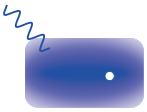
Theoretical Spectroscopy in exciting

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

Theoretical Spectroscopy

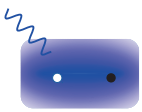
Charged Excitations



N → N-1

Photoemission Spectroscopy

Neutral Excitations

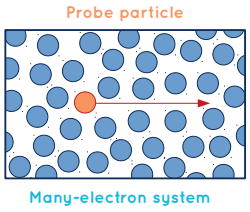


N → N

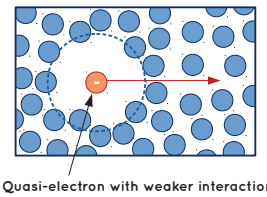
Absorption Spectroscopy

Charged Excitations: GW

Quasiparticles



Quasiparticles



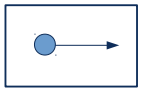
Perturbative Approach

$$\epsilon_{n\mathbf{k}}^{\mathrm{qp}} = \epsilon_{n\mathbf{k}} + \langle \psi_{n\mathbf{k}}(\mathbf{r}) | \Re \left[\Sigma\left(\mathbf{r}, \mathbf{r}'; \epsilon_{n\mathbf{k}}^{\mathrm{qp}}\right) \right] - V^{\mathrm{xc}}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') | \psi_{n\mathbf{k}}(\mathbf{r}') \rangle$$

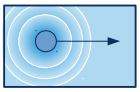
From DFT calculation

GW Approximation

$$\Sigma = GW$$



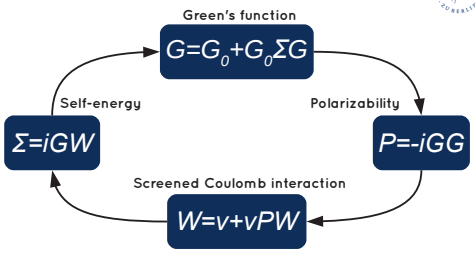
1-particle Green's function



Screened Coulomb interaction

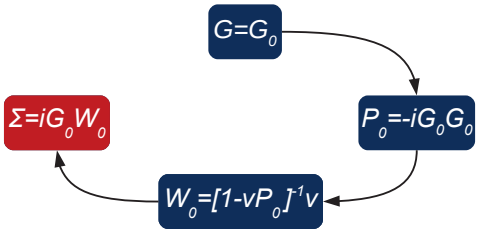
$$W(\mathbf{r}, \mathbf{r}', \omega)$$

Hedin's Equations



L. Hedin, Phys. Rev. 139, A796 (1965)
L. Hedin and B. I. Lundqvist, Solid State Phys. 23, 1 (1969)

G_0W_0 Approximation



L. Hedin, Phys. Rev. 139, A796 (1965)
L. Hedin and B. I. Lundqvist, Solid State Phys. 23, 1 (1969)

Screened Coulomb Interaction

RPA Polarizibility

$$P_0(\mathbf{r},\mathbf{r}';\omega) = \sum_{n\mathbf{k},m\mathbf{k}'} f(\epsilon_{n\mathbf{k}})\left[1-f(\epsilon_{m\mathbf{k}'})\right]\psi_{n\mathbf{k}}(\mathbf{r})\psi^*_{m\mathbf{k}'}(\mathbf{r})\psi^*_{n\mathbf{k}}(\mathbf{r}')\psi_{m\mathbf{k}'}(\mathbf{r}')$$
$$\times\left\{\frac{1}{\omega-\epsilon_{m\mathbf{k}'}+\epsilon_{n\mathbf{k}}+i\eta}-\frac{1}{\omega+\epsilon_{m\mathbf{k}'}-\epsilon_{n\mathbf{k}}-i\eta}\right\}$$

Dielectric function

$$\varepsilon(\mathbf{r},\mathbf{r}';\omega) = \delta(\mathbf{r},\mathbf{r}') - \int v(\mathbf{r},\mathbf{r}_1)\,P_0(\mathbf{r}_1,\mathbf{r}';\omega)\,d\mathbf{r}_1$$

Dynamically screened Coulomb interaction

$$W_0(\mathbf{r},\mathbf{r}';\omega) = \int \varepsilon^{-1}(\mathbf{r},\mathbf{r}_1;\omega)\,v(\mathbf{r}_1,\mathbf{r}')\,d\mathbf{r}_1$$

Implementation

Product-basis Representation

$$P_0(\mathbf{r},\mathbf{r}';\omega) = \sum_{n\mathbf{k},m\mathbf{k}'} f(\epsilon_{n\mathbf{k}})\left[1-f(\epsilon_{m\mathbf{k}'})\right]\psi_{n\mathbf{k}}(\mathbf{r})\psi^*_{m\mathbf{k}'}(\mathbf{r})\psi^*_{n\mathbf{k}}(\mathbf{r}')\psi_{m\mathbf{k}'}(\mathbf{r}')$$
$$\times\left\{\frac{1}{\omega-\epsilon_{m\mathbf{k}'}+\epsilon_{n\mathbf{k}}+i\eta}-\frac{1}{\omega+\epsilon_{m\mathbf{k}'}-\epsilon_{n\mathbf{k}}-i\eta}\right\}$$

Product-basis Representation

$$P_0(\mathbf{r},\mathbf{r}';\omega) = \sum_{nm}\sum_{\mathbf{k},\mathbf{q}} F_{nm}(\mathbf{k},\mathbf{q};\omega)\,\psi_{n\mathbf{k}}(\mathbf{r})\psi^*_{m\mathbf{k}-\mathbf{q}}(\mathbf{r})\,\psi^*_{n\mathbf{k}}(\mathbf{r}')\psi_{m\mathbf{k}-\mathbf{q}}(\mathbf{r}')$$

Basis function

$$\psi_{n\mathbf{k}}(\mathbf{r})\,\psi^*_{m\mathbf{k}-\mathbf{q}}(\mathbf{r}) = \sum_i M^i_{nm}(\mathbf{k},\mathbf{q})\,\chi^{\mathbf{q}}_i(\mathbf{r})$$

Expansion coefficients

$$P_{ij}(\mathbf{q},\omega) \equiv \int_V\int_V [\chi^{\mathbf{q}}_i(\mathbf{r})]^*\,P(\mathbf{r},\mathbf{r}';\omega)\chi^{\mathbf{q}}_j(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$$
$$= \sum_{\mathbf{k}}^{BZ}\sum_{nm} F_{nm}(\mathbf{k},\mathbf{q};\omega)M^i_{nm}(\mathbf{k},\mathbf{q})\left[M^j_{nm}(\mathbf{k},\mathbf{q})\right]^*$$

Mixed Basis in the MT Region

- Use only $u_{\alpha l}(r^\alpha)$ with $l \le l^{\mathrm{MB}}_{\mathrm{max}}$ → `/input/gw/mixbasis/@lmb`
- $v_{\alpha NL}(r^\alpha) = u_{\alpha l}(r^\alpha)u_{\alpha l'}(r^\alpha) : |l-l'| \le L \le l+l'$
- Form orthonormal basis + eliminate linearly dependent products
- Take in account the translational symmetry

$$\gamma^{\mathbf{q}}_{\alpha NLM}(\mathbf{r}) = \frac{1}{\sqrt{N_c}}\sum_{\mathbf{R}} e^{\lambda\mathbf{q}\cdot(\mathbf{r}_\alpha+\mathbf{R})}v_{\alpha NL}(r^\alpha)Y_{LM}(\hat{\mathbf{r}}^\alpha)$$

F. Aryasetiawan and O. Gunnarsson, Phys. Rev. B 49, 16214 (1994)
T. Kotani and M. van Schilfgaarde, Solid State Comm. 121, 461 (2002)

Mixed Basis in the Interstitial

- Form overlap matrix

$$\mathbb{O}_{\mathbf{G}\mathbf{G}'} = \frac{1}{\Omega}\int_\Omega \theta_l(\mathbf{r})\,e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}}\,d^3r$$

- Diagonalize

$$\sum_{\mathbf{G}'}\mathbb{O}_{\mathbf{G}\mathbf{G}'}S_{\mathbf{G}'i} = \lambda^l_i\,S_{\mathbf{G}i}$$

- Build an orthonormal basis set:

$$P^{\mathbf{q}}_i(\mathbf{r}) \equiv \frac{1}{\sqrt{\Omega}}\sum_{\mathbf{G}}^{G^{\mathrm{MB}}_{\mathrm{max}}} \tilde{S}_{\mathbf{G}i}e^{i(\mathbf{G}+\mathbf{q})\cdot\mathbf{r}}\theta_l(\mathbf{r}),\ \text{where}\ \tilde{S}_{\mathbf{G}i} \equiv \frac{S_{\mathbf{G}i}}{\sqrt{\lambda^l_i}}$$

→ `/input/gw/mixbasis/@gmb`

Parameters

Basis Set Quality

`/input/gw/mixbasis/@lmb`
`/input/gw/mixbasis/@gmb`

$$P_{ij}(\mathbf{q},\omega) = \sum_{\mathbf{k}}^{BZ}\sum_{n}^{occ}\sum_{m}^{unocc} F_{nm}(\mathbf{k},\mathbf{q};\omega)M^i_{nm}(\mathbf{k},\mathbf{q})\left[M^j_{nm}(\mathbf{k},\mathbf{q})\right]^*$$

→ `/input/gw/@nempty`

Generalized tetrahedron method (LIBBZINT library):
`/input/gw/@ngridq` + `/input/gw/@vqloff`

Parameters

Two contributions to Coulomb interaction

$$W^c_0(\mathbf{r},\mathbf{r}';\omega) = W_0(\mathbf{r},\mathbf{r}';\omega) - v(\mathbf{r},\mathbf{r}')$$

Two contributions to self-energy

$$\Sigma^x(\mathbf{r},\mathbf{r}') = \frac{i}{2\pi}\int G_0(\mathbf{r},\mathbf{r}';\omega')v(\mathbf{r}',\mathbf{r})e^{i\omega'\eta}d\omega'$$
$$= -\sum_{n\mathbf{k}} f_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})v(\mathbf{r}',\mathbf{r})\psi^*_{n\mathbf{k}}(\mathbf{r}')$$

Analytic integral over frequencies

$$\Sigma^c(\mathbf{r},\mathbf{r}';\omega) = \frac{i}{2\pi}\int G_0(\mathbf{r},\mathbf{r}';\omega+\omega')W^c_0(\mathbf{r}',\mathbf{r};\omega')\,d\omega'$$

Explicit Integral over frequencies → `/input/gw/@freqgrid`

Input File

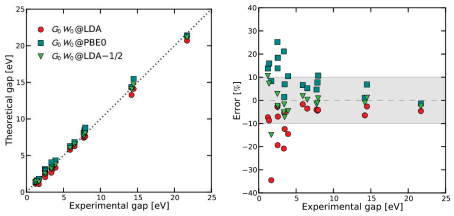
```
<gw
    taskname="g0w0"
    ngridq="2 2 2"
    nempty="22"
    ibgw="1"
    nbgw="10"
    >
  <mixbasis
      lmaxmb="3"
      gmb="3">
  </mixbasis>
</gw>
```

Type of calculations:
- "band" QP band-structure plot
- "dos" QP density of states

Quality of the product basis

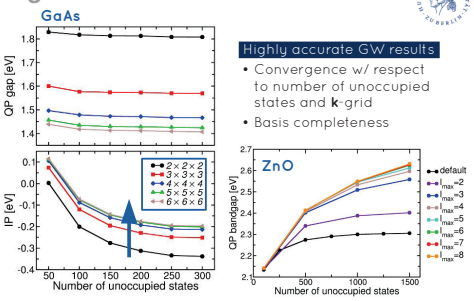
Examples

High-Precision GW Calculations



R.R. Pela, U. Werner, D. Nabok, and C. Draxl, Phys. Rev. B 94,235141 (2016)

High-Precision GW Calculations

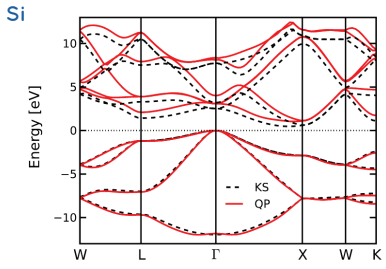


Highly accurate GW results

- Convergence w/ respect to number of unoccupied states and **k**-grid
- Basis completeness

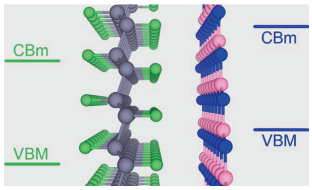
D. Nabok, A. Gulans, and C. Draxl, Phys. Rev. B 94 (3), 035118 (2016)

Bandstructure



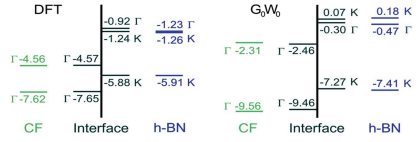
A. Gulans *et al.*, J. Phys.: Condens. Matter 26, 363202 (2014)

Level Alignment



Q. Fu, D. Nabok, and C. Draxl, J. Phys. Chem. C 120 (21), 11671-11678

Level Alignment

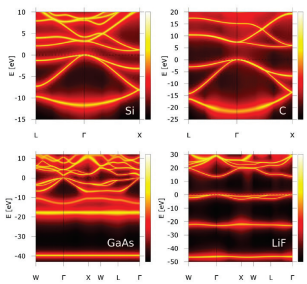


Very small change in band energies upon formation

Bands shifts of ~100 meV

Q. Fu, D. Nabok, and C. Draxl, J. Phys. Chem. C 120 (21), 11671-11678

Spectral Functions

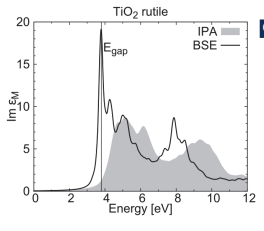


J. Gesenhues, D. Nabok, M. Rohlfing, and C. Draxl, Phys. Rev. B 96, 245124 (2017)

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)

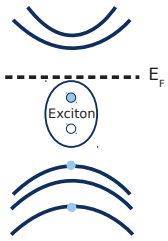
vs.

- 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

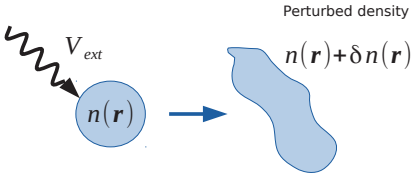
- Exciton – bound state of excited electron and the hole left behind
- Exciton binding energy:

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

Electron-hole correlation

- Screened Coulomb interaction
- Exchange interaction

Linear Response



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

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

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

Independent-particle transitions (IPA)

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

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

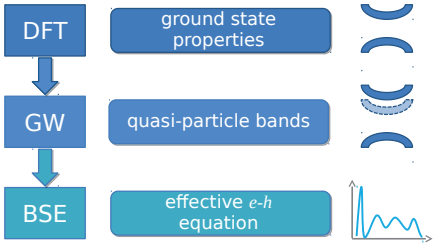
BSE approximation levels

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

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

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

Input file

```
<xs
   xstype='BSE'
   ngridk='4 4 4'
   vkloff='0.097 0.273 0.493'
   ngridq='4 4 4'
   nempty='30'
   gqmax='3.0'
   broad='0.007'
   scissor='0.20947'
   tevout='true'>

   <energywindow
      intv='0.0 1.0'
      points='1200'/>

   <screening
      screentype="full"
      nempty='100'/>

   <BSE
      bsetype="singlet"
      nstlbse='1 5 1 4' />

   <qpointset>
      <qpoint>0.0 0.0 0.0</qpoint>
   </qpointset>

   <storeexcitons HinNumberExcitons='1'
                  HaxNumberExcitons='5'/>
</xs>
```

perform an excited-state calculation

Input file

```
<xs
   xstype='BSE'
   ngridk='4 4 4'
   vkloff='0.097 0.273 0.493'
   ngridq='4 4 4'
   nempty='30'
   gqmax='3.0'
   broad='0.007'
   scissor='0.20947'
   tevout='true'>

   <energywindow
      intv='0.0 1.0'
      points='1200'/>

   <screening
      screentype="full"
      nempty='100'/>

   <BSE
      bsetype="singlet"
      nstlbse='1 5 1 4' />

   <qpointset>
      <qpoint>0.0 0.0 0.0</qpoint>
   </qpointset>

   <storeexcitons HinNumberExcitons='1'
                  HaxNumberExcitons='5'/>
</xs>
```

perform a BSE calculation

Input file

```
<xs
   xstype='BSE'
   ngridk='4 4 4'
   vkloff='0.097 0.273 0.493'
   ngridq='4 4 4'
   nempty='30'
   gqmax='3.0'
   broad='0.007'
   scissor='0.20947'
   tevout='true'>

   <energywindow
      intv='0.0 1.0'
      points='1200'/>

   <screening
      screentype="full"
      nempty='100'/>

   <BSE
      bsetype="singlet"
      nstlbse='1 5 1 4' />

   <qpointset>
      <qpoint>0.0 0.0 0.0</qpoint>
   </qpointset>

   <storeexcitons HinNumberExcitons='1'
                  HaxNumberExcitons='5'/>
</xs>
```

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

Input file

```
<xs
   xstype='BSE'
   ngridk='4 4 4'
   vkloff='0.097 0.273 0.493'
   ngridq='4 4 4'
   nempty='30'
   gqmax='3.0'
   broad='0.007'
   scissor='0.20947'
   tevout='true'>

   <energywindow
      intv='0.0 1.0'
      points='1200'/>

   <screening
      screentype="full"
      nempty='100'/>

   <BSE
      bsetype="singlet"
      nstlbse='1 5 1 4' />

   <qpointset>
      <qpoint>0.0 0.0 0.0</qpoint>
   </qpointset>

   <storeexcitons HinNumberExcitons='1'
                  HaxNumberExcitons='5'/>
</xs>
```

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

Input file

```
<xs
   xstype='BSE'
   ngridk='4 4 4'
   vkloff='0.097 0.273 0.493'
   ngridq='4 4 4'
   nempty='30'
   gqmax='3.0'
   broad='0.007'
   scissor='0.20947'
   tevout='true'>

   <energywindow
      intv='0.0 1.0'
      points='1200'/>

   <screening
      screentype="full"
      nempty='100'/>

   <BSE
      bsetype="singlet"
      nstlbse='1 5 1 4' />

   <qpointset>
      <qpoint>0.0 0.0 0.0</qpoint>
   </qpointset>

   <storeexcitons HinNumberExcitons='1'
                  HaxNumberExcitons='5'/>
</xs>
```

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:

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

Input file

```
<xs
   xstype='BSE'
   ngridk='4 4 4'
   vkloff='0.097 0.273 0.493'
   ngridq='4 4 4'
   nempty='30'
   gqmax='3.0'
   broad='0.007'
   scissor='0.20947'
   tevout='true'>

   <energywindow
      intv='0.0 1.0'
      points='1200'/>

   <screening
      screentype="full"
      nempty='100'/>

   <BSE
      bsetype="singlet"
      nstlbse='1 5 1 4' />

   <qpointset>
      <qpoint>0.0 0.0 0.0</qpoint>
   </qpointset>

   <storeexcitons HinNumberExcitons='1'
                  HaxNumberExcitons='5'/>
</xs>
```

Lorentzian broadening for the optical spectrum

Input file

```
<xs
   xstype='BSE'
   ngridk='4 4 4'
   vkloff='0.097 0.273 0.493'
   ngridq='4 4 4'
   nempty='30'
   gqmax='3.0'
   broad='0.007'
   scissor='0.20947'
   tevout='true'>

   <energywindow
      intv='0.0 1.0'
      points='1200'/>

   <screening
      screentype="full"
      nempty='100'/>

   <BSE
      bsetype="singlet"
      nstlbse='1 5 1 4' />

   <qpointset>
      <qpoint>0.0 0.0 0.0</qpoint>
   </qpointset>

   <storeexcitons HinNumberExcitons='1'
                  HaxNumberExcitons='5'/>
</xs>
```

scissors operator mimicking the quasi-particle gap

Input file

```
<gw
   taskname='skip'>
</gw>

<xs
   xstype='BSE'
   ngridk='4 4 4'
   vkloff='0.097 0.273 0.493'
   ngridq='4 4 4'
   nempty='30'
   gqmax='3.0'
   broad='0.007'
   tevout='true'>

   <energywindow
      intv='0.0 1.0'
      points='1200'/>

   <screening
      screentype="full"
      nempty='100'/>

   <BSE
      bsetype="singlet"
      nstlbse='1 5 1 4' />

   <qpointset>
      <qpoint>0.0 0.0 0.0</qpoint>
   </qpointset>

   <storeexcitons HinNumberExcitons='1'
                  HaxNumberExcitons='5'/>
</xs>
```

consider G_0W_0 quasi-particle enegies

Input file

```
<xs
   xstype='BSE'
   ngridk='4 4 4'
   vkloff='0.097 0.273 0.493'
   ngridq='4 4 4'
   nempty='30'
   gqmax='3.0'
   broad='0.007'
   scissor='0.20947'
   tevout='true'>

   <energywindow
      intv='0.0 1.0'
      points='1200'/>

   <screening
      screentype="full"
      nempty='100'/>

   <BSE
      bsetype="singlet"
      nstlbse='1 5 1 4' />

   <qpointset>
      <qpoint>0.0 0.0 0.0</qpoint>
   </qpointset>

   <storeexcitons HinNumberExcitons='1'
                  HaxNumberExcitons='5'/>
</xs>
```

energy window on which the spectrum is calculated

Input file

```
<xs
   xstype="BSE"
   ngridk="4 4 4"
   vkloff="0.097 0.273 0.493"
   ngridq="4 4 4"
   nempty="30"
   gqmax="3.0"
   broad="0.007"
   scissor="0.20947"
   tevout="true">

   <energywindow
      intv="0.0 1.0"
      points="1200"/>

   <screening
      screentype="full"
      nempty="100"/>

   <BSE
      bsetype="singlet"
      nstlbse="1 5 1 4" />

   <qpointset>
      <qpoint>0.0 0.0 0.0</qpoint>
   </qpointset>

   <storeexcitons HinNumberExcitons="1"
                  HaxNumberExcitons="5"/>
</xs>
```

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

```
<xs
   xstype="BSE"
   ngridk="4 4 4"
   vkloff="0.097 0.273 0.493"
   ngridq="4 4 4"
   nempty="30"
   gqmax="3.0"
   broad="0.007"
   scissor="0.20947"
   tevout="true">

   <energywindow
      intv="0.0 1.0"
      points="1200"/>

   <screening
      screentype="full"
      nempty="100"/>

   <BSE
      bsetype="singlet"
      nstlbse="1 5 1 4" />

   <qpointset>
      <qpoint>0.0 0.0 0.0</qpoint>
   </qpointset>

   <storeexcitons HinNumberExcitons="1"
                  HaxNumberExcitons="5"/>
</xs>
```

calculation of the screened Coulomb potential

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

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

Input file

```
<xs
   xstype="BSE"
   ngridk="4 4 4"
   vkloff="0.097 0.273 0.493"
   ngridq="4 4 4"
   nempty="30"
   gqmax="3.0"
   broad="0.007"
   scissor="0.20947"
   tevout="true">

   <energywindow
      intv="0.0 1.0"
      points="1200"/>

   <screening
      screentype="full"
      nempty="100"/>

   <BSE
      bsetype="singlet"
      nstlbse="1 5 1 4" />

   <qpointset>
      <qpoint>0.0 0.0 0.0</qpoint>
   </qpointset>

   <storeexcitons HinNumberExcitons="1"
                  HaxNumberExcitons="5"/>
</xs>
```

specific BSE parameters

Input file

```
<xs
   xstype="BSE"
   ngridk="4 4 4"
   vkloff="0.097 0.273 0.493"
   ngridq="4 4 4"
   nempty="30"
   gqmax="3.0"
   broad="0.007"
   scissor="0.20947"
   tevout="true">

   <energywindow
      intv="0.0 1.0"
      points="1200"/>

   <screening
      screentype="full"
      nempty="100"/>

   <BSE
      bsetype="singlet"
      nstlbse="1 5 1 4" />

   <qpointset>
      <qpoint>0.0 0.0 0.0</qpoint>
   </qpointset>

   <storeexcitons HinNumberExcitons="1"
                  HaxNumberExcitons="5"/>
</xs>
```

IPA	$H^{IPA} = H^{diag}$
RPA	$H^{RPA} = H^{diag} + H^{x}$
triplet	$H^{triplet} = H^{diag} + H^{c}$
singlet	$H^{singlet} = H^{diag} + 2H^{x} + H^{c}$

approximation level

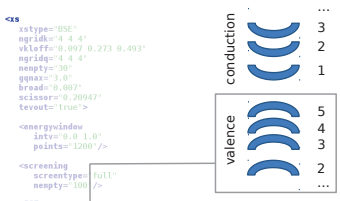
Input file

```
<xs
   xstype="BSE"
   ngridk="4 4 4"
   vkloff="0.097 0.273 0.493"
   ngridq="4 4 4"
   nempty="30"
   gqmax="3.0"
   broad="0.007"
   scissor="0.20947"
   tevout="true">

   <energywindow
      intv="0.0 1.0"
      points="1200"/>

   <screening
      screentype="full"
      nempty="100"/>

   <BSE
      bsetype="singlet"
      nstlbse="1 5 1 4" />

   <qpointset>
      <qpoint>0.0 0.0 0.0</qpoint>
   </qpointset>

   <storeexcitons HinNumberExcitons="1"
                  HaxNumberExcitons="5"/>
</xs>
```

range of valence and conduction bands

Input file

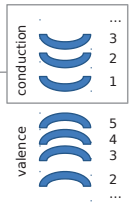
```
<xs
   xstype="BSE"
   ngridk="4 4 4"
   vkloff="0.097 0.273 0.493"
   ngridq="4 4 4"
   nempty="30"
   gqmax="3.0"
   broad="0.007"
   scissor="0.20947"
   tevout="true">

   <energywindow
      intv="0.0 1.0"
      points="1200"/>

   <screening
      screentype="full"
      nempty="100"/>

   <BSE
      bsetype="singlet"
      nstlbse="1 5 1 4" />

   <qpointset>
      <qpoint>0.0 0.0 0.0</qpoint>
   </qpointset>

   <storeexcitons HinNumberExcitons="1"
                  HaxNumberExcitons="5"/>
</xs>
```



range of valence and conduction bands

Input file

```
<xs
   xstype="BSE"
   ngridk="4 4 4"
   vkloff="0.097 0.273 0.493"
   ngridq="4 4 4"
   nempty="30"
   gqmax="3.0"
   broad="0.007"
   scissor="0.20947"
   tevout="true">

   <energywindow
      intv="0.0 1.0"
      points="1200"/>

   <screening
      screentype="full"
      nempty="100"/>

   <BSE
      bsetype="singlet"
      nstlbse="1 5 1 4" />

   <qpointset>
      <qpoint>0.0 0.0 0.0</qpoint>
   </qpointset>

   <storeexcitons HinNumberExcitons="1"
                  HaxNumberExcitons="5"/>
</xs>
```



range of valence and conduction bands

Input file

```
<xs
   xstype="BSE"
   ngridk="4 4 4"
   vkloff="0.097 0.273 0.493"
   ngridq="4 4 4"
   nempty="30"
   gqmax="3.0"
   broad="0.007"
   scissor="0.20947"
   tevout="true">

   <energywindow
      intv="0.0 1.0"
      points="1200"/>

   <screening
      screentype="full"
      nempty="100"/>

   <BSE
      bsetype="singlet"
      nstlbse="1 5 1 4" />

   <qpointset>
      <qpoint>0.0 0.0 0.0</qpoint>
   </qpointset>

   <storeexcitons HinNumberExcitons="1"
                  HaxNumberExcitons="5"/>
</xs>
```

In `exciting carbon` $\mathbf{q} \neq 0$ is possible only in TDDFT

definition of the $\mathbf{q}$-points

Input file

```
<xs
   xstype="BSE"
   ngridk="4 4 4"
   vkloff="0.097 0.273 0.493"
   ngridq="4 4 4"
   nempty="30"
   gqmax="3.0"
   broad="0.007"
   scissor="0.20947"
   tevout="true">

   <energywindow
      intv="0.0 1.0"
      points="1200"/>

   <screening
      screentype="full"
      nempty="100"/>

   <BSE
      bsetype="singlet"
      nstlbse="1 5 1 4" />

   <qpointset>
      <qpoint>0.0 0.0 0.0</qpoint>
   </qpointset>

   <storeexcitons HinNumberExcitons="1"
                  HaxNumberExcitons="5"/>
</xs>
```

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

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

```
<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 Analysis

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

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

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="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 block

electron block

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>
```

specify hole position:

it should be slightly shifted with respect to the atom position

Exciton Analysis

```
<xs ...>
  ...
  <plan>
    <doonly task='writebsevec'/>
    <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

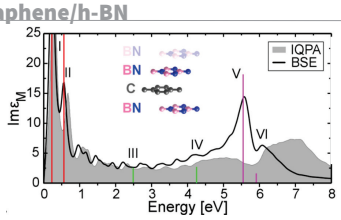
Exciton Analysis

```
<xs ...>
  ...
  <plan>
    <doonly task='writebsevec'/>
    <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

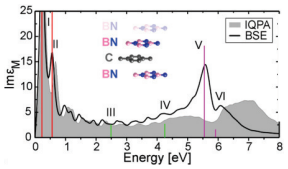
Graphene/h-BN

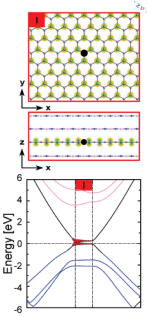


- Graphene/hexagonal boron nitride (h-BN) van der Waals heterostructure
- Quasi-particle gap of 250 meV opened in graphene through interaction with h-BN
- Three types of excitations can be identified

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

Graphene/h-BN

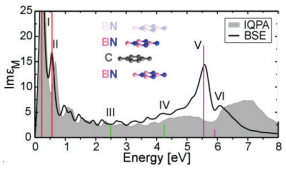


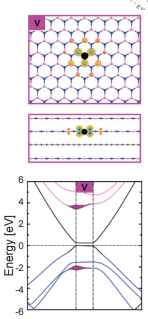


- IR region: interband transitions within graphene layer
- Delocalized excitations with electron and hole in the same layer exhibiting π-π* character

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

Graphene/h-BN

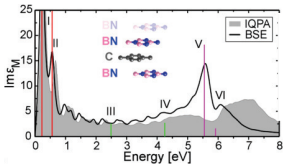


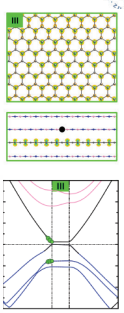


- UV region: strongly bound h-BN intralayer excitons
- Spatially confined e-h pairs with large oscillator strength within h-BN layer

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

Graphene/h-BN



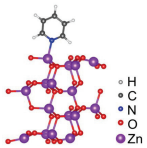


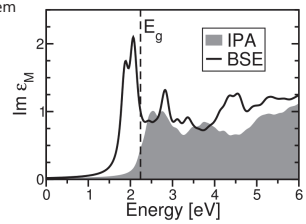
- Fingerprints of the heterostructure in the visible region: charge-transfer excitations
- Delocalized excitations with hole located on h-BN and electron on the carbon layer and vice versa

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

Py@ZnO(10-10)

Prototypical hybrid organic/inorganic system

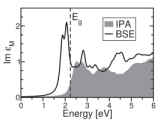


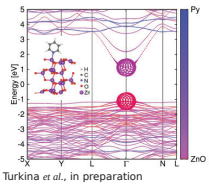


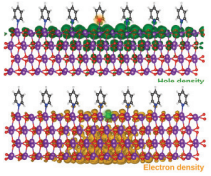
O. Turkina *et al.*, in preparation

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



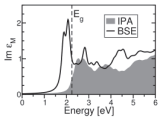


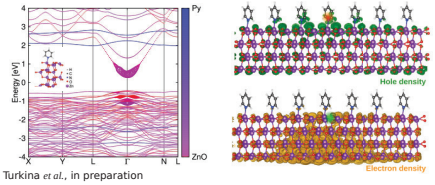


O. Turkina *et al.*, in preparation

Py@ZnO(10-10)

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

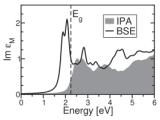


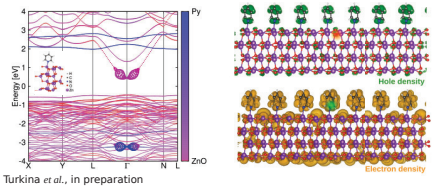


O. Turkina *et al.*, in preparation

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

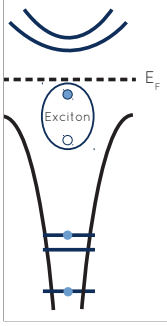
- Optical excitations described by Bethe-Salpeter equation
- Applicable to complex materials

Ongoing Development

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

Core Spectroscopy

Introduction



Core-Level Spectroscopy

Sensitive probe for

- Unoccupied electronic structure
- Local chemical environment
- Symmetry, bonding ...

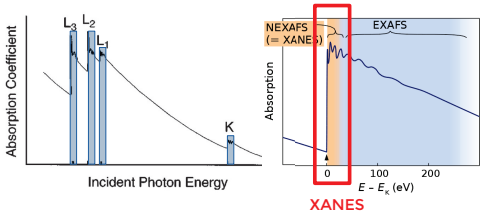
Correlation Effects

Electron-hole correlation

Two contributions:

- Screened Coulomb interaction
- Exchange interaction

X-ray Absorption Spectroscopy

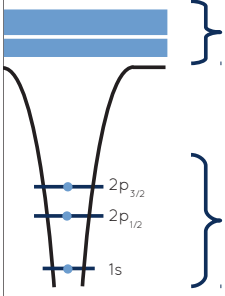


XANES

X-ray Absorption Near-Edge Structure

Rehr, J.J.; Albers, R.C.: Rev. Mod. Phys. 72 (2000), 621-654.
https://commons.wikimedia.org/w/index.php?curid=832879

Ab initio Core Spectroscopy



- Extended unoccupied states
- Spin-unpolarized, non-magnetic system

Linearized Augmented Planewaves (LAPW) Basis Set

- Strongly bound states
- Spherical symmetric potential
- Strong spin-orbit coupling

Radial Dirac equation in spherical potential

Input File

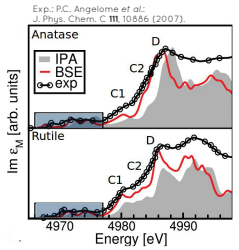
```
<BSE
  xas="true"                    → XANES calculation
  xasspecies="1"
  xasatom="2"                   → absorbing atom
  xasedge="L23"                 → Initial states
  bsetype="singlet"
  nstlxas="1 20"/>              → Final states
```

```
<species speciesfile="T1.xml" rmt="1.8000">
   <atom coord="0.0000000000      0.0000000000      0.0000000000"/>
   <atom coord="0.5000000000      0.5000000000      0.5000000000"/>
</species>
<species speciesfile="O.xml" rmt="1.8000">
   <atom coord="0.3050853616      0.3050853616      0.0000000000"/>
   <atom coord="0.6949146384      0.6949146384      0.0000000000"/>
   <atom coord="0.1949146384      0.8050853616      0.5000000000"/>
   <atom coord="0.8050853616      0.1949146384      0.5000000000"/>
</species>
```


Examples

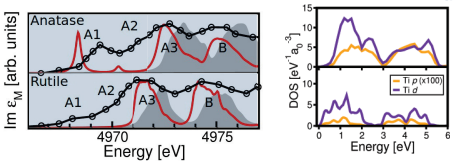
Ti K Edge of TiO_2

- BSE spectra in good agreement with experimental ones
- Systematic red-shift of BSE spectra compared to IPA ones
- No distinct fingerprint of the two phases



C. Vorwerk, C. Cocchi, and C. Draxl, Phys. Rev. B **95**, 155121 (2017).

Pre-Edge Analysis



Bound excitons

- Require many-body treatment
- Bright in anatase, dark in rutile

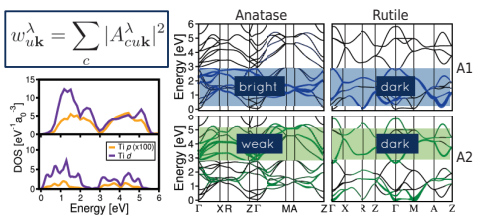
Transitions into lowest band

- Mostly Ti 3d character
- Allowed due to hybridization with Ti *p* states
- Qualitatively described by IPA

C. Vorwerk, C. Cocchi, and C. Draxl, Phys. Rev. B **95**, 155121 (2017).

Pre-Edge Analysis

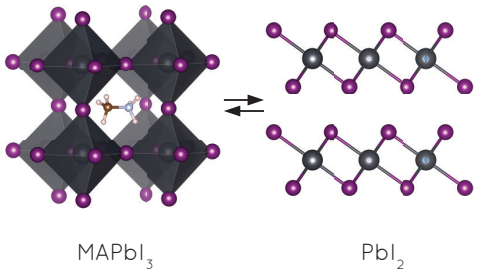
$$w^{\lambda}_{v\mathbf{k}} = \sum_{c} |A^{\lambda}_{cv\mathbf{k}}|^2$$



Good Agreement with previous works

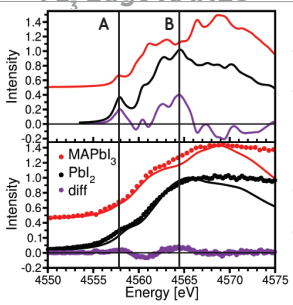
E. L. Shirley, J. Electron Spectrosc. Relat. Phenom. **136**, 77 (2004).
T. Mizoguchi et al., Micron **41**, 695 (2010).

Hybrid Perovskite: $MAPbI_3$



$MAPbI_3$ PbI_2

I L_3 Edge XANES



A

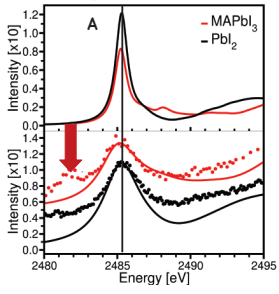
- Feature due to bound excitons in both material
- Binding energies of 480 meV ($MAPbI_3$) 450 meV (PbI_2)

B

- Band-like transitions to I *d* states
- Distinct peak in PbI_2 traced back to electronic structure

C. Vorwerk, C. Hartmann, C. Cocchi, G. Sadoughi, S. Habisreutinger, R. Felix, R.G. Wilks, H. Snaith, M. Bär, and C. Draxl: *preprint* (2017).

Pb M_5 Edge XANES

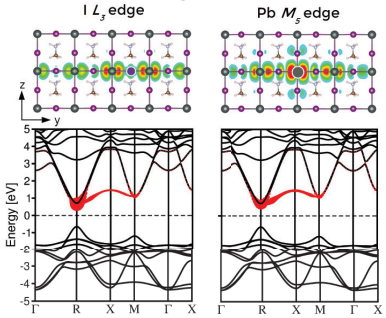


A

- Strong excitonic feature formed by transitions to Pb p states
- Binding energies of 860 meV ($MAPbI_3$) 950 meV (PbI_2)
- Additional experimental feature at lower transition energies

C. Vorwerk, C. Hartmann, C. Cocchi, G. Sadoughi, S. Habisreutinger, R. Felix, R.G. Wilks, H. Snaith, M. Bär, and C. Draxl: *preprint* (2017).

Exciton Analysis



Commercial

HoW exciting! 2018

DFG European Science Foundation

Workshop & Hands-on Tutorial on Excitations in Solids

Berlin, July 31 – August 9, 2018

See exciting-code.org

Invited speakers:

John J. Rehr	Kieron Burke	Patrick Rinke	Maria A. Loi
Lucia Reining	Peter Puschnig	Andrivo Rusydi	Kristian Thygesen
Feliciano Giustino	Julia Stähler	Ralph Erstdorfer	Christoph Friedrich
Marco Grioni	Ulrich Hohenester	Weitao Yang	Ludger Wirtz
Timo Thonhauser	Anna Köhler	Gitti Frey	

Thank you for your attention!