

# Modelling Charge Complexes in 2D Materials & Their Heterostructures

Northern Quantum Meeting II

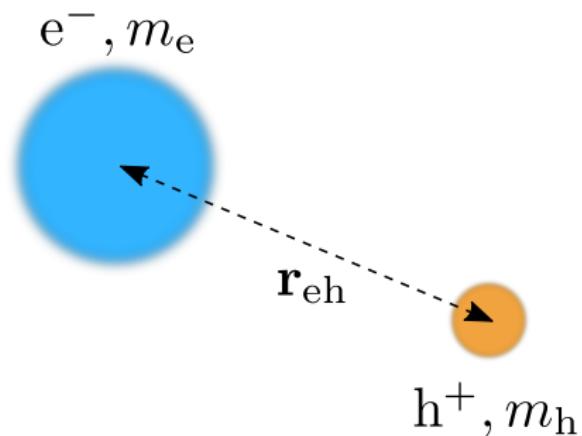
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15<sup>th</sup> December, 2017



# What are charge complexes, why study them?

- ▶ Charge-carrier complexes are **bound states** of two or more charges in a host material.
- ▶ Common example is an exciton.

**Figure 1:** Schematic view of an exciton - a bound state comprised of one electron and one hole.



- ▶ At low enough temperatures, charge complexes **dominate** the optical response of semiconductors.

# Effective mass approximation

- ▶ In conventional semiconductors,<sup>1</sup> the binding of excitons may be described in the **effective mass approximation**.
- ▶ The electronic band structures of these materials serve to supply effective masses for electrons and holes.
- ▶ We then solve Schrödinger equations analogous to those for the hydrogen atom:

$$\left[ -\sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{i < j} V(\mathbf{r}_{ij}) \right] \Psi(\{\mathbf{r}_i\}) = E \Psi(\{\mathbf{r}_i\}) \quad (1)$$

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<sup>1</sup>Take III-Vs as an explicit example.

# Electromagnetism in Flatland

- ▶ If we lived in flatland (bona fide 2D space), electromagnetism would be a **very different beast**.
- ▶ Poisson's equation would look the same, however, it's (two-dimensional) solution would predict a “logarithmic Coulomb potential” between pairs of point charges.<sup>2</sup>

$$\nabla^2 \phi(\mathbf{r}) = -\frac{\rho(\mathbf{r})}{\epsilon_0}. \quad (2)$$

$$V_q(\mathbf{r}) \propto -q \ln |\mathbf{r}|. \quad (3)$$

- ▶ But we don't live in flatland, so we **don't get this** ☹
- ▶ We **do** have to consider screening, however.

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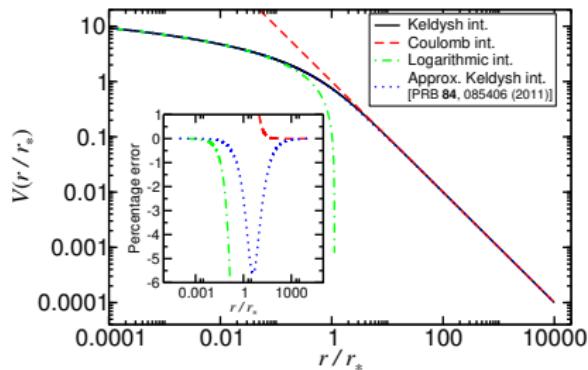
<sup>2</sup> Explanation for technical people: look at the inverse Fourier transform of the Green's function  $G(k) = 1/k^2$  in 2D and 3D. By power counting you can see that this is the case. EM in 1D is even stranger.

# The Keldysh Interaction

- Keldysh<sup>3</sup> showed that the effective interaction between charges in a polarisable 2D material has a special form

$$V_K(\mathbf{r}) = \frac{q_1 q_2}{8\epsilon_r \epsilon_0 r_*} \left[ H_0 \left( \frac{r}{r_*} \right) - Y_0 \left( \frac{r}{r_*} \right) \right], \quad (4)$$

with  $r_*$  a material parameter (usually **inferred** from *ab initio* DFT or *GW* calculations of  $\epsilon(\mathbf{q}, \omega)$ ).

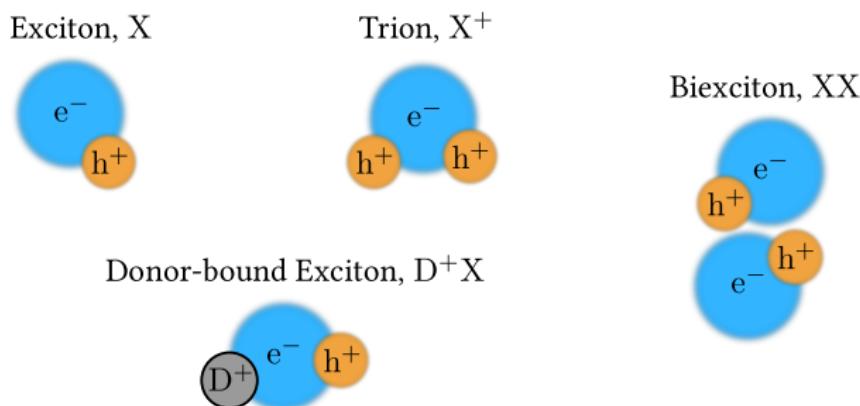


**Figure 2:** The Keldysh interaction.  
Notice we have recovered a  
log-dependence at short-range...

<sup>3</sup> L. V. Keldysh. In: JETP Letters 29 (1979).

# Complexes in Monolayers

- ▶ It turns out that the Keldysh interaction permits numerous bound states to exist, for typical  $r_*$  values ( $\mathcal{O}(50 \text{ \AA})$ , vacuum).



**Figure 3:** A few of the charge carrier complexes which can exist in 2D semiconductors.

# Our Model

& some of its limitations

- ▶ Taking monolayers as a goal, for now, we seek to solve

$$\left[ -\sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{i < j} V_k(\mathbf{r}_{ij}) \right] \Psi(\{\mathbf{r}_i\}) = E \Psi(\{\mathbf{r}_i\}), \quad (5)$$

for various complexes. We then compare total energies  $E$  in order to evaluate binding energies (experimentally relevant).

- ▶ We ignore exchange effects, but can add them back in as a **perturbative correction** (requires pair distribution functions, and unknown parameters...).
- ▶ We are assuming that both the E.M.A. holds, and that the Keldysh interaction is a good approximation for real materials.

# Solving the few-body problem: Quantum Monte Carlo

- ▶ We solve our few-body effective mass Schrödinger equations by using the variational and diffusion quantum Monte Carlo methods (VMC, DMC).
- ▶ In VMC, estimates of high-dimensional integrals are formed from (cleverly weighted) random sampling. **The results are as good as the trial wave function.**

$$E[|\Psi\rangle] = \frac{\langle\Psi|\hat{\mathcal{H}}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \int d\mathbf{R} \Pi(\mathbf{R}) E_L(\mathbf{R})$$
$$\Pi(\mathbf{R}) = \frac{|\Psi(\mathbf{R})|^2}{\int d\mathbf{R} |\Psi(\mathbf{R})|^2}, \quad E_L = \frac{\hat{\mathcal{H}}\Psi(\mathbf{R})}{\Psi(\mathbf{R})} \quad (6)$$

## Quantum Monte Carlo II - VMC

- ▶ VMC is usually only ever done as a prelude to DMC.
- ▶ In these models, we start with **educated guesses** at the trial wave function which are of **Jastrow** form

$$\Psi_T(\mathbf{R}) = \exp [\mathcal{J}_{\{\alpha\}}(\mathbf{R})] \quad (7)$$

where  $\{\alpha\}$  are a set of optimisable parameters.

- ▶ In practice, we vary the  $\{\alpha\}$  such that some property of the wave function is **optimal** (minimise E, variance of E, or MAD of E).

# Quantum Monte Carlo III - DMC

- ▶ In DMC, a trial function is propagated in imaginary time,<sup>4</sup> such that any excited state components it may contain are removed. The results are **independent of the trial function (in our cases), and offer improvement over VMC results.**
- ▶ We exploit (with  $t = i\tau$ )

$$\lim_{\tau \rightarrow \infty} \exp \left[ -\tau \hat{\mathcal{H}} \right] |\Psi_T\rangle \sim |\Psi_{GS}\rangle \quad (8)$$

- ▶ DMC is **exact for nodeless wave functions.**

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<sup>4</sup>Details not important - but we do this by interpreting the problem as a *statistical* one.

# Fairness: How else might one do this?

Other approaches for solving these kinds of problems exist. I won't talk about these, but for completeness I will mention them.

- ▶ *GW*-BSE: Solve the Bethe-Salpeter equation for the spectral function of a material including two-body effects.
- ▶ First-principles QMC: Solve the many-electron Schrödinger equation for the interacting system. Few people have ever actually done this (I'm one!).

There's a good book covering both of these by Martin, Reining, and Ceperley.<sup>5</sup>

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<sup>5</sup> R. M. Martin, L. Reining, and D. M. Ceperley. Cambridge University Press, 2016.

# Results: Monolayers

TMDC	DMC	$E_{X^-}^b$ (meV)		$E_{X^+}^b$ (meV)	
		Exp.	DMC	Exp.	DMC
$\text{MoS}_2$	35.0	40, 18.0(15), 43		34.9	
$\text{MoSe}_2$	34.5		30	34.4	30
$\text{WS}_2$	33.5	34, 36, 10–15, 30, 45		33.6	
$\text{WSe}_2$	29.6		30	29.6	30, 24

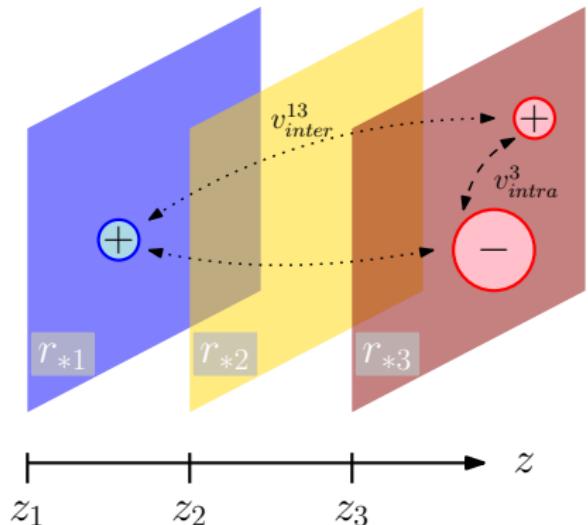
**Table 1:** Some trion binding energy results from our paper. Refs. and comparative results may be found therein.<sup>a</sup>

<sup>a</sup> E. Mostaani et al. In: Phys. Rev. B 96 (2017).

- We also enjoy good agreement with other theoretical studies, based on DMC, PIMC, SVM, heavy-hole approx., and variational calculations.

# Heterostructures: multilayer interactions

**Figure 4:** A tri-layer heterostructure of 2D semiconductors. There are  $N$  layer potentials, and  $N(N - 1)/2$  inter-layer potentials.



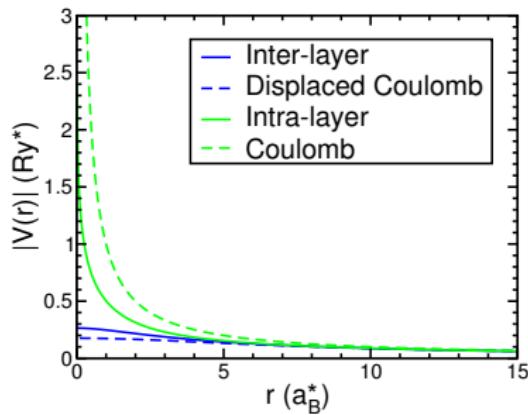
- ▶ Fourier components can be determined,<sup>6</sup> but real-space potentials obtained numerically (Hankel transform).

<sup>6</sup>Analytically, upto  $N = 4$ . Possibly higher  $N$  in special cases, or, as always, with symmetry.

# Bilayers of 2D semiconductors

How do charges interact in bilayers? More special functions?

**Figure 5:** Exact inter-layer and intra-layer interaction potentials versus distance. Parameters taken from an experimentally relevant MoSe<sub>2</sub>/WSe<sub>2</sub> geometry.



- ▶ The screened interactions start to get cumbersome:

$$v_{\text{intra}}(\mathbf{q}) = \frac{(1 + r_{*j}q) \exp(qD) - r_{*j}q \exp(-qD)}{2\bar{\epsilon}q [(1 + r_{*j}q)(1 + r_{*i}q) \exp(qD) - r_{*i}r_{*j}q^2 \exp(-qD)]} \quad (9)$$

# Bilayers of 2D semiconductors: Results

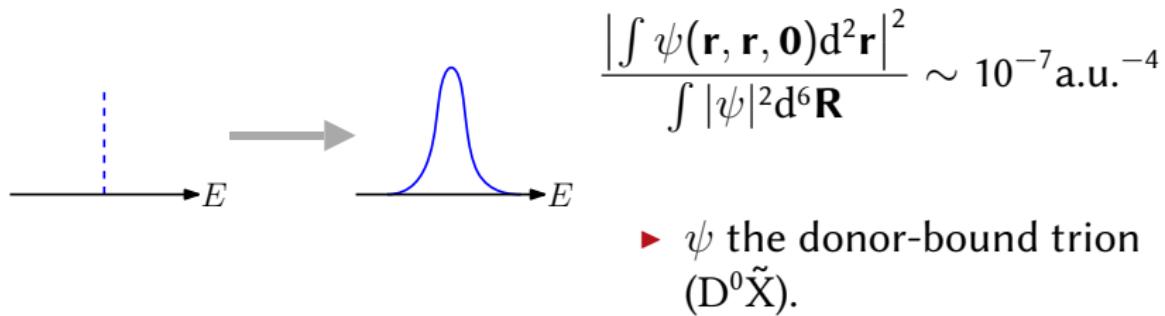
- ▶ We have studied various complexes in various dielectric environments (act to renormalize  $r_*$ ).
- ▶ Are able to explain positions and widths (see later) of three candidate peaks relevant to a recent experiment.

Complex	Binding Energy (meV)
$\tilde{X}$	103.95863(8)
$D_e^0$	163.247871(3)
$\tilde{X}e \rightarrow \tilde{X} + e$	4.226(4)
$D_e^0\tilde{X} \rightarrow D_e^0 + \tilde{X}$	11.41(3)

**Table 2:** Binding energies of various complexes of interest in an hBN/MoSe<sub>2</sub>/WSe<sub>2</sub>/hBN system.

# What else can QMC do for us?

- ▶ Whilst we're still on the topic of model systems, **is there anything useful QMC can do beyond calculate binding energies?**
- ▶ In collaboration with Mark Danovich, David Ruiz-Tijerina, and Volodya Fal'ko, we've<sup>7</sup> used QMC + pen-and-paper to form estimates of *lifetimes* in perturbation theory.



<sup>7</sup>Myself, Neil Drummond and Marcin Szyniszewski.

# First-principles QMC: Phosphorene

## First-Principles Excited State QMC

For a  $n \times m$  supercell of phosphorene unit cells, ground and (singlet) excited states could be modelled by:

$$\begin{aligned}\Psi(\mathbf{R}) &= \exp [\mathcal{J}(\mathbf{R})] \times \mathcal{D}_{\uparrow}(\mathbf{R}) \times \mathcal{D}_{\downarrow}(\mathbf{R}), \\ \Psi^*(\mathbf{R}) &= \exp [\mathcal{J}(\mathbf{R})] \times \mathcal{D}_{\uparrow}^*(\mathbf{R}) \times \mathcal{D}_{\downarrow}(\mathbf{R}).\end{aligned}\quad (10)$$

$\mathcal{D}^*$  is a Slater determinant of single-particle orbitals which has had one orbital replaced with an excited orbital.<sup>8</sup>

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<sup>8</sup>The important point in phosphorene is the  $\Gamma$  point...

# First-principles QMC: cont.

The *excitonic* and *quasiparticle* energy gaps are then:

$$\begin{aligned}\Delta_x &= E[\Psi_N^*] - E[\Psi_N] \\ \Delta_Q &= E[\Psi_{N+1}] + E[\Psi_{N-1}] - 2E[\Psi_N]\end{aligned}\quad (11)$$

But it's not<sup>9</sup> clear QMC can do this "cleanly"...

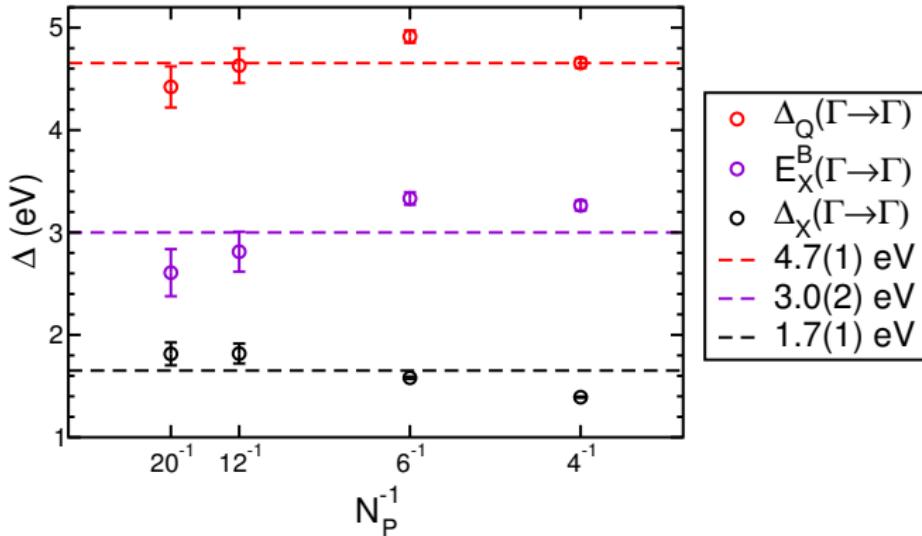
- ▶ Periodic BCs
  - ▶ Need to remove **finite-size** effects.
  - ▶ & balance resources...
- ▶ Variational Principles
  - ▶ Excitonic energies **don't** have them...
  - ▶ Quasiparticle energies **do**.

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<sup>9</sup>Or, *wasn't*.

# First-principles QMC: cont.

We find in phosphorene<sup>10</sup> that we **can** do this sensibly.



**Figure 6:** DMC quasiparticle and excitonic gaps for phosphorene. Their difference is the exciton binding energy,  $E_X^B$ .

<sup>10</sup>But have also studied hBN, Bulk hBN, Si,  $\text{SiO}_2$ , c-BN.

# Future (relevant) Research Avenues

- ▶ Electron-hole droplets in TMDCs? There's been recent interest in studying "electron-hole droplets".<sup>11</sup> These might show up in TMDC bilayers. I'd like to find out.<sup>12</sup>
- ▶ Electron gases in metallic TMDCs? Lots of literature on 2DEGs in context of III-Vs, but presumably metallic 2D materials will one day be of interest. Requires periodic Keldysh interaction.

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<sup>11</sup> L. V. Keldysh. In: Contemporary Physics 27.5 (1986), A. E. Almand-Hunter et al. In: Nature 506.7489 (2014).

<sup>12</sup>This requires "Ewaldising" the bilayer Keldysh interaction - i.e. making lattice sums of its  $1/r$  component absolutely convergent. I've recently done this for monolayers....

# Credits

C → charge-complexes (various)

X → first-principles excitations in QMC.

## Lancaster

- ▶ N. Drummond (C, X)
- ▶ M. Szyniszewski (C, X)
- ▶ O. Witham (C)
- ▶ E. Mostaani (C)

## UoM - NGI

- ▶ M. Danovich (C)
- ▶ D. Ruiz-Tijerina (C)
- ▶ V. Fal'ko (C, X)
- ▶ V. Zólyomi (X)

## Japan - JAIST

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- ▶ G. Prayogo (X)

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