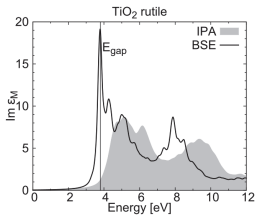
Optical spectroscopy with BSE in exciting

Olga Turkina, Christian Vorwerk, and Claudia Draxl
Humboldt-Universität zu Berlin

Introduction



O. Turkina, Master thesis

Optical Spectroscopy

- Independent particle approximation (IPA)

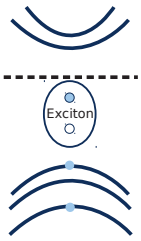
vs.

- Bethe-Salpeter equation (BSE) containing many-body effects

New features arise at the absorption onset that can not be described within IP picture:

Excitonic effects

Introduction



Optical Spectroscopy

- Exciton – bound state of excited electron and the hole left behind
- Exciton binding energy:

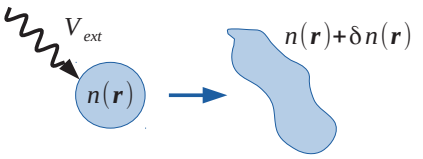
$$E_B = E^{\lambda} - E_{gap}$$

Electron-hole correlation

- Screened Coulomb interaction
- Exchange interaction

Linear Response

Perturbed density



$$\chi = \frac{\delta n}{\delta V_{ext}} \rightarrow \dots \rightarrow \epsilon_M(\omega) = 1 - v\bar{\chi}(\omega)$$

Density response function — Dielectric function

Green's function

$$\begin{aligned}\chi(1,2) &= -i\langle \Psi_0^N | \hat{\tilde{n}}(1)\hat{\tilde{n}}(2) | \Psi_0^N \rangle \\ &= i[G_2(1,2,1',2') - G_1(1,1')G_1(2,2')] \\ &= -iL(1,2;1',2')\end{aligned}$$

Two-particle correlation function

Matrix formulation

in many-body perturbation theory

$$L_{\alpha,\beta}(\omega) = L^0_{\alpha,\beta}(\omega) + \sum_{\gamma,\delta} L^0_{\alpha\gamma}(\omega)\Xi_{\gamma,\delta}L_{\delta\beta}(\omega)$$

Two-particle basis $\alpha = (vc\boldsymbol{k})$

Solution

$$\boldsymbol{L} = [(\boldsymbol{L^0}(\omega))^{-1} - \Xi]^{-1} = [\boldsymbol{H^{BSE}} - \omega]^{-1}$$

Bethe-Salpeter Equation (BSE)

G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).
S. Sagmeister and C. Draxl, Phys. Chem. Chem. Phys. **11**, 4451-4457 (2009).

BSE Hamiltonian

$$\sum_{v'c'\mathbf{k}'} H^{BSE}_{vc\mathbf{k},v'c'\mathbf{k}'} A^{\lambda}_{v'c'\mathbf{k}'} = E^{\lambda} A^{\lambda}_{vc\mathbf{k}}$$

$$t_\lambda = \sum_{vc\mathbf{k}} A^{\lambda}_{vc\mathbf{k}} \frac{< v\mathbf{k}|\hat{\mathbf{p}}|c\mathbf{k} >}{\epsilon_{v\mathbf{k}} - \epsilon_{v\mathbf{k}}}$$

Transition coefficients

$$\mathrm{Im}\,\epsilon_M(\omega) = \frac{8\pi^2}{\Omega}\sum_{\lambda}|t_\lambda|^2\delta(w - E^{\lambda})$$

Absorption spectrum

$$H^{BSE} = H^{diag} + 2\gamma_x H^x + \gamma_c H^c$$

Diagonal — Exchange — Direct

Matrix elements

$$H^{diag}_{vc\mathbf{k},v'c'\mathbf{k}'} = (\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}})\,\delta_{vv'}\,\delta_{cc'}\,\delta_{\mathbf{k}\mathbf{k}'}$$

Independent-particle transitions (IPA)

$$H^x_{vc\mathbf{k},v'c'\mathbf{k}'} = \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \sum_{\sigma} \psi_{c\mathbf{k}\sigma}(\mathbf{r})\,\psi^*_{v\mathbf{k}\sigma}(\mathbf{r})\,\bar{v}(\mathbf{r},\mathbf{r}') \sum_{\sigma'} \psi^*_{v'\mathbf{k}'\sigma'}(\mathbf{r}')\,\psi_{c'\mathbf{k}'\sigma'}(\mathbf{r}')$$

Repulsive exchange term with bare Coulomb potential

$$H^c_{vc\mathbf{k},v'c'\mathbf{k}'} = -\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \sum_{\sigma} \psi_{v\mathbf{k}\sigma}(\mathbf{r})\,\psi^*_{v'\mathbf{k}'\sigma}(\mathbf{r})\,W(\mathbf{r},\mathbf{r}') \sum_{\sigma'} \psi^*_{c\mathbf{k}\sigma'}(\mathbf{r}')\,\psi_{c'\mathbf{k}'\sigma'}(\mathbf{r}')$$

Attractive term with statically screened Coulomb potential

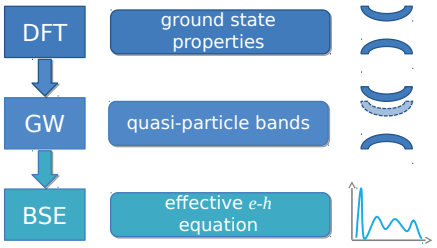
BSE approximation levels

$$H^{BSE} = H^{diag} + 2\gamma_x H^x + \gamma_c H^c$$

independent-particle transitions $\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}}$ — bare Coulomb potential $\bar{v}(\mathbf{r},\mathbf{r}')$ — screened Coulomb potential $W(\mathbf{r},\mathbf{r}')$

IPA	$H^{IPA} = H^{diag}$	only independent particle
RPA	$H^{RPA} = H^{diag} + H^x$	only exchange effects
triplet	$H^{triplet} = H^{diag} + H^c$	only screening effects
singlet	$H^{singlet} = H^{diag} + 2H^x + H^c$	exchange + screening effects

Workflow



Usage

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perform an excited-state calculation

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ngridk
ngridq

define the **k**- and **q**- mesh for the BSE calculation

vkloff

determines the shift of the **k**-mesh to improve the sampling of the Brillouin Zone by avoiding the high-symmetry points

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number of empty states available for the construction of the BSE Hamiltonian

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G-vector cutoff for plane wave matrix elements – **local field effects**:

$$M_{nm\mathbf{k}}(\mathbf{q}+\mathbf{G}) = \sum_{\sigma}\langle\psi_{n\mathbf{k}\sigma}|\exp(-i(\mathbf{q}+\mathbf{G}))|\psi_{m(\mathbf{k}+\mathbf{q})\sigma}\rangle$$

Cut-off condition:

$$|\mathbf{G}+\mathbf{q}| \leq \boxed{|\mathbf{G}+\mathbf{q}|_{\max}}$$

Input file

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Lorentzian broadening for the optical spectrum

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scissors operator mimicking the quasi-particle gap

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consider G_0W_0 quasi-particle enegies

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energy window on which the spectrum is calculated

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calculation of the screened Coulomb potential

$$W_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) = \epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) v_{\mathbf{G}'}(\mathbf{q})$$

Input file

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calculation of the screened Coulomb potential

$$W_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) = \epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) v_{\mathbf{G}'}(\mathbf{q})$$

$$\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) = \sum_{v\textcircled{c}\mathbf{k}'} \dots$$

Input file

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specific BSE parameters

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approximation level

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range of valence and conduction bands

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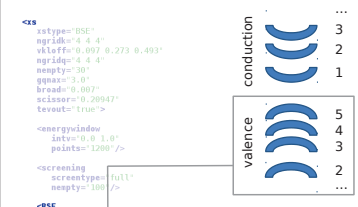

range of valence and conduction bands

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range of valence and conduction bands

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In `exciting carbon` **q**≠0 is possible only in TDDFT

definition of the **q**-points

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$$\sum_{v'c'\mathbf{k}'} H^{BSE}_{vc\mathbf{k},v'c'\mathbf{k}'} A^{\lambda}_{v'c'\mathbf{k}'} = E^{\lambda} A^{\lambda}_{vc\mathbf{k}}$$

store exciton eigenvectors for detailed exciton analysis

Exciton Analysis

BSE Hamiltonian $$\sum_{v'c'\mathbf{k}'} H^{BSE}_{vc\mathbf{k},v'c'\mathbf{k}'} A^{\lambda}_{v'c'\mathbf{k}'} = E^{\lambda} A^{\lambda}_{vc\mathbf{k}}$$

In real space - two-particle exciton wavefunction

$$\Psi^{\lambda}(\mathbf{r_e}, \mathbf{r_h}) = \sum_{vc\mathbf{k}} A^{\lambda}_{vc\mathbf{k}} \psi_{c\mathbf{k}}(\mathbf{r_e}) \psi^{*}_{v\mathbf{k}}(\mathbf{r_h})$$

In reciprocal space - exciton weights

$$w^{\lambda}_{v\mathbf{k}} = \sum_{c} |A^{\lambda}_{vc\mathbf{k}}|^2$$

$$w^{\lambda}_{c\mathbf{k}} = \sum_{v} |A^{\lambda}_{vc\mathbf{k}}|^2$$

Exciton Analysis

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Exciton Analysis

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               <origin coord=' -1.0  -1.0  -1.0'/>
               <point  coord='  2.0  -1.0  -1.0'/>
               <point  coord=' -1.0   2.0  -1.0'/>
               <point  coord=' -1.0  -1.0   2.0'/>
            </box>
         </plot3d>
      </electron>
   </excitonPlot>
</xs>
```

print exciton coefficients for reciprocal space analysis

Exciton Analysis

```
<xs ...>
   ...
   <plan>
      <doonly task='writebevec'/>
      <doonly task='excitonWavefunction'/>
   </plan>

   <writeexcitons HinNumberExcitons='1'
                  HaxNumberExcitons='5'/>

   <excitonPlot epstol='1d-2'>
      <exciton lambda='1' fix='hole'/>
      <hole>
         <plot1d>
            <path steps='1'>
               <point coord=' 0.52  0.52  0.52'/>
            </path>
         </plot1d>
      </hole>
      <electron>
         <plot3d>
            <box grid='40 40 40'>
               <origin coord=' -1.0  -1.0  -1.0'/>
               <point  coord='  2.0  -1.0  -1.0'/>
               <point  coord=' -1.0   2.0  -1.0'/>
               <point  coord=' -1.0  -1.0   2.0'/>
            </box>
         </plot3d>
      </electron>
   </excitonPlot>
</xs>
```

exciton wave function plot

Exciton Analysis

```
<xs ...>
   ...
   <plan>
      <doonly task='writebevec'/>
      <doonly task='excitonWavefunction'/>
   </plan>

   <writeexcitons HinNumberExcitons='1'
                  HaxNumberExcitons='5'/>

   <excitonPlot epstol='1d-2'>
      <exciton lambda='1' fix='hole'/>
      <hole>
         <plot1d>
            <path steps='1'>
               <point coord=' 0.52  0.52  0.52'/>
            </path>
         </plot1d>
      </hole>
      <electron>
         <plot3d>
            <box grid='40 40 40'>
               <origin coord=' -1.0  -1.0  -1.0'/>
               <point  coord='  2.0  -1.0  -1.0'/>
               <point  coord=' -1.0   2.0  -1.0'/>
               <point  coord=' -1.0  -1.0   2.0'/>
            </box>
         </plot3d>
      </electron>
   </excitonPlot>
</xs>
```

cut-off for exciton eigenvectors

Exciton Analysis

```
<xs ...>
   ...
   <plan>
      <doonly task='writebevec'/>
      <doonly task='excitonWavefunction'/>
   </plan>

   <writeexcitons HinNumberExcitons='1'
                  HaxNumberExcitons='5'/>

   <excitonPlot epstol='1d-2'>
      <exciton lambda='1' fix='hole'/>
      <hole>
         <plot1d>
            <path steps='1'>
               <point coord=' 0.52  0.52  0.52'/>
            </path>
         </plot1d>
      </hole>
      <electron>
         <plot3d>
            <box grid='40 40 40'>
               <origin coord=' -1.0  -1.0  -1.0'/>
               <point  coord='  2.0  -1.0  -1.0'/>
               <point  coord=' -1.0   2.0  -1.0'/>
               <point  coord=' -1.0  -1.0   2.0'/>
            </box>
         </plot3d>
      </electron>
   </excitonPlot>
</xs>
```

exciton index λ

Exciton Analysis

```
<xs ...>
   ...
   <plan>
      <doonly task='writebevec'/>
      <doonly task='excitonWavefunction'/>
   </plan>

   <writeexcitons HinNumberExcitons='1'
                  HaxNumberExcitons='5'/>

   <excitonPlot epstol='1d-2'>
      <exciton lambda='1' fix='hole'/>
      <hole>
         <plot1d>
            <path steps='1'>
               <point coord=' 0.52  0.52  0.52'/>
            </path>
         </plot1d>
      </hole>
      <electron>
         <plot3d>
            <box grid='40 40 40'>
               <origin coord=' -1.0  -1.0  -1.0'/>
               <point  coord='  2.0  -1.0  -1.0'/>
               <point  coord=' -1.0   2.0  -1.0'/>
               <point  coord=' -1.0  -1.0   2.0'/>
            </box>
         </plot3d>
      </electron>
   </excitonPlot>
</xs>
```

hole or electron position fixed

Exciton Analysis

```
<xs ...>
   ...
   <plan>
      <doonly task="writehdfvar"/>
      <doonly task="excitonWavefunction"/>
   </plan>

   <writeexcitons HinNumberExcitons="1"
                  HaxNumberExcitons="5"/>

   <excitonPlot epstol="1d-2">
      <exciton lambda="1" fix="hole"/>
      <hole>
         <plot1d>
            <path steps="1">
               <point coord=" 0.52  0.52  0.52"/>
            </path>
         </plot1d>
      </hole>
      <electron>
         <plot3d>
            <box grid="40 40 40">
               <origin coord=" -1.0  -1.0  -1.0"/>
               <point  coord="  2.0  -1.0  -1.0"/>
               <point  coord=" -1.0   2.0  -1.0"/>
               <point  coord=" -1.0  -1.0   2.0"/>
            </box>
         </plot3d>
      </electron>
   </excitonPlot>
</xs>
```

hole block

electron block

Exciton Analysis

```
<xs ...>
   ...
   <plan>
      <doonly task="writehdfvar"/>
      <doonly task="excitonWavefunction"/>
   </plan>

   <writeexcitons HinNumberExcitons="1"
                  HaxNumberExcitons="5"/>

   <excitonPlot epstol="1d-2">
      <exciton lambda="1" fix="hole"/>
      <hole>
         <plot1d>
            <path steps="1">
               <point coord=" 0.52  0.52  0.52"/>
            </path>
         </plot1d>
      </hole>
      <electron>
         <plot3d>
            <box grid="40 40 40">
               <origin coord=" -1.0  -1.0  -1.0"/>
               <point  coord="  2.0  -1.0  -1.0"/>
               <point  coord=" -1.0   2.0  -1.0"/>
               <point  coord=" -1.0  -1.0   2.0"/>
            </box>
         </plot3d>
      </electron>
   </excitonPlot>
</xs>
```

specify hole position:

it should be slightly shifted with respect to the atom position

Exciton Analysis

```
<xs ...>
   ...
   <plan>
      <doonly task="writehdfvar"/>
      <doonly task="excitonWavefunction"/>
   </plan>

   <writeexcitons HinNumberExcitons="1"
                  HaxNumberExcitons="5"/>

   <excitonPlot epstol="1d-2">
      <exciton lambda="1" fix="hole"/>
      <hole>
         <plot1d>
            <path steps="1">
               <point coord=" 0.52  0.52  0.52"/>
            </path>
         </plot1d>
      </hole>
      <electron>
         <plot3d>
            <box grid="40 40 40">
               <origin coord=" -1.0  -1.0  -1.0"/>
               <point  coord="  2.0  -1.0  -1.0"/>
               <point  coord=" -1.0   2.0  -1.0"/>
               <point  coord=" -1.0  -1.0   2.0"/>
            </box>
         </plot3d>
      </electron>
   </excitonPlot>
</xs>
```

define supercell for 3D plot of the electron distribution

Exciton Analysis

```
<xs ...>
   ...
   <plan>
      <doonly task="writehdfvar"/>
      <doonly task="excitonWavefunction"/>
   </plan>

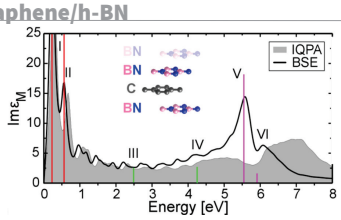
   <writeexcitons HinNumberExcitons="1"
                  HaxNumberExcitons="5"/>

   <excitonPlot epstol="1d-2">
      <exciton lambda="1" fix="hole"/>
      <hole>
         <plot1d>
            <path steps="1">
               <point coord=" 0.52  0.52  0.52"/>
            </path>
         </plot1d>
      </hole>
      <electron>
         <plot3d>
            <box grid="40 40 40">
               <origin coord=" -1.0  -1.0  -1.0"/>
               <point  coord="  2.0  -1.0  -1.0"/>
               <point  coord=" -1.0   2.0  -1.0"/>
               <point  coord=" -1.0  -1.0   2.0"/>
            </box>
         </plot3d>
      </electron>
   </excitonPlot>
</xs>
```

define the sampling of the supercell

Examples

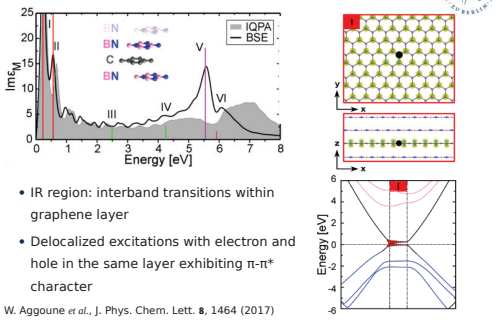
Graphene/h-BN



- Graphene/hexagonal boron nitride (h-BN) van der Waals heterostructure
- Quasi-particle gap of 250 meV opened in graphene through interaction with h-BN
- Three types of excitations can be identified

W. Aggoune *et al.*, J. Phys. Chem. Lett. **8**, 1464 (2017)

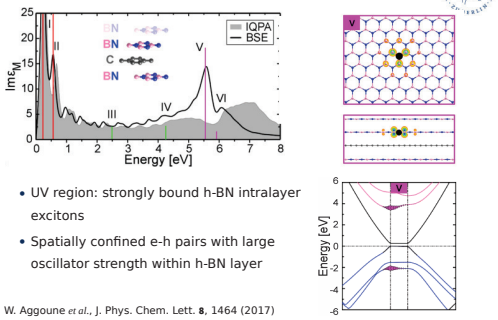
Graphene/h-BN



- IR region: interband transitions within graphene layer
- Delocalized excitations with electron and hole in the same layer exhibiting π-π* character

W. Aggoune *et al.*, J. Phys. Chem. Lett. **8**, 1464 (2017)

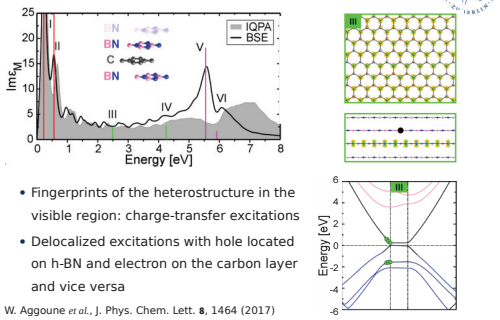
Graphene/h-BN



- UV region: strongly bound h-BN intralayer excitons
- Spatially confined e-h pairs with large oscillator strength within h-BN layer

W. Aggoune *et al.*, J. Phys. Chem. Lett. **8**, 1464 (2017)

Graphene/h-BN

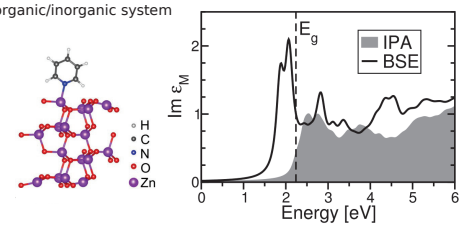


- Fingerprints of the heterostructure in the visible region: charge-transfer excitations
- Delocalized excitations with hole located on h-BN and electron on the carbon layer and vice versa

W. Aggoune *et al.*, J. Phys. Chem. Lett. **8**, 1464 (2017)

Py@ZnO(10-10)

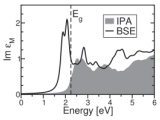
Prototypical hybrid organic/inorganic system

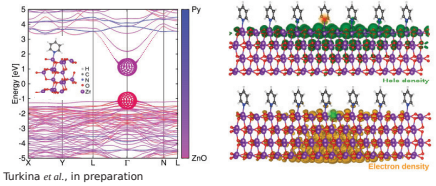


O. Turkina *et al.*, in preparation

Py@ZnO(10-10)

- Lowest bound exciton E_b= 0.4 eV at E = 1.8 eV with highest intensity
- Main contribution: transition from ZnO-like VBM to hybridized CBM

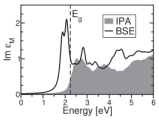


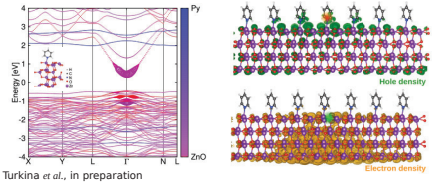


O. Turkina *et al.*, in preparation

Py@ZnO(10-10)

- Hybrid exciton at E = 2.5 eV
- Main contribution: transition from hybridized valence band to hybridized CBM at Γ

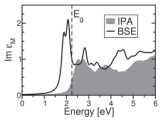


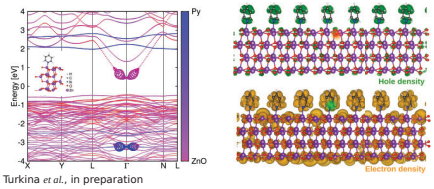


O. Turkina *et al.*, in preparation

Py@ZnO(10-10)

- Charge-transfer exciton at E = 5.5 eV
- Main contribution: transition from Py(HOMO-1) to hybridized CBM





O. Turkina *et al.*, in preparation

Conclusions

Conclusions

- Optical excitations described by Bethe-Salpeter equation
- Applicable to complex materials

Ongoing Development

- Going beyond Tamm-Dancoff approximation
- Finite momentum transfer
- More efficient/parallelized version