

# Quantum Monte Carlo Studies of Electronic Bandgaps

## Introduction

- Quantum Monte Carlo (QMC) methods offer an accurate means of probing both the **ground** and **excited state** properties of semiconductors from first-principles.
- In this series of projects, we have benchmarked the predictive power of QMC - and proven that the method can be successfully applied in **numerous** cases of interest.

## QMC Methods

- In Variational MC, trial many-e<sup>-</sup> wavefunctions  $\Psi_T(\mathbf{R})$  are formed from **Slater** determinants  $\mathcal{D}(\mathbf{R})$  and **Jastrow** factors  $e^{J(\mathbf{R})}$

$$\Psi_T(\mathbf{R}) = e^{J(\mathbf{R})} \mathcal{D}(\mathbf{R}). \quad (1)$$

The Jastrow exponent  $J$  depends on parameters, which are **optimised** by stochastic techniques.

- In Diffusion MC,  $|\Psi_T\rangle$  is evolved in imaginary time - with excited states dying away exponentially

$$|\Psi^{\text{DMC}}(\tau)\rangle = \sum_{i=0}^{\infty} c_i e^{-(\epsilon_i - E_T)\tau} |\Phi_i(0)\rangle. \quad (2)$$

- Excited state DMC is non-trivial, and energies are not always variational [1]. In our work, the **nodes** of  $\Psi_T(\mathbf{R})$  are fixed and the **topology** of the (fixed) nodal surface determines energies.

## Which Gap...?

- The **quasiparticle** gap is defined as

$$\Delta_{QP} = E_{N+1} + E_{N-1} - 2E_N, \quad (3)$$

- The **excitonic** gap is defined as

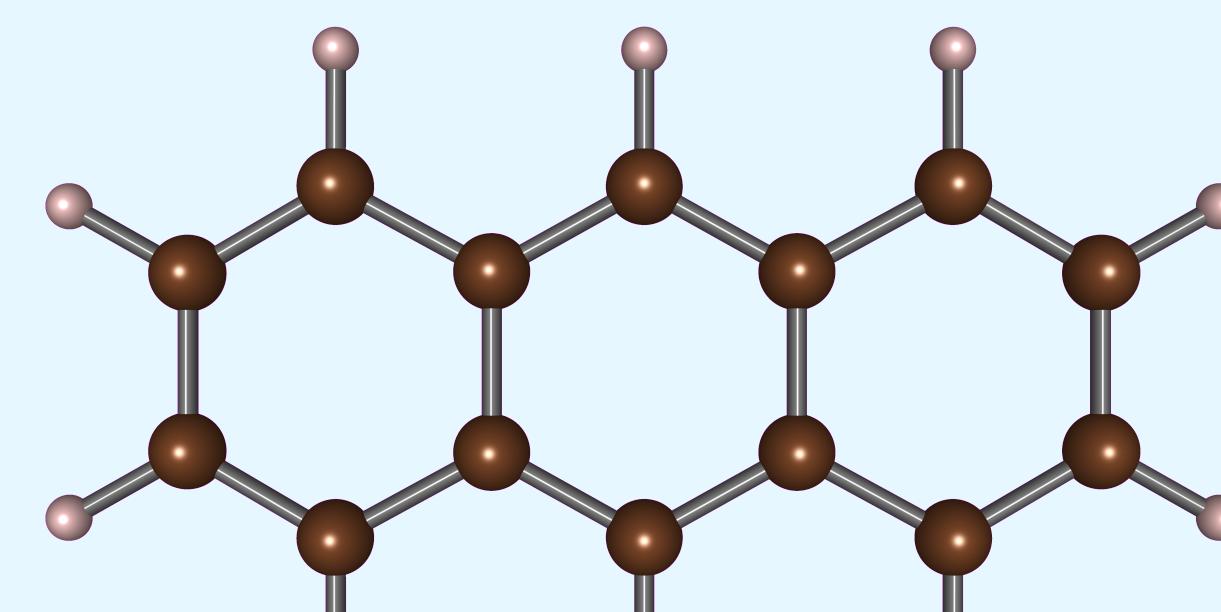
$$\Delta_{Ex} = E_N^+ - E_N, \quad (4)$$

- Their difference is the **exciton binding**,  $E_X = \Delta_{QP} - \Delta_{Ex}$ .

## Molecular Systems<sup>[3]</sup>

- We have calculated the QP gaps of several small molecules, incl. **Anthracene**, via QMC.

**Figure 1:** The (DFT-relaxed) structure of Anthracene, a molecule of interest in molecular electronics.



Method	Expt.	DFT-LDA	$G_0W_0^\star$	GW	DMC
$\Delta_{QP} / \text{eV}$	6.9	2.25	6.15-6.86	6.74	6.89(6)

**Table 1:** Experimental and theoretical  $\Delta_{QP}$  for Anthracene (GW from [2]).

\* These gaps are orbital dependant.

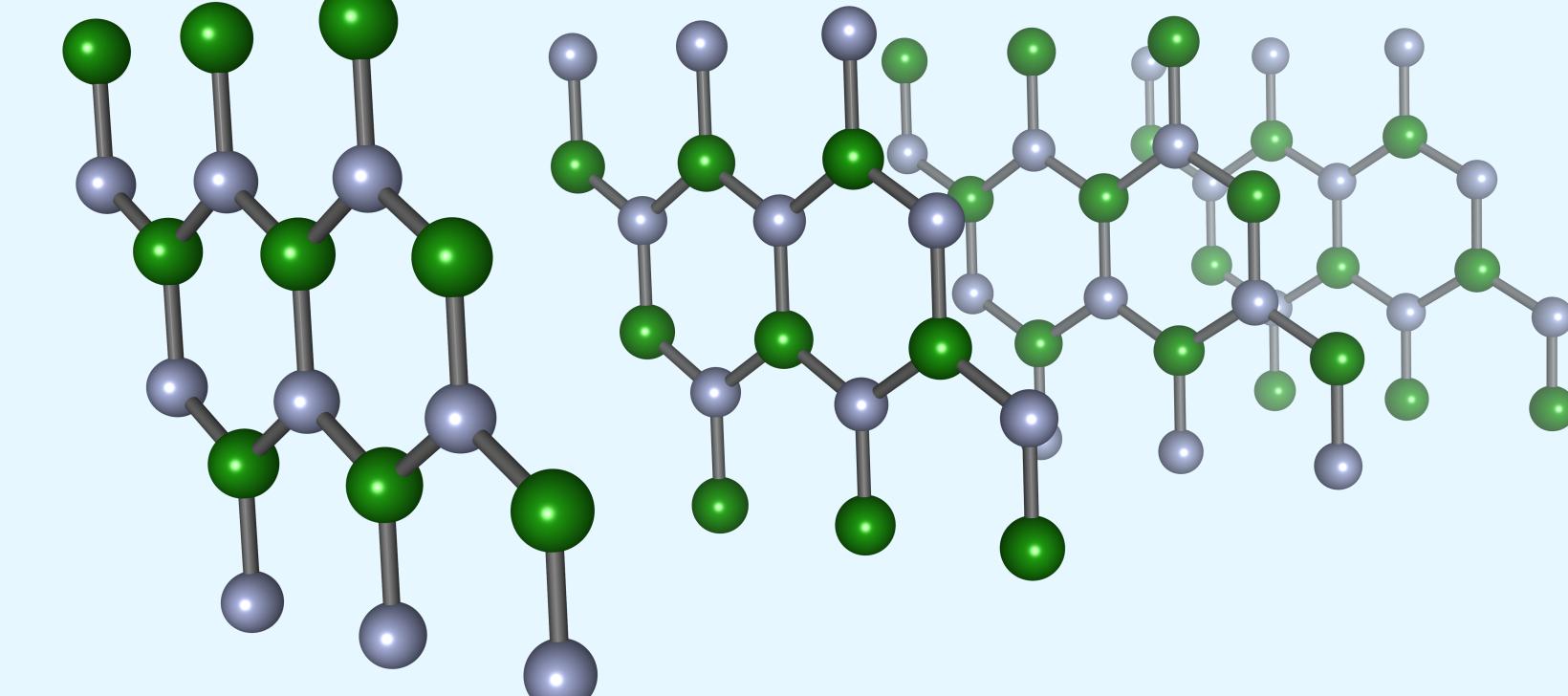
- Potential caveats:** Jahn-Teller effect, phonon renormalisation - each of these could affect our (static-nucleus) results.

## References

1. Foulkes, W. M. C., et al. PRB **60** (1999): 4558.
2. Blase, X., et al. PRB **83** (2011): 115103.
3. Hunt, R. J., Drummond, N. D. Manuscript in preparation, (2016).
4. Hunt, R. J., et al. Manuscript in preparation, (2016).

## Boron Nitride<sup>[4]</sup>

- We have calculated both the **excitonic** and **quasiparticle** gaps of bulk and monolayer hBN.



**Figure 2:** An example (288 e<sup>-</sup>) supercell used in our bulk simulations.

- Main Point:** Gaps are **strongly** enhanced in the monolayer

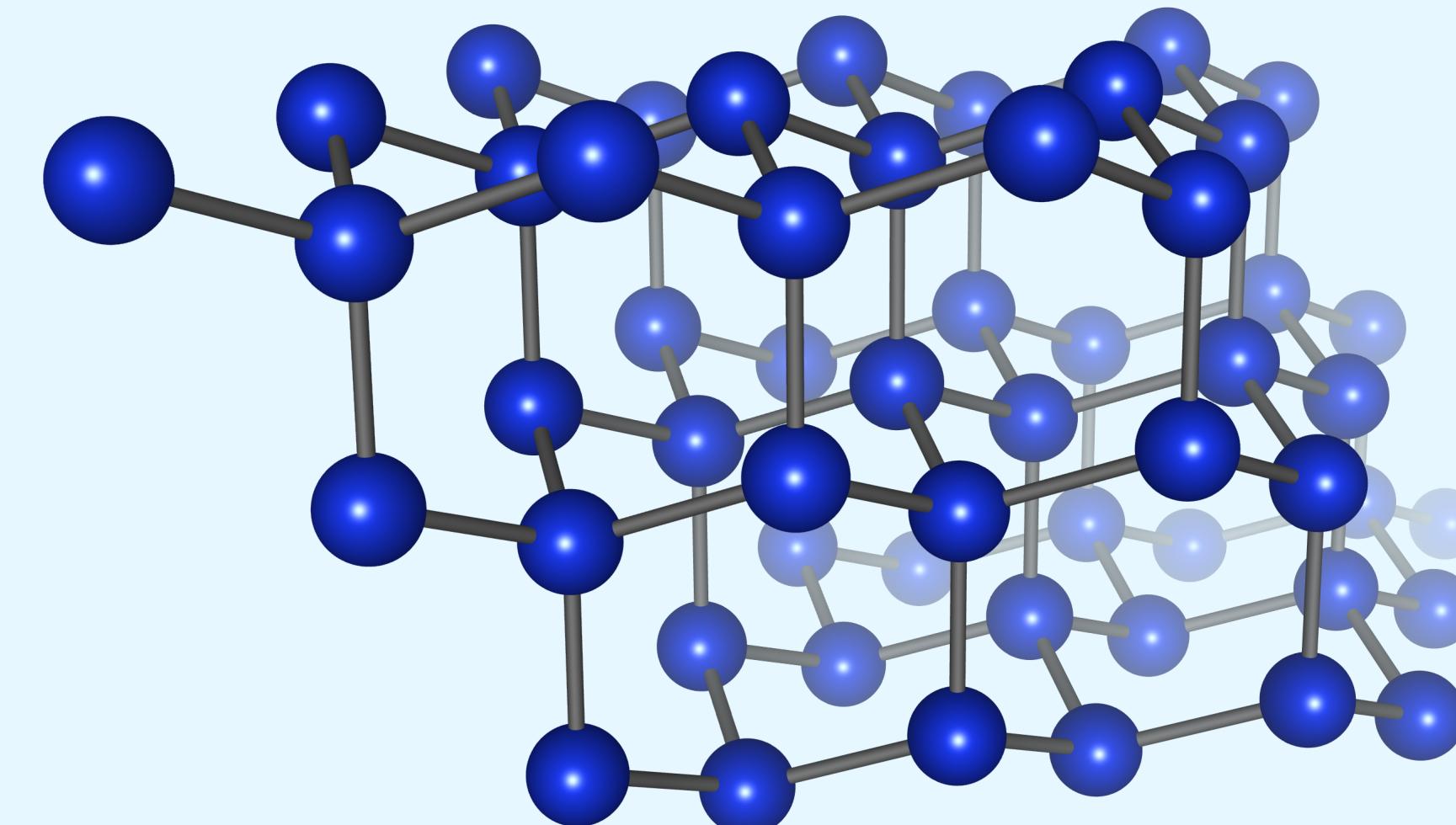
System →	Bulk	Monolayer
$\Delta_{Ex}(K_v \rightarrow K_c) / \text{eV}$	5.8(1)	8.7(3)
$\Delta_{Ex}(K_v \rightarrow \Gamma_c) / \text{eV}$	5.69(8)	7.5(3)

**Table 2:** A subset of our hBN results. The calculated monolayer exciton binding is 2.0(3) eV, with the bulk value to be determined.

- First QMC gap calculation for a **layered**, and a **2D** material.
- First analysis of **finite size effects** in QMC energy gaps.

## Bulk Silicon et al.<sup>[3]</sup>

- Silicon in the diamond structure is perhaps *the* most widely studied semiconductor.



**Figure 3:** An example (216 e<sup>-</sup>) supercell used in our simulations.

- Our ongoing simulations hope to act as thorough benchmarks of the DMC method as used in gap calculations.
- We have also opted to study cubic BN and  $\alpha$ -SiO<sub>2</sub>. Both have sizeable gaps, and cubic BN hosts a well-bound exciton.

## Conclusions

- QMC methods are robust and accurate, and may be used to calculate energy gaps for semiconductors of any dimensionality.
- QMC is also capable of describing systems bonded by a variety of means - including by van der Waals interactions.

## Acknowledgements

- QMC calculations were performed with the **CASINO** code, and DFT trial wavefunctions were obtained with **CASTEP**.
- All calculations were performed on the **HEC** facility at Lancaster and the **N8 HPC**.