

# Quantum Monte Carlo Methods in Solid State Physics

Ryan Hunt  
Physically Speaking  
20<sup>th</sup> June, 2017



# Outline

## The (Quantum) Many-Body Problem

Why is this relevant for solid state physics?

Why is this a hard problem?

## Quantum Monte Carlo Methods

Variational Monte Carlo

Diffusion Monte Carlo

## Examples

Charge complexes in semiconductor heterostructures

*Grown-up QMC:* 500+ quantum particles

# Solid State Physics

Solid State Physics is intrinsically many-body in nature.  
Solids comprise of *many bodies*.

“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.”

– Paul Dirac (1929).



# The Quantum Many-Body Problem

## Problem Statement

- ▶ Solve:

$$\hat{\mathcal{H}}|\Psi_\lambda\rangle = E_\lambda|\Psi_\lambda\rangle, \quad (1)$$

with

$$\begin{aligned} \hat{\mathcal{H}} = & -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ & - \cancel{\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2}^0 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}. \end{aligned} \quad (2)$$

for  $E_\lambda$  and  $|\Psi_\lambda\rangle$ . Hint: don't really try this.

# Why is this hard?

- ▶ Let  $\mathbf{R} = \{\mathbf{r}_1, \dots, \mathbf{r}_{N_e}\}$  be a set of  $e^-$  positions in  $3N_e$ -dimensions.
- ▶ **Curse of dimensionality:**  $\Psi(\mathbf{R})$  doesn't factorise, the # of antisymmetric combinations of basis functions<sup>1</sup> needed to express  $\Psi$  goes like  $e^{N_e}$ .



“I cannot foresee an advance in computer science which can minimize a quantity in a space of  $10^{150}$  dimensions.”  
– Walter Kohn, Nobel Lecture (1998).

---

<sup>1</sup>Also known as *Slater determinants*.

# Outline

## The (Quantum) Many-Body Problem

Why is this relevant for solid state physics?

Why is this a hard problem?

## Quantum Monte Carlo Methods

Variational Monte Carlo

Diffusion Monte Carlo

## Examples

Charge complexes in semiconductor heterostructures

*Grown-up QMC:* 500+ quantum particles

# Quantum Monte Carlo (QMC) Methods

- ▶ Solid State theory has taken a lot from “single-particle” theories.
- ▶ We’ve learned that these **fail** to describe certain important bits of physics (many-body effects, electronic correlation).<sup>2</sup>
- ▶ Quantum Monte Carlo methods are **strikingly different**.

---

<sup>2</sup>Major consequences include: misclassification of metals / semiconductors, systematic underestimation of energy gaps, systematic failure to describe dispersion interactions, and the inability to describe many-particle bound states.

# Variational MC

- ▶ In Variational MC, we evaluate various quantities, e.g.

$$E_T = \frac{\int d\mathbf{R} |\Psi_T(\mathbf{R})|^2 \overbrace{\left[ \Psi_T(\mathbf{R})^{-1} \hat{\mathcal{H}} \Psi_T(\mathbf{R}) \right]}^{\text{“Local Energy”}}}{\int d\mathbf{R} |\Psi_T(\mathbf{R})|^2} \quad (3)$$

with stochastic techniques (Metropolis algorithm to sample  $|\Psi_T|^2$ , Monte Carlo integration with subsequent samples).

- ▶ This allows us to evaluate the energies, variances, *etc* of **trial wavefunctions**,  $\Psi_T$ .

# VMC Trial Wavefunctions

- ▶ We obviously don't want to add combinations of determinants. Walter Kohn is still correct.
- ▶ What we can do, however, is build on a single Slater determinant,  $\mathcal{D}$ , and form

$$\Psi_{SJ} = \exp [\mathcal{J}_{\{\alpha\}}(\mathbf{R})] \cdot \mathcal{D}(\mathbf{R}), \quad (4)$$

with  $\mathcal{J}$  the **Jastrow exponent** (describes correlation, amongst other things).

- ▶ Aside: one of these “other things” is called the **Kato cusp condition** – an important property of exact many-body wavefunctions.

# Diffusion Monte Carlo

- ▶ I spent some time telling you about how single-particle theories fail, then I used a Slater determinant in VMC.  
**Why is this reasonable?**
- ▶ VMC is not the whole story. Whilst useful, it is usually done as a prelude to DMC.
- ▶ DMC is a **projector-based** method, relying on the general fact:<sup>3</sup>

$$|\Psi_{GS}\rangle = \lim_{\tau \rightarrow \infty} \exp(-\tau \hat{\mathcal{H}}) |\Psi_T\rangle. \quad (5)$$

---

<sup>3</sup>This is imaginary time evolution,  $t = i\tau$ .

# Diffusion Monte Carlo (II)

- Q** How do we do enact this projection? How do we *evolve* in imaginary time?
- A** An approximate (interacting) Green's function,

$$\Psi(\mathbf{R}, \tau + \Delta\tau) = \int G(\mathbf{R} \leftarrow \mathbf{R}', \Delta\tau) \Psi(\mathbf{R}', \tau) d\mathbf{R}'. \quad (6)$$

- ▶ We **don't represent / store**  $\Psi$ , we store configurations *distributed* as  $|\Psi|^2$ .<sup>4</sup>
- ▶ **Caveats:** Relies on interpretation of  $\Psi$  as a probability density - have to treat +/- regions separately!<sup>5</sup>

---

<sup>4</sup>This is how we get away with what Dr. Kohn rightly said was impossible!

<sup>5</sup>This is the *fixed-node approximation* - and is our way of avoiding the so-called "sign-problem" for fermions.

# Diffusion Monte Carlo (III)

Credit where credit is due...

“...as suggested by Fermi, the time-independent Schrödinger equation ...can be interpreted as describing the behaviour of a system of particles each of which performs a random walk, i.e., diffuses isotropically and at the same time is subject to a multiplication...”

– **Nicholas Metropolis**  
& Stanislaw Ulam (1949).



# Outline

## The (Quantum) Many-Body Problem

Why is this relevant for solid state physics?

Why is this a hard problem?

## Quantum Monte Carlo Methods

Variational Monte Carlo

Diffusion Monte Carlo

## Examples

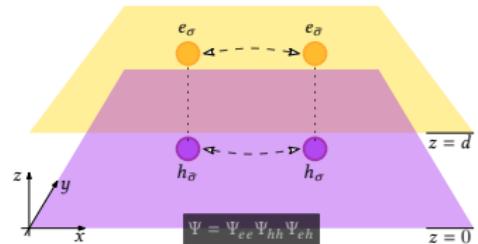
Charge complexes in semiconductor heterostructures

*Grown-up QMC:* 500+ quantum particles

# Trion Formation in Coupled Quantum Wells

w/ Oliver Witham, and Neil Drummond

- ▶ Experimentalists are interested in shining lasers on “real” CQWs, and looking for Bose-Einstein condensates of excitons.<sup>6</sup>
- ▶ They’ve yet to find anything conclusive: Why?



**Figure 1:** A schematic of the system in question, and the problem setup for the ground-state biexciton.

<sup>6</sup>A particularly good group who have studied this extensively is that of Ronen Rapaport. They shy away from calling what they have found a BEC, instead naming it a “correlated quantum liquid”.

# What have we done?

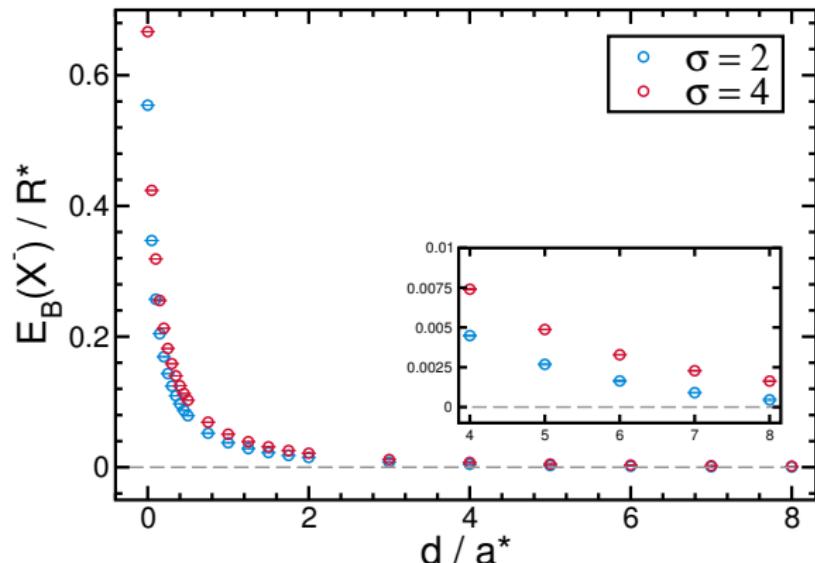
- ▶ Previously, the biexciton was thought to hinder the formation of a condensate. It is stable for very large  $d$  values.
- Q** Is it **safe** to assume that the charged trions are less stable than the neutral biexcitons?
- A** **Nope.**

## What have we done? (II)

- By solving the three-body Schrödinger equation for this system *exactly* in DMC, we have found,

$$d_{\text{crit}}(X^\pm) \sim 10 \cdot d_{\text{crit}}(XX) \quad (7)$$

**Figure 2:** Trion binding energies against  $d$  for two experimentally relevant  $e^-/h^+$  mass ratios,  $\sigma$ .



# *Grown-up QMC: 500+ quantum particles*

w/ Neil Drummond, Marcin Szyniszewski, and Ryo Maezono

- ▶ Modern Solid State Physics is now an arena in which we routinely simulate the properties of **large**, **realistic** systems.
- ▶ Traditionally, excited state properties have been very interesting: excitonic effects, band gaps, ...
- ▶ QMC is the most accurate means we have of studying these properties for remotely realistic systems: competitor methods scale as high powers of system size,<sup>7</sup> or get the **wrong answer**.<sup>8</sup>

---

<sup>7</sup>Often  $\mathcal{O}(N_e^{6-7})$ , vs. QMC - which is usually  $\mathcal{O}(N_e^3)$ .

<sup>8</sup>For reasons that we now largely understand: correlation effects are critical!

# What have we done?

- ▶ By using DMC for large supercells of solid systems, we have calculated:<sup>9</sup>
  - ▶ Quasiparticle and Excitonic energy gaps of **hexagonal BN**, cubic BN, diamond Si, SiO<sub>2</sub> ( $\alpha$ -quartz), phosphorene.
  - ▶ Charge-complex binding energies (excitons, and biexcitons) - *without* any over-simplifying approximations.
- ▶ We have found that such large-scale excited state calculation are possible, however, *they can bite.*

---

<sup>9</sup>or, are still calculating!

# Finite Size Effects

- In large-scale QMC simulations, we are limited by  $N_e$ . We therefore study systems of  $\mathcal{O}(10)$  unit cells.

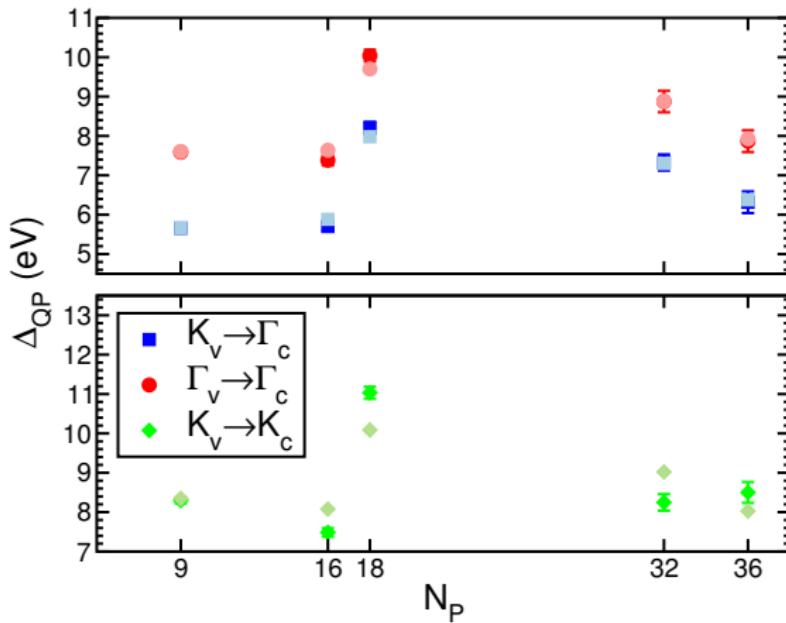
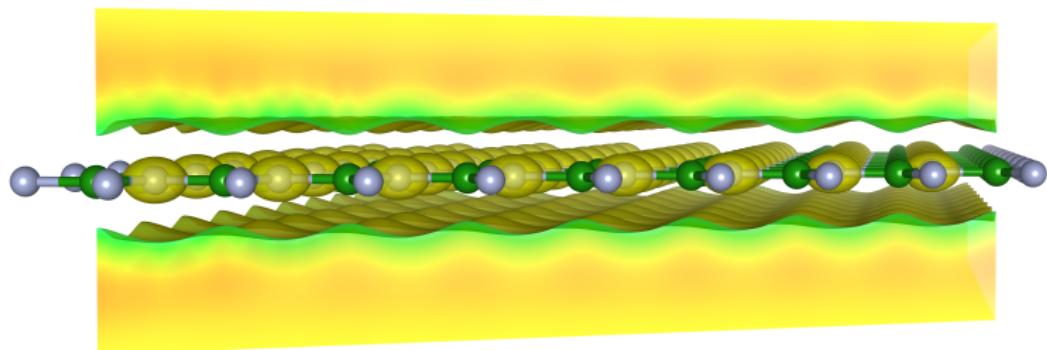


Figure 3: Quasiparticle energy gaps in bulk hBN vs. system size.

# Is all hope lost?

- ▶ Probably not - hBN is, realistically, a **worst-case** scenario. Why?
  - ▶ Localisation vs. delocalisation of quasiparticles.
  - ▶ Anisotropic dielectric screening.
  - ▶ Flat bands, with **unusual features**.



**Figure 4:** Band charge density isosurface of the (delocalised)  $\Gamma_c$  band in bulk hBN. This quasi-electron is almost *free*.

# Thank you all for listening

Incidentally, the QMC community is quite small. You all now know more this topic than most condensed matter physicists!