Diffusion Monte Carlo Study of Charge Carrier Complexes in Two-Dimensional Semiconductors

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Outline

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2. Effective interaction between charge carriers
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Charge carrier complexes in transition-metal dichalcogenides

- Large exciton binding energies in TMDCs
- Experimentalists observe lines in absorption spectra ascribed to trions and biexcitons\(^1\)
- There are bright and dark complexes, whether recombination is allowed by spin and momentum conservation
- Neglect indistinguishable carriers: they are weakly bound anyway

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![Diagram of exciton, trion, and biexciton complexes](image)

\(\Delta_{so}\) Difference in spin polarisation

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Effective interaction

- Coulomb interaction between charge carriers is greatly modified\(^{[2]}\) by the in-plane susceptibility of the material.
- Consider charge density \(\rho(x, y)\delta(z)\) in a 2D semiconductor. By using the Gauss’s law and assuming the polarisation field is only in-plane, the potential becomes:

\[
v(r) = \frac{1}{r} \frac{\pi}{2r_*} \left( H_0 \left(\frac{r}{r_*}\right) - Y_0 \left(\frac{r}{r_*}\right) \right), \quad r_* = 2\pi \chi_\perp
\]

**Short range:** Logarithmic interaction

\[
V(x) = -\log x/2 - \gamma
\]

**Long range:** Coulomb interaction

\[
V(x) = \frac{1}{x}
\]

Units

- Parameter $r_*$ related to susceptibility, can range from 0 to $\infty$ and has units of length. Let us measure it in the units of the excitonic Bohr radius $r_*/a_B^*$ is invariant under charge conjugation.
- Mass ratio $m_e/m_h$ is already dimensionless, but can range from 0 to $\infty$.
- Mapping into $[0,1]$ patch:
  
  $$\frac{r_*/a_B^*}{1 + r_*/a_B^*} = \frac{r_*}{r_* + a_B^*}, \quad \frac{m_e/m_h}{1 + m_e/m_h}$$

- **Exciton** binding energy should be measured in units that remove the mass dependence:
  
  $$\frac{e^2}{4\pi \varepsilon_0 a_B^*} = 2Ry^*$$

- **Trion and biexciton** binding energy
  
  $$\frac{e^2}{(4\pi \varepsilon_0 (r_* + a_B^*))}$$

  Goes to $e^2/4\pi \varepsilon_0 r_*$ for logarithmic limit and to $2Ry^*$ for Coulomb.
Limits for a negative trion

- **Logarithmic limit (large susceptibility)**
- **Coulomb limit (no susceptibility)**
- **Heavy electron limit**
  - Born-Oppenheimer approximation for a negative trion: separation of fixed particles must be determined
  - Square root behaviour in \( \frac{m_e}{m_h} \)

**Light electron limit**
- Negative trion resembles an \( H^- \) ion
- Linear in mass ratio

**Space of our parameters**

\[
\frac{m_e}{m_h} = 1 + \frac{m_e}{m_h} \left( r_*/(r_* + a_B) \right)
\]

**Square root behaviour** in mass ratio.
Details of Quantum Monte Carlo

- **CASINO**\(^3\) used for all our QMC calculations
- We start with a **trial wave function** of the Jastrow form:
  \[
  \psi = \exp J(\vec{R})
  \]
  where the Jastrow exponent contains pairwise sum of terms \(u_0\) and two- and three-body polynomial terms\(^4\)
  \[
  u_0(r) = \frac{c_1r^2 \log r + c_2r^2 + c_3r^3}{1 + c_4r^2}
  \]
- **Distinguishable** particles \(\to\) ground-state wave function is **nodeless**
- Use **variational MC** to optimise the free parameters in the w.f. by unreweighted variance and energy minimisation
- **Diffusion MC** calculations performed using time steps in the ratio 1:4 with corresponding configuration population 4:1 \(\to\) extrapolate linearly to zero time step and infinite population

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\[4\] Drummond et al., PRB 70, 235119 (2004); López Rios et al., PRE 86, 036703 (2012)
Exciton binding energy

\[ E_X = \frac{e^2}{4\pi\varepsilon_0 a_B^*} \left( \frac{r_*/a_B^*}{1 + r_*/a_B^*} \right) \]

Fit behaviour using results of [5]

Trion binding energy

Previous results:
- Logarithmic limit [5]
- Coulomb limit [6]
- $m_e = m_h$ [7]

\[
E_X = \frac{e^2}{4\pi\varepsilon_0} \left( r_\ast^2 + a_B^\ast \right)
\]

\[
\frac{m_e}{m_h} \quad 0.0 
0.2 
0.4 
0.6 
0.8 
1.0
\]

\[
\frac{r_\ast/a_B^\ast}{1 + r_\ast/a_B^\ast}
\]

Steep decrease

Comparison with experiments

<table>
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<th>Material</th>
<th>$\frac{m_e}{m_h}$</th>
<th>$r_*$ [Å]</th>
<th>Trion binding energy [meV]</th>
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Donor+exciton binding energy

\[ E_{D+x} [e^2 / 4\pi\varepsilon_0 (r^* + a_B^*)] \]

\[ \frac{r^*/a_B^*}{1 + r^*/a_B^*} \]

\[ \frac{m_e/m_h}{1 + m_e/m_h} \]

Biexciton

\[ E_{XX} \left[ \frac{e^2}{4\pi\varepsilon_0} \left( \frac{r_*}{a_B^*} \right) \right] \]

\[
\frac{m_e/m_h}{1 + m_e/m_h}
\]

\[
\frac{r_*/a_B^*}{1 + r_*/a_B^*}
\]
Contact interaction

- Energy penalty when charge carriers overlap
- First-order perturbation theory: correction to the energy is
  \[ A_{eh}\rho_{eh}(0) + A_{ee}\rho_{ee}(0) \]
- In our calculations we collected results for pair densities

- Determining \( A_{ij} \) by \textit{ab initio} calculations would be challenging, so we’ll leave that to experimentalists.
Contact pair density

\[ \rho_{eh} \left[ \frac{1}{a_B^2} \right] = \rho_X \left[ \frac{1}{a_B^2} \right] + \frac{\rho_X}{2} \left[ \frac{1}{a_B^2} \right] \]

\[ \frac{r_*/a_B^*}{1 + r_*/a_B^*} \]

\( m_e/m_h \)
- 0.5
- 1.0
- 2.0
- 5.0
Summary & Outlook

• Excitons, trions and biexcitons are crucial in optoelectronics of 2D semiconductors
  • Nonlocal screening effects modify the Coulomb interaction
• Using the Diffusion Monte Carlo approach we have calculated the binding energies of charge carrier complexes
• Contact pair densities extracted, to enable the analysis of the contact interactions in these systems

Future work:
• For biexcitons there’s only one type of the complex with distinguishable particles
• Modifying the trial wave function:
  • Slater determinant
  • W.f. is no longer nodeless
Thanks for listening!

Acknowledgements:

and

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