# QMC Studies of Real Systems

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Real Systems

- There have been many important applications of QMC to **model systems** (e.g. electron gases, jellium surfaces and spheres).

- **Real systems** (atoms, molecules and solids) usually require more computational effort.

- QMC is most accurate first-principles total-energy method for systems of more than a few tens of electrons.

- QMC is becoming an important tool in *ab initio* studies of real systems.
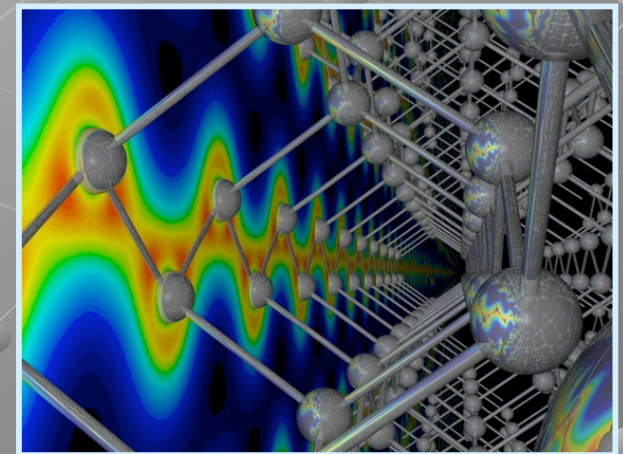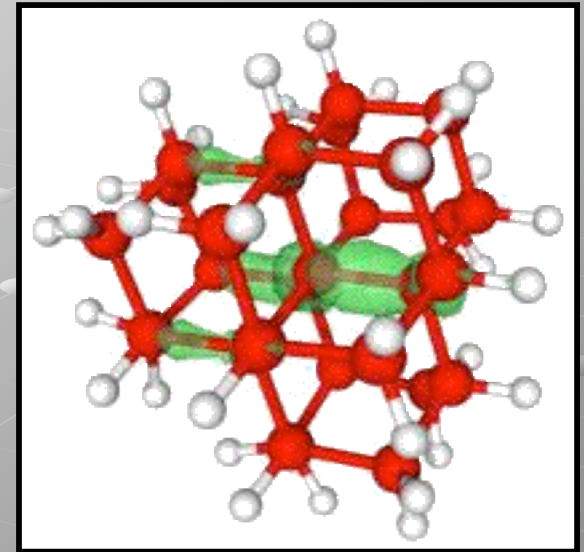
Electronic-Structure Methods
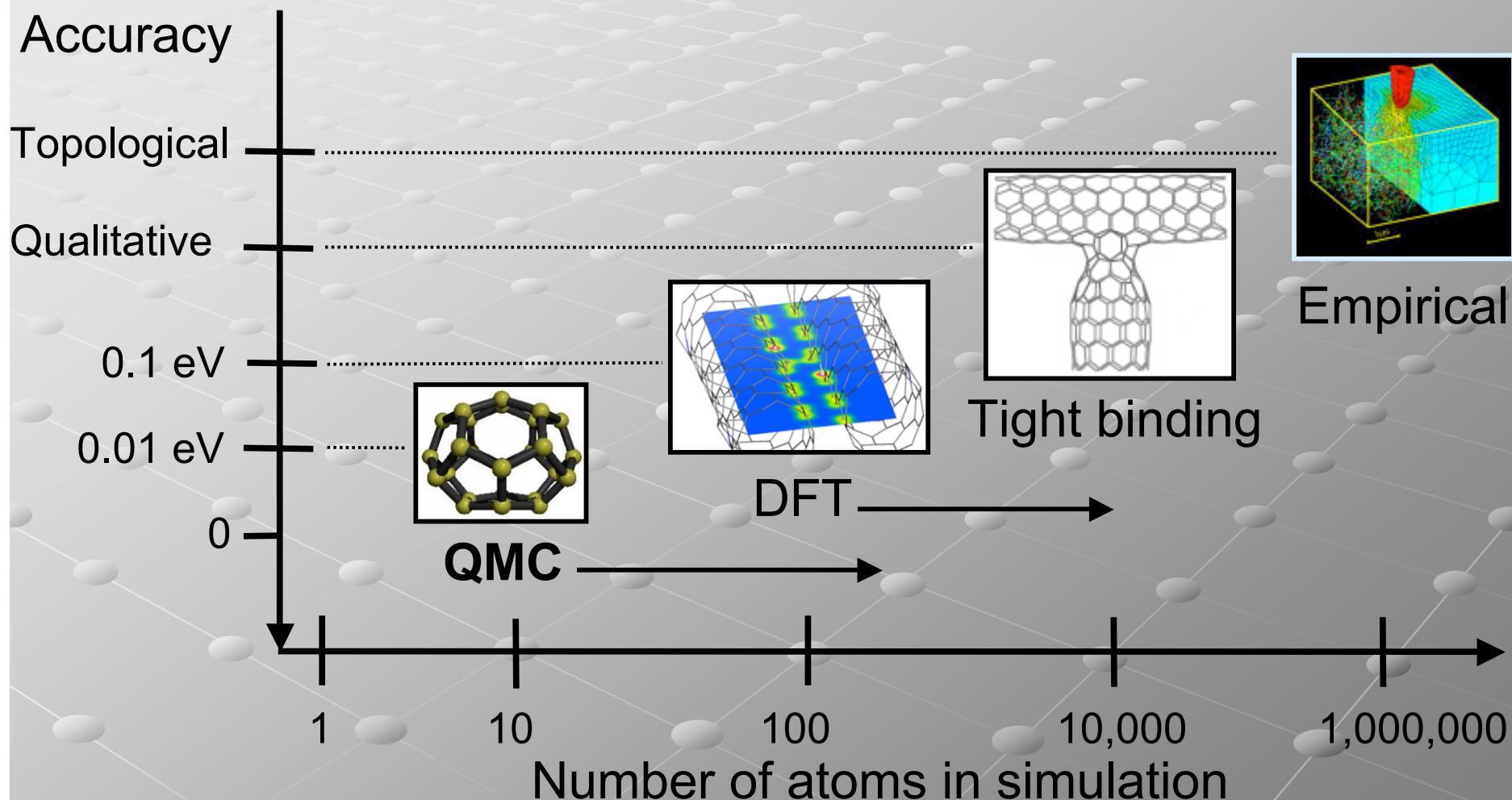
Outline of Talk + References

- QMC studies of <u>solid diamond</u> [Maezono *et al*., PRL **98**, 025701].

- QMC studies of <u>solid neon</u> [Drummond & Needs, PRB **73**, 024107].

- QMC calculations of optoelectronic properties of <u>diamondoids</u> [Drummond *et al*., PRL **95**, 096801].

- *Ex nihilo* structure prediction (<u>silane</u> & <u>solid hydrogen</u>) [Pickard & Needs PRL **97**, 045504; Pickard & Needs, Nature Physics (online)]
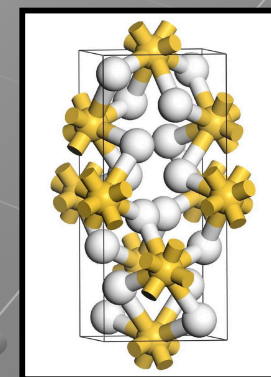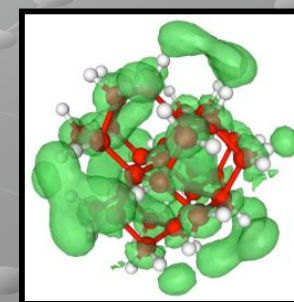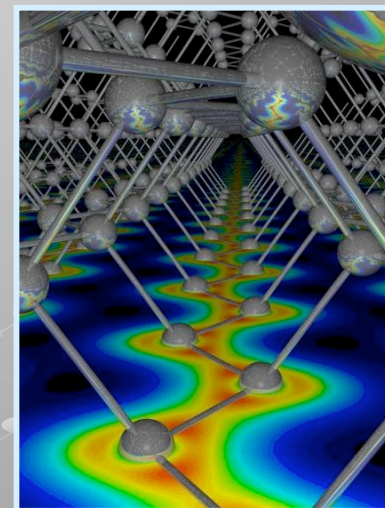
Solid Diamond

- Zero-temperature equation of state of diamond is imperfectly characterised.

- Knowledge of EoS is important in design of diamond anvil cells.

- Raman frequency: zone-centre optic-phonon frequency, measured in Raman spectroscopy.

- Raman spectroscopy of diamond could be used as a pressure gauge if Raman frequency as a function of pressure were known

- Use QMC to calculate EoS and Raman frequency of diamond.
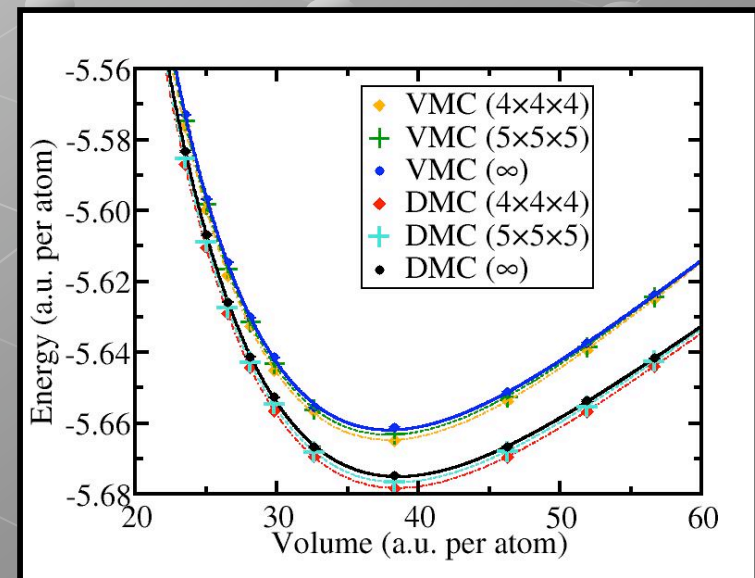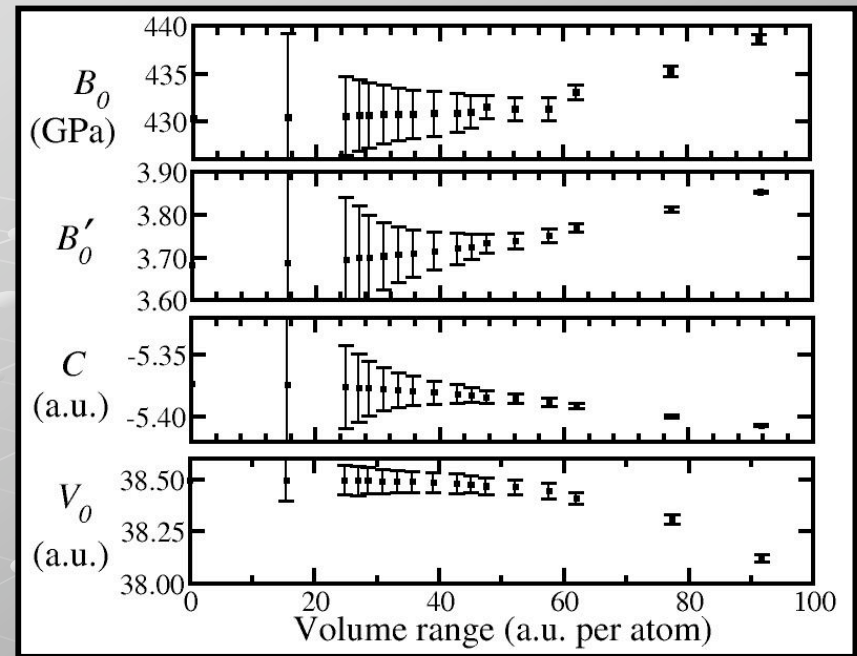
Heart of eternity

Diamond anvil cell

Designing the Calculations

- Calculate QMC energy at different volumes and fit Vinet EoS.

- Like particle-physics experiments, QMC calculations are <u>expensive</u>.

- Simulate fitting of EoS to data from DFT EoS with added noise and identify the volume range that allows the EoS parameters to be determined with maximum accuracy.

The QMC Calculations

- Use Dirac-Fock pseudopotentials for C^{4+} cores.

- Use simulation cells consisting of 4_4_4 & 5_5_5 primitive cells (128 & 250 atoms).

- Use plane-wave DFT calculations, then re-express orbitals in a blip basis.

- Single-particle finite-size errors are small; extrapolate to infinite system size using $E(N)=E(\infty)+b/N$.

- Add DFT quasiharmonic free energy at 300 K.

- Compare with experimental results: McSkimin & Andreatch, J. Appl. Phys. **43**, 2944; Occelli *et al*., Nat. Mater. **2**, 151.

Equation of State

	LDA	PBE	VMC	DMC	Exp.
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(5), 3.0(1)
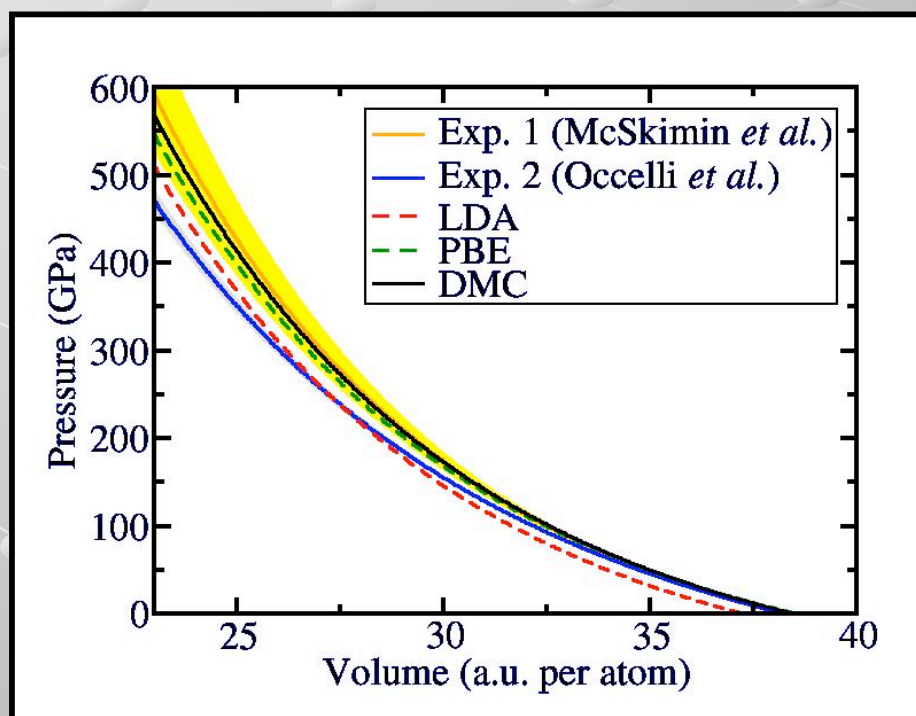
- VMC and DMC in good agreement.
- DFT and QMC in good agreement.
- Need to refine ruby pressure scale?

Raman Frequency

- Frozen phonon method used.
- Cubic anharmonicity determined, and renormalised phonon frequencies found.
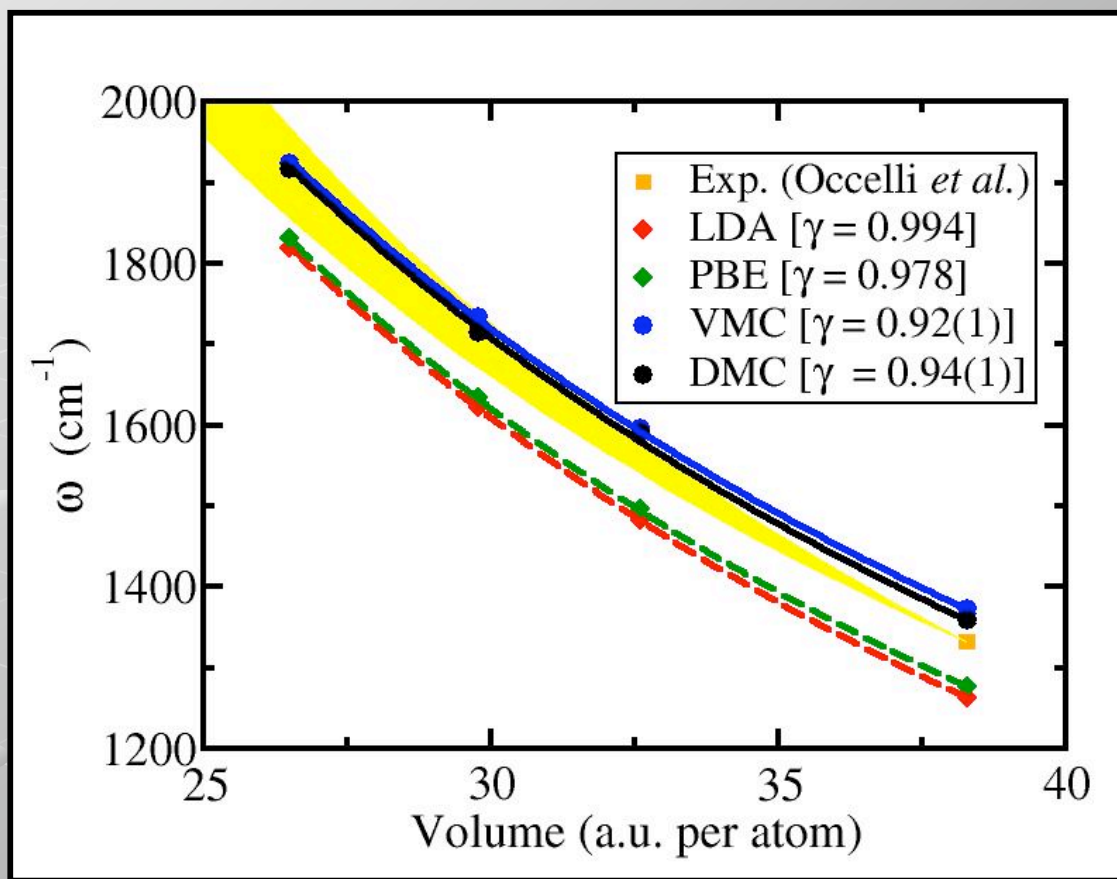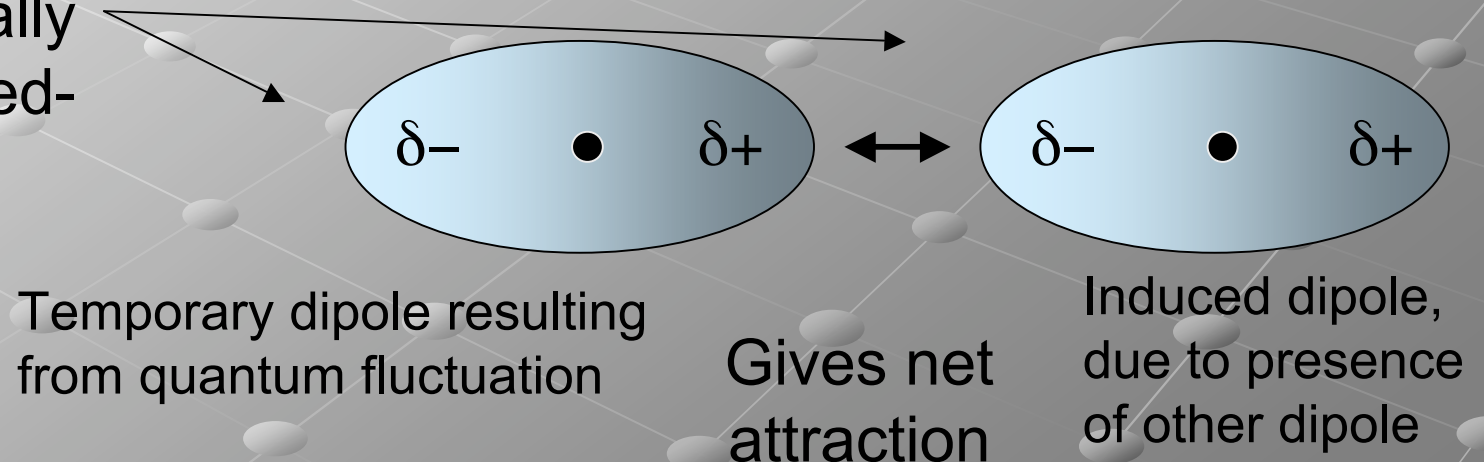

	LDA	PBE	VMC	DMC	Exp.
ω (cm^{-1}) [harm.]	1281	1292	1389(3)	1375(4)	N/A
ω (cm^{-1}) [ren.]	1263	1277	1373(4)	1359(4)	1333

Neon

- The chemistry of the noble gas **neon** is simple.
- When atoms are brought together, their electron clouds overlap, giving a **hard-core repulsion**.
- Atoms are weakly attracted to one another by **van der Waals** forces.
- *Can QMC methods describe van der Waals forces?*

Two electrically neutral, closed-shell atoms

$\delta-$ • $\delta+$ ↔ $\delta-$ • $\delta+$

Temporary dipole resulting from quantum fluctuation

Gives net attraction

Induced dipole, due to presence of other dipole

Solid Neon

- At low temperatures or high pressures, neon forms a crystalline solid with the face-centred cubic structure.
- Highly accurate experimental data are available.
- Solid neon has long been used as a test system for theoretical many-body physics.
- Accurate pressure-volume data at high pressures may be of relevance to diamond-anvil experiments.

Diamond anvil

Metal gasket

Pressure-conducting medium, e.g. neon

Sample
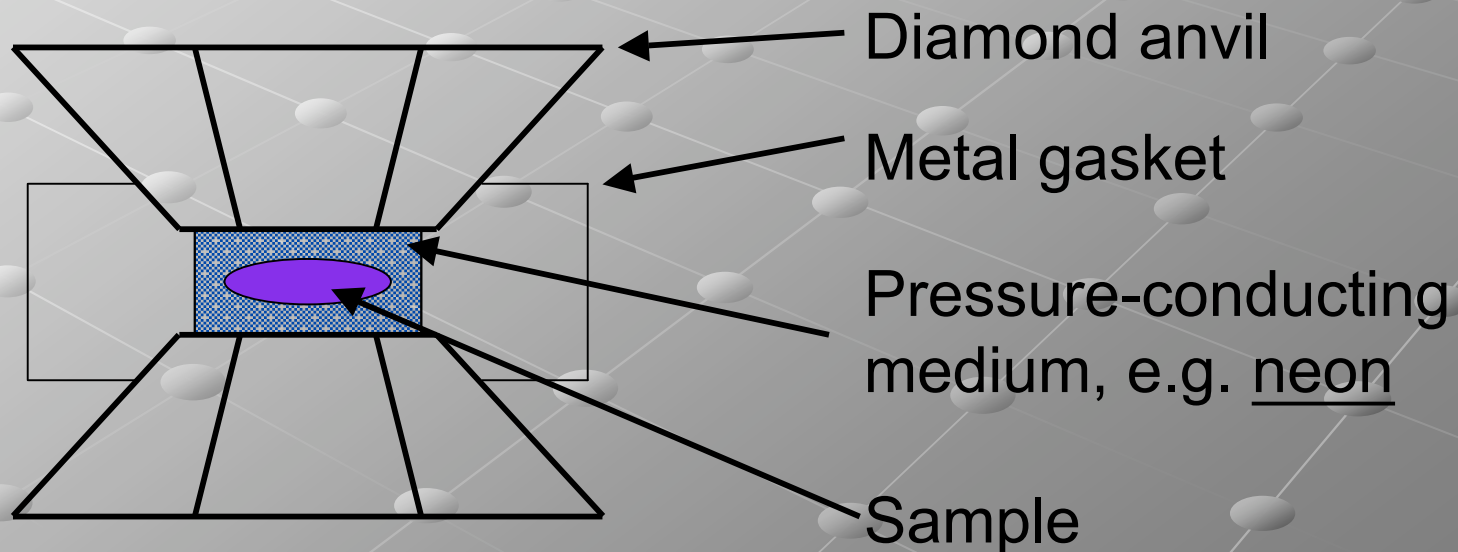
QMC Calculations I

- Used DFT-LDA orbitals in a Slater-Jastrow trial wave function (CASINO).

- Used HF neon pseudopot.

- Appreciable time-step bias in DMC energies.

- Used same time step in all DMC EoS calculations; bias in energy nearly same at each density; *hence there is very little bias in the pressure*.

- Verified this by calculating EoS at two different time steps: clear that EoS has converged.
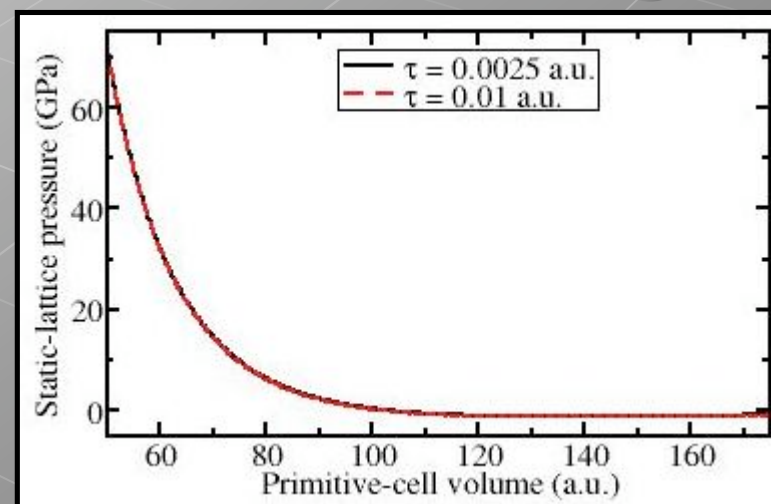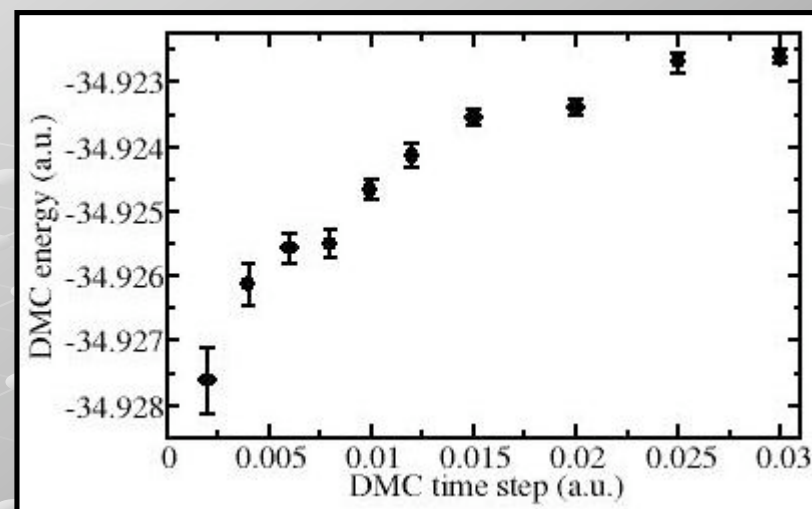
QMC Calculations II

- Single-particle finite-size effects are negligible in our QMC results; verified by studying convergence of DFT energy with respect to **k**-point sampling.

- Long-ranged kinetic-energy and Coulomb finite-size biases go as $1/N$, where N is the number of electrons.

- Vinet EoSs were fitted to QMC results in simulation cells of 3x3x3 and 4x4x4 primitive unit cells, and the assumed form of the finite-size bias was used to extrapolate the EoS to infinite system size.

Equation of State of Solid Neon
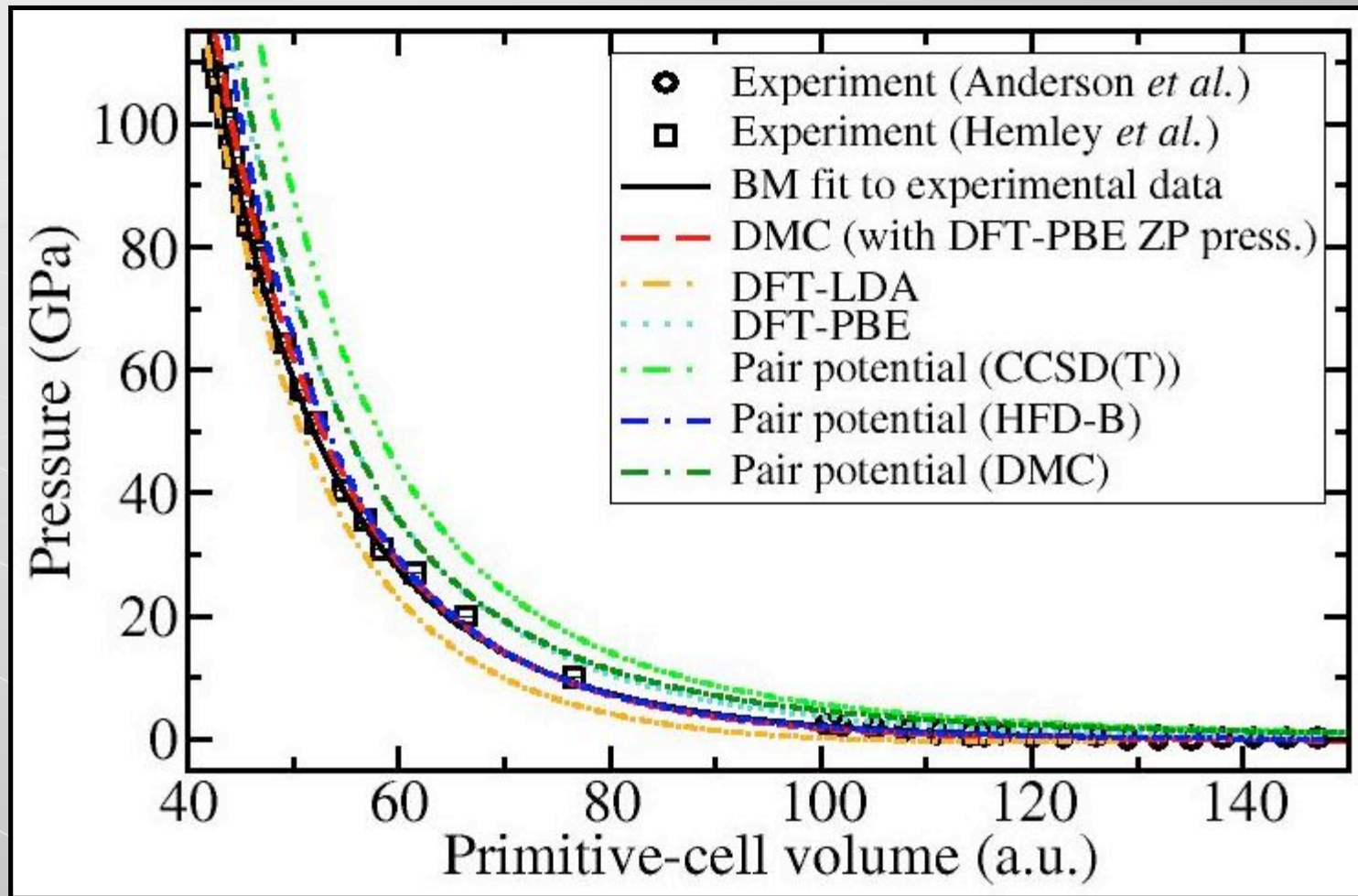
DFT-LDA and DFT-PBE results disagree significantly.

Equation of State of Solid Neon (II)
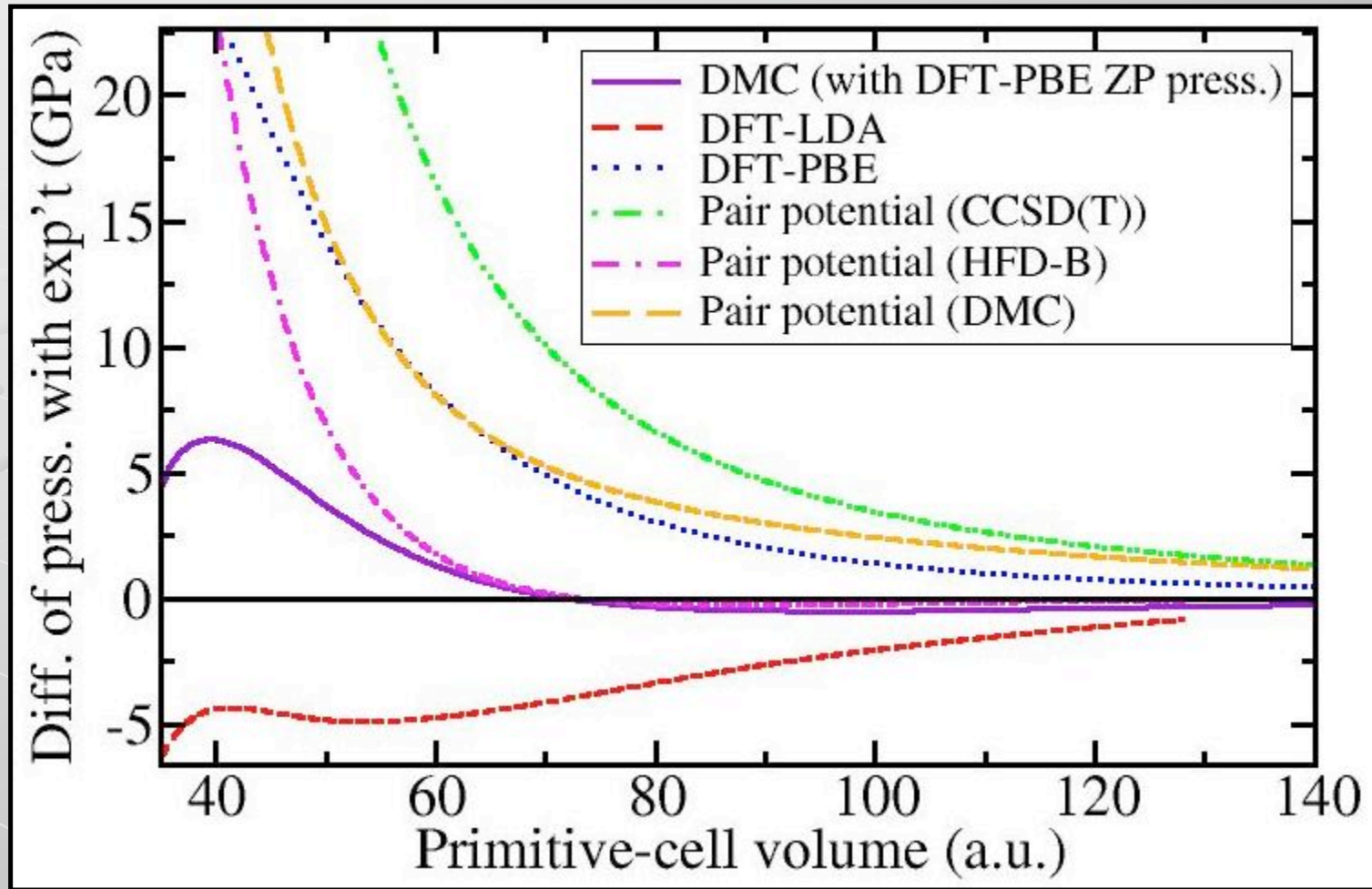
QMC, unlike DFT, gives an accurate description of van der Waals attractions. Unlike the empirical pair potential, QMC is accurate at high pressure.
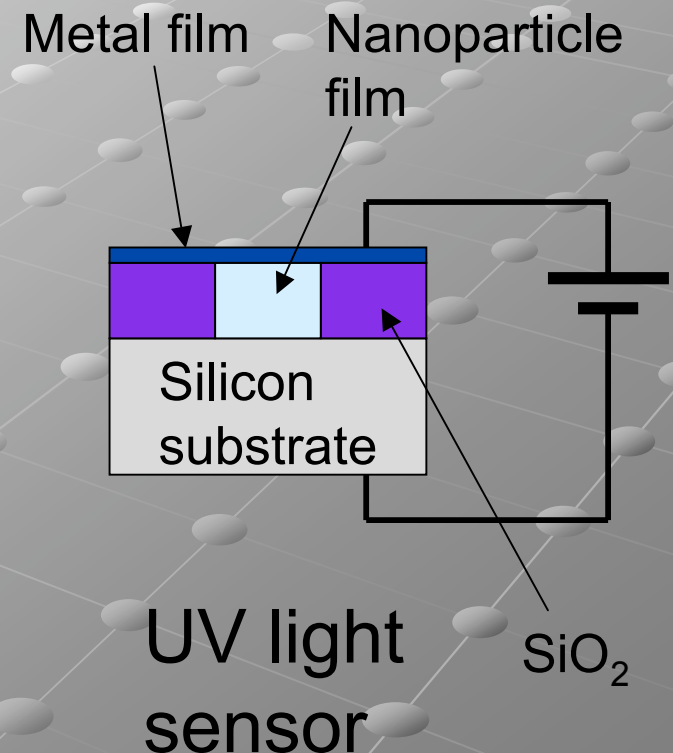
Semiconductor Nanoparticles for Optoelectronic Devices (I)

- *Optical gap* (OG): difference between ground-state and first-excited-state energies.

- **Quantum-confinement** (QC) effects should raise OGs of **nanoparticles** above the corresponding bulk band gaps.

- QC caused by quadratic increase in KE of states when <u>spatially confined</u>.
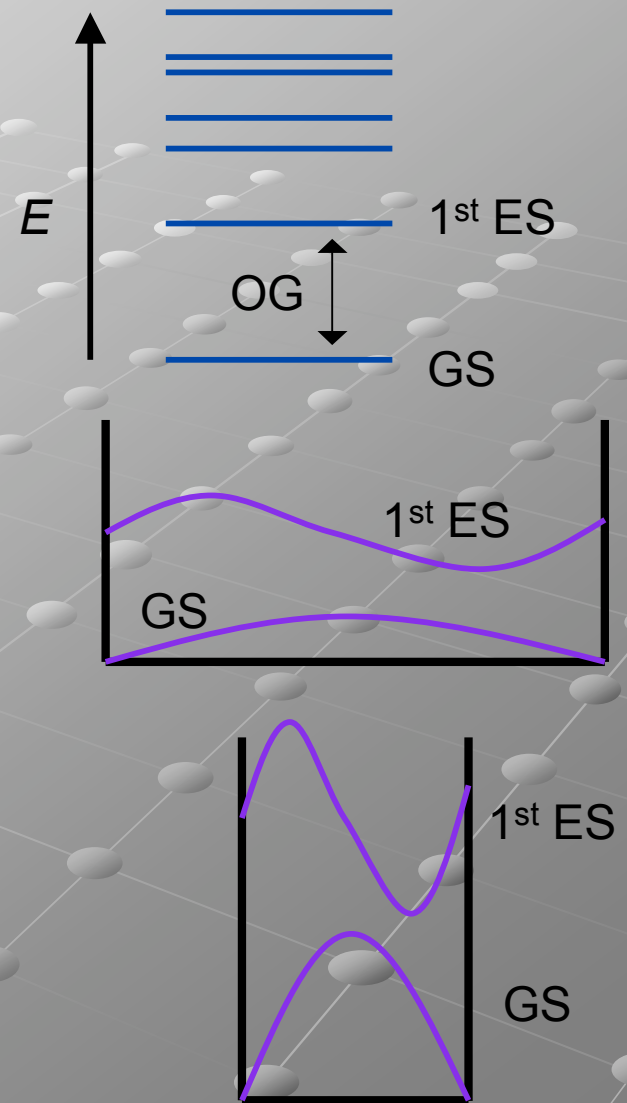
Semiconductor Nanoparticles for Optoelectronic Devices (II)

- Films of nanoparticles can be used to make **UV sensors**.

- Si and Ge nanoparticles have been studied extensively; can be integrated with existing device-fabrication techniques.

- Until recently, carbon nanoparticles have been more difficult to synthesise and study.

- Diamond band gap (5.47 eV) is in the UV range.

- QC might push the OGs of carbon nanoparticles even further into the UV range: new range of UV sensors.

Metal film   Nanoparticle film

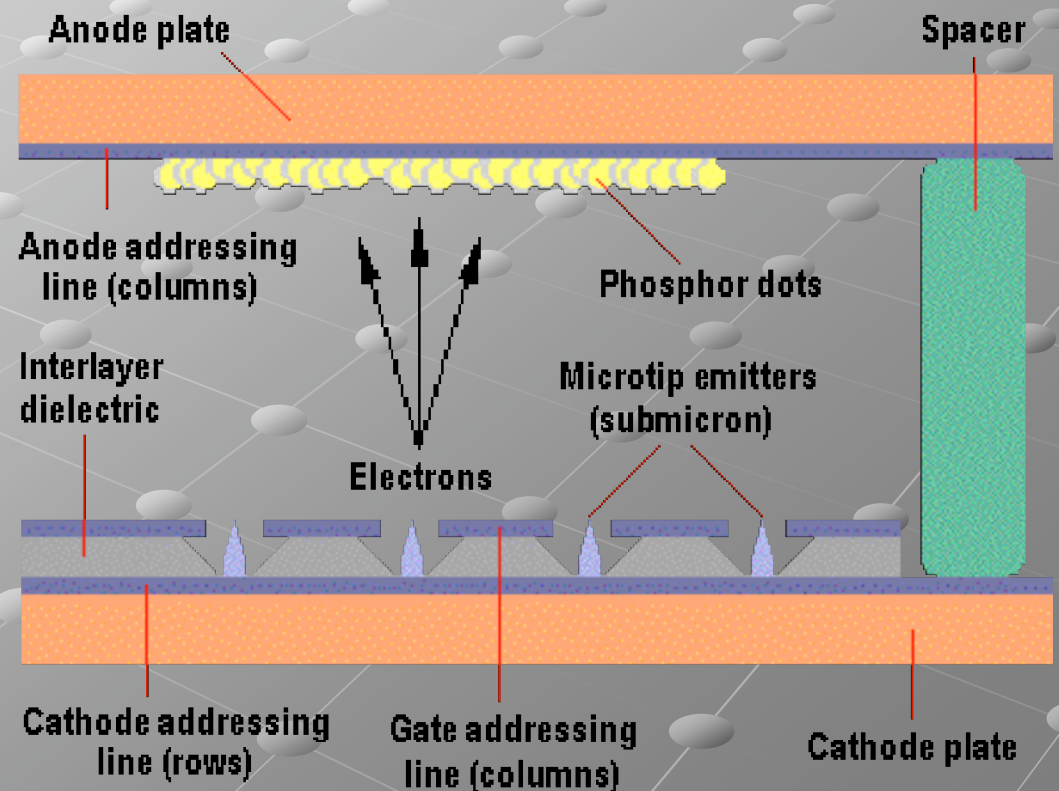Silicon substrate

SiO$_2$

UV light sensor

Semiconductor Nanoparticles for Electron-Emission Devices

- *Electron affinity* (EA) of a molecule: energy released when molecule and a free electron form an ion.

- EA of a semiconductor: difference between conduction-band minimum and vacuum level.

- Some hydrogen-terminated diamond surfaces have **negative** EAs.

- <u>Hydrogen-terminated carbon nanoparticles should have low or negative EAs.</u>

Molecule $^+$

e$^-$

Molecule $^-$ + **EA**

Vacuum level

EA

E

Conduction -band min

Band gap

Valence- band max
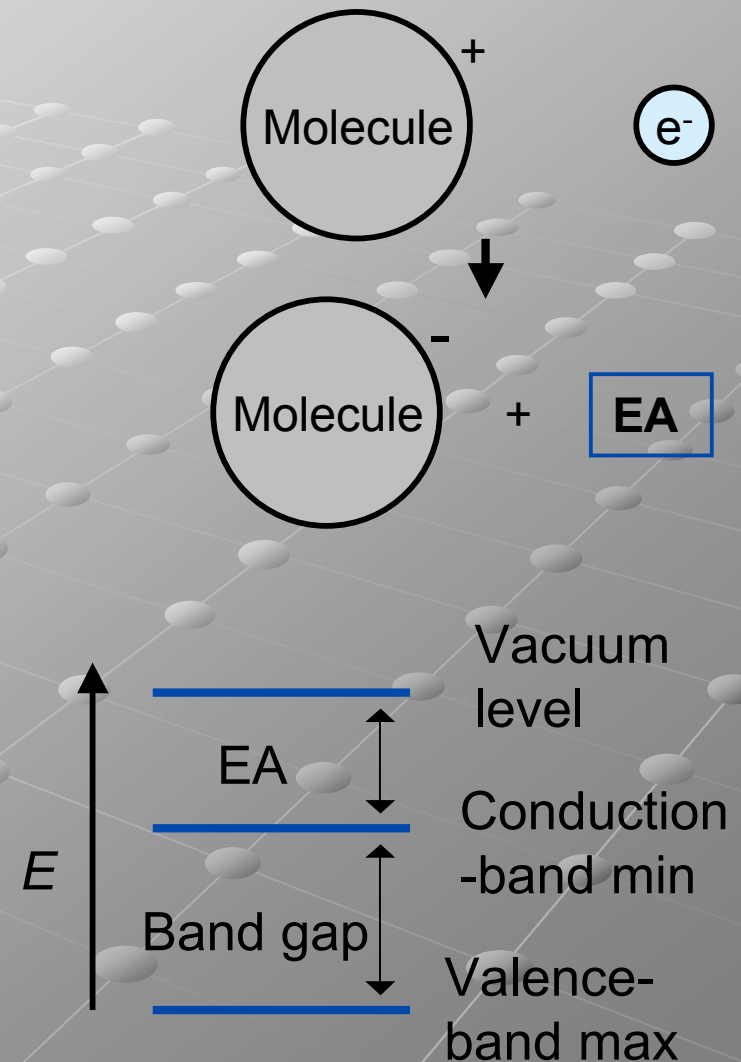
Field-Emission Devices (I)

- **Field-emission display** (FED) devices: attractive alternative to CRT or LCD displays.

- CRTs are very unwieldy and power-hungry.

- LCDs have slow response times, limited viewing angles, limited size and are power-hungry.

- Existing (prototype) FED devices use electric fields to pull electrons off cold, micron-sized metal tips towards phosphor dots.

- Very strong fields required, and tips get damaged.

Anode plate

Spacer

Anode addressing line (columns)

Phosphor dots

Interlayer dielectric

Microtip emitters (submicron)

Electrons

Cathode addressing line (rows)

Gate addressing line (columns)

Cathode plate

Field-Emission Devices (II)
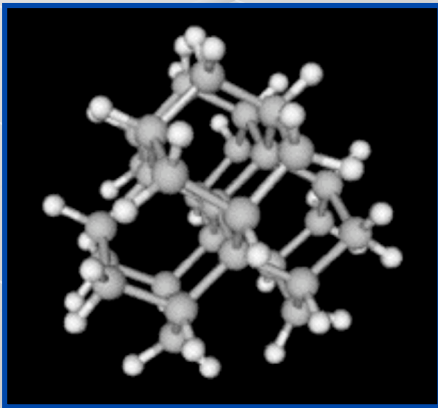
- Materials with <u>negative electron affinities</u> will readily emit conduction electrons.
- Electric field required to pull electrons off such materials does not need to be especially strong.
- Tips are not required (pixels smaller & more robust).
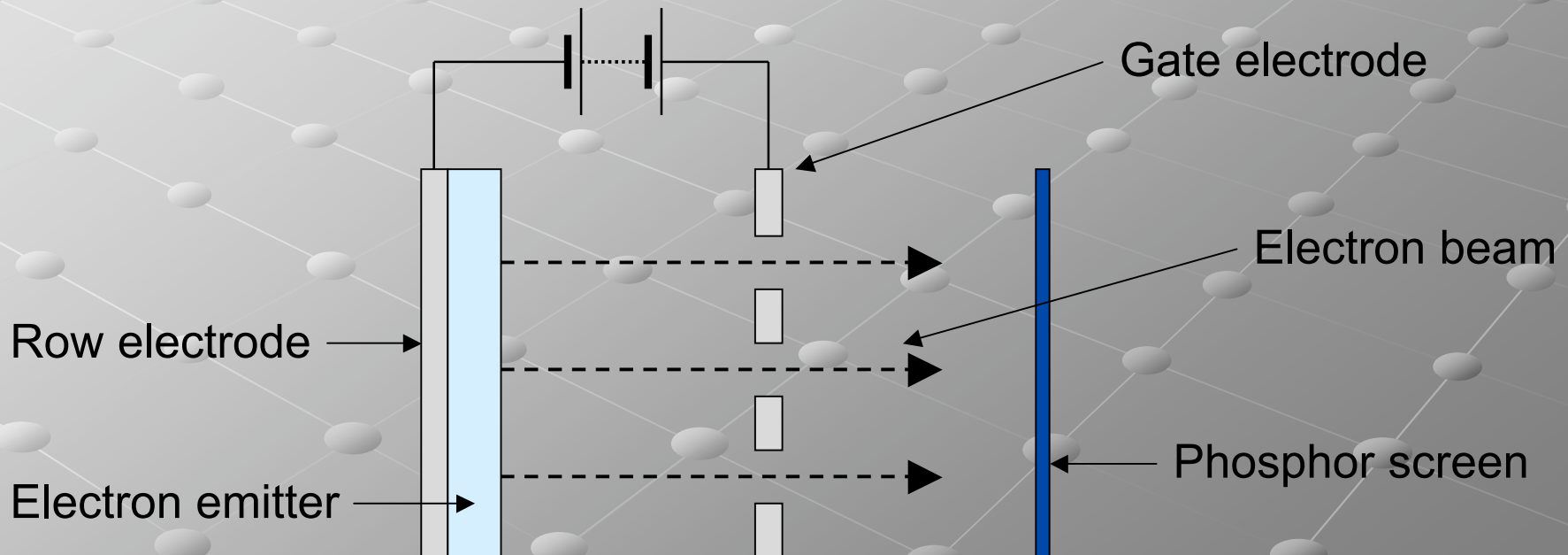
Diamondoids (I)

- Hydrogen-terminated carbon nanoparticles are called *diamondoids*.

$C_{29}H_{36}$
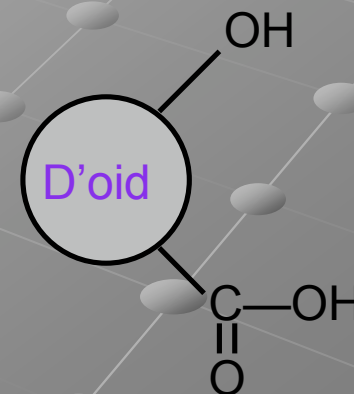

$C_{66}H_{64}$

$C_{87}H_{76}$
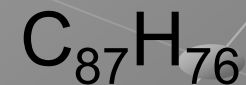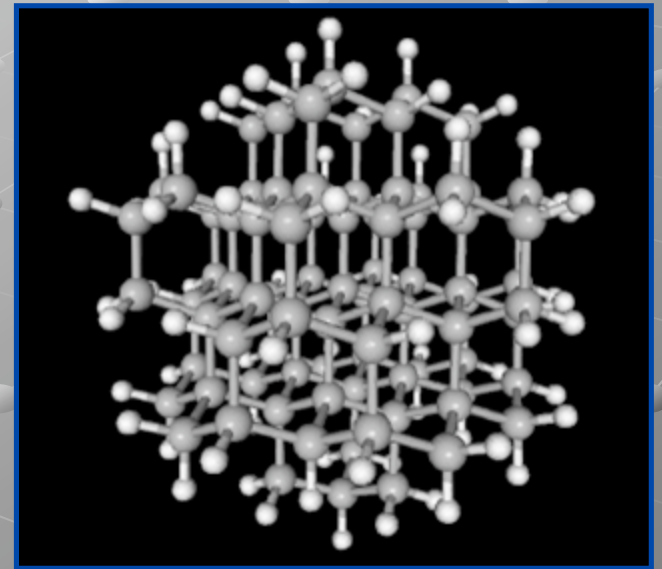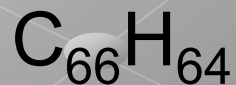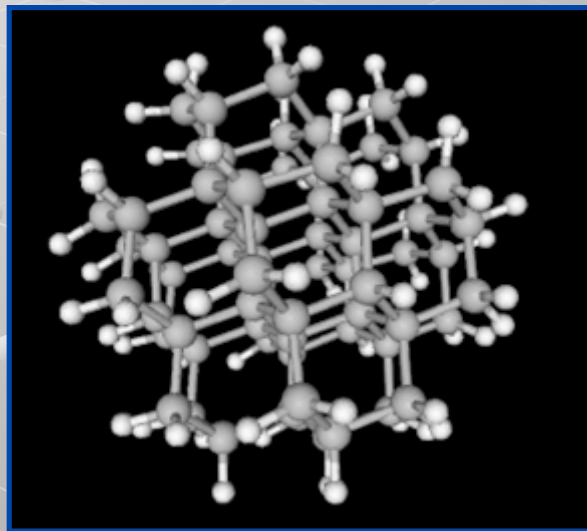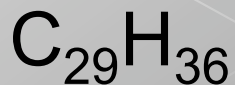
Diamondoids (II)

- Diamondoids have been isolated from petroleum [Dahl *et al.*, Science **299**, 96].

- **Crystals** of diamondoids have been grown.

- **Functional groups** have been added to diamondoids.

- Hence it is possible to produce **polymers** and **self-assembled monolayers** of diamondoids.

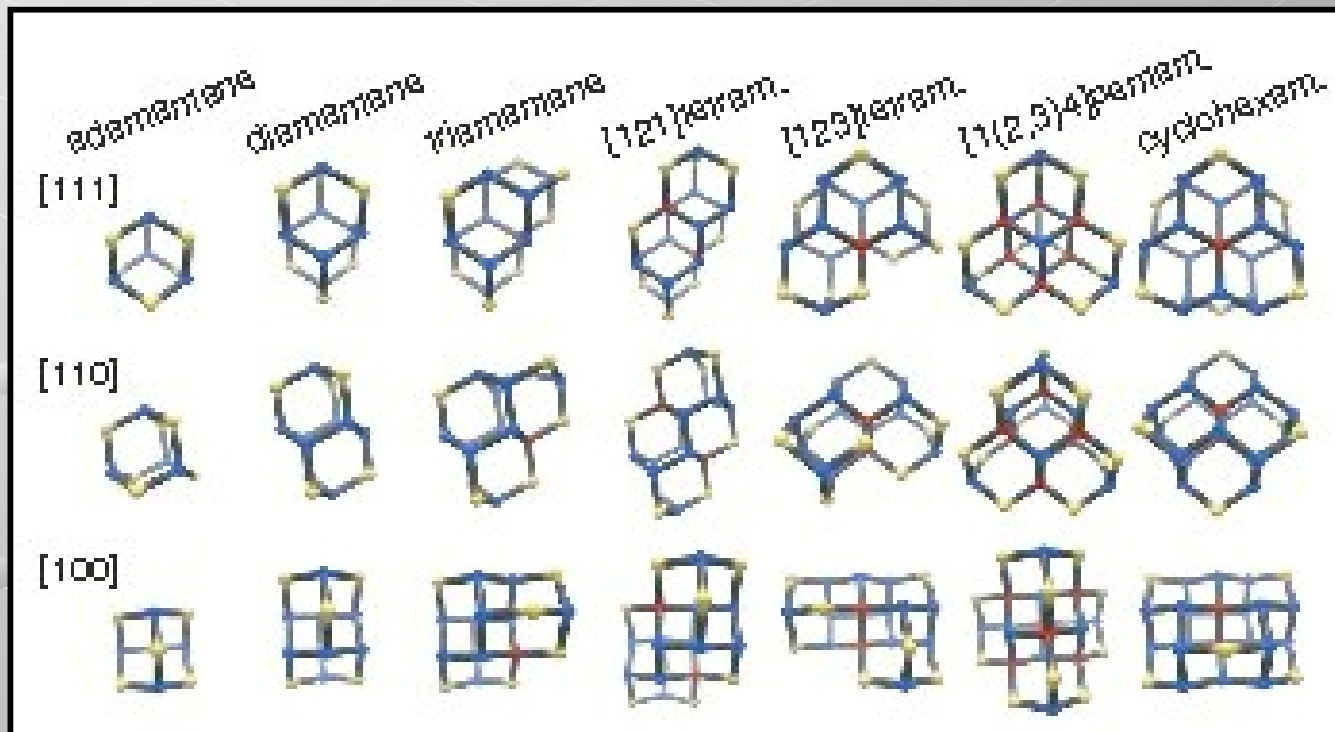Crystals of $C_{26}H_{32}$.

D'oid — OH

C—OH
‖
O

Diamondoids (III)

- Experimentally isolated diamondoids are members of a <u>series</u>.
- We have used some of these structures in our calculations.

From Willey *et al.*, PRL **95**, 113401.

Experimental Results

- XANES: substantial QC in diamondoids up to several nanometres in diameter [Chang *et al.*, PRL **82**, 5377].

- NEXAFS: no evidence of QC in such nanoparticles [Raty *et al.*, PRL **90**, 037401].

- No experimental studies of electron affinities of carbon nanoparticles.

- Several technologically important questions, but experimental results are contradictory or nonexistent.

- Accurate first-principles simulations are clearly required!

Previous DFT Simulations

- DFT OGs are always underestimated: infamous "band-gap" problem.

- One DFT study predicted that diamondoid OGs fall off rapidly as their diameter increases [Raty *et al*., PRL **90**, 037401].

- At 1 nm the OGs were predicted to lie *below* the band gap of diamond.

- Another DFT study found that the OGs of the same molecules are substantially higher than the diamond gap [McIntosh *et al*., PRB **70**, 045401].

- More accuracy required? Then use QMC!

The QMC Calculations (I)

- DFT pseudopotentials were used for C and H.

- Very large simulation boxes (side-length 35-50 a.u.) and plane-wave cutoff energies (35-50 Ry) were used in the DFT calculations.

- Orbitals were represented by splines in real space to improve scaling of QMC calculations with system size.

- DMC time step was 0.02 a.u.; resulting errors in the gaps are negligible.

The QMC Calculations (II)

- Changing XC functional used to generate nanoparticle geometry and trial wave function altered DMC OG by 0.3 eV.

- HOMO was replaced by LUMO in spin-down Slater determinant to give excited state. Introduces an error of 0.1-0.2 eV into excited-state DMC energy.

- **Overall, DMC OG expected to be within about 0.5 eV of true gap.**

Optical-Gap Results
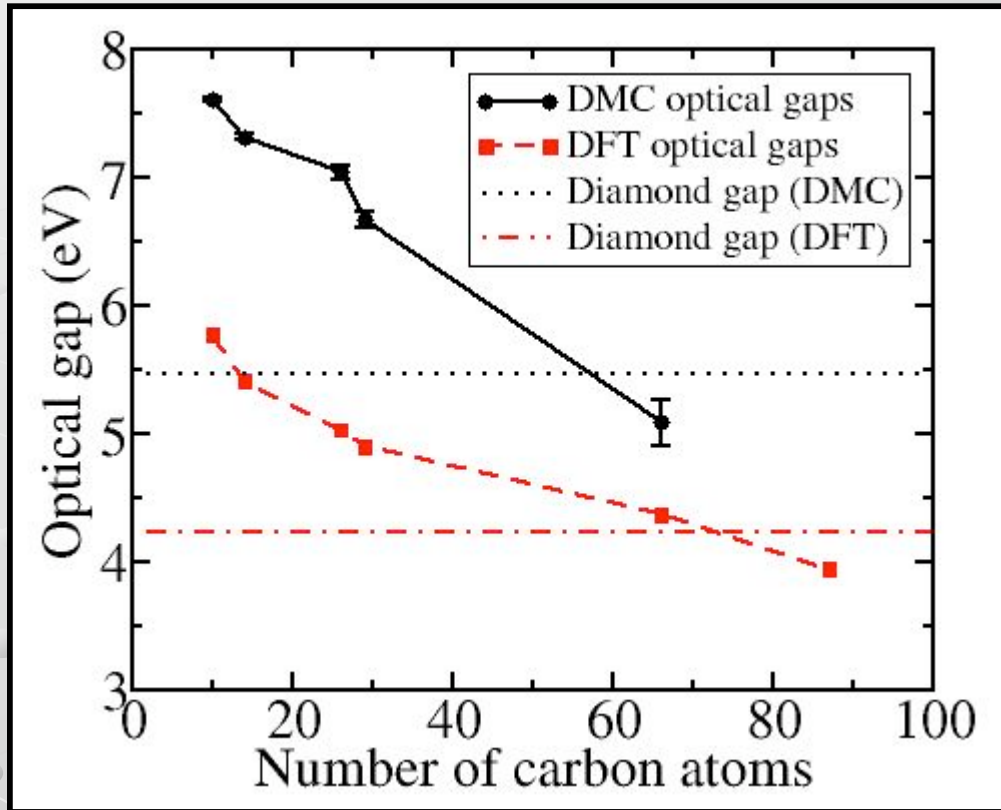
- DFT OGs are lower than DMC gaps by about 2 eV.
- DMC OGs decrease rapidly with cluster size, falling **below** bulk gap at a diameter of **1 nm**.

- Differs from OG behaviour of Si and Ge nanoparticles.
- DFT <u>qualitatively</u> (but not <u>quantitatively</u>) correct.

Nature of the HOMO and LUMO for Diamondoids (I)

$C_{29}H_{36}$
HOMO

$C_{29}H_{36}$
LUMO

- **HOMO** is located on the atoms and bonds **within** nanoparticle.
- **LUMO** is a diffuse **surface** state for diamondoids; not the case for Si or Ge clusters.
- HOMO evolves into the valence-band maximum as cluster size increases.
- LUMO does **not** evolve into the conduction-band minimum. It's like a surface or impurity state within the band gap.
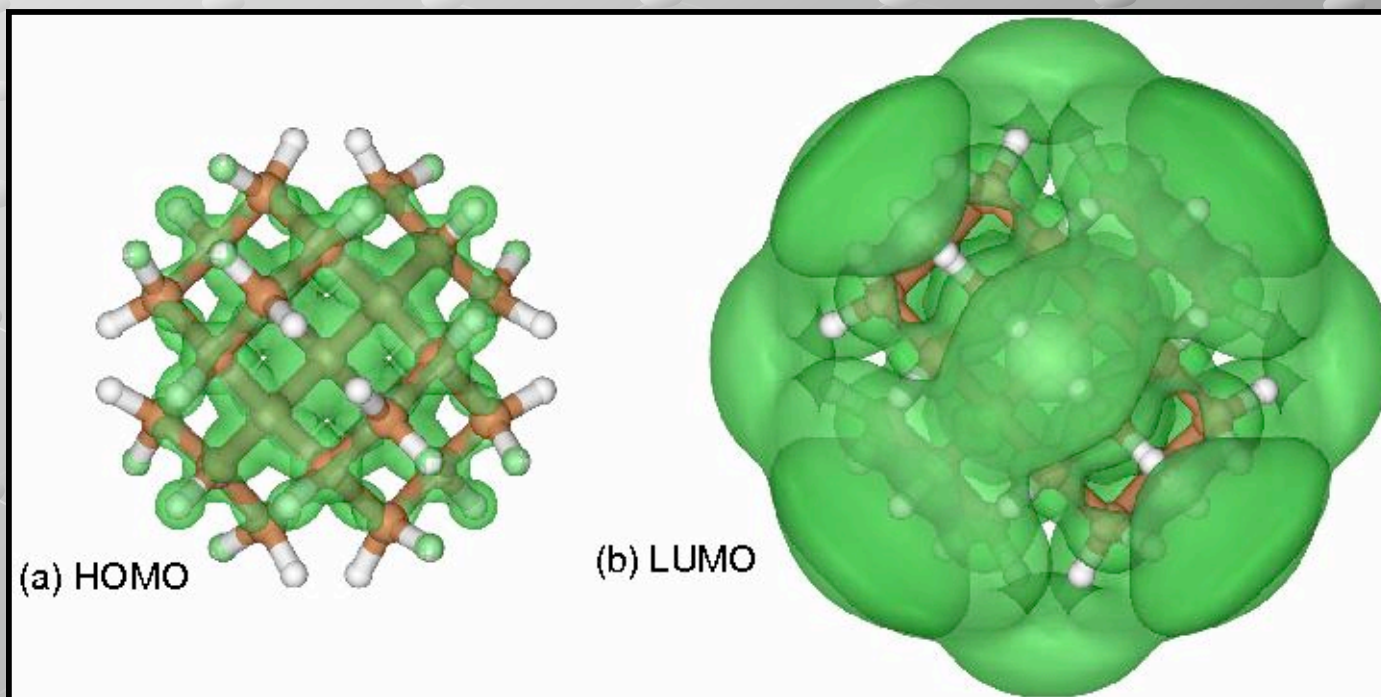- *LUMO is clearly not confined.*
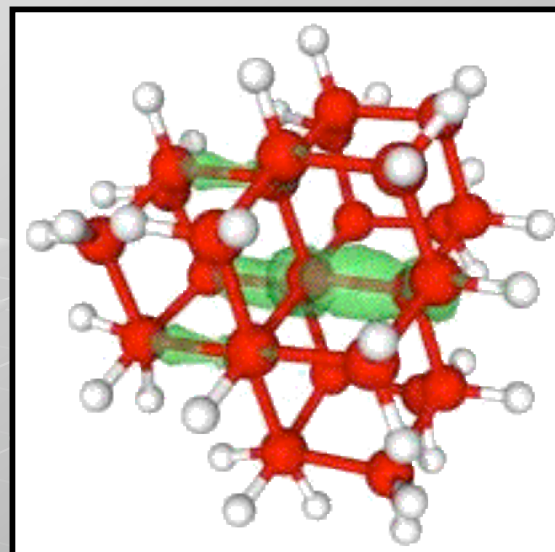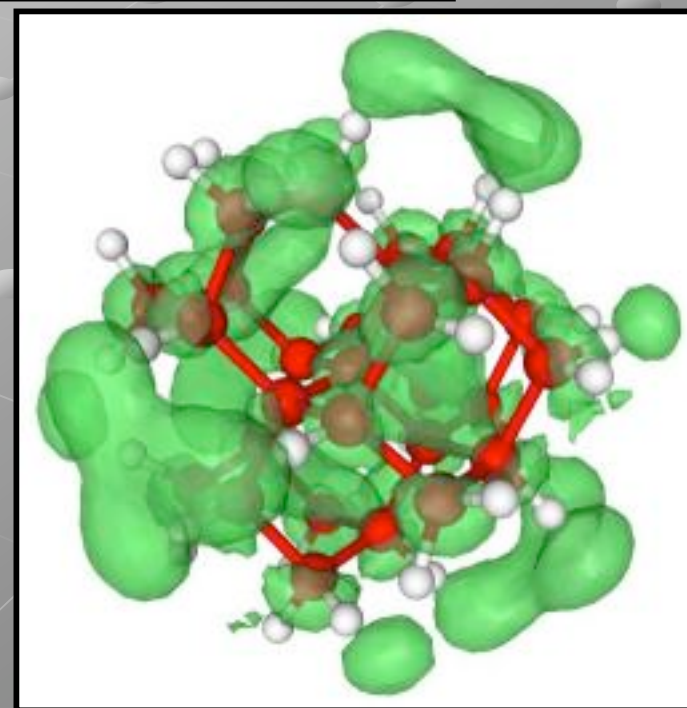
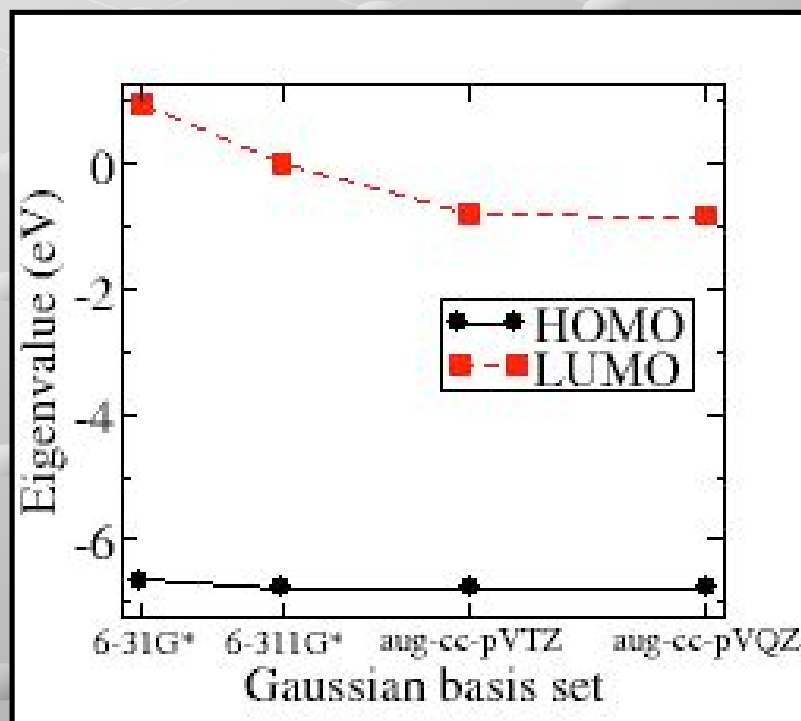# Nature of the HOMO and LUMO for Diamondoids (II)

- LUMO is essentially unbound, suggesting EA will be small or negative.

$C_{29}H_{36}$:

(a) HOMO   (b) LUMO

Nature of the HOMO and LUMO for Diamondoids (III)

- Disagreement between previous DFT results arose because one group used an inadequate Gaussian basis set to describe LUMO.

- LUMO artificially localised _ spurious QC effect.

Convergence of HOMO and LUMO eigenvalues with Gaussian basis set

Electron Affinities of Diamondoids

Molecule	DMC electron affinity (eV)	DMC ionisation potential (eV)
$C_{10}H_{16}$	_0.13(2)	10.15(3)
$C_{29}H_{36}$	_0.29(6)	7.63(5)

- DFT EAs and IPs agree with DMC results.
- The EAs are **negative**, as was hoped.
- *Diamondoids are therefore candidates for use as low-voltage electron emitters.*
- Other candidates exist (e.g. CVD diamonds & carbon nanotubes).

Recent Experimental Results

- Recent studies of small diamondoids [Willey *et al.*, PRL **95**, 113401; Willey *et al.*, PRB **74**, 205432; Yang *et al.*, Science **316**, 1460] have confirmed our predictions.

- LUMO energy is almost indep. of system size.

- Diamondoids have negative electron affinities and are good electron emitters.
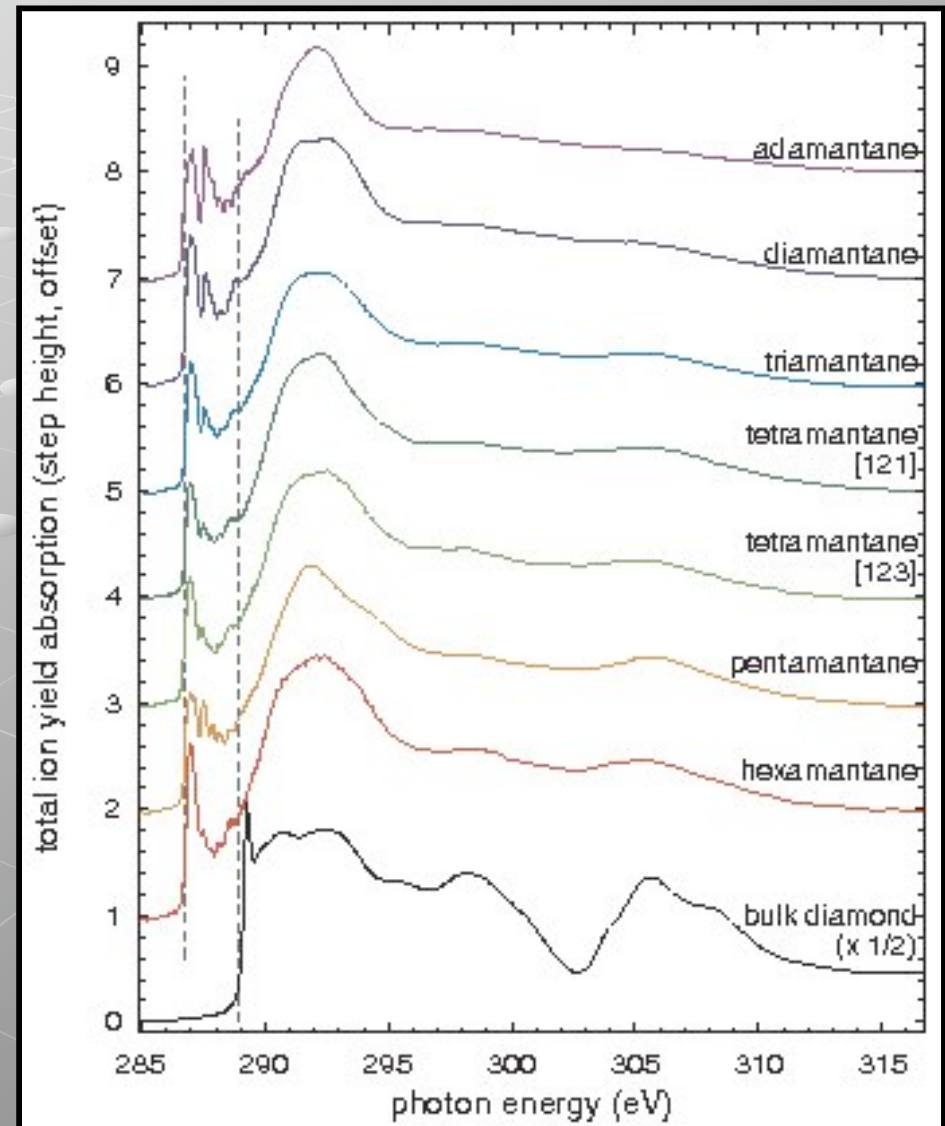
Ex Nihilo Structure Searching (I)

- Locating lowest-enthalpy structure within DFT is difficult (NP-hard).

- Structures are usually identified by either experiment, analogy with similar materials, clever methods for moving between local minima or chemical intuition.

- New, simple and surprisingly successful method: choose cell vectors randomly, then scale to give desired volume; choose atom coordinates randomly in cell; then relax all coordinates in DFT. Repeat many times.

- *Why has nobody tried this before?*

Ex Nihilo Structure Searching (II)

- *Although the number of local minima rises exponentially with system size, many systems of interest are sufficiently simple that this simple random-searching method works.*

- Continue generating random configurations until the relaxed structures with low enthalpies are generated several times.

- Where possible, look for known "marker" structures.

- Implications for QMC: new phases for several different materials are being predicted; where energy differences between phases are small, use QMC to decide between competing phases.

Silane at High Pressure

- Find lowest enthalpy structures with 2 SiH_4 units per cell (larger cells have too many degrees of freedom).

- Having found candidate phases, calculate enthalpies with greater accuracy.

- BCS suggests C2/c phase may be high-T superconductor.
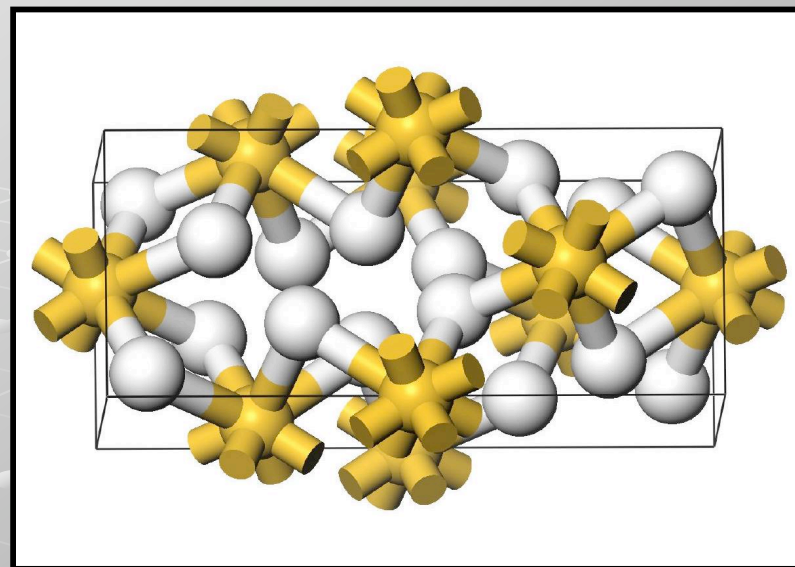
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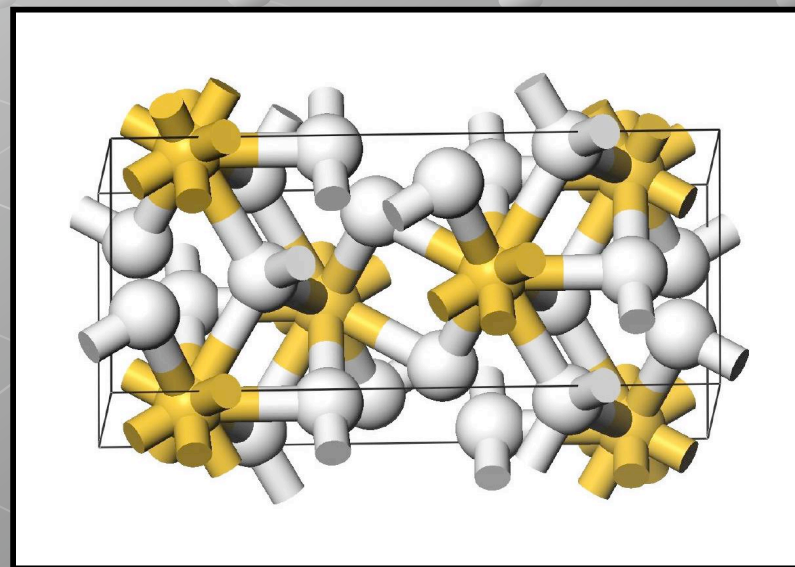
C2/c

Phase Diagram of Hydrogen (I)

- Hydrogen: most abundant element in universe and one of the most heavily studied.

- H atoms scatter X-rays weakly: *experiments are difficult*.

- Energy differences between phases are small and zero-point energy is important: *theory is difficult*.

- Random-structure searching has led to a major revision of the DFT phase diagram of hydrogen.

- ZPE is included within the harmonic approximation. Let's hope that anharmonic effects cancel between phases.

Phase Diagram of Hydrogen (II)
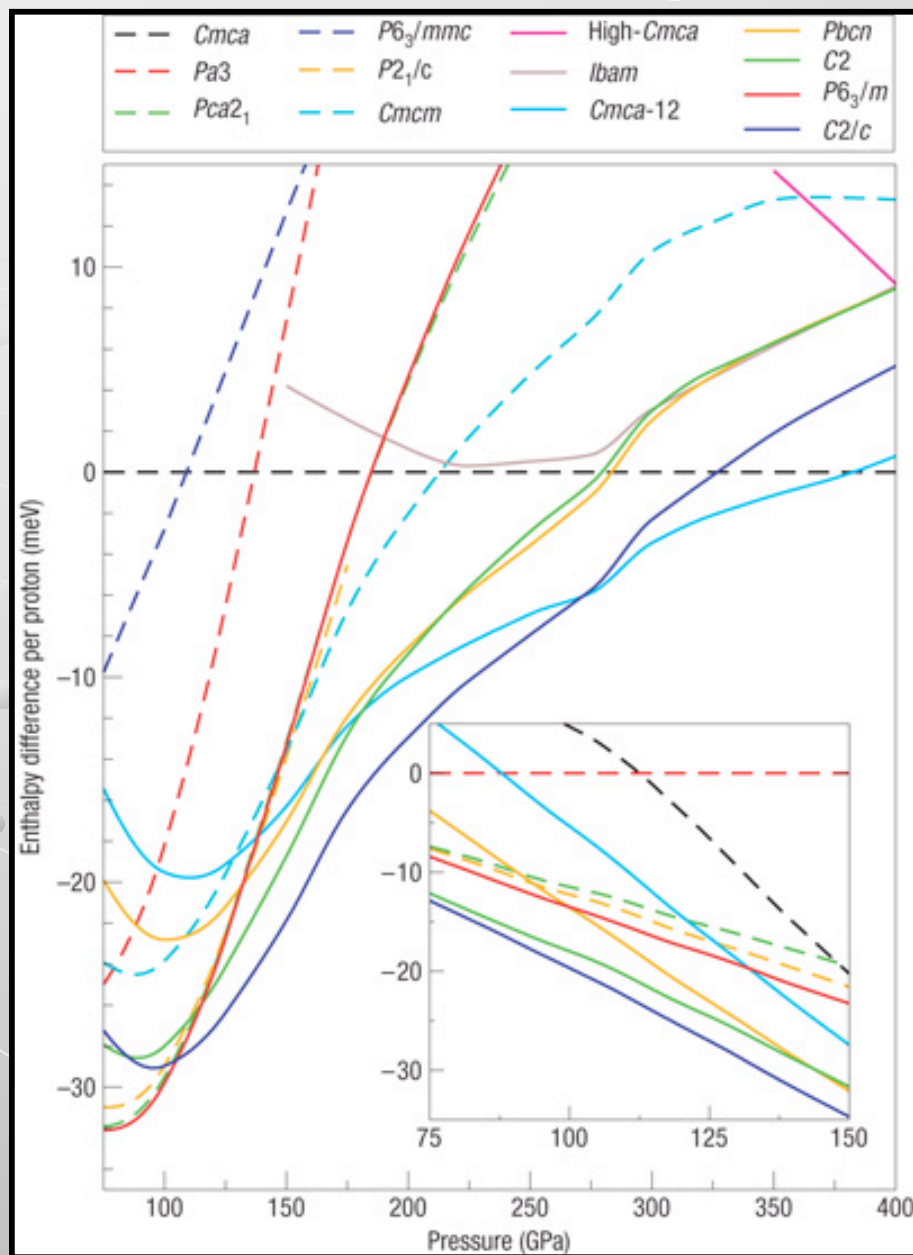
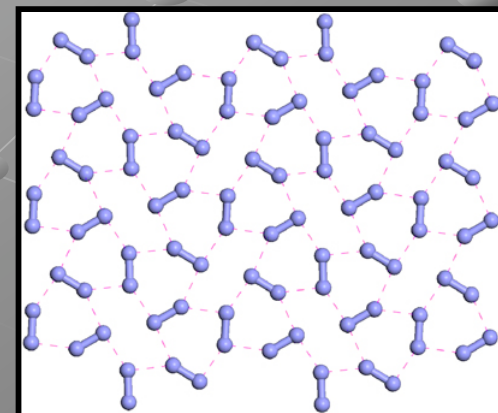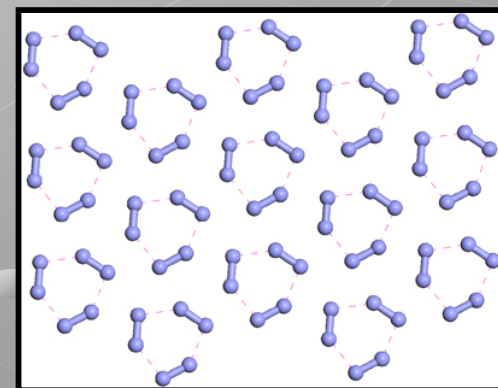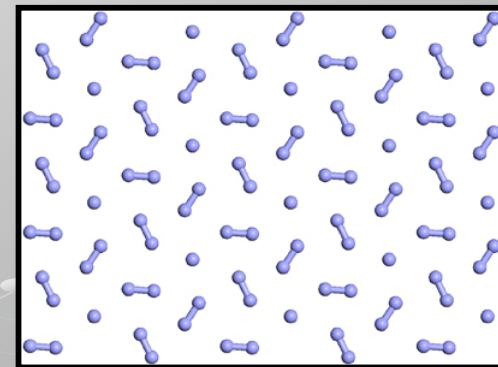Solid lines: *new phases*;

Dashed lines: *phases that have been considered previously*.

ZPE included in inset.

P6$_3$/m

C2/c

Cmca-12

Summary & Outlook

- *QMC provides quantitative accuracy where DFT cannot*: optical gaps, comparing structures/phases with different bonding, van der Waals forces,...

- *QMC can be used to study systems that are completely inaccessible to quantum chemistry methods*: solids, clusters, nanoparticles, ...

- Computer power is growing exponentially, QMC technology is advancing rapidly and QMC community is growing exponentially.