GW-BSE Calculation of the Optical Response of Spin-polarized Materials and Nanostructures

Li Yang

- Department of Physics, University of California at Berkeley
- Materials Sciences Division, Lawrence Berkeley National Laboratory

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Outline

- GW+BSE method with the spin degree of freedom included.
- The optical response of spin-polarized zigzag-edged graphene nanoribbons (ZGNRs).
- The electronic structure and optical response of NiO.

I. An Introduction of the GW+BSE Method with the Spin Degree of Freedom Included

Kohn-Sham Equation

The Hamiltonian of *N* electrons :

$$\boldsymbol{H} = \sum_{i=1}^{N}[-\frac{1}{2}\nabla_i^2 + V_{ext}(\mathbf{r}_i)] + \sum_{i<j}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

The Kohn-Sham formulation of density functional theory:

$$[-\frac{1}{2}\nabla^2 + V_h + V_{ext} + V_{xc}]\psi_i = \varepsilon_i\psi_i$$

with the exchange-correlation potential under the local density approximation (LDA) or the general gradient approximation (GGA). It is very successful to describe the ground state properties of solids.

For excited states, LDA or GGA systematically underestimates the band gap of semiconductors and insulators. In addition, the optical response is not well described by the above method.

Many-body Perturbation Theory (Single-particle Excitations)

Quasiparticle (Dyson) Equation:

$$[T+V_h+V_{ext}]\Psi_{n,k}(\mathbf{r})+\int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}';E_{n,k})\Psi_{n,k}(\mathbf{r}')=E_{n,k}\Psi_{n,k}(\mathbf{r})$$

Σ : Self-energy operator; $E_{n,k}$: Quasiparticle energy.

Hedin (1965): Perturbation series in screen Coulomb inteaction:

$$\Sigma = iGW + \ldots$$

G: dressed Green's function
W: screened Coulomb interaction $W = \epsilon^{-1}v$

Self-energy is evaluated by:

$$\Sigma(r,r';E)=\frac{i}{2\pi}\int dE'\, exp(-i\delta E')\, G(r,r';E-E')W(r,r';E')$$

Many-body perturbation Theory (single-particle excitations)

Approximations for G and W (Hybertsen and Louie, 1986):

- Random phase approximation (RPA) for the dielectric function.
- General plasmon-pole model for dynamical screening.

$G \approx G^{LDA}$, use the LDA results as the a starting point:

Dyson's equation

$$(T + V_{ext} + V_H)\Psi_{n,k}(r) + \int dr'\, \Sigma(r, r'; E_{n,k})\, \Psi_{n,k}(r') = E_{n,k}\, \Psi_{n,k}(r)$$

becomes

$$(T + V_{ext} + V_H + V_{xc})\, \Psi_{n,k}(r)$$
$$+ \int dr'\, [\, \Sigma(r, r'; E_{n,k}) - \delta(r, r') V_{xc}(r)\,]\, \Psi_{n,k}(r') = E_{n,k}\, \Psi_{n,k}(r)$$

Include the Spin Degree of Freedom in GWA

By random-phase approximation, the static polarizability with spin degree of freedom (no spin-orbital interaction included) is

$$P^{\sigma\sigma'}_{G,G'}(\boldsymbol{q},\omega=0)=\delta_{\sigma,\sigma'}\sum_{nn'\boldsymbol{k}}\frac{\langle n\sigma,\boldsymbol{k}|e^{-i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}}|n'\sigma,\boldsymbol{k}-\boldsymbol{q}\rangle\langle n'\sigma,\boldsymbol{k}-\boldsymbol{q}|e^{i(\boldsymbol{q}+\boldsymbol{G}')\cdot\boldsymbol{r}'}|n\sigma,\boldsymbol{k}\rangle}{E^{DFT}_{n'\sigma\boldsymbol{k}-\boldsymbol{q}}-E^{DFT}_{n\sigma\boldsymbol{k}}}.$$

So we only need consider the diagonal term in spin space. $P_{\sigma\sigma'}=\begin{pmatrix}P^{\uparrow\uparrow} & 0\\ 0 & P^{\downarrow\downarrow}\end{pmatrix}$

The dielectric matrix has the form: $\epsilon = I - v_{\alpha\alpha'}P^{\alpha\alpha'}$

And the bare Coulomb interaction is spin-blind: $v_{\alpha\alpha'}=\begin{pmatrix}v & v\\ v & v\end{pmatrix}$

Therefore, the static dielectric function with the spin degree of freedom included is given by:

$$\epsilon = 1 - v\tilde{P}\text{ , and }\quad \tilde{P}=P^{\uparrow\uparrow}+P^{\downarrow\downarrow}$$

Many-body Perturbation Theory (electron-hole excitations)

Exciton wave function:

$$\chi_S(\vec{x}_e, \vec{x}_h) = \sum_k^{hole} \sum_v^{elec} \sum_c A^S_{vck} \psi_{ck}(\vec{x}_e) \psi^*_{vk}(\vec{x}_h)$$

A^S_{vck}: Exciton amplitude

$\psi_{ck}(\vec{x}_e)$: Electron wave function

$\psi^*_{vk}(\vec{x}_h)$: Hole wave function

Bethe-Salpeter equation (BSE):

$$(E_{ck} - E_{vk}) A^S_{vck} + \sum_{k'v'c'} \langle vck | K^{eh} | v'c'k' \rangle A^S_{v'c'k'} = \Omega^S A^S_{vck}$$

$K^{eh}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}, \mathbf{r_4}, \Omega^S)$: a four-point energy-dependent electron-hole interaction kernel (Onida, et al., 1995; Albrecht, et al., 1997; Rohlfing, et al., 1998; Benedict, et al., 1998)

Include the Spin Degree of Freedom in BSE

The interaction kernel can be split into two parts, the direct term and exchange term (with the spin index included):

$$\langle v^{\mu}c^{\nu}|K^{d}(\Omega_S)|v'^{\alpha}c'^{\beta}\rangle = \int d\mathbf{x}d\mathbf{x}'\psi_c^{\nu *}(\mathbf{x})\psi_{c'}^{\beta}(\mathbf{x})\psi_v^{\mu}(\mathbf{x}')\psi_{v'}^{\alpha *}(\mathbf{x}')$$
$$\times\frac{i}{2\pi}\int d\omega e^{-i\omega 0^+}W(\mathbf{x},\mathbf{x}',\omega)$$
$$\times[\frac{1}{\Omega_S-\omega-(E_{c'}^{\beta}-E_{v'}^{\alpha})+i0^+}+\frac{1}{\Omega_S+\omega-(E_c^{\nu}-E_v^{\mu})+i0^+}]$$

$$\langle v^{\mu}c^{\nu}|K^{x}|v'^{\alpha}c'^{\beta}\rangle = \int d\mathbf{x}d\mathbf{x}'\psi_c^{\nu *}(\mathbf{x})\psi_v^{\mu}(\mathbf{x})v(\mathbf{x},\mathbf{x}')\psi_{c'}^{\beta}(\mathbf{x}')\psi_{v'}^{\alpha *}(\mathbf{x}')$$

Include the Spin Freedom in BSE

In spin subspace, the Hamiltonian is

$$H^{eh} = \begin{pmatrix} D+K^d+K^x & 0 & 0 & K^x \\ 0 & D+K^d & 0 & 0 \\ 0 & 0 & D+K^d & 0 \\ K^x & 0 & 0 & D+K^d+K^x \end{pmatrix} \begin{matrix} (\leftrightarrow v\uparrow c\uparrow) \\ (\leftrightarrow v\uparrow c\downarrow) \\ (\leftrightarrow v\downarrow c\uparrow) \\ (\leftrightarrow v\downarrow c\downarrow) \end{matrix},$$

Where *D* is the quasiparticle energy difference: $D = (E_c - E_v)$

Therefore, for a spin-polarized system, we have to evaluate the direct and exchange terms with different spin components and diagonalize the above Hamiltonian to solve BSE.

Optical spectrum

For optical frequencies we need the complex dielectric function

$$\varepsilon(\vec{q} \to 0, \omega) = \varepsilon_1(\omega) + i\,\varepsilon_2(\omega)$$

No electron-hole interaction:

$$\epsilon_2^{(0)}(\omega) = \frac{16\pi^2 e^2}{\omega^2} \sum_k^{hole} \sum_v^{elec} \sum_c \left| \vec{\lambda} \cdot \langle vk|\vec{v}|ck\rangle \right|^2 \delta(\omega - (E_{c,k} - E_{v,k}))$$

$\vec{\lambda}$: Polarization vector

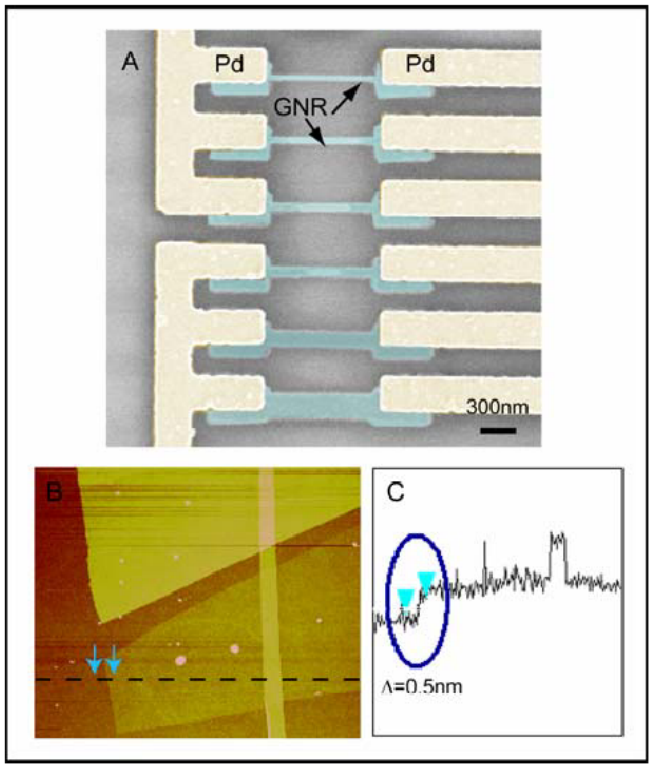
$\vec{v}$: Current operator $\vec{v} = 1/\hbar\,[H, \vec{r}]$

With electron-hole interaction:

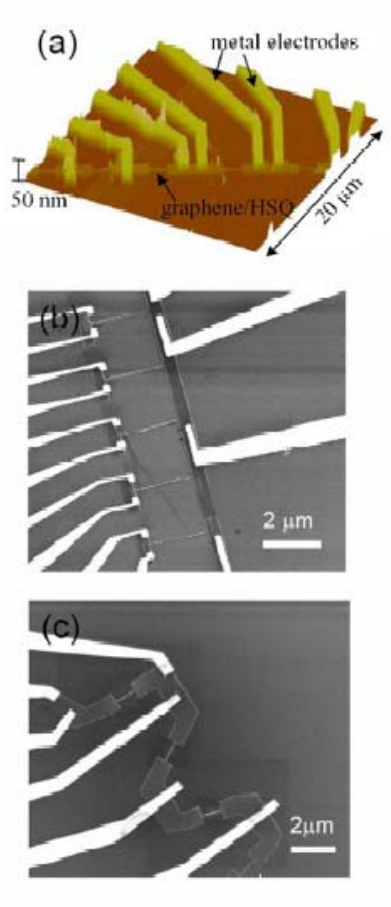
$$\epsilon_2(\omega) = \frac{16\pi^2 e^2}{\omega^2} \sum_S \left| \vec{\lambda} \cdot \left(\sum_k^{hole} \sum_v^{elec} \sum_c A^S_{vck} \langle vk|\vec{v}|ck\rangle \right) \right|^2 \delta(\omega - \Omega^S)$$

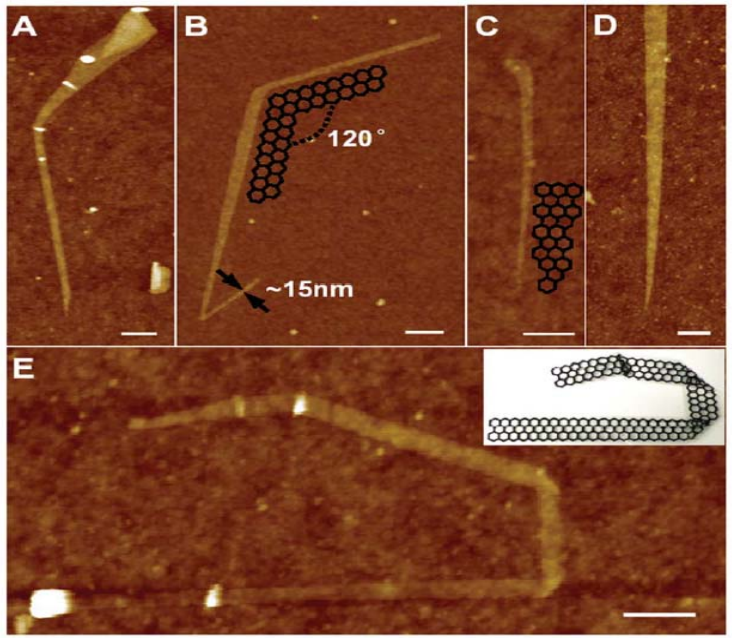
II. Quasiparticle Energies and Excitonic Effects of Graphene Nanoribbons

Graphene Nanoribbons (GNRs)



P. Avouris, et al., Physica E, 40, 228 (2007)

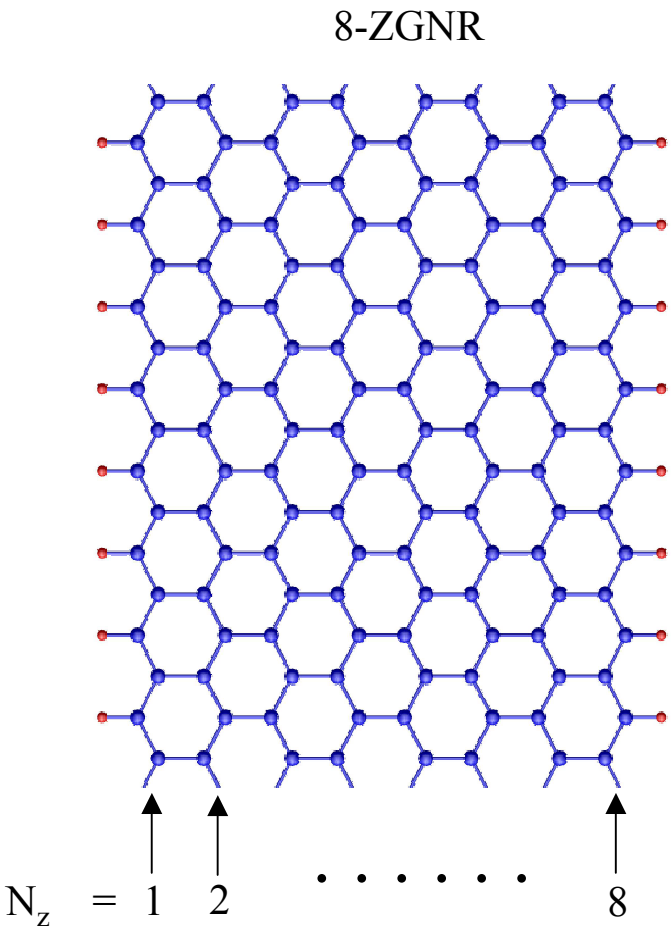


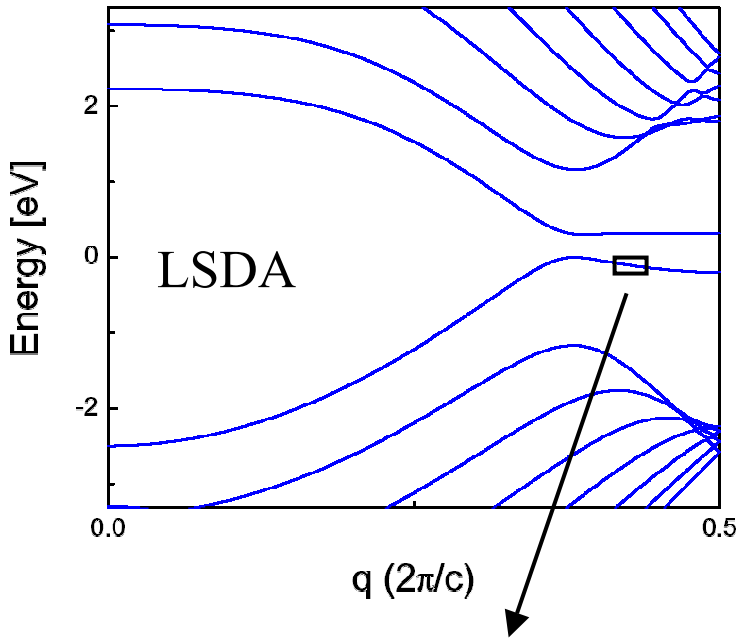


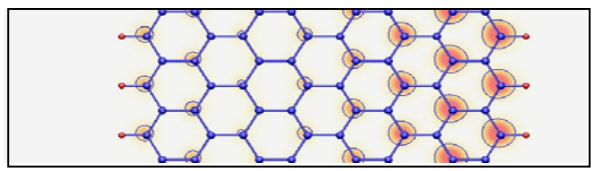
Hongjie Dai, et al., Science express, (2008).

P. Kim, et al., PRL, 98, 206805 (2007)

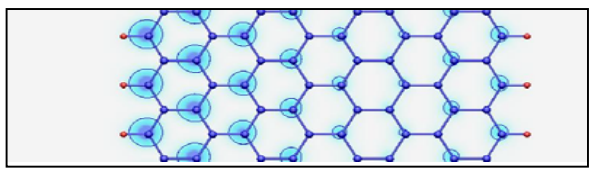
Zigzag-edged GNRs (ZGNRs)





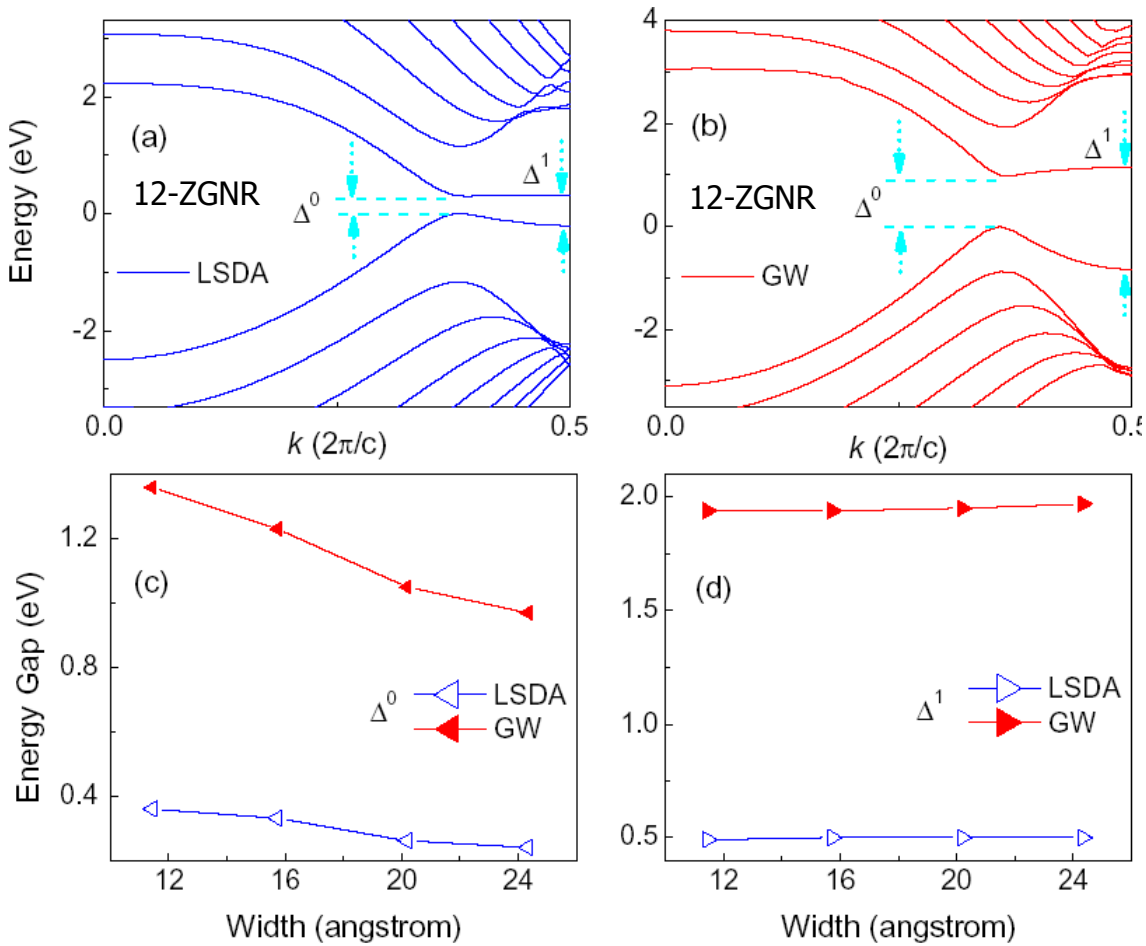


Spin up



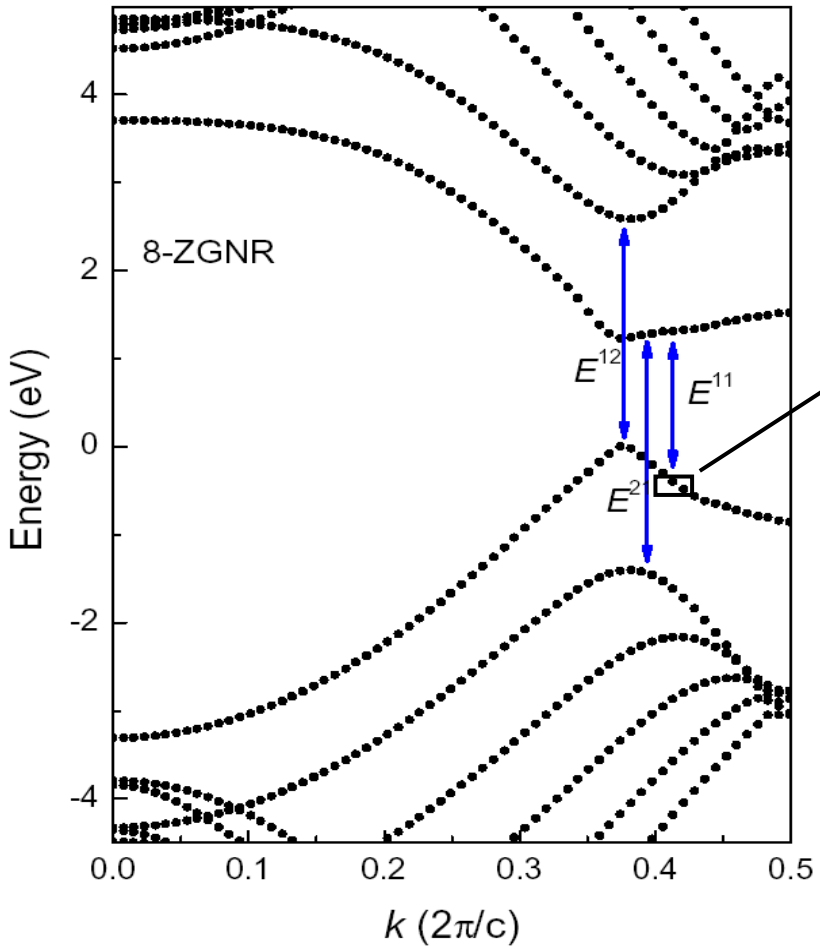
Spin down

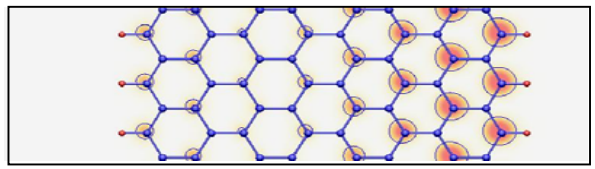
Quasiparticle Energies of ZGNRs



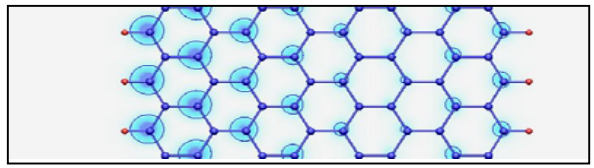
- The single-shoot GW calculation with the spin degree of freedom included.
- Significant self-energy corrections are found in ZGNRs.
- The calculated effective mass of spin-polarized edge state is decreased.
- The self-energy correction depends on the localization of electronic states.

Spin-polarized edge states in ZGNRs

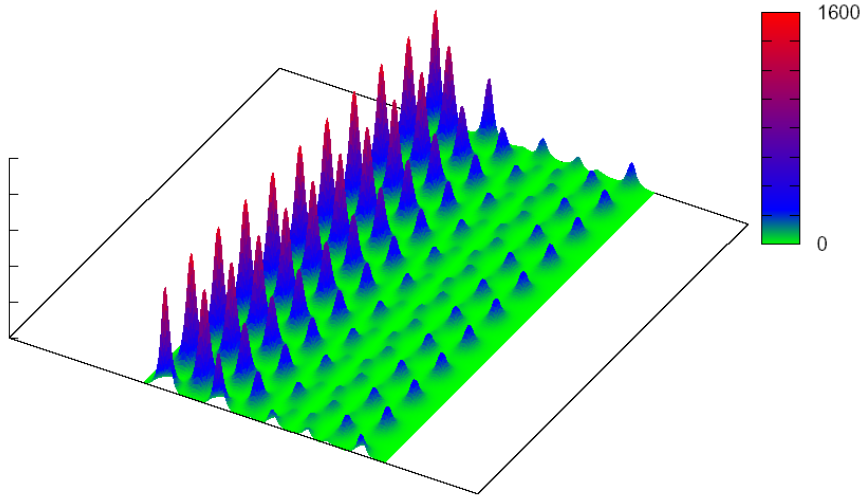




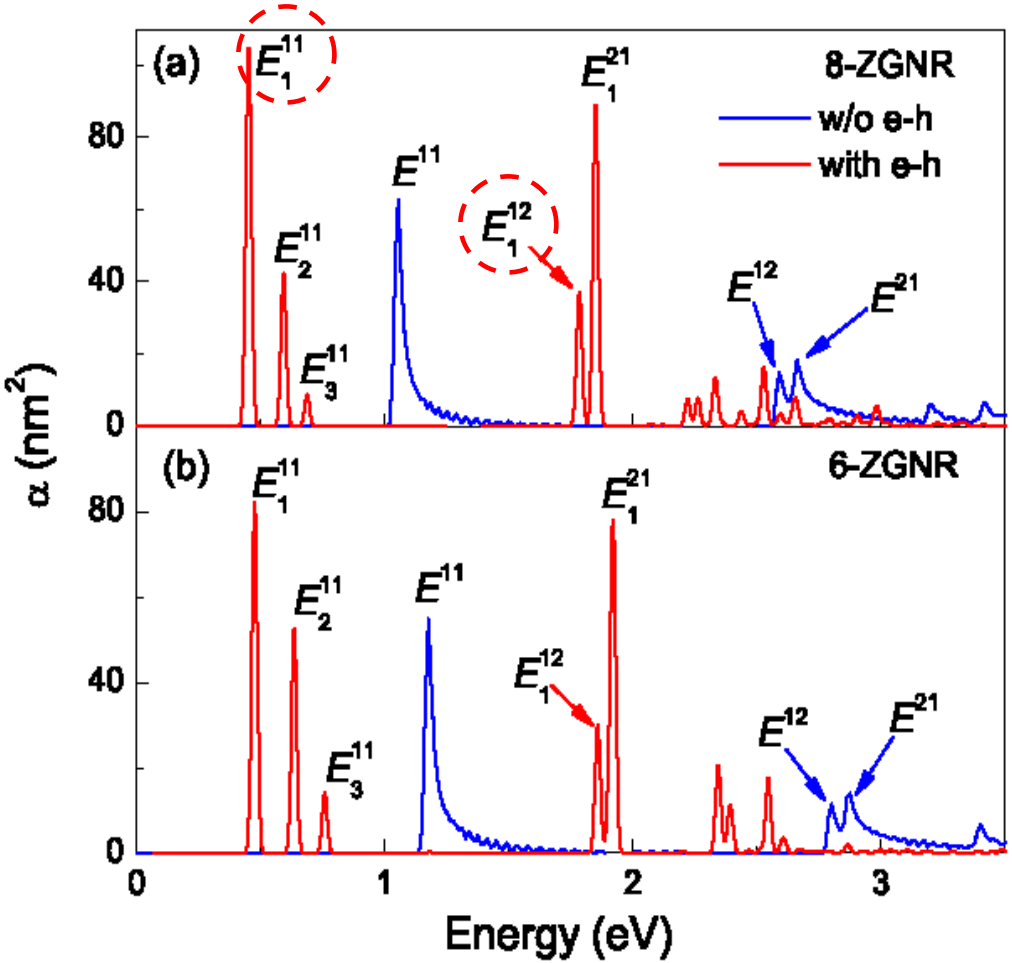
Spin up



Spin down

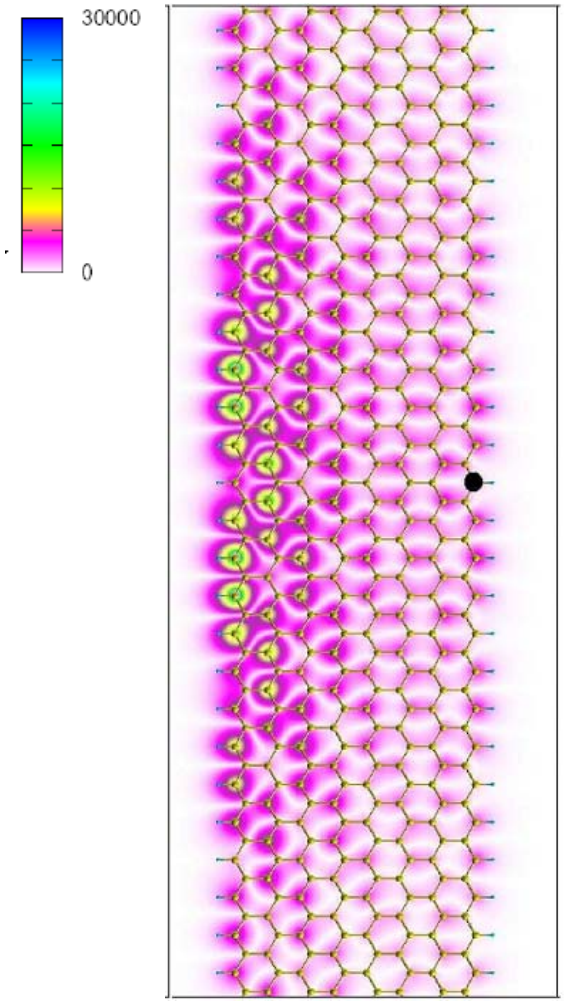


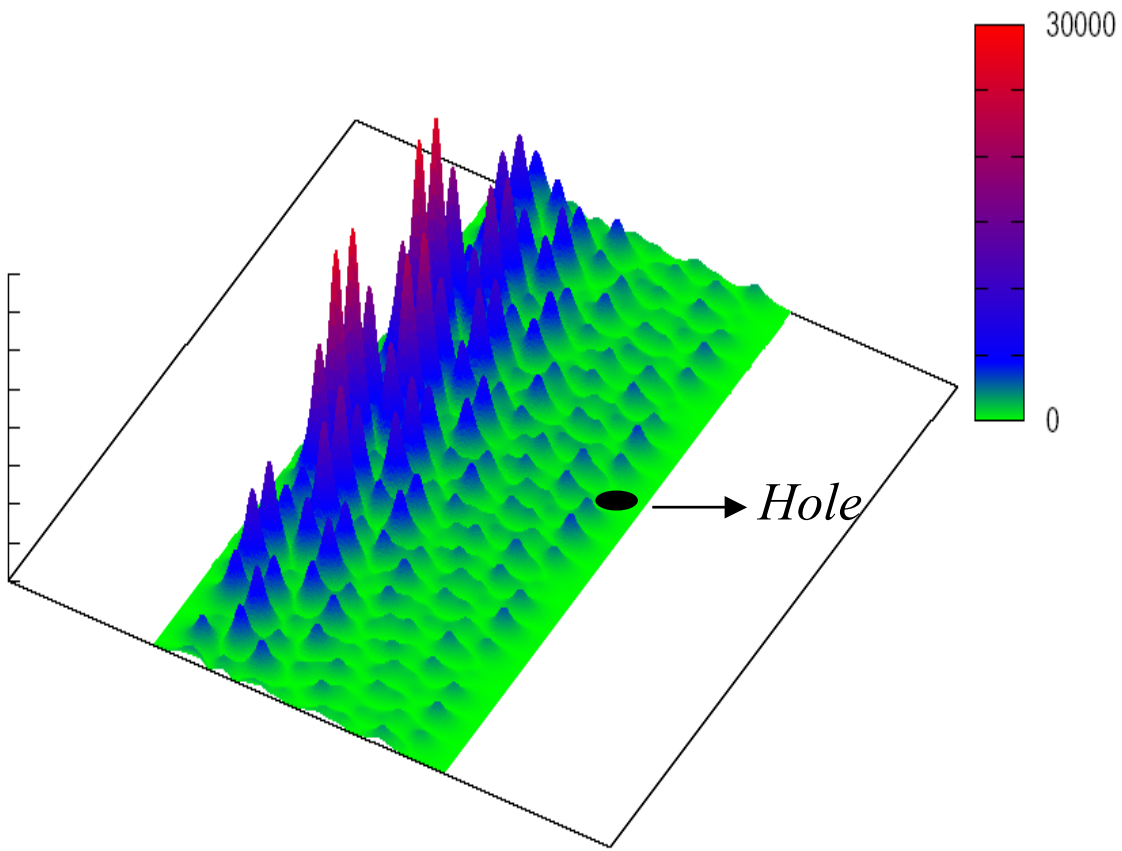
Optical Absorption Spectra of ZGNRs



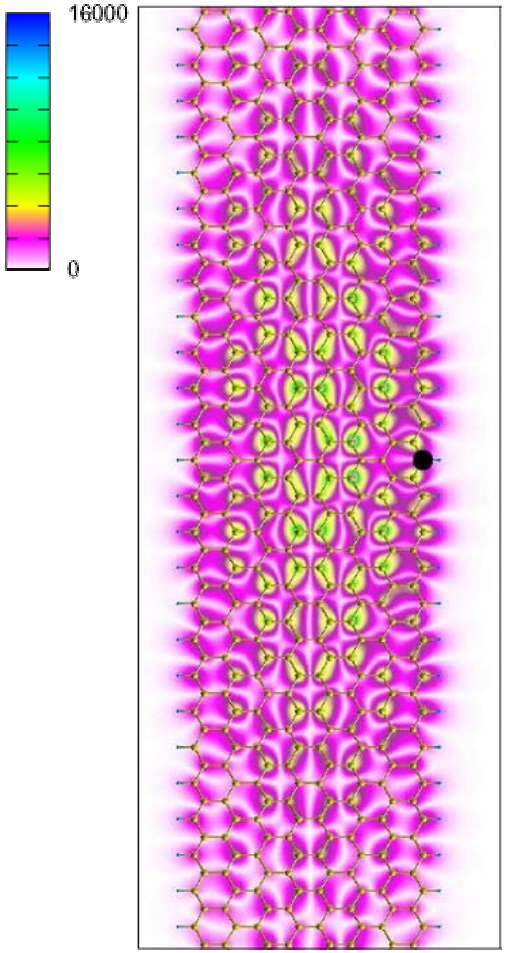
- The BSE is solved within a 1x1x256 k-grid with the spin degree of freedom included.
- The spectra are dominated by edge-state excitons (E^{11}_i series) with a significant e-h binding energy.

Exciton E_1^{11} (8-ZGNR)





Exciton E_1^{12} (8-ZGNR)



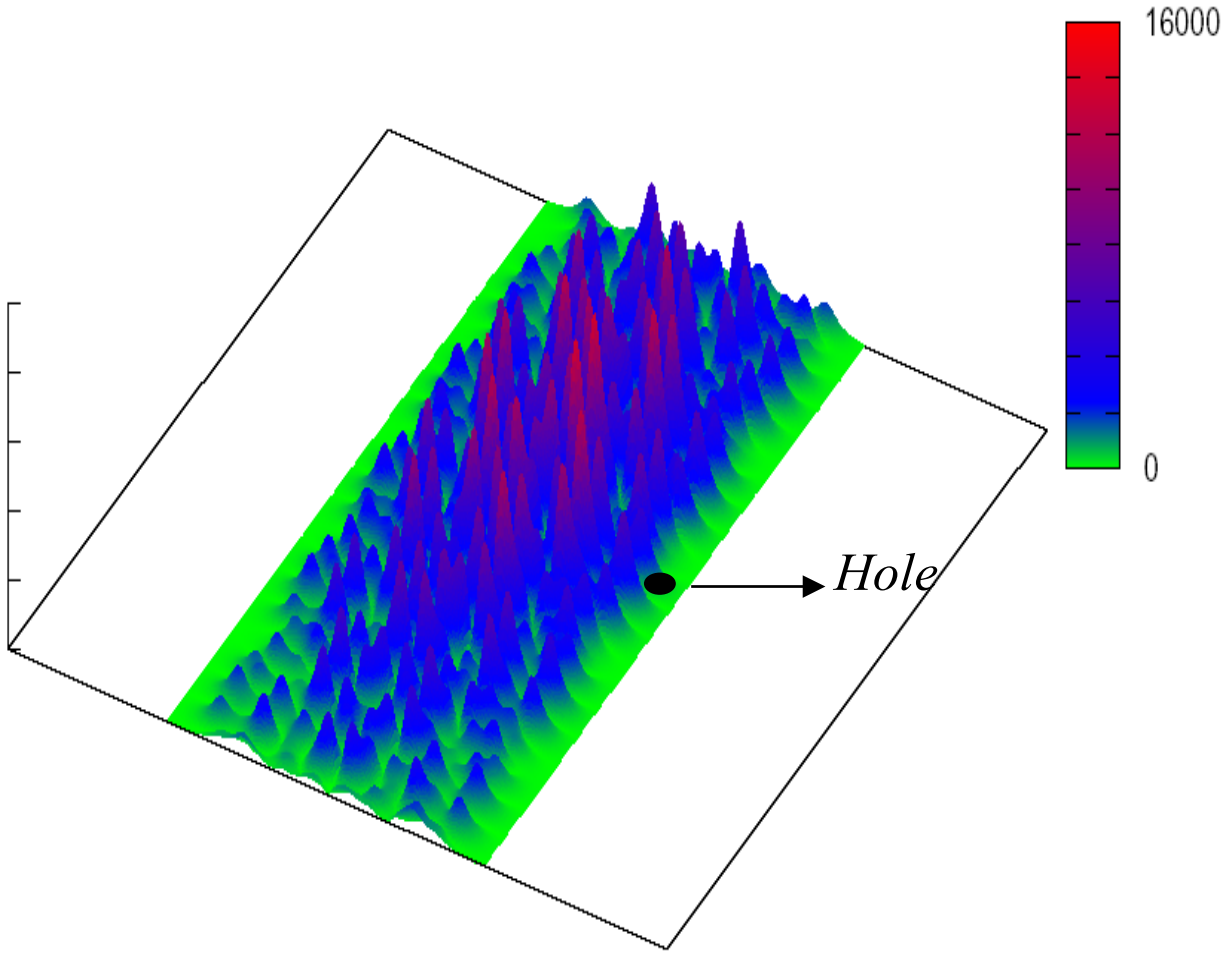
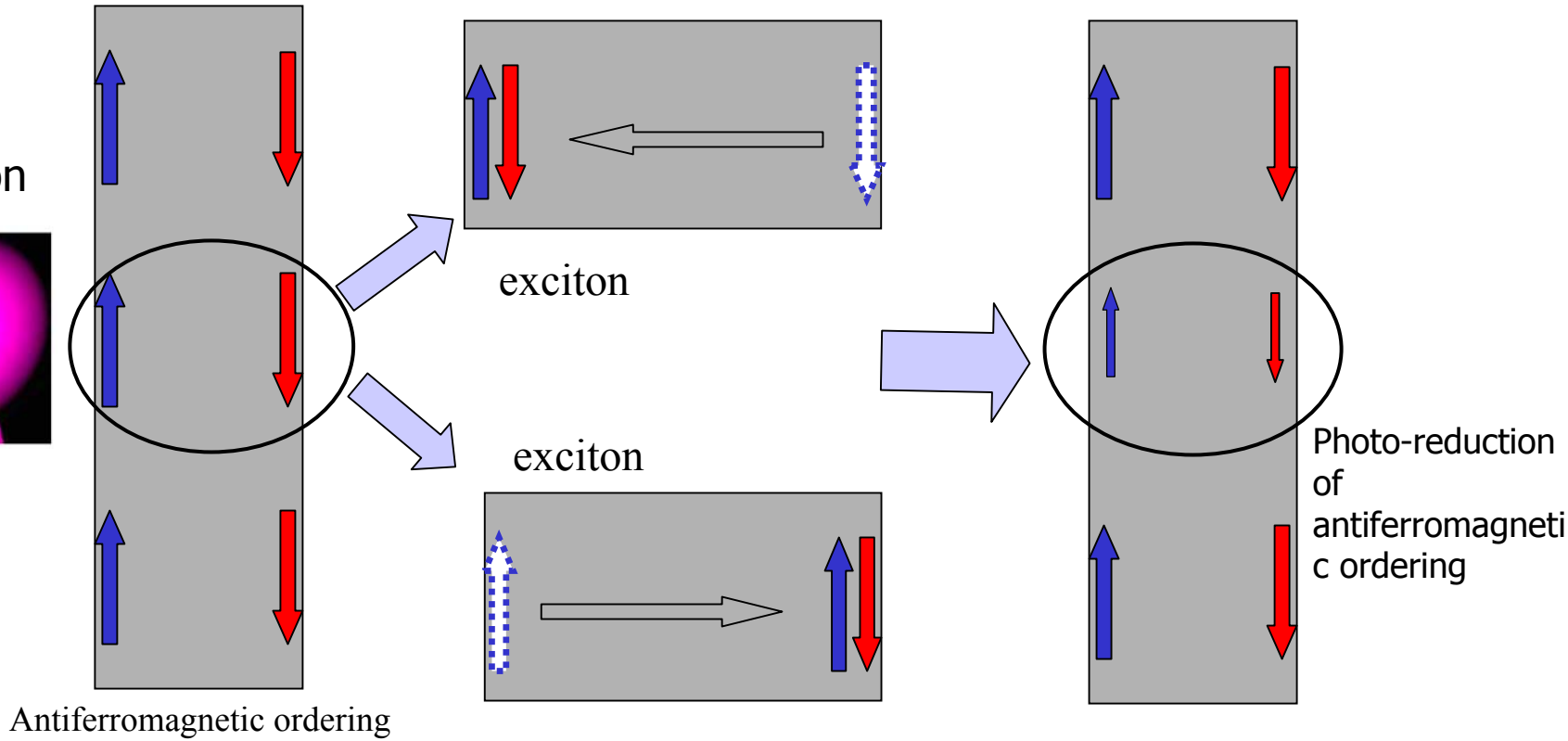


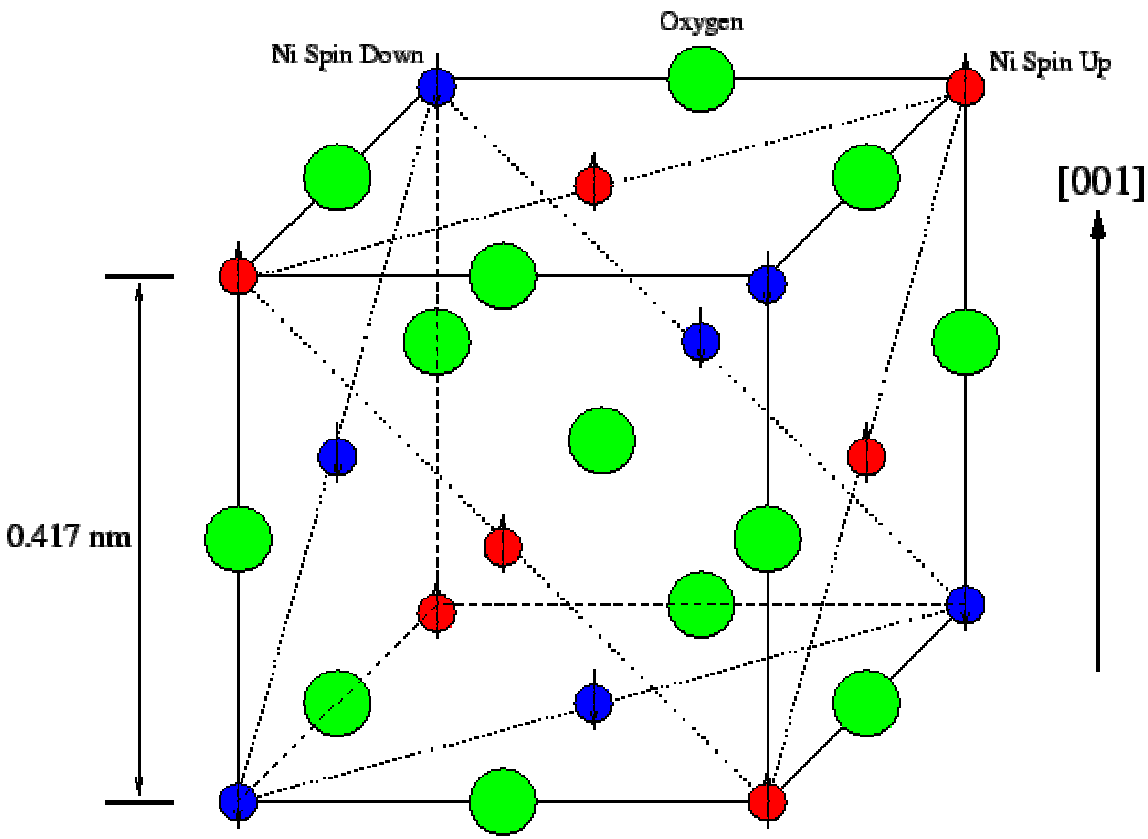
Photo-induced Charge and Spin Transfers in ZGNRs



- Charge transfer and corresponding spin transfer induced by excitons formed from spin-polarized edge states.
- Magnetic ordering reduced by exciting singlet excitons.

III. The Electronic Structure and Optical Response of NiO

Structure of NiO Crystal



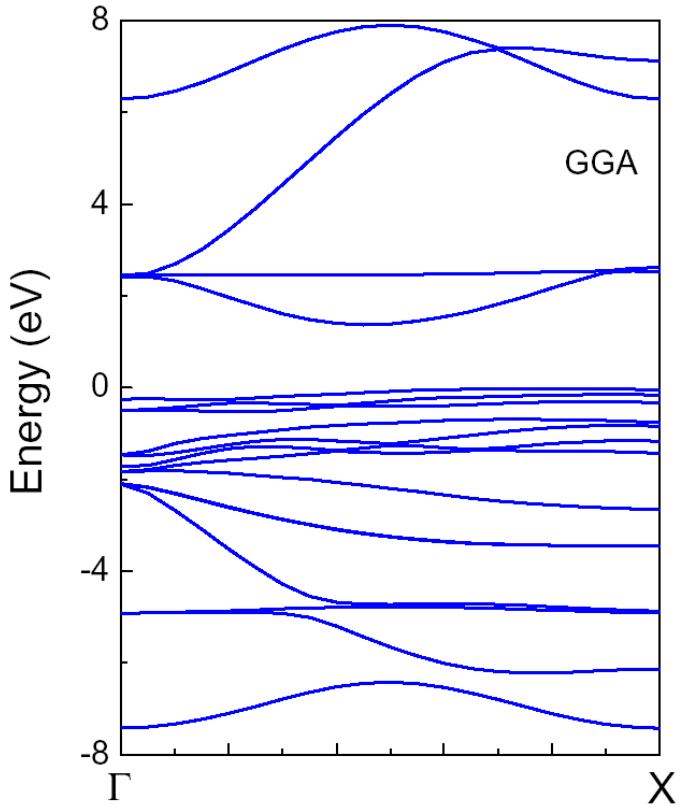
- A (Nearly) cubic structure (rocksalt) with a lattice constant of 0.417 nm.
- NiO has an antiferro
  -magnetic insulating ground state below the Neel temperture.
- The spins of Ni atoms are ferromagnetically aligned within the {111} plane, but in antiferromagnetic array along the [111] direction.

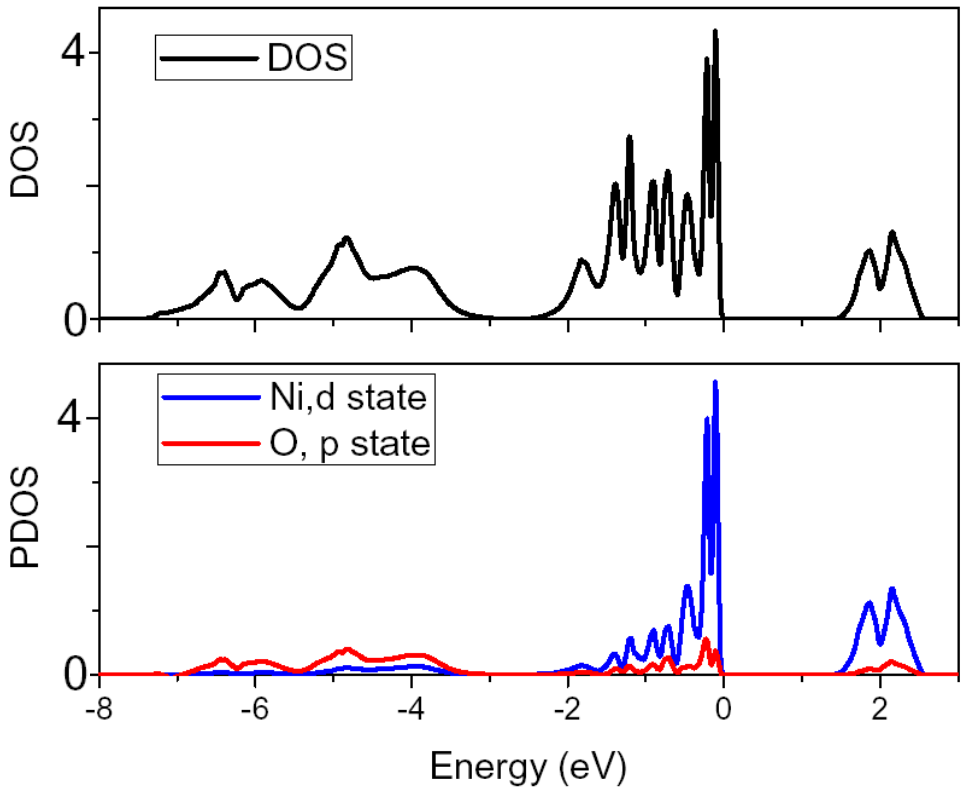
Review of Past *ab initio* Studies

	d-d Band Gap* (eV)	Magnetic Moment (μ_B)
GW [Aryasetiawan, et al., 1995]	5.5	1.60
model GW [Massidda, et al., 1997]	3.7	1.56
SCGW (all e) [Faleev, et al., 2004]	4.8	1.72
GGA+GW [Je-Luen Li, et al., 2005]	4.3	1.60
LDA+DMFT [Ren, et al., 2006]	4.3	1.70
Expt.	$4.0 \sim 4.3$	$1.64 \sim 1.90$

The discrepancy between above GW calculated result is due to the underlying different approximations, self-consistency, and assumptions used.

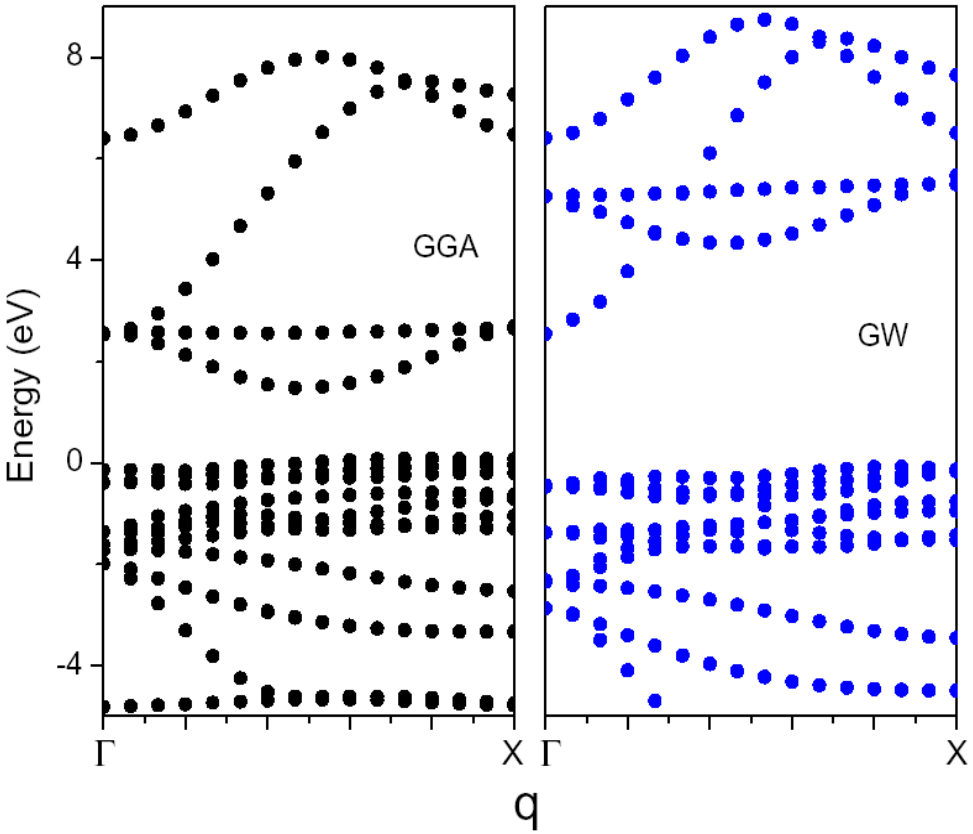
GGA Results

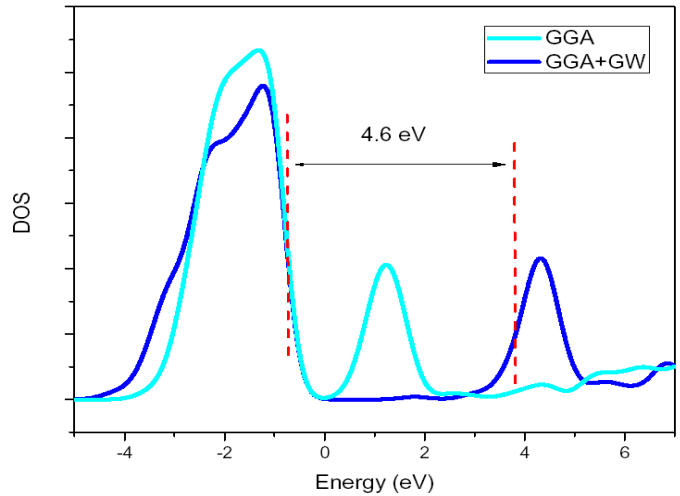


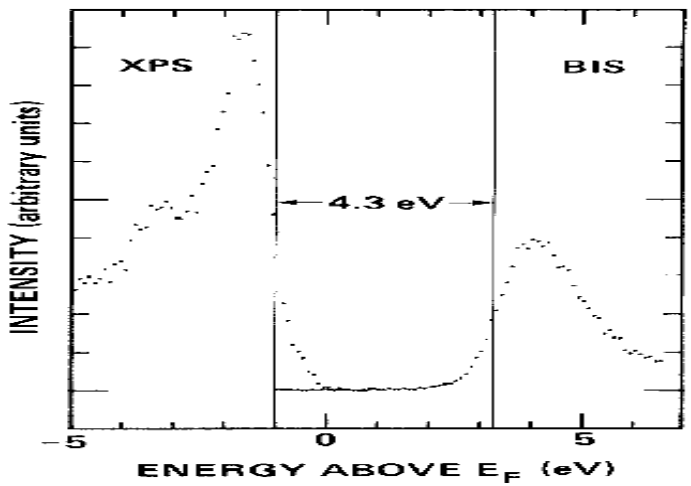


- We include 3s and 3p as valence electrons for pseudopotential generation.
- The direct d-d band gap is around 1.4 eV.
- Significant hybridization between the Ni 3d and O 2p is found for the bands close to the band gap.

GW Results





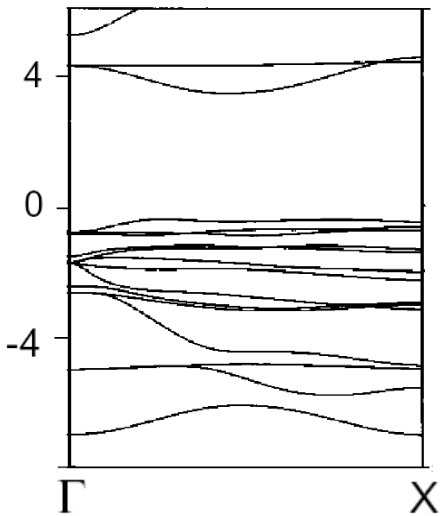


[Sawatzky, et al., 1984]

- The d – d band gap is increased from 1.4 eV to 4.3 eV.
- The d – s band gap is increased from 2.5 eV to 2.9 eV.

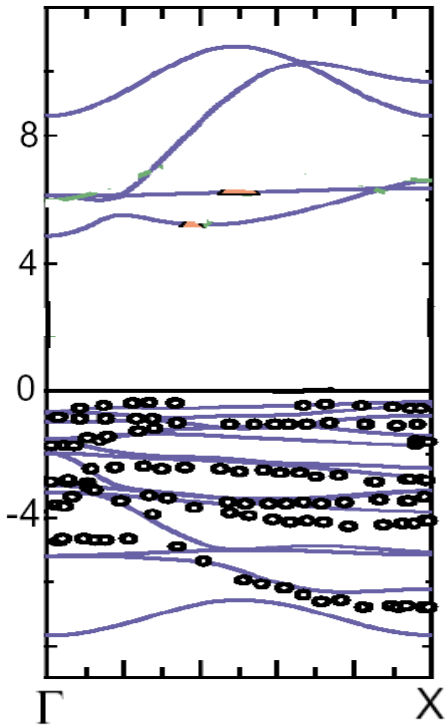
Compare with Previous Works

[Massidda, et al., 1997]



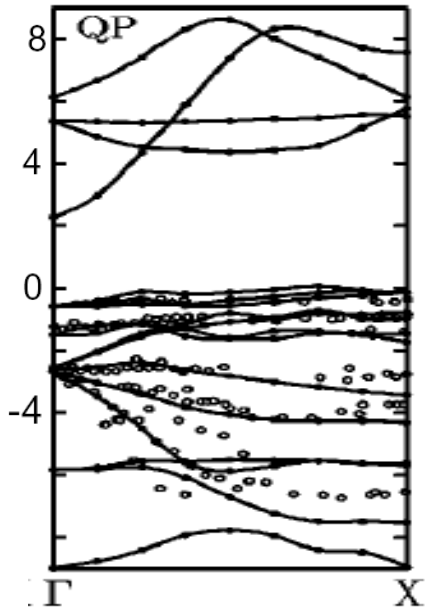
Model GW

Faleev, et al., 2004



LSDA_SCGW

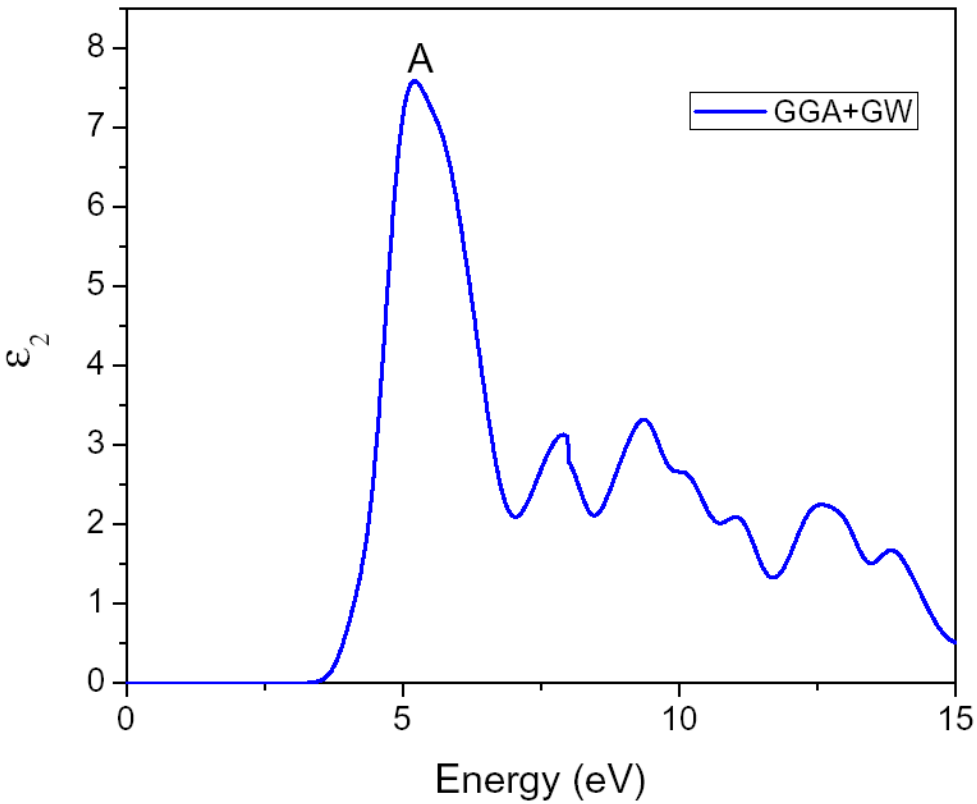
This work

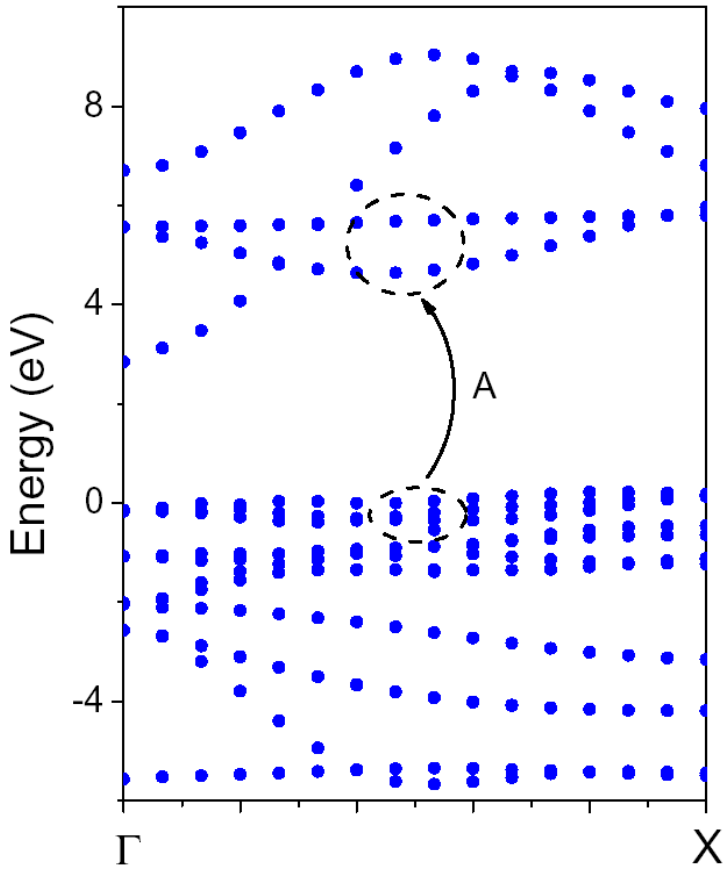


GGA+GW

- Significant difference of the d - s band gap between this work and previous ones.

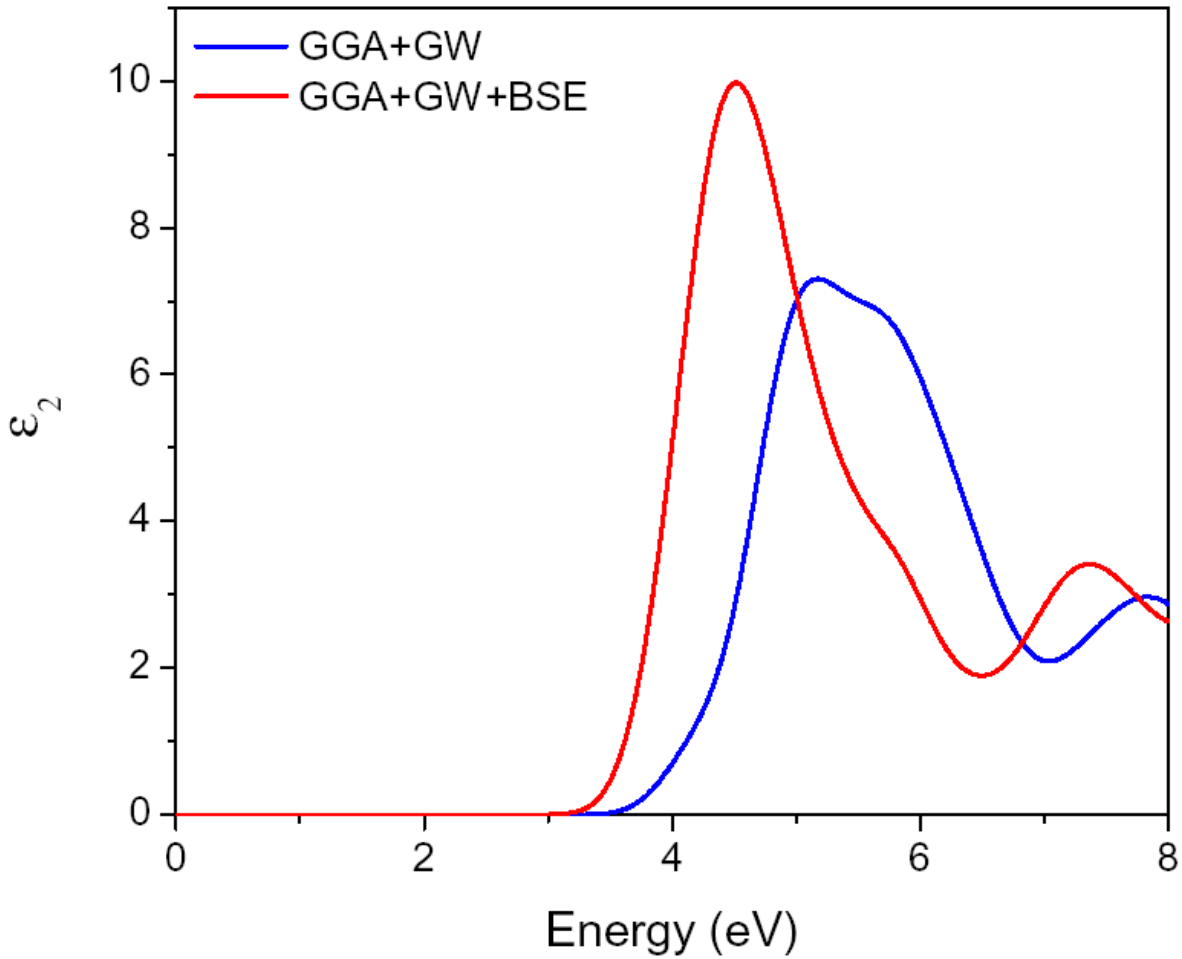
Optical Absorption without e-h





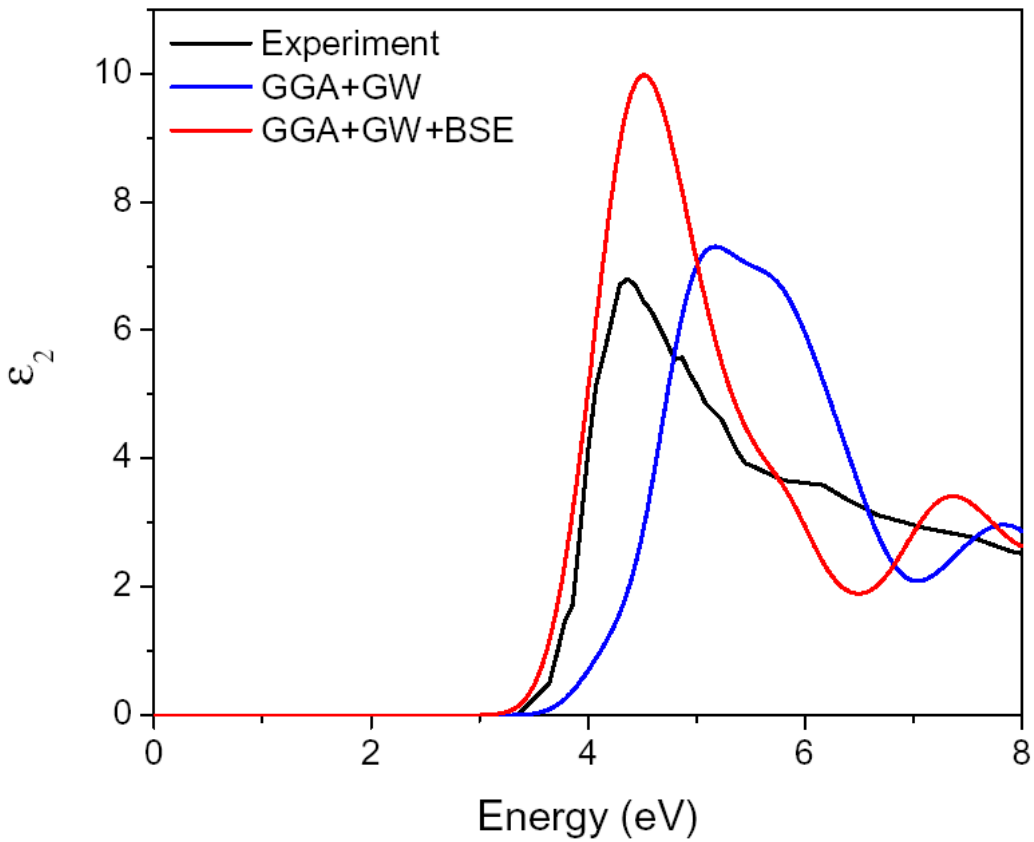
- The most prominent absorption peak A is consisted of a lot contribution from d electron states.

Optical Absorption with e-h



- Significant excitonic effects are found in the optical absorption spectrum. The most prominent peak is changed from 5.1 eV to 4.5 eV.
- This enhanced excitonic effect is due to the nature of localized d electron states.

Compare with Experiment



[experiment from Power, et al., 1970]

- The position of the most prominent peak in experiment is located at 4.2 eV, while our calculated peak is at 4.5 eV.

Summary

- The framework of GW+BSE method with the spin degree of freedom included is introduced.
- The optical absorption spectra of ZGNRs are found to be dominated by the magnetic-edge excitons.
- The edge-state excitons are charge-transfer excitons and they induce a spin-transfer across the ribbon at the same time.
- We have performed the spin-polarized GGA+GW method to obtain the quasiparticle band structure of NiO, which is in good agreement with experimental measurements.
- Significant excitonic effects are found in the optical response of NiO, which improve the agreement of the calculated spectrum with the experimental result.

Acknowledge

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- Dr. Jeff Neaton (LBNL)
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