0\times10^5$ systems from the nodes of a linear combination of polarized and unpolarized deter-




TREX




Ceperley

# Changes in work

- Unix operating system (1980)
- LATEX 1986
- Internet started being useful in 1980's
  - Sent files to Europe in 1985
- Work from home
  - IBM PC in 1985
- Moved to UIUC in 1987
  - Open environment
  - Lots of students/postdocs/visitors


Silent-700 Terminal


Ceperley-Martin group reunion, APS March 1997

TRANSFERING FILES TO ITALY

1) First transfer files to MFE
   a) Get files on a 7600 but in CRAY format (do not do TRANS).
   b) write tape
      ADT +tname flist
   c) Get tape from Bldg 113 and take to MFECC operator in 451.
   d) Log on to MFE "A" machine (7600), read tape and store away files.
   Phone number for 300 baud is 26070.
      A 7117 A 430CRA "z" IKHIKU :Ceperley's account "z"=control z
      RDFILES tname SEVEN, ALL. :read tape
      FILEM
      WRITE .TRENTO flist
2) Send files over arpanet and bitnet.
   a) login to C machine and retrieve files.
      C 7117 A 430CRA "z" IKHIKU
      FILEM
      READ .TRENTO flist
   b) use trixgl to make sure files are still in CRAY format and find number of lines.
   c) Send files using TELL. Look in TELL document for full description. There are two routes, Berkeley and Wisconsin. I have only tried Berkeley.
      TELL VY6A%ICINECA.BITNET@UCB-VAX.ARPA FILE=fname
      or
      TELL VY6A%ICINECA.BITNET@WISCVM.ARPA FILE=fname
   You can then type in an 80 character header line. Include name of program and total number of lines. After this type S to send fname.
3) Log into my account occasionaly to check for mail from me or returned mail. The system will prompt you on login if there are any messages. Type help if you are unfamiliar with the MFECARS

# Top reasons why quantum Monte Carlo is not widely used (N.B. list from 1995)

12. We need forces, dummy!
11. Try getting $O_2$ to bind at the variational level.
10. How many graduate students lives have been lost optimizing wavefunctions?
9. It is hard to get 0.01 eV accuracy by throwing dice.
8. Most chemical problems have more than 50 electrons.
7. Who thought LDA or HF pseudopotentials would be any good?
6. How many spectra have you seen computed by QMC?
5. QMC is only exact for energies.
4. Multiple determinants. We can't live with them, we can't live without them.
3. After all, electrons are fermions.
2. Electrons move.
1. QMC isn't included in Gaussian 90. Who programs anyway?

# Developments in QMC since 1995

- Forces including zero variance zero bias.
- Pseudo potentials
- trial functions: Multi-determinant, backflow, neutral-net trial functions, optimization techniques
- QMC Methods: auxiliary field, reptation, coupled-electron ion MC, restricted Path Integrals
- Methods for Excited states, complex trial functions with fixed-phase
- Finite size error corrections, Twist Average Boundary Conditions
- Codes: QMCPACK, CASINO, CHAMP, TURBO-RVB…

- Many methods for lattice models.

# Improved Wavefunctions

11. Try getting $O_2$ to bind at the variational level.
7. Who thought LDA or HF pseudopotentials would be any good?
4. Multiple determinants. We can't live with them, we can't live without them.

These things have been addressed.

# Problems that will be solved

9. It is hard to get 0.01 eV accuracy by throwing dice.
8. Most chemical problems have more than 50 electrons.

Computer time, scaling up of algorithms, software tools have been addressed by more capable computers

1. QMC isn't included in Gaussian 90. Who programs anyway?

Long term support needed to develop open source production and research codes. QMC cannot expand its usefulness with the current state of the software. This is the surest way to accelerate growth of QMC.

Several codes are now available.

# Technical Problems

12. We need forces, dummy!
10. How many graduate student's lives have been lost optimizing wavefunctions?
8. Most chemical problems have more than 50 electrons.
5. QMC is only exact for energies.

**The community has been slow to solve these problems and implement them in codes.**

**They can be solved by systematic, applied math research.**

**(Very important progress since 1995 in energies and properties)**

# Difficult problems

6. How many spectra have you seen computed by QMC?
3. After all, electrons are fermions.
2. Electrons move.

The "sign problem" is a key problem in computational physics. Its solution would be a major advance.

The fixed-node method can be very accurate and can be improved upon since correlation is built in at the beginning. This is a key advantage of QMC.

The "dynamics" problems is hardly touched. Some dynamics problems are not too hard (linear-response, scattering) Which dynamical methods are hard and which are easy?

# Machine learning is great opportunity

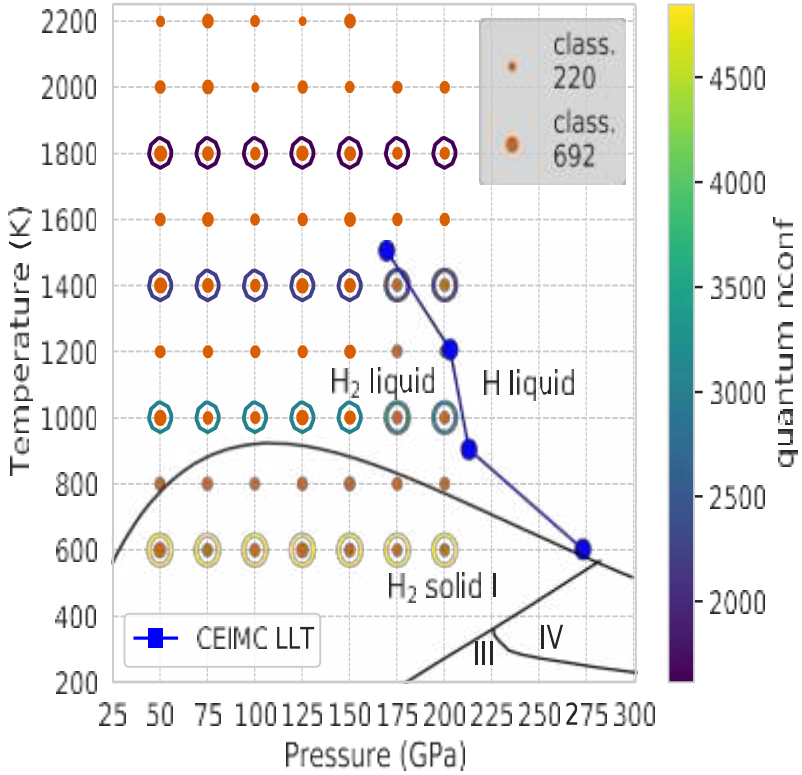
- First principles accuracy at empirical potential cost: can treat longer length and time scales.
- Bespoke potentials can be tailored to precise conditions and ingredients.
- But we need accurate **data** to construct ML potentials.
- Potentials needed beyond the **electronic ground state.**

## Quantum MC for ML data is a great application

- Lower bias than DFT (i.e. generally higher accuracy).
- Can model exotic quantum states, e.g. superconductivity.
- Continuum basis set (VMC, DMC, PIMC) is better for disordered systems, e.g. liquids.
- Naturally parallel

# QMC hydrogen database

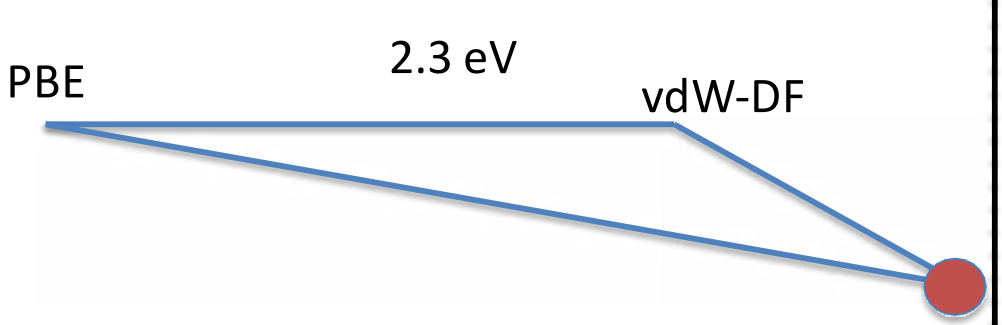
**Large-scale publicly accessible database of QMC force calculations for dense hydrogen enabling more accurate machine-learned potentials.**

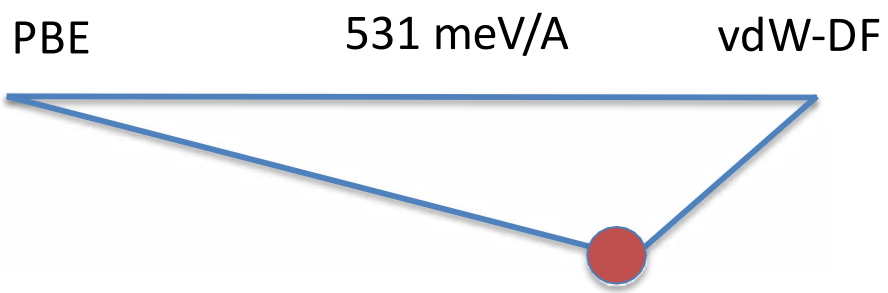



- Database of 100,000 configurations for 96 protons generated with MD and CEIMC.
- Forces from DFT with PBE and vdW functionals
- 20,000 configurations selected for accurate QMC calculations (~5.8M data items).
- QMC forces using Chiesa estimator with extrapolated electron density

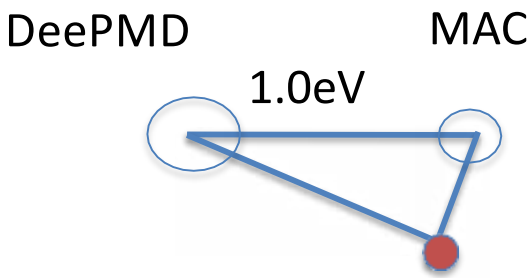
https://qmc-hamm.hub.yt

# Comparisons of Models using the hydrogen database

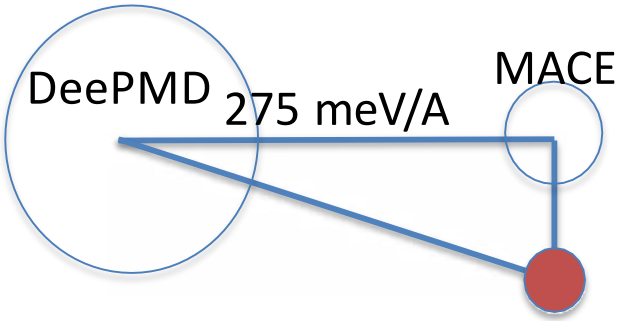



**Energy error of 96 atoms**




**Force errors**




Cross-validation error

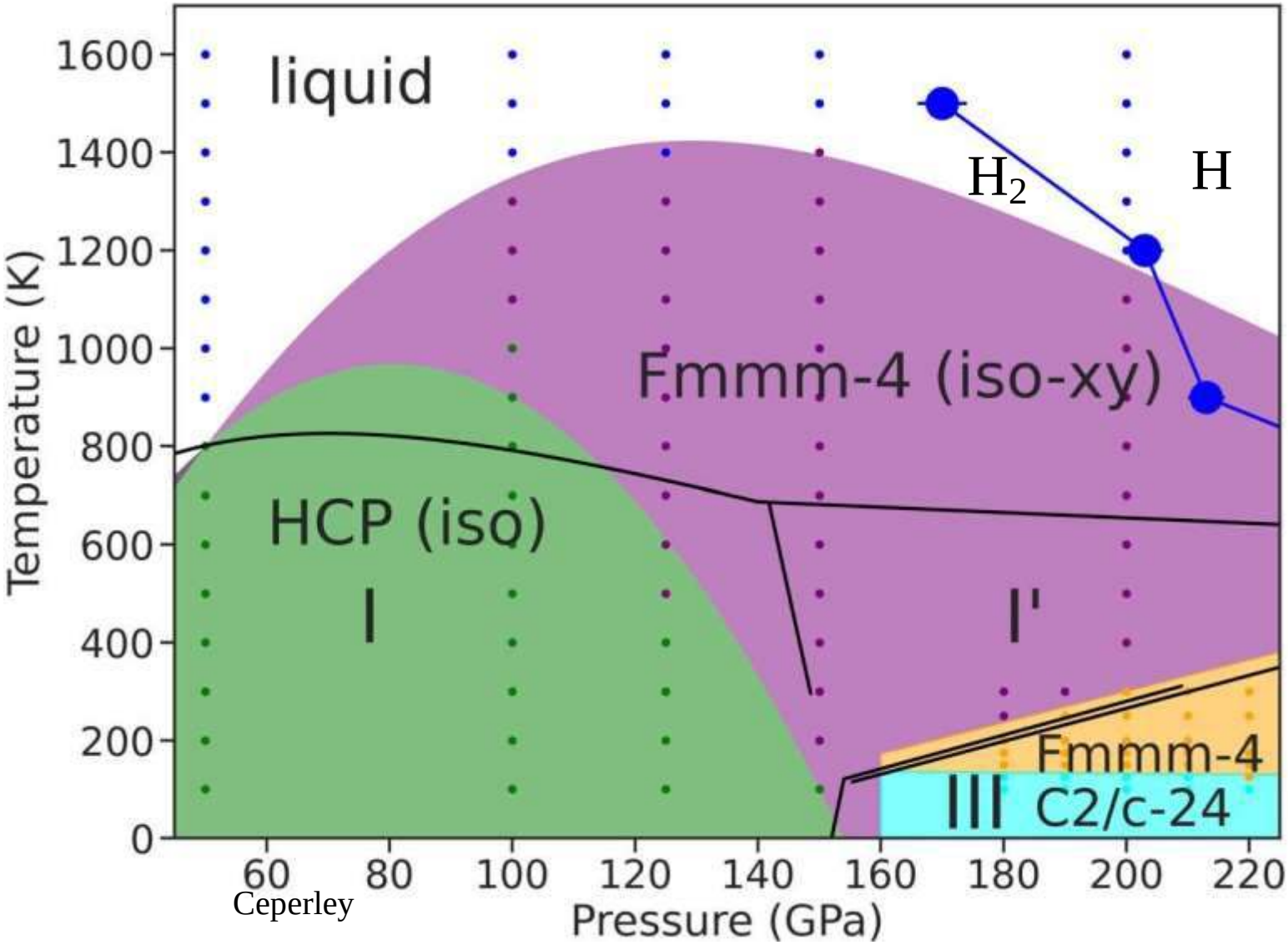
FN-QMC model in direction out of plane

$\sigma_V$ = 0.01eV

$\sigma_F$ = 77meV/A

We discovered a new dominant crystal structure with a higher melting temperature! Different from DFT and experiment!

Y. Yang, H. Niu, DMC, S. Jensen, M. Holzmann, C. Pierleoni PRL 130, 76102, 2023.



# Challenges for QMC&ML

- What type of QMC  is best? VMC,DMC,RMC?
- How to select configurations?  How many?
- What estimator to use for forces?  Its bias?
- Need to speed up QMC (speed of data generation)
  - Need robust but lightweight QMC
  - A simplified trial function
  - Minimize wavefunction optimization
- What model to fit to?  e.g. 2 level Δ-model.
- How to put physical constraints in the model?
  - Long-range properties, e.g. dielectric screening in metal phases.
  - Dispersion (van der Waals), quadrupole-quadrupole interaction.
- Quantify errors of the resulting model.

# Collaborators

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