Multiple Exciton Generation in Si and Ge Nanoparticles with High Pressure Core Structures

S. Wippermann, M. Vörös, D. Rocca, A. Gali, G. Zimanyi, G. Galli
Multiple Exciton Generation (MEG)

**MEG**: hot exciton relaxes by exciting another exciton.

Promising pathway to exceed Shockley-Queisser limit in 3rd generation solar cells.

**Multiple Exciton Generation (MEG)**

MEG: hot exciton relaxes by exciting another exciton

Promising pathway to exceed Shockley-Queisser limit in 3rd generation solar cells

enhanced MEG in quantum-confined nanostructures, e.g. nanocrystals

**Multiple Exciton Generation (MEG)**

**MEG:** hot exciton relaxes by exciting another exciton

Promising pathway to exceed Shockley-Queisser limit in 3rd generation solar cells

enhanced MEG in quantum-confined nanostructures, e.g., nanocrystals

---

**Key problem**

- Quantum confinement required for efficient MEG, but pushes electronic gap beyond solar spectrum
- MEG observed in Si and Ge: gap/wavefunction engineering possible?

=> investigate nanocrystals with high pressure core structures

---

Allotropes of Si and Ge

$c_{35}H_{36}$
$(X=Si,Ge)$

Cubic diamond, semiconductor
Allotropes of Si and Ge

- **cubic diamond, semiconductor**
- **BC8, semimetal**
- **$X_{34}H_{38}$ (X=Si,Ge)**

Allotropes of Si and Ge

- **cubic diamond**, semiconductor
- **BC8**, semimetal
- **X$_{34}$H$_{38}$**
- **X$_{35}$H$_{36}$** $(X=\text{Si, Ge})$
- **ST12**
- **X$_{46}$H$_{52}$**


Reduced gaps for BC8 and ST12 nanocrystals

![Graph showing the reduced gaps for BC8 and ST12 nanocrystals. The graph compares the energy gap (E_{gap-LDA} [eV]) against the NP diameter (nm) with different symbols and lines representing Si-I (cd) and Si-III (BC8).]
BC8 is semimetal in the bulk, quantum confinement opens small gap in BC8 nanocrystals => significantly reduced gaps compared to Si-I
Reduced gaps for BC8 and ST12 nanocrystals

BC8 is semimetal in the bulk, quantum confinement opens small gap in BC8 nanocrystals => significantly reduced gaps compared to Si-I.
BC8 is semimetal in the bulk, quantum confinement opens small gap in BC8 nanocrystals => significantly reduced gaps compared to Si-I

Ge ST12 features reduced gaps for \( d < 2.5\,\text{nm} \), significantly increased electronic density of states at band edges
BC8 is semimetal in the bulk, quantum confinement opens small gap in BC8 nanocrystals => significantly reduced gaps compared to Si-I.

Ge ST12 features reduced gaps for $d < 2.5\text{nm}$, significantly increased electronic density of states at band edges.

Get realistic estimate of electronic gaps from quasiparticle calculations in GW approximation.
GW for large systems

Calculation, storage & inversion of dielectric matrix $\varepsilon$ is major computational bottleneck $\Rightarrow$ spectral representation of $\varepsilon$ (RPA)

$$\tilde{\varepsilon} = \sum_{i=1}^{N} \tilde{v}_i \lambda_i \tilde{v}_i^H = \sum_{i=1}^{N} \tilde{v}_i (\lambda_i - 1) \tilde{v}_i^H + I$$

GW for large systems

Calculation, storage & inversion of dielectric matrix $\varepsilon$ is major computational bottleneck $\Rightarrow$ spectral representation of $\varepsilon$ (RPA)

$$\tilde{\varepsilon} = \sum_{i=1}^{N} \tilde{\nu}_i \lambda_i \tilde{\nu}_i^H = \sum_{i=1}^{N} \tilde{\nu}_i (\lambda_i - 1) \tilde{\nu}_i^H + I$$

Calculating eigenvectors/-values does NOT require explicit knowledge of the matrix itself; knowing the action of $\varepsilon$ on an arbitrary vector is sufficient

In linear response: $(\varepsilon - I) \Delta V_{SCF} = -v_c \Delta n$

Charge density response $\Delta n$ to perturbation of self-consistent field $\Delta V_{SCF}$ can be evaluated from density functional perturbation theory

GW for large systems

Calculation, storage & inversion of dielectric matrix \( \varepsilon \) is major computational bottleneck \( \Rightarrow \) spectral representation of \( \varepsilon \) (RPA)

\[
\tilde{\varepsilon} = \sum_{i=1}^{N} \tilde{\nu}_i \lambda_i \tilde{\nu}_i^H = \sum_{i=1}^{N} \tilde{\nu}_i (\lambda_i - 1) \tilde{\nu}_i^H + I
\]

Calculating eigenvectors/-values does NOT require explicit knowledge of the matrix itself; knowing the action of \( \varepsilon \) on an arbitrary vector is sufficient

In linear response: \( (\varepsilon - I) \Delta V_{SCF} = -\nu_c \Delta n \)

Charge density response \( \Delta n \) to perturbation of self-consistent field \( \Delta V_{SCF} \) can be evaluated from density functional perturbation theory

Orthogonal iteration procedure to obtain eigenvector/-value pairs, using \( \Delta V_{SCF} \) as trial potentials

In RPA fast monotonous decay of dielectric eigenvalue spectrum

Single parameter \( N_{eig} \) to control numerical accuracy

No summation over empty states, no inversion

GW for large systems

Calculation, storage & inversion of dielectric matrix $\epsilon$ is major computational bottleneck $\Rightarrow$ spectral representation of $\epsilon$ (RPA)

$$\tilde{\epsilon} = \sum_{i=1}^{N} \tilde{v}_i \lambda_i \tilde{v}_i^H = \sum_{i=1}^{N} \tilde{v}_i (\lambda_i - 1) \tilde{v}_i^H + I$$

Calculating eigenvectors/-values does NOT require explicit knowledge of the matrix itself; knowing the action of $\epsilon$ on an arbitrary vector is sufficient

In linear response: $(\epsilon - I) \Delta V_{SCF} = -v_c \Delta n$

Charge density response $\Delta n$ to perturbation of self-consistent field $\Delta V_{SCF}$ can be evaluated from density functional perturbation theory

Orthogonal iteration procedure to obtain eigenvector/-value pairs, using $\Delta V_{SCF}$ as trial potentials

In RPA fast monotonous decay of dielectric eigenvalue spectrum

Single parameter $N_{eig}$ to control numerical accuracy

No summation over empty states, no inversion

D. Rocca, H.-V. Nguyen, T.A. Pham (UCD)

Optimum gap for MEG in 4-8nm BC8 NPs

GW calculations up to d=1.6nm (Si$_{144}$H$_{114}$) confirm trends observed in LDA

Optimum gap for PV cells employing MEG ($E_g = 0.5-1.0$ eV) [5] found for BC8 NPs within typical experimental size range of d = 4-8 nm (extrapolation of GW gaps)

Calculating Multiple Exciton Generation (MEG) Rates

Impact Ionization (II) is dominating contribution to MEG [6]

=> approximate MEG rates with II rates [7]

Calculate II rates from Fermi’s Golden Rule:

\[ \Gamma_{ii}^{II} = \frac{2\pi}{\hbar} \sum_{f} \left| \langle X_i | W | XX_f \rangle \right|^2 \delta(E_i - E_f) \]

Approximate initial exciton \((X_i)\) and final biexciton states \((XX_f)\) as singly and doubly excited Slater determinants, built up from DFT orbitals

Screened Coulomb interaction \(W\) calculated using same technique as during GW calculations


Impact Ionization (II) is dominating contribution to MEG [6] => approximate MEG rates with II rates [7]

Calculate II rates from Fermi’s Golden Rule:

\[
\Gamma^{II}_i = \frac{2\pi}{\hbar} \sum_f |\langle X_i | W | XX_f \rangle|^2 \delta(E_i - E_f)
\]

Approximate initial exciton \((X_i)\) and final biexciton states \((XX_f)\) as singly and doubly excited Slater determinants, built up from DFT orbitals

Screened Coulomb interaction \(W\) calculated using same technique as during GW calculations


Optimum gap for MEG in 4-8nm BC8 NPs
Optimum gap for MEG in 4-8nm BC8 NPs

BC8 NPs feature lower activation threshold on absolute energy scale & order of magnitude higher impact ionization rate at same energies and same NP size!
Multiple Exciton Generation in Ge allotrope nanocrystals

relative energy scale

\( \langle T \rangle \) (1/ps)

\begin{align*}
\text{ST12}_{46} & \\
\text{ST12}_{60} & \\
\text{ST12}_{124} & \\
diamond_{66} & \\
diamond_{78} & \\
diamond_{124} & \\
\end{align*}

Energy / \( E_g \)
Multiple Exciton Generation in Ge allotrope nanocrystals

ST12 II rates size-independent

Increasing EDOS at band edges counterbalances loss of confinement
Multiple Exciton Generation in Ge allotrope nanocrystals

**Relative energy scale**

- ST12_{46}
- ST12_{60}
- ST12_{124}
- diamond_{66}
- diamond_{78}
- diamond_{124}

**Absolute energy scale**

- ST12_{60}
- ST12_{124}
- diamond_{66}
- diamond_{78}
- diamond_{124}

**ST12 II rates size-independent**

- Increasing EDOS at band edges counterbalances loss of confinement
- Simultaneously lower electronic gaps and higher relative II efficiency translate to significantly improved MEG on absolute energy scale
(Metastable) high pressure phases of elemental semiconductors allow for gap engineering of nanoparticles, while retaining efficient MEG (Si-BC8 and Ge-ST12).

Nanoparticles with high pressure core structures can attain optimum gap range for MEG-based solar energy conversion.

High pressure nanoparticles can be formed via the high pressure route or directly at ambient pressure in solution by chemical bottom-up synthesis from a precursor.

Talk on Si NPs embedded in charge transport matrix today at 12:30pm, Tre Ma
Acknowledgements

Giulia Galli and her group at UChicago, especially Marton Vörös and Tuan Anh Pham

Francois Gygi (UC Davis), Gergely Zimanyi (UC Davis), Adam Gali (Budapest Univ.), Dario Rocca (Univ. Lorraine)
Additional Slides
Optical properties (TD-DFT RPA)

- **red-shifted optical absorption** onset for high density phases (BC8, R8, Ibam)
- less pronounced for ST12 and low density phases (bct, hd)
cubic diamond vs. ST12

\[
\Gamma^I \propto \frac{2\pi}{\hbar} \sum_f \left| \langle X_i | W | XX_f \rangle \right|^2 \delta(E_i - E_f) \\
= \frac{2\pi}{\hbar} |W_{eff}^i|^2 \cdot TDOS_i
\]

**cubic diamond**: NP size increase reduces Coulomb interaction \(W_{eff}\), trion DOS almost constant

\[\Rightarrow\] impact ionization rate drops

**ST12**: \(W_{eff}\) reduced as for cubic diamond, *but TDOS increases*

\[\Rightarrow\] impact ionization rate remains almost constant with increasing size
Density functional theory (DFT):

Hohenberg-Kohn theorem:

\[ E_e[n] = T_0[n] + \frac{1}{2} \int \frac{n(r)n(r')}{|r - r'|} \, dr \, dr' + \int n(r)V(r) \, dr + E_{XC}[n] \]

\[ E_{XC}[n] \approx E_{XC}^{LDA}[n] = \int n(r)\epsilon_{XC}^{hom}(n(r)) \, dr \]

[Walter Kohn, Nobel Prize for chemistry in 1998]
Density functional theory (DFT):

**Hohenberg-Kohn theorem:**

\[
E_{e}[n] = T_0[n] + \frac{1}{2} \int \frac{n(r)n(r')}{|r - r'|} dr \, dr' + \int n(r)V(r) \, dr + E_{XC}[n]
\]

[Walter Kohn, Nobel Prize for chemistry in 1998]

\[
E_{XC}[n] \approx E_{XC}^{LDA}[n] = \int n(r)\epsilon_{XC}^{\text{hom}}(n(r)) \, dr
\]

\[
\n(r) = \frac{1}{2} \nabla^2 + \int \frac{n(r')}{|r - r'|} \, dr' + V(r) + \frac{\delta E_{XC}^{LDA}}{\delta n(r)} \psi_j(r) = \epsilon_j \psi_j(r)
\]

\[
n(r) = \sum_{occ.} \sum_j |\psi_j(r)|^2
\]

**Kohn-Sham self-consistent electron structure**

atomic positions
**Density functional theory (DFT):**

**Hohenberg-Kohn theorem:**

\[ E_{e}[n] = T_0[n] + \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} d\mathbf{r} d\mathbf{r}' + \int n(r)V(r) d\mathbf{r} + E_{XC}[n] \]

[Starting point: initial geometry]

- Interatomic forces
- External potential
- Kohn-Sham self-consistent electron structure
- Structurally relaxed ground-state

**Density functional equation:**

\[ -\frac{\nabla^2}{2} + \int \frac{n(r')}{|r-r'|} d\mathbf{r}' + V(\mathbf{r}) + \left( \frac{\delta E_{LDA}^{XC}}{\delta n(\mathbf{r})} \right) \psi_j(\mathbf{r}) = \epsilon_j \psi_j(\mathbf{r}) \]

**Occupied states:**

\[ n(\mathbf{r}) = \sum_{j} |\psi_j(\mathbf{r})|^2 \]

[Walter Kohn, Nobel Prize for chemistry in 1998]
Density functional theory (DFT):

**Hohenberg-Kohn theorem:**

\[
E_{e}[n] = T_0[n] + \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} dr\,dr' + \int n(r)V(r)dr + E_{XC}[n]
\]

\[
E_{XC}[n] \approx E_{XC}^{LDA}[n] = \int n(r)e_{xc}^{hom}(n(r))dr
\]

[Walter Kohn, Nobel Prize for chemistry in 1998]

**Starting point:** initial geometry

\[\n\]

external potential

interatomic forces

Kohn-Sham self-consistent electron structure

\[
\left\{ -\frac{\nabla^2}{2} + \int \frac{n(r')}{|r-r'|} dr' + V(r) + \frac{\delta E_{XC}^{LDA}}{\delta n(r)} \right\} \psi_j(r) = \epsilon_j \psi_j(r)
\]

structurally relaxed ground-state

\[\]

vibrational and thermal properties

electronic properties

spectroscopic and transport properties
Excited states (GW/BSE)

DFT disregards screened e⁻⁻ interaction and e⁻⁻h interaction for excited states => band gap underestimation, wrong distribution of spectral weights
Excited states (GW/BSE)

- DFT disregards screened e⁻–e⁻ interaction and e⁻–h interaction for excited states ⇒ band gap underestimation, wrong distribution of spectral weights

- Perturbative approaches for including screening (GW) and e⁻–h interaction (Bethe-Salpeter), starting from Quantum Liouville equation

\[
\frac{id\hat{\rho}(t)}{dt} = \left[ \hat{\mathcal{H}}(t), \hat{\rho}(t) \right]
\]

\[
\rho(r, r', t) = \sum_v \phi_v^*(r, t) \phi_v(r', t)
\]

single particle occ. orbitals

\[
\int \hat{\mathcal{H}}(r, r', t) \phi(r', t) \, dr' = \left( -\frac{1}{2} \nabla^2 + v_H(r, t) + v_{ext}(r, t) \right) \phi(r, t)
\]

+ \int \Sigma(r, r', t) \phi(r', t) \, dr'

time-dep. perturbation, i. e. electromagn. field
Excited states (GW/BSE)

- DFT disregards screened $e^-e^-$ interaction and $e^-h$ interaction for excited states $\Rightarrow$ band gap underestimation, wrong distribution of spectral weights

- Perturbative approaches for including screening (GW) and $e^-h$ interaction (Bethe-Salpeter), starting from Quantum Liouville equation

$$i \frac{d \hat{\rho}(t)}{dt} = \left[ \hat{\mathcal{H}}(t), \hat{\rho}(t) \right]$$

$$\rho(\mathbf{r}, \mathbf{r}', t) = \sum_v \phi_v^*(\mathbf{r}, t) \phi_v(\mathbf{r}', t)$$

Single particle occ. orbitals

$$\int \hat{\mathcal{H}}(\mathbf{r}, \mathbf{r}', t) \phi(\mathbf{r}', t) d\mathbf{r}' = \left( -\frac{1}{2} \nabla^2 + \nu_H(\mathbf{r}, t) + \nu_{ext}(\mathbf{r}, t) \right) \phi(\mathbf{r}, t)$$

+ $$\int \Sigma(\mathbf{r}, \mathbf{r}', t) \phi(\mathbf{r}', t) d\mathbf{r}'$$

Self-energy

$$\Sigma_{COH}(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \delta(\mathbf{r} - \mathbf{r}') W_p(\mathbf{r}, \mathbf{r}')$$

$$\Sigma_{SEX}(\mathbf{r}, \mathbf{r}', t) = -\sum_v \phi_v(\mathbf{r}, t) \phi_v^*(\mathbf{r}', t) W(\mathbf{r}, \mathbf{r}')$$

Statically screened Bethe-Salpeter equation (BSE)
Excited states (GW/BSE)

DFT disregards screened $e^−-e^−$ interaction and $e^−-h$ interaction for excited states $\Rightarrow$ band gap underestimation, wrong distribution of spectral weights

Perturbative approaches for including screening (GW) and $e^−-h$ interaction (Bethe-Salpeter), starting from Quantum Liouville equation

$$i\frac{d\hat{\rho}(t)}{dt} = \left[\hat{\mathcal{H}}(t), \hat{\rho}(t)\right]$$

$$\rho(r, r', t) = \sum_{\nu} \phi_{\nu}^*(r, t) \phi_{\nu}(r', t)$$

$\rho(r, r', t)$: single particle occ. orbitals

$$\int \hat{\mathcal{H}}(r, r', t) \phi(r', t) dr' = \left(-\frac{1}{2} \nabla^2 + v_H(r, t) + v_{ext}(r, t)\right) \phi(r, t)$$

$$+ \int \Sigma(r, r', t) \phi(r', t) dr'$$

$\Sigma(r, r', t)$: time-dep. perturbation, i. e. electromagn. field

$\Sigma_{COH}(r, r') = \frac{1}{2} \delta(r - r') W_p(r, r')$

$\Sigma_{SEX}(r, r', t) = -\sum_{\nu} \phi_{\nu}(r, t) \phi_{\nu}^*(r', t) W(r, r')$

$W(r, r')$: statically screened Bethe-Salpeter equation (BSE)

$\phi_{\nu}(r, t)$: screened Coulomb interaction
Excited states (GW/BSE)

To correct for DFT’s band gap underestimation, quasiparticle energies can be obtained in GW approximation from

$$\Sigma_{GW}(\mathbf{r}, \mathbf{r}'; i\omega) = \frac{1}{2\pi} \int G(\mathbf{r}, \mathbf{r}'; i(\omega - \omega')) W(\mathbf{r}, \mathbf{r}'; i\omega') d\omega'$$
Excited states (GW/BSE)

To correct for DFT's band gap underestimation, quasiparticle energies can be obtained in GW approximation from

\[ \Sigma_{GW}(r, r'; i\omega) = \frac{1}{2\pi} \int G(r, r'; i(\omega - \omega')) W(r, r'; i\omega') d\omega' \]

Screened Coulomb interaction required (in random phase (RPA) approx.)

\[ W(r, r') = \int \epsilon^{-1}(r, r'') v_{c}(r'', r') dr'' \]
Excited states (GW/BSE)

To correct for DFT's band gap underestimation, quasiparticle energies can be obtained in GW approximation from

$$\Sigma_{GW}(\mathbf{r}, \mathbf{r}'; i\omega) = \frac{1}{2\pi} \int G(\mathbf{r}, \mathbf{r}'; i(\omega - \omega')) W(\mathbf{r}, \mathbf{r}'; i\omega') d\omega'$$

Screened Coulomb interaction required (in random phase (RPA) approx.)

$$W(\mathbf{r}, \mathbf{r}') = \int \epsilon^{-1}(\mathbf{r}, \mathbf{r}'') v_c(\mathbf{r}'', \mathbf{r}') d\mathbf{r}''$$

Bottleneck: calculation, storage & inversion of dielectric matrix is very computationally demanding, involves large sums over empty states and is hard to converge.
Excited states (GW/BSE)

To correct for DFT’s band gap underestimation, quasiparticle energies can be obtained in GW approximation from

$$\Sigma_{GW}(\mathbf{r}, \mathbf{r}'; i\omega) = \frac{1}{2\pi} \int G(\mathbf{r}, \mathbf{r}'; i(\omega - \omega')) W(\mathbf{r}, \mathbf{r}'; i\omega') d\omega'$$

Screened Coulomb interaction required (in random phase (RPA) approx.)

$$W(\mathbf{r}, \mathbf{r}') = \int \epsilon^{-1}(\mathbf{r}, \mathbf{r}'') v_c(\mathbf{r}'', \mathbf{r}') d\mathbf{r}''$$

Bottleneck: calculation, storage & inversion of dielectric matrix is very computationally demanding, involves large sums over empty states and is hard to converge

Solution: spectral representation of RPA dielectric matrix; obtain matrix from directly calculating eigenvectors and eigenvalues

$$\tilde{\epsilon} = \sum_{i=1}^{N} \tilde{\mathbf{v}}_i \lambda_i \tilde{\mathbf{v}}_i^H = \sum_{i=1}^{N} \tilde{\mathbf{v}}_i (\lambda_i - 1) \tilde{\mathbf{v}}_i^H + I$$

=> no summation over empty states, no inversion, storage of eigenvector/-value pairs only!
Obtaining the eigenvectors/-values does **NOT** require explicit knowledge of the matrix; knowledge of the **action of the matrix** on an arbitrary vector is sufficient!

in linear response: 
\[
(\epsilon - I) \Delta V_{SCF} = -v_c \Delta n
\]

charge density response \(\Delta n\) to perturbation of self-consist. field \(\Delta V_{SCF}\) can be evaluated from density functional perturbation theory

orthogonal iteration procedure to obtain eigenvectors/-values, using \(\Delta V_{SCF}\) as trial potentials

in RPA fast monotonous decay of dielectric eigenvalue spectrum

single parameter \(N_{eig}\) to control numerical accuracy

\[
\tilde{\epsilon} = \sum_{i=1}^{N} \tilde{v}_i \lambda_i \tilde{v}_i^H = \sum_{i=1}^{N} \tilde{v}_i (\lambda_i - 1) \tilde{v}_i^H + I
\]

[H. Wilson et al., PRB 79, 245106 (2009); D. Rocca et al., J. Chem. Phys. 133, 164109 (2010); H.-V. Nguyen et al., PRB 85, 081101 (2012)]