The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific
and Cultural Organization

International Atomic
Energy Agency

SMR.1824 - 18

**13th International Workshop on
Computational Physics and Materials Science:
Total Energy and Force Methods**

11 - 13 January 2007

Equation of state and raman frequency of diamond from quantum Monte Carlo

Richard NEEDS
Cambridge University
Theory of Condensed Matter Group
Cavendish Laboratory
Department of Physics
Madingley Road
Cambridge, CB3 0HE
U.K.

Equation of state and Raman frequency of diamond from quantum Monte Carlo

Ryo Maezono

National Institute for Materials Science, Tsukuba, Japan

Andrea Ma, Mike Towler, Richard Needs

University of Cambridge, United Kingdom

Diffusion Monte Carlo (DMC)

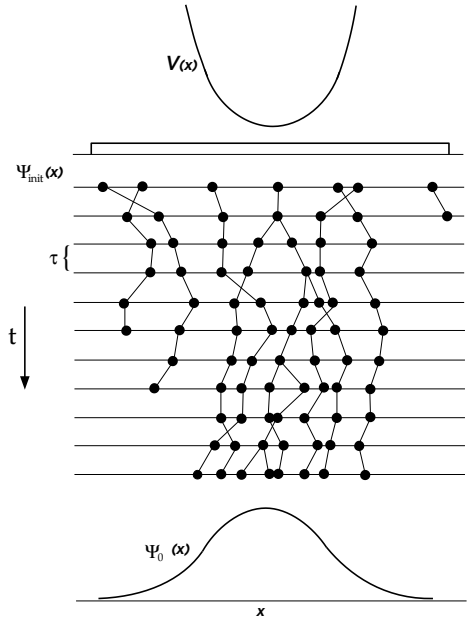
Consider imaginary time Schrödinger equation

$$\left(-\frac{1}{2}\nabla^2 + V\right)\Psi(\mathbf{R},t) = -\frac{\partial\Psi(\mathbf{R},t)}{\partial t}$$

Expand $\Psi(\mathbf{R},t)$ in eigenfunctions of $\hat{H}$

$$\Psi(\mathbf{R},t) = \sum_{n=0}^{\infty} c_n\,\phi_n(\mathbf{R})\,e^{-E_n t}$$

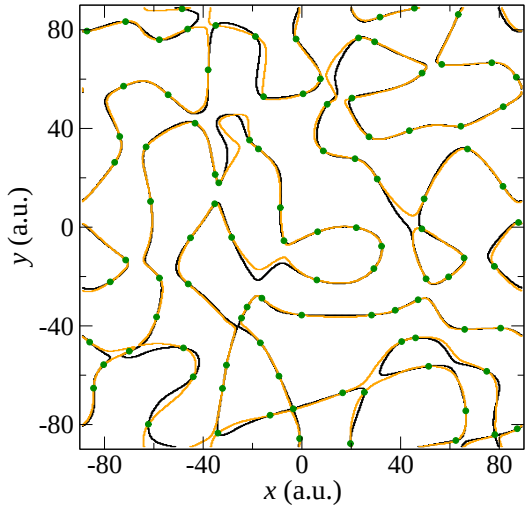
Kinetic term: diffusion process Potential term: rate process



Importance sampling in DMC

Problem 1: Ψ is not a probability distribution $\longrightarrow$ fermion sign problem
Problem 2: Rate process is poorly behaved

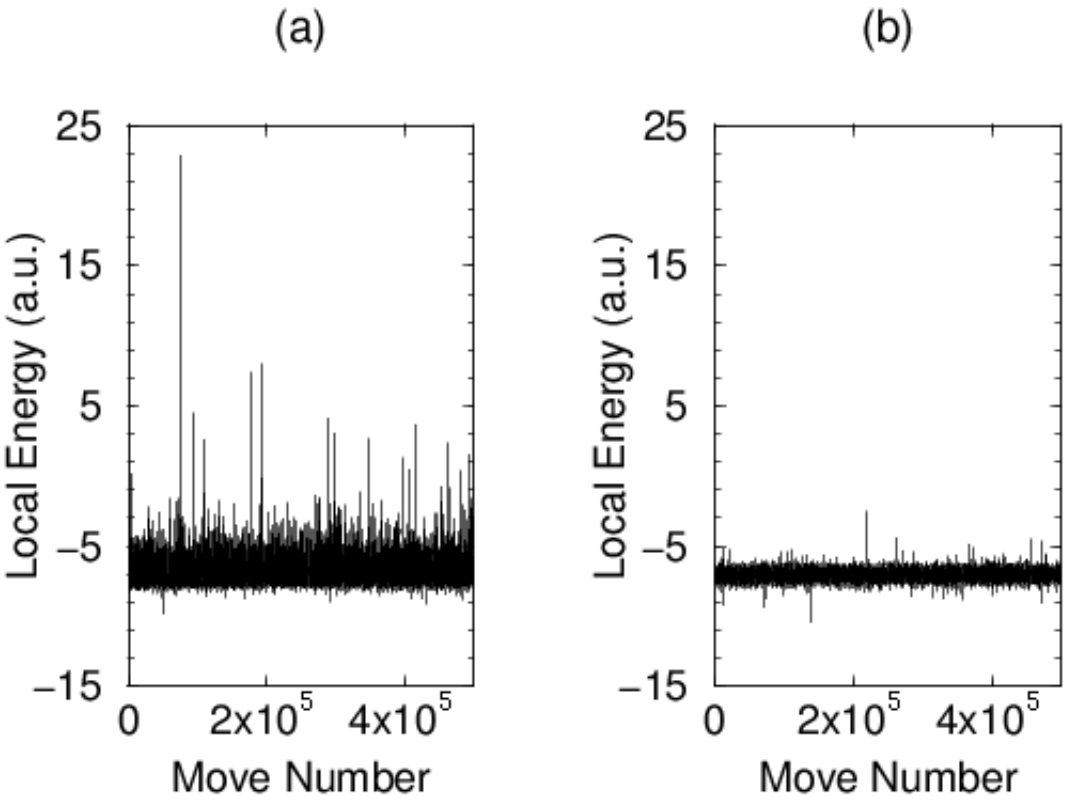
Solution: Work with distribution $f(\mathbf{R}, \tau) = \Psi(\mathbf{R}, \tau)\Phi_T(\mathbf{R})$ and deal with sign problem via fixed-node approximation



Hartree-Fock (black) and backflow (orange) nodes for 101 same-spin free fermions in a square box at a density of $r_s = 10$
Pablo Lopez Rios $et\ al.$, Phys Rev E 74, 066701 (2006)

The Slater-Jastrow wave function

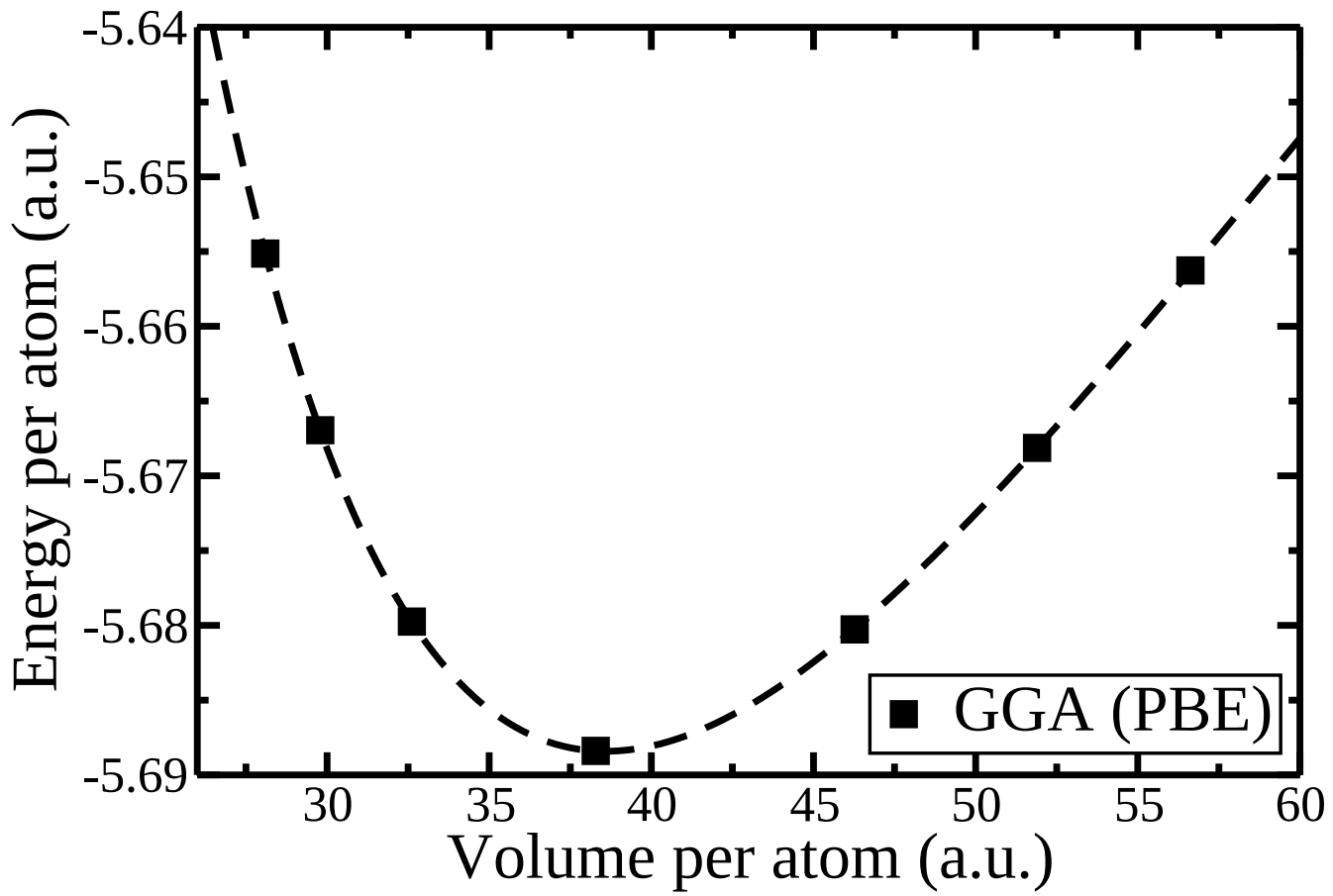
$$\Phi_T = \det(\phi_i)\, \exp\left[\mathcal{J}(r_{ij}, r_{iI}, r_{jI})\right]$$



Local energy $\Phi_T^{-1} \hat{H} \Phi_T$ of a silane molecule

(a) without Jastrow factor (b) with Jastrow factor

Equation of State of Diamond



Vinet equation of state:

$$E(V) = -\frac{4B_0V_0}{(B_0'-1)^2}\left(1-\frac{3}{2}(B_0'-1)\left(1-(V/V_0)^{1/3}\right)\right)e^{\left(\frac{3}{2}(B_0'-1)\left(1-\left(\frac{V}{V_0}\right)^{1/3}\right)\right)}+C$$

Equation of State of Diamond

- Understanding the physical properties of diamond at high pressures is important for the design and operation of diamond anvil cells

- Equilibrium volume and bulk modulus of diamond are well established from experiment

- Pressure derivative of the bulk modulus is not well established

  $B_0' = 4.0 \pm 0.5$ McSkimin and Andreatch (1972)

  $B_0' = 3.0 \pm 0.1$ Occelli *et al.* (2003)

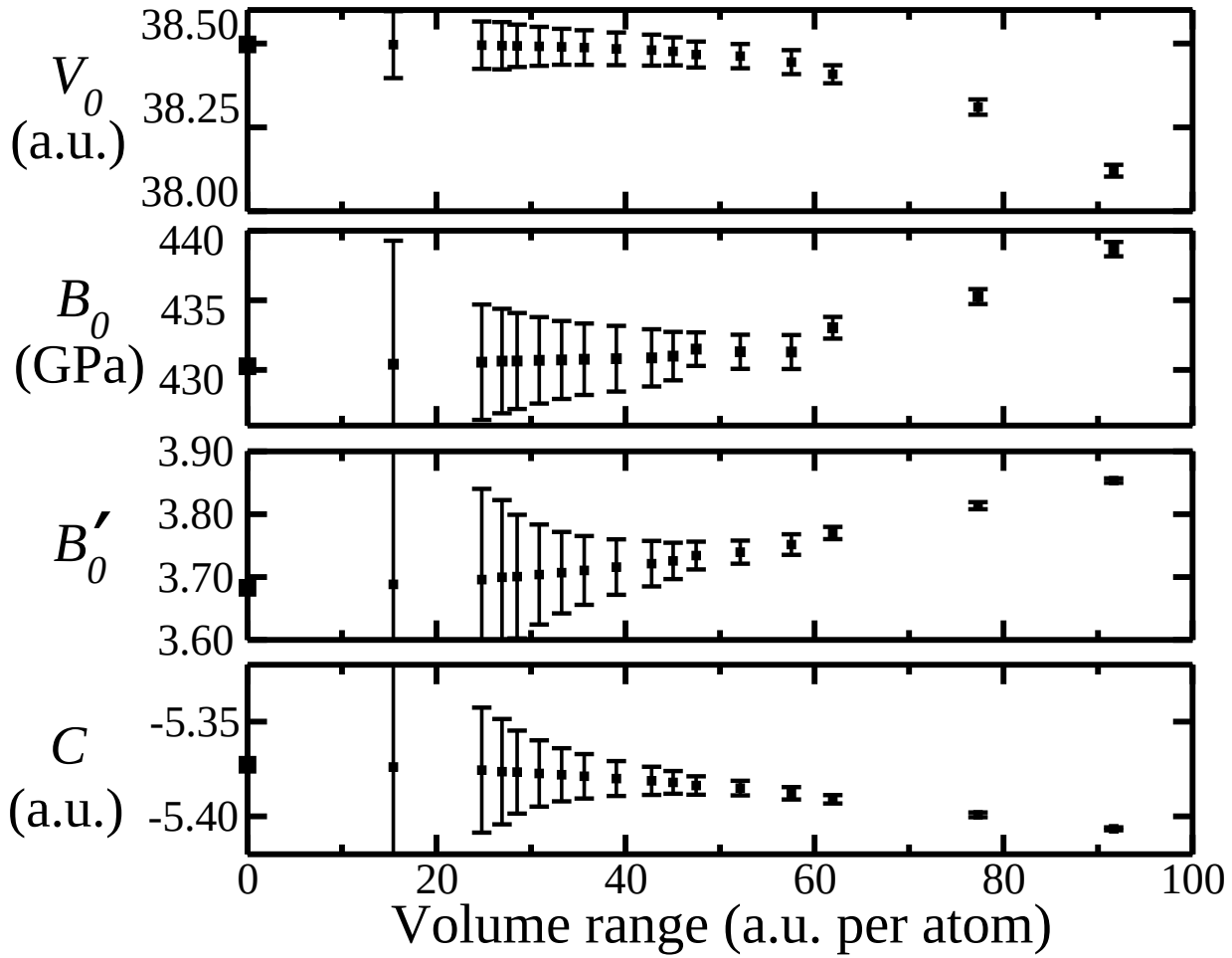
- $B_0' = 4.0 \pm 0.5$ is preferred, but the error bar is very large

- Perform QMC calculations of energy as a function of volume

- Include zero-point energy and finite temperature effects at the DFT level

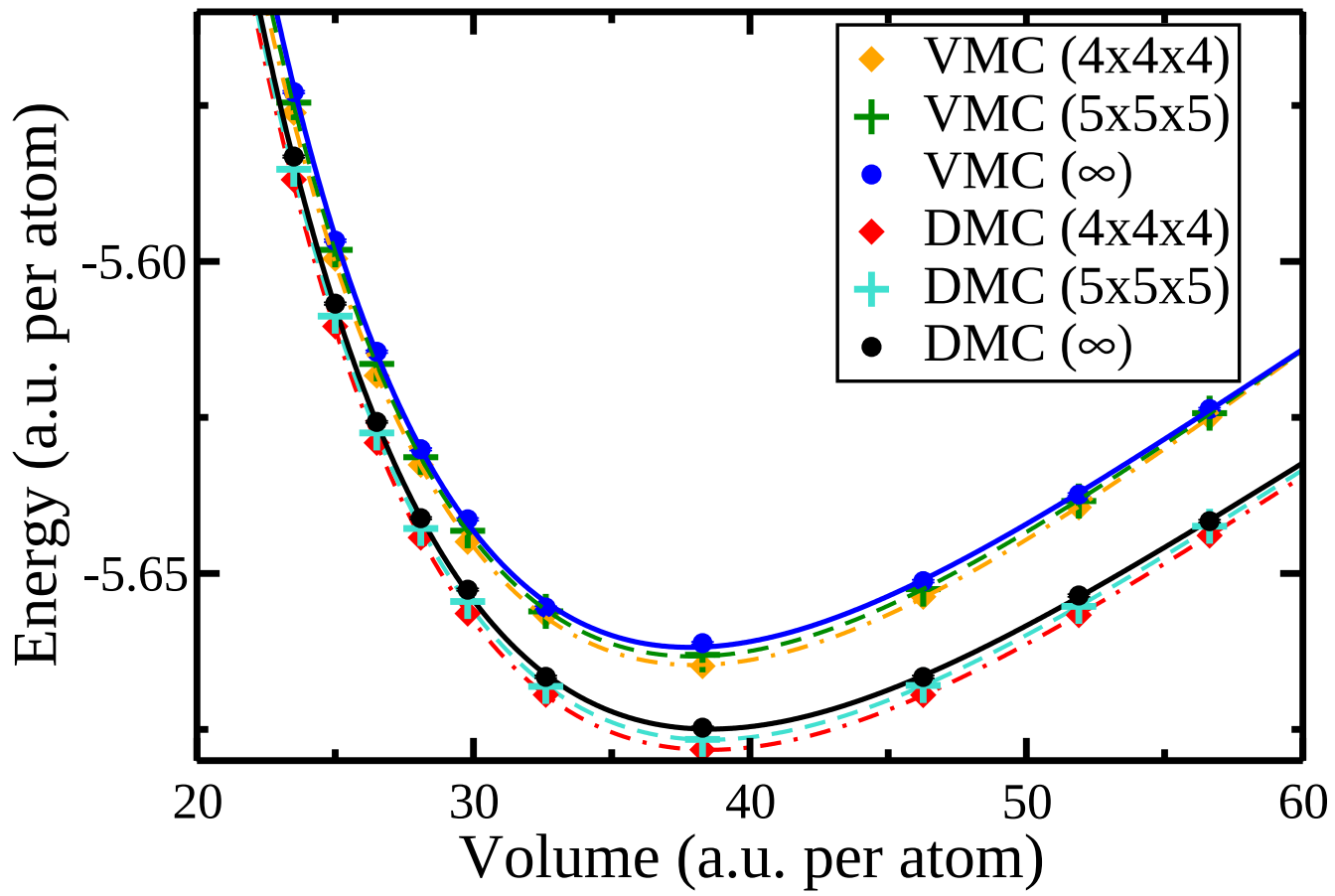
Equation of State of Diamond

Calculate energy over a large volume range to reduce the effect of statistical errors $\Rightarrow$ systematic error in the parameters



Assume statistical noise of 0.0001 a.u. per atom

Equation of State of Diamond

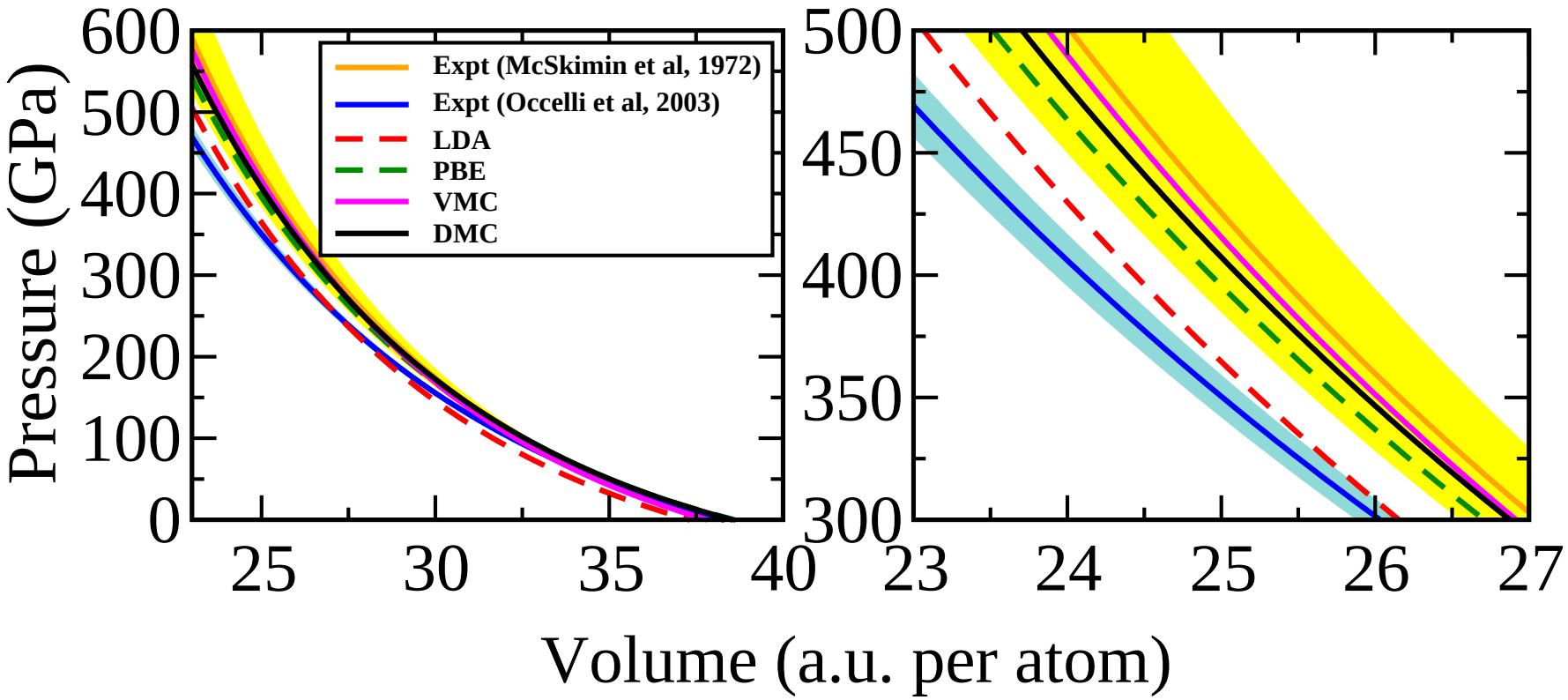


CASINO QMC code

Hartree-Fock pseudopotentials, 128 atom and 250 atom simulation cells

PBE-GGA orbitals, plane waves $\Rightarrow$ "B-splines"

Equation of State of Diamond



	LDA	PBE	VMC	DMC	Expt. (300 K)
V_0 (a.u.)	37.31	38.61	37.82(6)	38.54(6)	38.284
B_0 (GPa)	454	422	472(4)	437(3)	442(4)
B_0'	3.65	3.72	3.8(1)	3.7(1)	4.0(5), 3.0(1)

Pressure dependence of Raman frequency of diamond

- Can use volume dependence of the Raman frequency as a pressure gauge in diamond anvil cell experiments

- DMC calculations with the frozen phonon method

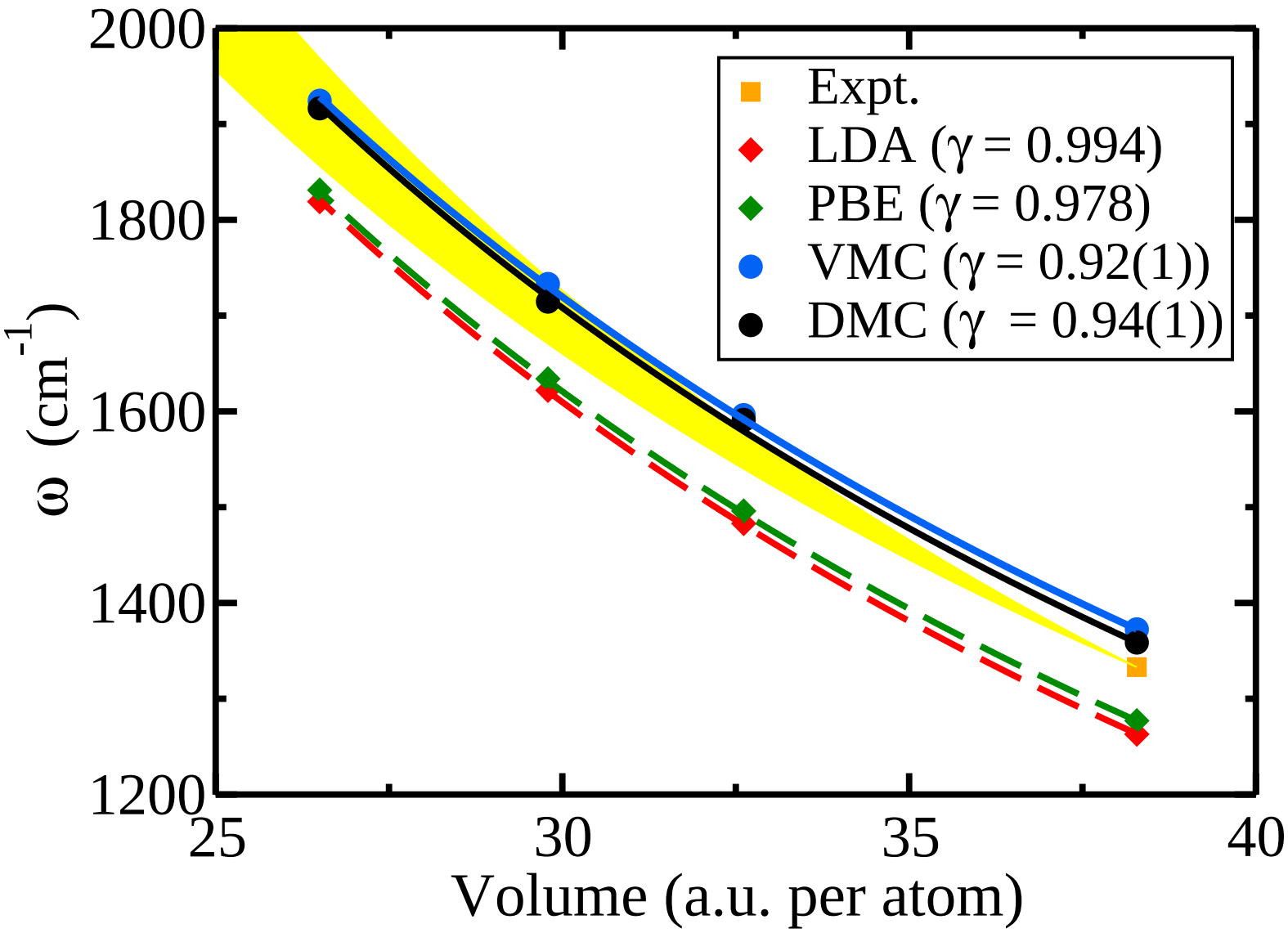
- Use large displacements, 0.17-0.35 a.u., to reduce the effects of noise

- Must correct for anharmonicity $\Rightarrow$ calculate third order anharmonicity in QMC, use DFT for (small) fourth order term

- Remove anharmonic effects, then use perturbation theory to add back realistic anharmonic renormalisation effect
Our theoretical values: -18.0 cm^{-1} (LDA), -15.6 cm^{-1} (PBE-GGA), $-16.8(3)$ cm^{-1} (DMC + DFT fourth order)

- Anharmonic renormalisation from experiment at zero pressure:
$\simeq -20$ cm^{-1} Herchen and Capelli (1991)

Pressure dependence of Raman frequency of diamond



Shaded yellow region from Gruneisen parameters in range γ=0.9-1.06

Summary

- Have calculated the equation of state of diamond up to high pressures. DMC, VMC, GGA-DFT, and LDA-DFT consistent with B_0' a little below 4

- Have calculated the Raman frequency as a function of volume

- Incremental improvements in QMC methodology and increased availability of parallel computers have led to much improved results

- These calculations were done with "last year's methodology", which has already been improved upon!

Team Quantum Monte Carlo and Friends