

Ryan J. Hunt<sup>1</sup>, M. Szyniszewski<sup>1</sup>, G. I. Prayogo<sup>2</sup>, R. Maezono<sup>2</sup> & N. D. Drummond<sup>1</sup>  
<sup>1</sup>Department of Physics, Lancaster University, <sup>2</sup>JAIST, Japan

## Quantum Monte Carlo Methods

- Quantum Monte Carlo (QMC) methods offer an **accurate** means of solving the many-electron Schrödinger equation for **ground** and **excited** state properties from first principles.
- In Variational MC (VMC), expectation values of quantum mechanical operators are taken with respect to **trial wavefunctions** of arbitrary form. The **Slater-Jastrow** form is by far the most common

$$\Psi_{SJ} = \exp [\mathcal{J}_\alpha(\mathbf{R})] \cdot \mathcal{D}(\mathbf{R}).$$

- In Diffusion MC (DMC), trial wavefunctions are **projected forward in imaginary time**, such that "excited state" components die away

$$|\Psi(\tau)\rangle = \sum_{i=0}^{\infty} c_i \exp [-(\epsilon_i - E_T)\tau] |\Phi_i(0)\rangle.$$

- So how can we study excited states? In practice, we make the **fixed-node approximation**, which means that we only remove "excited states" w.r.t. a fixed **trial nodal surface**. These differ for excited states - and so we can extract excitation energies by taking **energy differences** obtained in calculations with different nodal surfaces.

## Atoms & Molecules

- Calculations on atomic and molecular systems do not suffer **finite size** and **vibrational effects** to the same extent as those on solids. They are ideal for the testing of our methods!

Table 1: Calculated ionization potentials of Ne at various levels of QMC theory, and with "exact non-relativistic" results from [1]. Mean absolute errors (MAE) are taken over all  $n$  values.

$n$	Exact NR IP	SJ-VMC	SJB-VMC	SJ-DMC	SJB-DMC
1	21.61333	22.08(2)	21.96(2)	21.72(1)	21.72(1)
2	40.99110	41.48(2)	41.39(2)	41.10(1)	41.06(1)
3	63.39913	63.44(2)	63.23(1)	63.35(2)	63.39(1)
4	97.29312	97.91(2)	97.78(1)	97.75(2)	97.72(1)
5	126.28846	126.85(2)	126.72(2)	126.85(1)	126.79(1)
6	157.80001	158.43(2)	158.30(1)	158.25(2)	158.34(1)
7	207.04137	204.48(2)	204.56(1)	205.04(2)	205.26(1)
8	238.78949	238.10(1)	238.49(1)	238.70(2)	238.79(1)
Avg. MAE		0.83%	0.67%	0.38%	0.34%

- For the Hydrogen atom, we have explicitly demonstrated **negative nodal error** [2] in an excited state calculation.

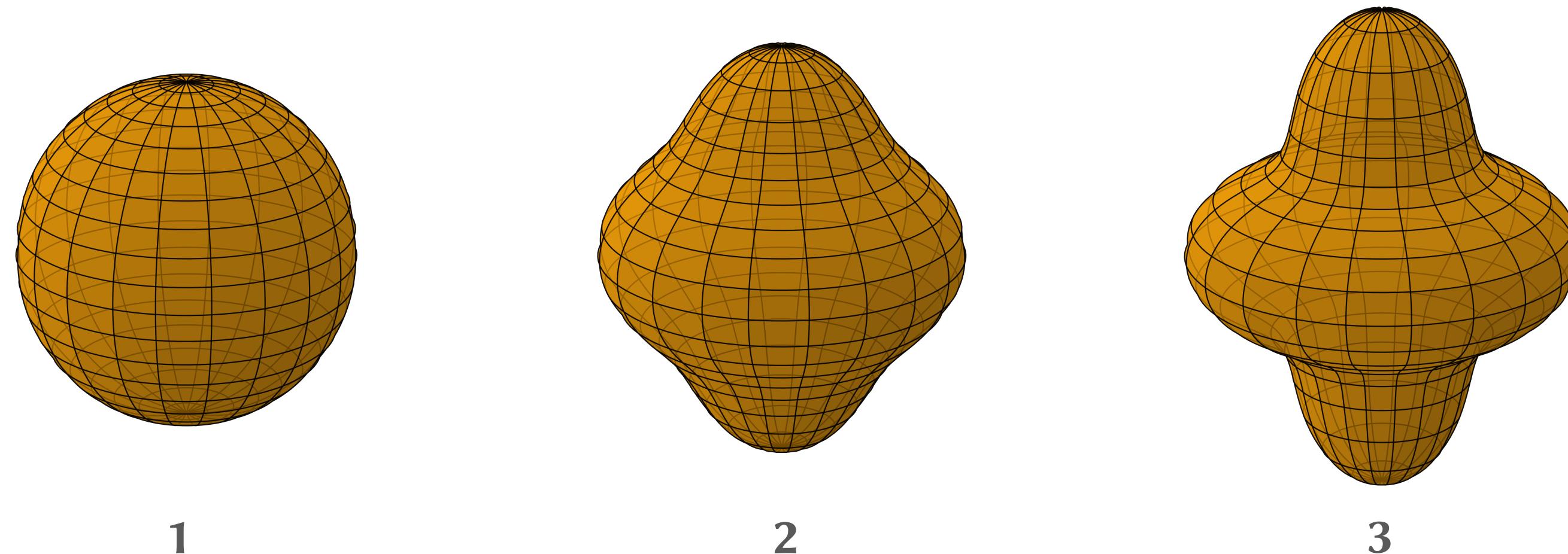


Figure 1: The nodal surfaces of a model excited state for the Hydrogen atom. Far left is the exact 2S state node (case 1), and from left to right we add increasingly stronger  $L=4$  perturbations, finding that  $E_1 > E_2 > E_3$ .

- We have also evaluated ionization potentials for various molecular systems, finding that DMC routinely obtains an accuracy with respect to experiment of <1%.

## References

- [1] Chakravorty, S. J., *et al.*, Phys. Rev. A **47**(5), 3649-3670 (1993).
- [2] Foulkes, W. M. C., *et al.*, Phys. Rev. B **60**(7), 4558 (1999).
- [3] Monserrat, B., *et al.*, Phys. Rev. B **87**(14), 144302 (2013).
- [4] Chang, E. K. *et al.*, Phys. Rev. Lett. **85**(12), 2613-2616 (2000).

## Energy Gaps in Phosphorene

- When we use QMC to perform excited state calculations for solids, we are interested in two main quantities, the **excitonic** (EX) and **quasiparticle** (QP) energy gaps

$$\Delta_{\text{QP}} = E(N+1) + E(N-1) - 2E(N) \stackrel{\text{Phos.}}{=} 4.8(4) \text{ eV}$$

$$\Delta_{\text{EX}} = E^*(N) - E(N) \stackrel{\text{Phos.}}{=} 2.6(2) \text{ eV}$$

- We find, additionally to known sources of error, there are residual **quasirandom** finite size errors that scale as  $L^{-1}$ , "L" being the linear size of the simulation cell. These are the **dominant** source of error in our gap calculations.

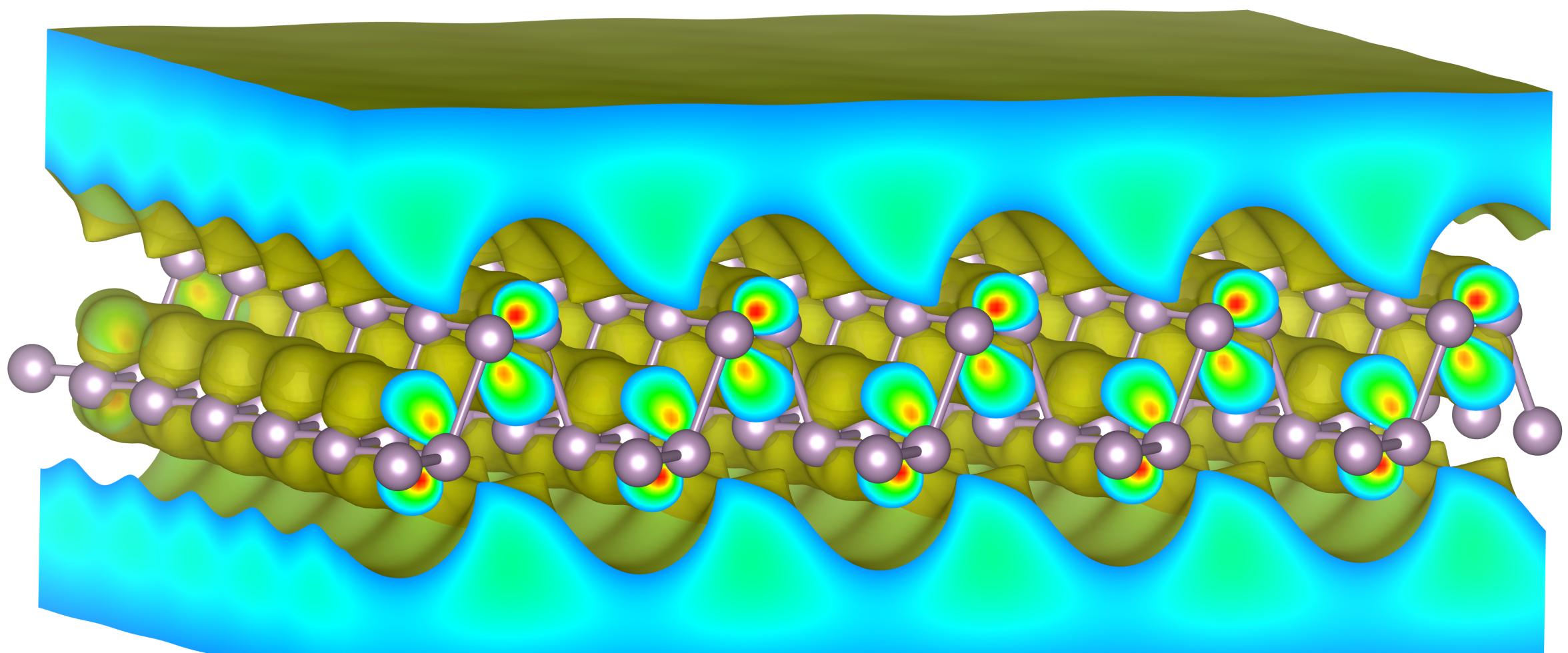


Figure 2: The DFT-PBE charge density associated with the conduction band in phosphorene at the  $\Gamma$  point. Here, the effective mass approximation applies, and carriers do not localise on particular atoms.

- Knowing the physical sources of finite size effects in these systems is critical if we are to correctly take our simulation data to the **thermodynamic limit** (as in our quoted values).
- The **exciton binding** can then be determined as

$$E_B^X = \Delta_{\text{QP}} - \Delta_{\text{EX}} \stackrel{\text{Phos.}}{=} 2.3(3) \text{ eV}$$

- NB: direct comparison to experiment for theoretical methods in which **phonons** have been neglected is **ill advised** [3].

## Bulk Solids

- In this work, we have studied the **excitonic energy gaps** and **exciton binding** energies of cubic (and hexagonal, in other work) Boron Nitride, Silicon dioxide, and Silicon.

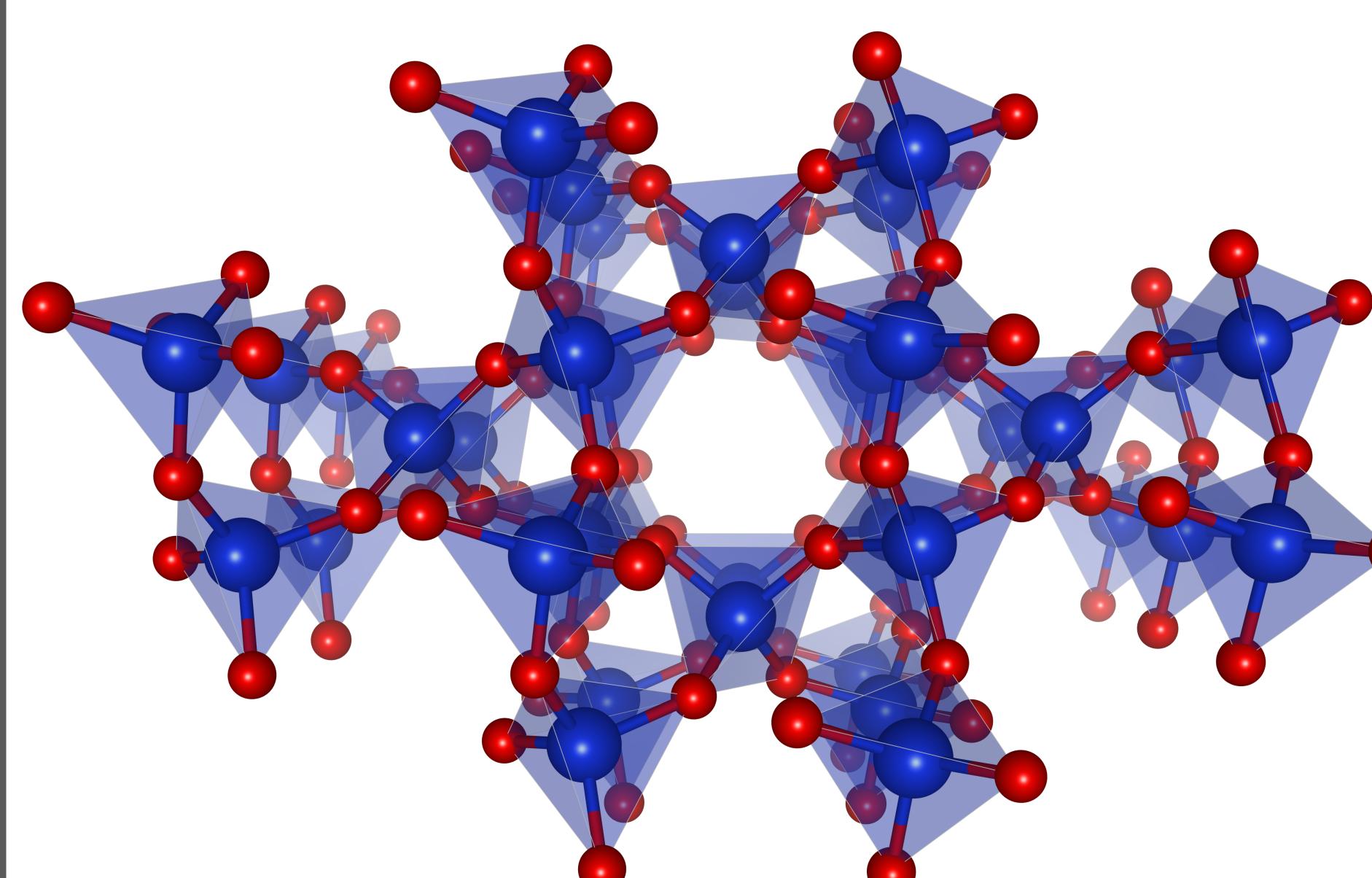


Figure 4:  $\alpha$ -SiO<sub>2</sub> is the stable SiO<sub>2</sub> polymorph under normal conditions. We specifically aim to uncover the properties of a putative excitonic state [4] residing at the  $\Gamma$  point of the Brillouin zone.

- Our ongoing (large-scale!) calculations aim to shed light on the **excitonic properties** of cubic BN and of SiO<sub>2</sub>, and to probe the nature of **finite-size effects** in QMC calculations on cubic materials.

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r.hunt4@lancaster.ac.uk | ryan.hunt@postgrad.manchester.ac.uk