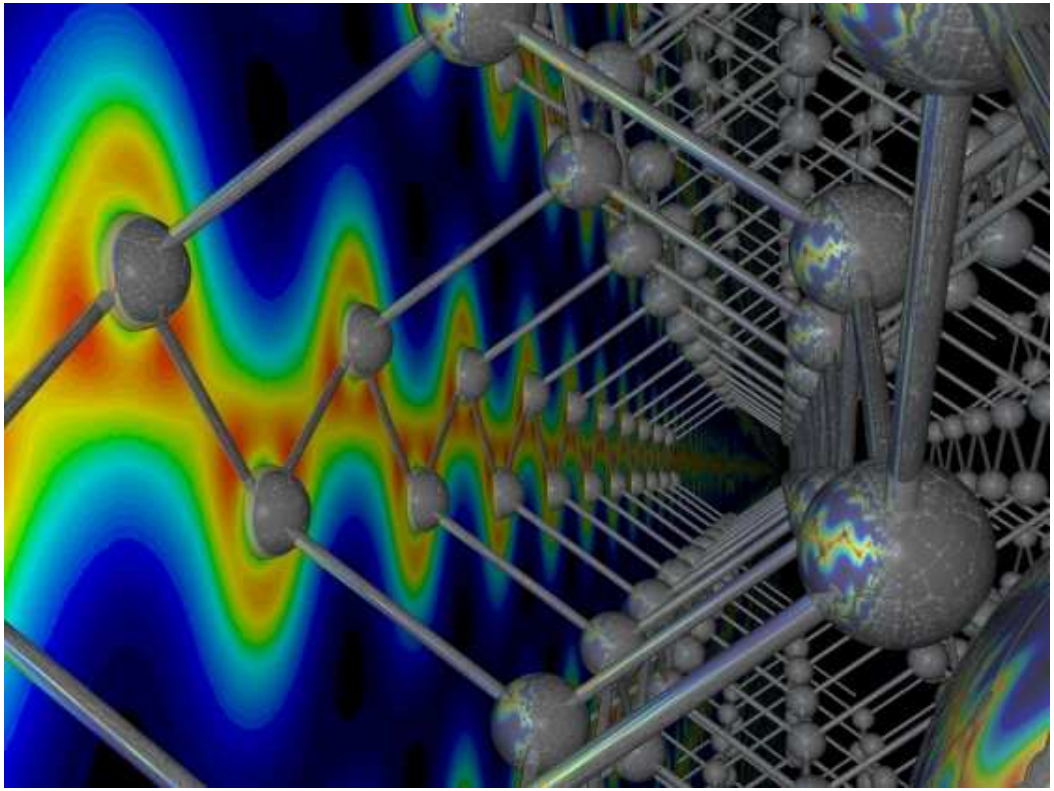
Some applications of diffusion quantum Monte Carlo



Richard Needs

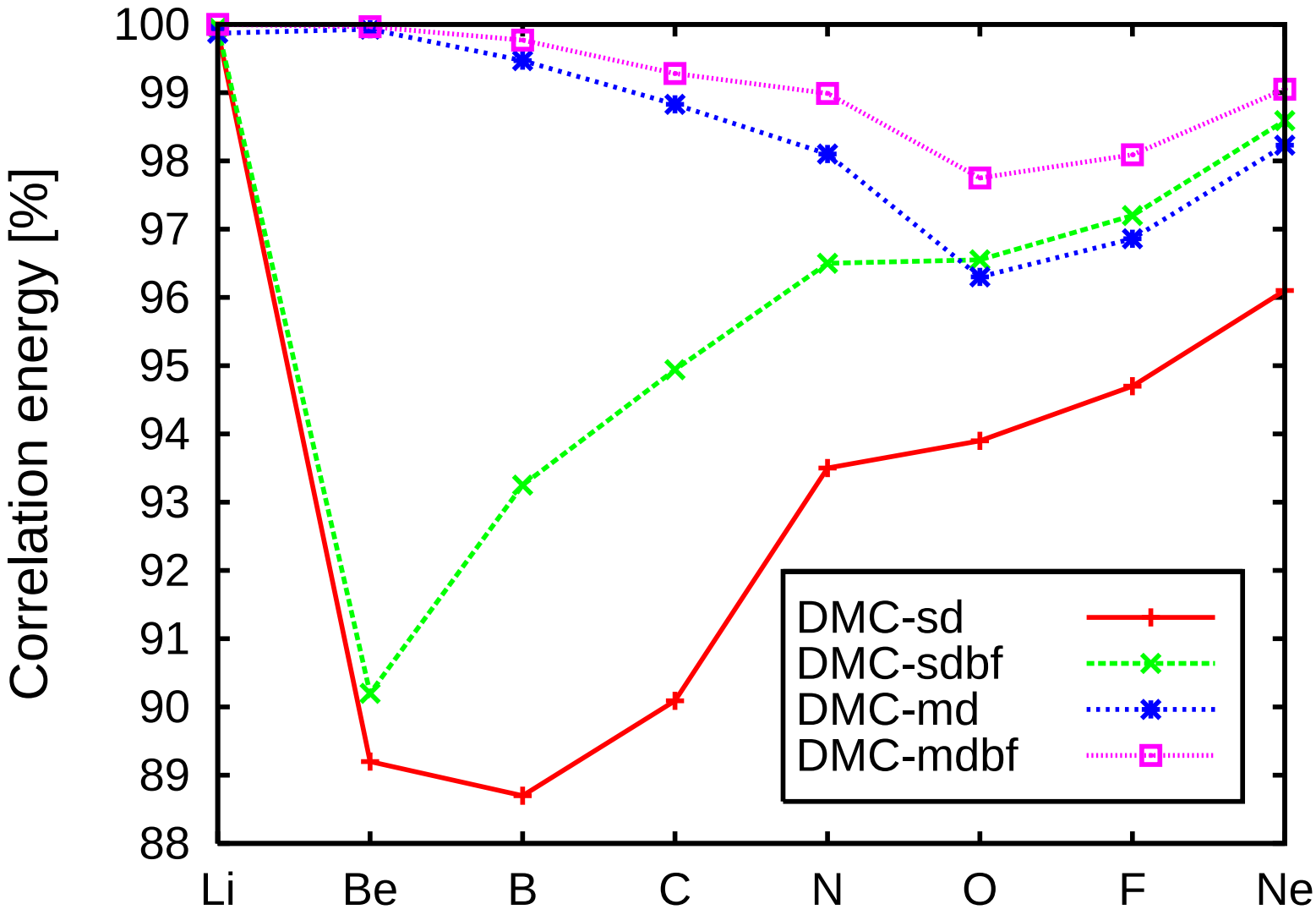
Theory of Condensed Matter Group
Cavendish Laboratory
University of Cambridge

Many-Body Wave functions

$$
\begin{aligned}
\text{Slater} - \text{Jastrow} \quad & \Phi_{\mathrm{SJ}}(\mathbf{R}) &= & \; e^{J(\mathbf{R})} \det\left[\phi_i(\mathbf{r}_i^{\uparrow})\right] \det\left[\phi_i(\mathbf{r}_j^{\downarrow})\right] \\
\text{Multi} - \text{Det} \quad & \Phi_{\mathrm{MD}}(\mathbf{R}) &= & \; e^{J(\mathbf{R})} \sum c_n \det\left[\phi_n(\mathbf{r}_i^{\uparrow})\right] \det\left[\phi_n(\mathbf{r}_j^{\downarrow})\right] \\
\text{Singlet Pairing} \quad & \Phi_{\mathrm{SP}}(\mathbf{R}) &= & \; e^{J(\mathbf{R})} \det\left[\psi(\mathbf{r}_i^{\uparrow}, \mathbf{r}_j^{\downarrow})\right] \\
\text{Backflow} \quad & \Phi_{\mathrm{BF}}(\mathbf{R}) &= & \; e^{J(\mathbf{R})} \det\left[\phi_i(\mathbf{r}_i^{\uparrow} + \xi_i(\mathbf{R}))\right] \det\left[\phi_i(\mathbf{r}_j^{\downarrow} + \xi_j(\mathbf{R}))\right]
\end{aligned}
$$

Can make Jastrow-pairing-backflow wave functions etc.

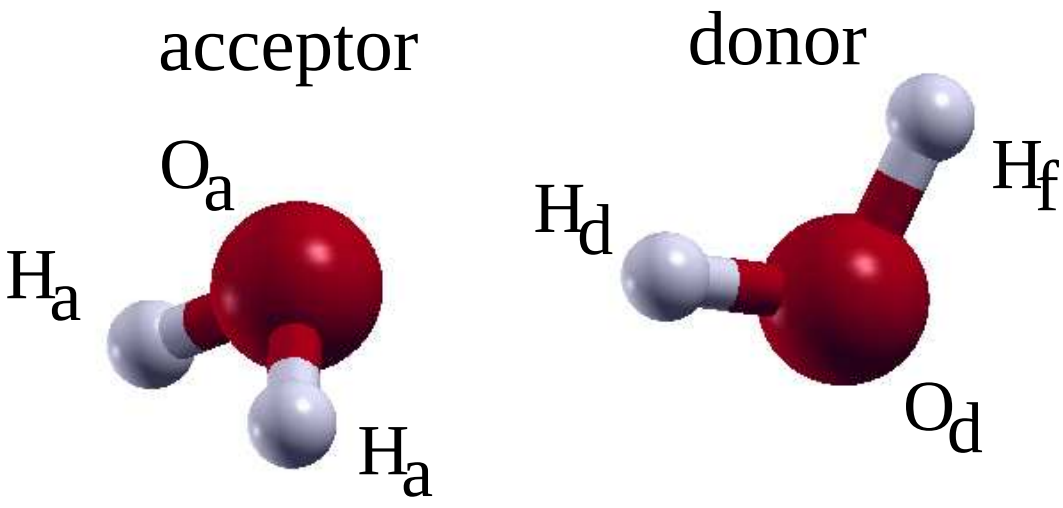
All-electron atoms Li-Ne



Multi-dets: 20 CSFs

Brown, Trail, López Ríos, and RJN, J Chem Phys 126, 224110 (2007)

Dissociation energy of the water dimer



Weak hydrogen bond

Experimental dissociation energy minus calculated vibrational effects:

5.44 ± 0.7 kcal/mol	or	5.00 ± 0.7 kcal/mol	or	5.14 kcal/mol
0.236 ± 0.03 eV	or	0.217 ± 0.03 eV	or	0.223 eV

The water monomer

All-electron VMC and DMC calculations using CCSD(T) geometry

Method	Wave function	Error in Energy (eV)	Error in Energy (kcal/mol)
VMC	SJ	1.65(5)	38.1(12)
VMC	SJB	0.94(5)	21.7(12)
DMC	SJ	0.28(14)	6.5(32)
DMC	SJB	0.26(14)	6.0(32)

Errors in total energy for water molecule (total energy is $\simeq$2080 eV)

Dissociation energy of the water dimer

Method	Wave function	D_e (eV)	D_e (kcal/mol)
AE-CCSD(T)		0.218(2)	5.02(5)
AE-DMC	SJ	0.224(4)	5.16(10)
AE-DMC	SJB	0.232(4)	5.35(10)
PP-DMC	SJ	0.220(3)	5.07(7)
PP-DMC	SJB	0.233(3)	5.38(8)

Dissociation energy of water dimer

AE $\equiv$ All-electron
PP $\equiv$ Pseudopotential

CCSD(T) value from Klopper *et al.* Phys Chem Chem Phys 2, 2227 (2000)

Gurtubay and RJN, J Chem Phys 127, 124306 (2007)

Van der Waals energies for wires and sheets

Van der Waals interaction energies between separated objects may be evaluated as a sum of $1/R^6$ interactions between atoms or volume elements

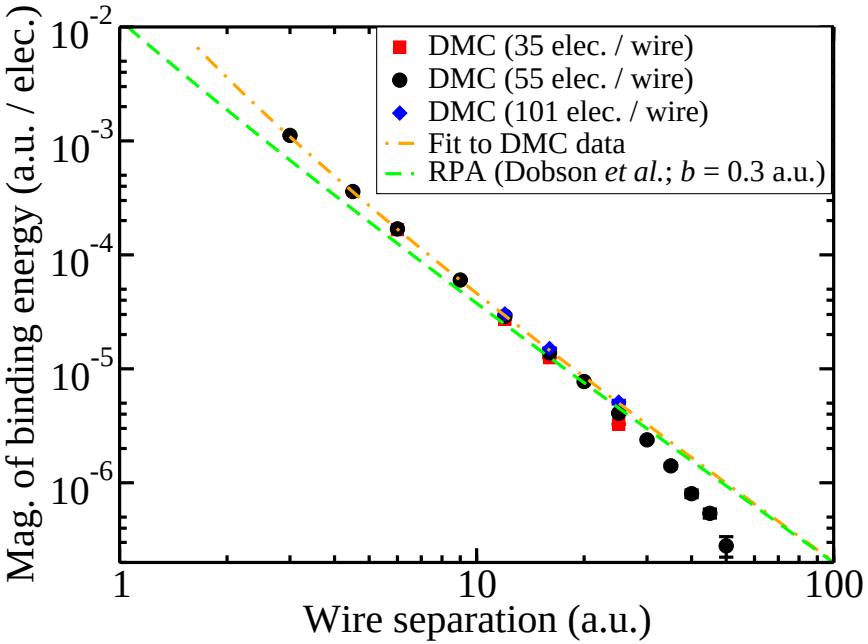
This is not correct for metals which are spatially extended in at least one dimension (to allow long-wavelength charge fluctuations) but are small in another dimension (to reduce e-e screening)

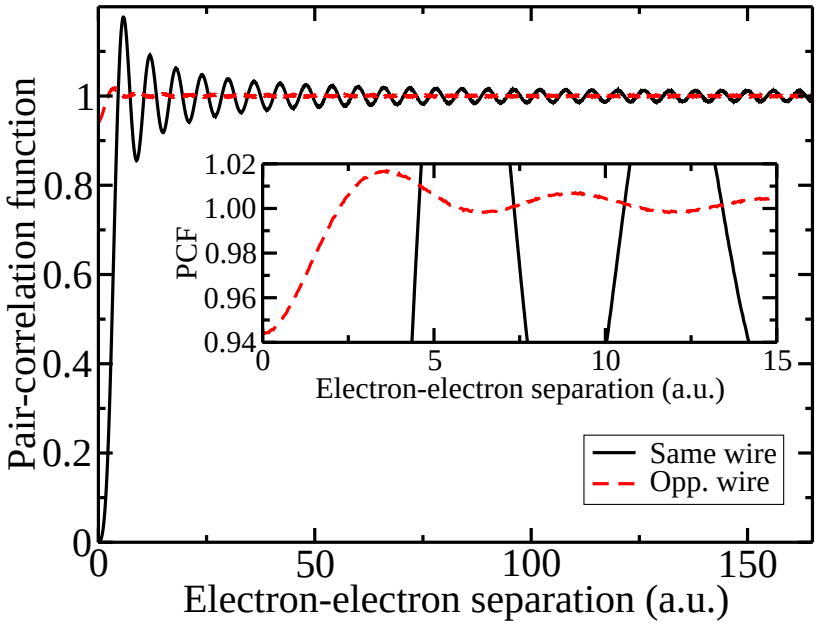
Random Phase Approximation (RPA) calculations:
Sernelius and Björk, Phys Rev B 57, 6592 (1998)
Dobson, White, and Rubio, Phys Rev Lett 96, 073201 (2006)

System	RPA	Standard
Two parallel metallic wires	$-d^{-2}(\ln(Kd))^{-3/2}$	$-d^{-5}$
Two parallel metallic sheets	$-d^{-5/2}$	$-d^{-4}$

Asymptotic behaviour of van der Waals energy

Two parallel electron wires





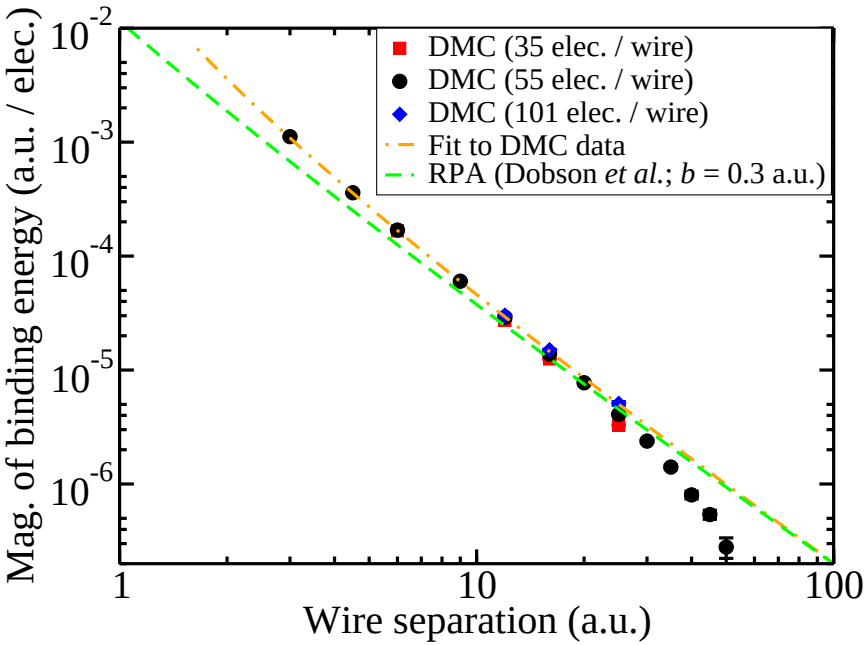
Two parallel 1D HEG wires, density $r_s = 3$ a.u.
PCF at wire separation $z = 3$ a.u.

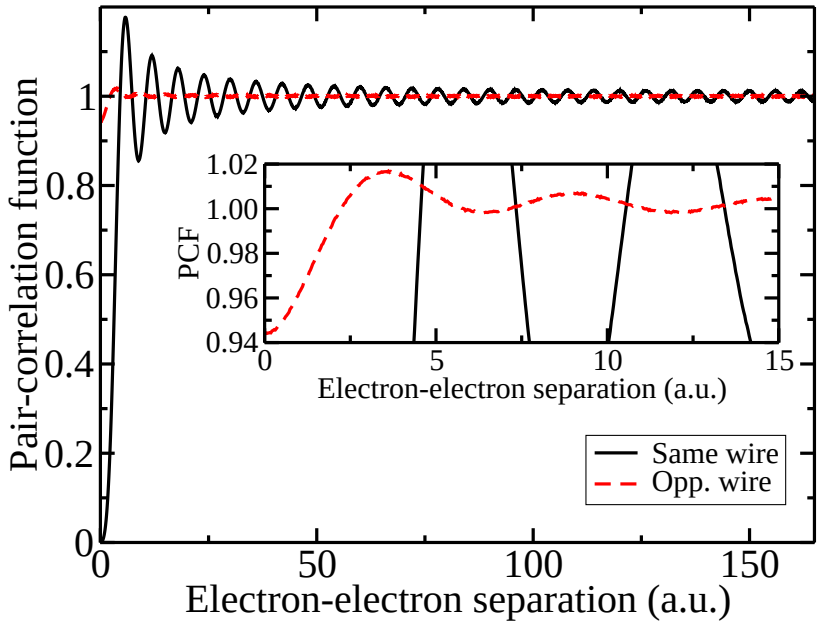
$$U_{\mathrm{RPA}}(z) \approx -\frac{\sqrt{r_s}/(16\pi)}{z^2\left[\log(2.39z/b)\right]^{3/2}}$$

$$U_{\mathrm{DMC}}(z) = -\frac{0.0225}{z^{1.98}\left[\log(1.95z)\right]^{3/2}}$$

Drummond and RJN, Phys Rev Lett 99, 166401 (2007)

Two parallel electron sheets





Two parallel 2D HEG wires, density $r_s = 10$ a.u.
PCF at wire separation $z = 3$ a.u.

$$U_{\mathrm{RPA}}(z) \approx -\frac{0.012562\sqrt{\pi}r_s}{2z^{5/2}}$$

$$U_{\mathrm{DMC}}(z) = -\frac{0.0388}{z^{2.64}}$$

Drummond and RJN, Phys Rev Lett 99, 166401 (2007)

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, but the pressure derivative of the bulk modulus is not

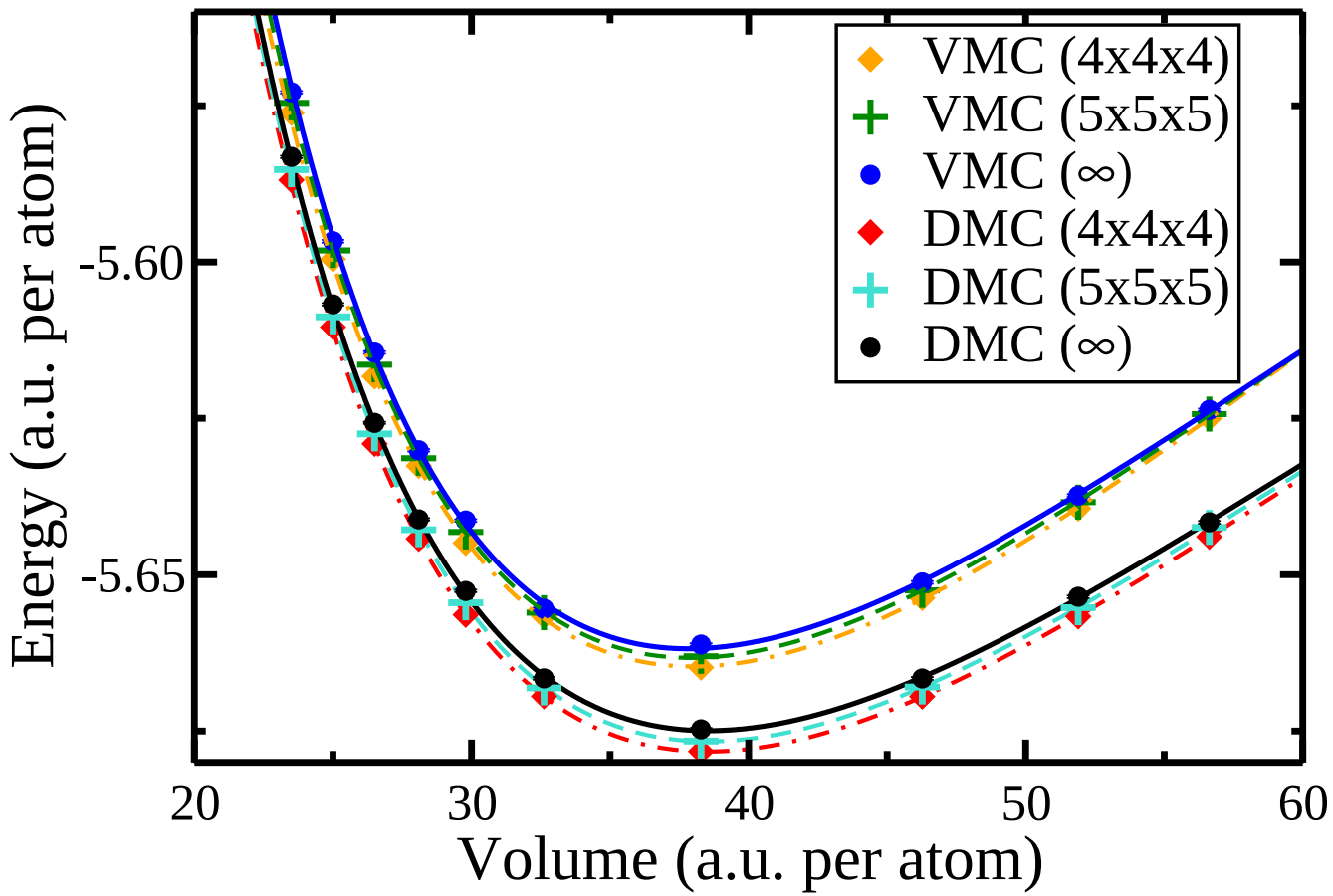
$B_0' = 4.0 \pm 0.5$ McSkimin and Andreatch (1972)
$B_0' = 3.0 \pm 0.1$ Occelli *et al.* (2003)

• Datchi *et al.* (2007) fitted data of Occelli *et al.* to new ruby scales
Five scales dating from 2003 to present give

$B_0 = 432(3) - 444(2)$ GPa
$B_0' = 3.66(7) - 4.05(7)$

• Could use pressure dependence of the Raman frequency and equation of state of diamond to determine pressure in the diamond anvil cell

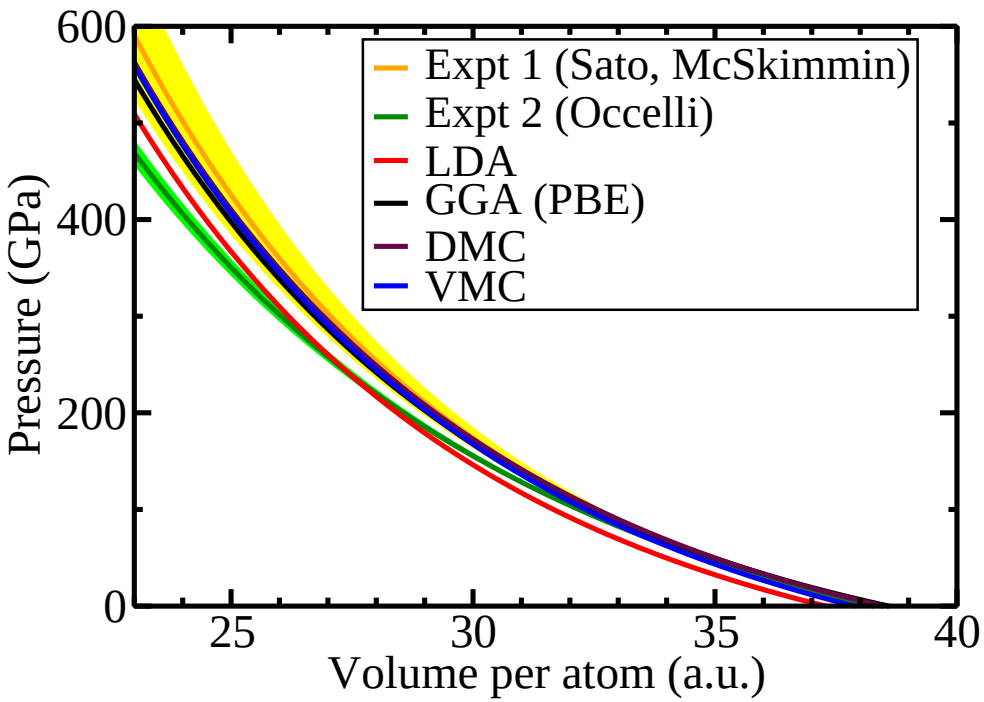
Equation of State of Diamond from QMC



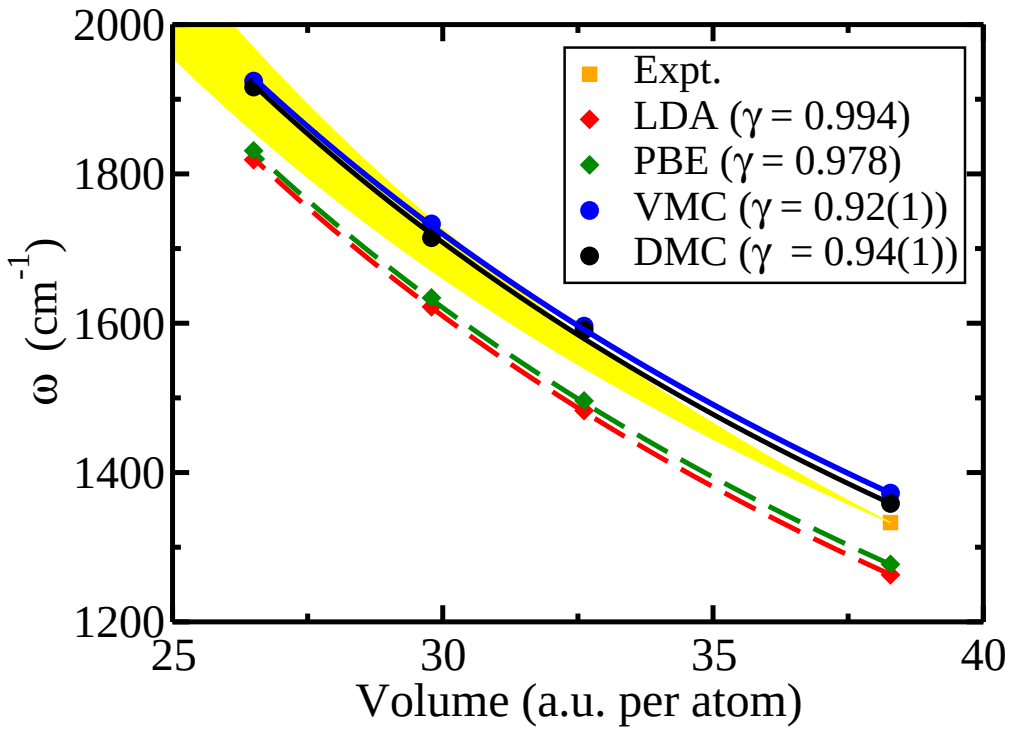
Hartree-Fock pseudopotentials, 128 atom and 250 atom simulation cells
PBE-GGA orbitals, plane waves ⇒ "B-splines"

Maezono, Ma, Towler, and RJN, Phys Rev Lett 98, 025701 (2007)

Equation of State of Diamond from QMC



Pressure-volume relation



Raman frequency $\omega(V)$

	LDA	PBE	VMC	DMC	Expt. (295 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)	432(3)-444(2)
B_0'	3.65	3.72	3.8(1)	3.7(1)	3.66(7)-4.05(7)

Conclusions

- DMC is a very general method, one can treat fermions and bosons with any interactions and any form of wave function

- DMC is feasible for large systems

- DMC is the most accurate method known for computing the total energies of large assemblies of interacting quantum particles

- DMC is expensive - but worth it!