

Modelling Charge Complexes in 2D Materials & Their Heterostructures

Graphene NOWNANO CDT Monthly Seminar

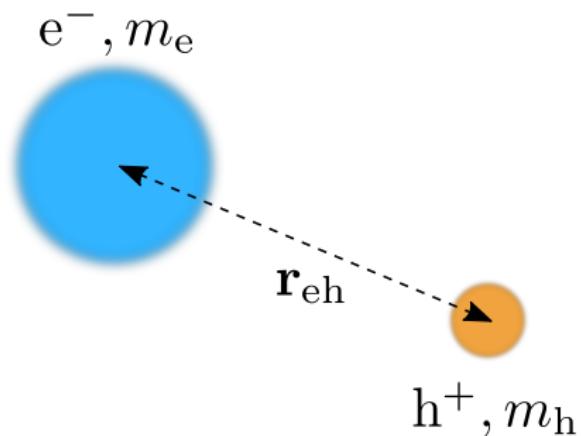
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What are charge complexes, why study them?

- ▶ 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,¹ 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:

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

¹Take 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.²

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

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

- ▶ But we don't live in flatland, so we **don't get this** ☹

² 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.

Reality: 3D space, and electrostatic screening

...or do we? In any realistic model, and in every experiment ever done on 2D materials, one other factor is very important: **screening**.

- ▶ Electrostatic screening is the suppression in electric field strength due to the presence of mobile charges.
- ▶ Screening is lessened for 2D materials that are taken from their parent compound - interactions between charges are stronger.

The Keldysh Interaction

- Keldysh³ showed that the effective interaction between charges in a 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 $\epsilon(\mathbf{q}, \omega)$).

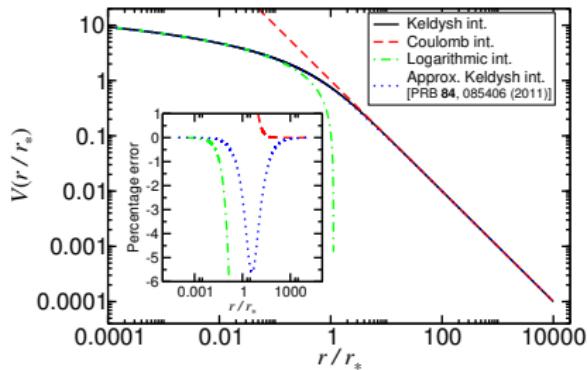


Figure 2: The Keldysh interaction.
Notice we have recovered a
log-dependence at short-range...

³ 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).

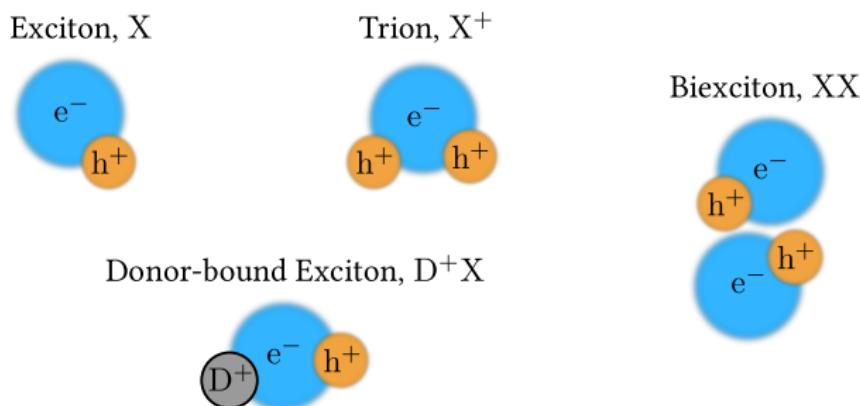


Figure 3: A few of the charge carrier complexes which can exist in 2D semiconductors.

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,⁴ 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.**

⁴Details 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.⁵

⁵ 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
MoS_2	35.0	40, 18.0(15), 43		34.9	
MoSe_2	34.5		30	34.4	30
WS_2	33.5	34, 36, 10–15, 30, 45		33.6	
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.^a

^a 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.

Results: Monolayers II

- ▶ Another aspect of this paper was the study of higher complexes. Surprisingly, we find that such systems are bound...

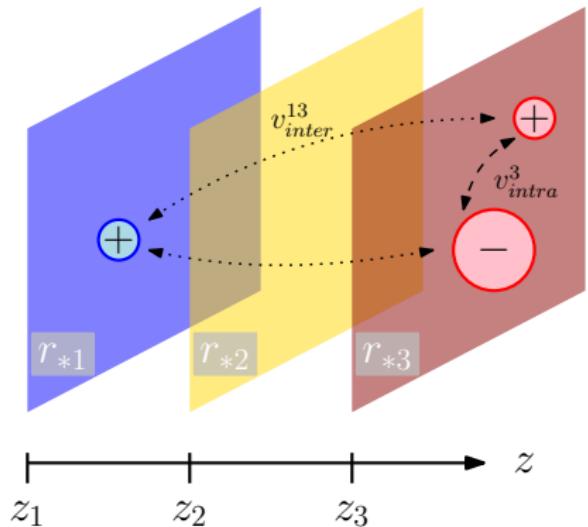
TMDC	Binding energy (meV)		
	XX^- (eehh)	D^-X (Deehh)	D^0XX (Deehh)
MoS_2	58.6(6)	84.4(4)	61.6(6)
MoSe_2	57.0(4)	57.9(2)	56.9(9)
WS_2	57.4(3)	59.2(4)	58.2(6)
WSe_2	52.5(7)	51.3(4)	51(1)

Table 2: Binding energies of BIG complexes in different TMDCs.
Note: these aren't necessarily PL peak positions.

- ▶ Biex. problem: Big things end up being called “biexcitons”?

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.



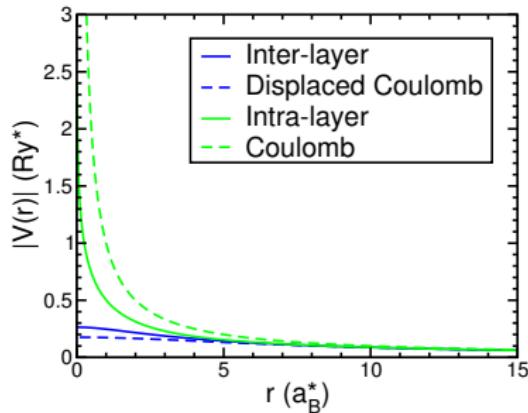
- ▶ Fourier components can be determined,⁶ but real-space potentials obtained numerically (Hankel transform).

⁶Analytically, 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 MoSe₂/WSe₂ geometry.



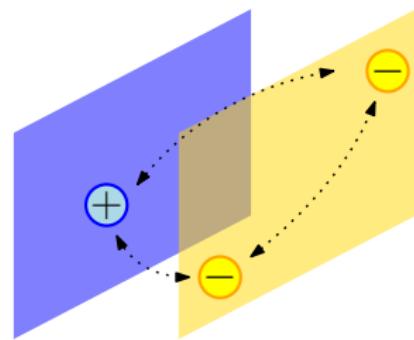
- ▶ The screened interactions start to get a little cumbersome here:

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

A Quick Tangent

- ▶ The interactions are qualitatively similar to the (displaced) Coulomb interactions. We expect similar physics to that in CQWs of III-Vs.

Figure 6: Schematic of an indirect trion in a coupled quantum well.



- ▶ These were originally studied as the “ideal testbed” for finding BECs of excitons. We’ve studied them before.⁷

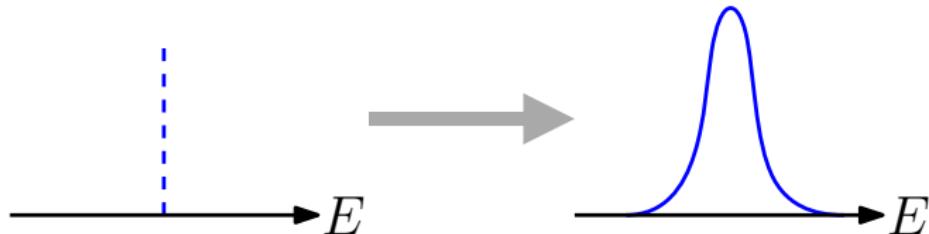
⁷ O. Witham, R. J. Hunt, and N. D. Drummond. In: [arXiv 1707.09427 \(submitted\)](#) (July 2017).

Bilayers: cont.

- ▶ Our work with bilayers is ongoing, but we find that we are capable of explaining at least one set of experimental results. [In fairness, many relevant experimental results now exist].
- ▶ We currently use an approximation to the bilayer interactions - but now have access to the full solution to Poisson's equation (i.e. we can do a little better?).
- ▶ We've also managed to generalise this to the case of N -layers. We may study higher heterostructures in future.

What else can QMC do for us?

- ▶ Could try to solve full many-body Schrödinger equation?
Is expensive. Failing that, **is there anything useful
QMC can do beyond calculate binding energies?**
- ▶ In collaboration with Mark Danovich, David Ruiz-Tijerina, and Volodya Fal'ko, we've⁸ used QMC + pen-and-paper to form estimates of *lifetimes* in perturbation theory.



⁸Myself, Neil Drummond and Marcin Szyniszewski.

Future (relevant) Research Avenues

- ▶ Excited states of few-body complexes: some of these could be bound, and (theoretically, I admit) show up in PL spectra. I'm interested in using the Faddeev equations and/or QMC to try to study these states.⁹
- ▶ e-h droplets in TMDCs? There's been recent interest in studying “electron-hole droplets”.¹⁰ These might show up in TMDC bilayerss. I'd like to find out.¹¹
- ▶ Possible multi-component electron gases in TMDCs?
Requires periodic Keldysh interaction.

⁹ L. D. Faddeev. In: Sov. Phys. JETP 12.5 (1961).

¹⁰ L. V. Keldysh. In: Contemporary Physics 27.5 (1986), A. E. Almand-Hunter et al. In: Nature 506.7489 (2014).

¹¹This requires “Ewaldising” the Keldysh interaction - i.e. making lattice sums of its $1/r$ component absolutely convergent. I'm doing this as I write the presentation, ask me how its going...

Thank you all for listening!