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

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Outline

1. Introduction to charge carrier complexes
2. Effective interaction between charge carriers
3. Units
4. Details of QMC
5. Results: binding energies
6. Comparison with experiments
7. Results: pair densities
8. Summary & outlook
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

\[\text{EXCITON} \quad \text{TRION} \quad \text{BIEXCITON}\]

\[\begin{align*}
\text{EXCITON} & : e^+ e^- \\
\text{TRION} & : \text{Positive } X^+ \\
\text{BIEXCITON} & : XX \\
\end{align*}\]

\[\begin{align*}
D^+ e^- & \\
A^- e^+ & \\
D^+ X & \\
D^+ A^- e^+ & \\
D^+ A^- e^- & \\
A^- X & \\
\ldots & \\
\end{align*}\]

\[\Delta_{\text{so}} \quad \Delta \]

\[\Delta \]

\[\Delta_{\text{so}} \]

Effective interaction

• Coulomb interaction between charge carriers is greatly modified\textsuperscript{[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:

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

Short range: Logarithmic interaction

$$V(x) = -\log x/2 - \gamma$$

Long range: Coulomb interaction

$$V(x) = 1/x$$

\textsuperscript{[2]} Keldysh, JETP Lett. 29, 658 (1979)
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
    \[
    e^2/(4\pi\varepsilon_0 (r_* + a_B^*))
    \]
    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)
- Heavy electron limit
  - Born-Oppenheimer approximation for a negative trion: separation of fixed particles must be determined
  - Square root behaviour in $m_e/m_h$
- Coulomb limit (no susceptibility)

Space of our parameters

- Light electron limit
  - Negative trion resembles an $H^-$ ion
  - Linear in mass ratio
Details of Quantum Monte Carlo

- CASINO\textsuperscript{[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\textsuperscript{[4]}
  \[ u_0(r) = \frac{c_1 r^2 \log r + c_2 r^2 + c_3 r^3}{1 + c_4 r^2} \]
- Distinguishable particles \( \rightarrow \) 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 \( \rightarrow \) extrapolate linearly to zero time step and infinite population

\textsuperscript{[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

Trion binding energy $E_X = \frac{e^2}{4\pi\epsilon_0} \left( \frac{r^*_e}{a_B^*} + \frac{1}{1 + r^*_e/a_B^*} \right)$

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

Steep decrease

## Comparison with experiments

<table>
<thead>
<tr>
<th>Material</th>
<th>$\frac{m_e}{m_h}$</th>
<th>$r_*$ [Å]</th>
<th>Trion binding energy [meV]</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>This work</td>
<td>Log</td>
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<td>$X^-$</td>
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<td></td>
<td></td>
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<tr>
<td>MoS2</td>
<td>0.7</td>
<td>41.5</td>
<td>35</td>
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<td>51.7</td>
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<tr>
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<td>60.0</td>
<td>26</td>
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<tr>
<td>WS2</td>
<td>0.6</td>
<td>37.9</td>
<td>36</td>
</tr>
<tr>
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<td>45.1</td>
<td>31</td>
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<tr>
<td>WTe2</td>
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<td>Phosphorene</td>
<td>1.1</td>
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<td>$X^+$</td>
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<td>131</td>
<td></td>
</tr>
</tbody>
</table>

$^\text{[8]}$ Berkelbach et al., PRB 88, 045318 (2013).
Donor+exciton binding energy

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

Biexciton

\[ E_{XX} \equiv \frac{e^2}{4\pi \varepsilon_0} \left( r_0 + a_B^* \right) \]

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

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

\[ \rho_{eh}[1/a_B^2] \]

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

\[ \rho_{eh} \left[ \frac{1}{a_B^*} \right] = \frac{\rho_X \left[ \frac{1}{a_B^*} \right]}{1 + \frac{r_*/a_B^*}{1 + \frac{r_*/a_B^*}{m_e/m_h}}} \]

Graph showing the relationship between contact pair density and \( \frac{r_*/a_B^*}{1 + \frac{r_*/a_B^*}{m_e/m_h}} \) for different values of \( m_e/m_h \): 0.5, 1.0, 2.0, and 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 for the funding!