Multiscale modeling of optical and transport properties of solids and nanostructures

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Outline

• Optical excitations of solids/nanostructures modeled by: density-functional theory (DFT), tight-binding (TB), k.p model, and effective bond-orbital model (EBOM)

• Transport and thermoelectric properties of nanostructure junctions modeled by non-equilibrium Green function method, including correlation

• Examples: zincblende/cubic semiconductors, quantum wires, and QDs and QD tunnel junctions
Excitation spectra

Flow chart of BSE calculation for excitation spectra

[ G. Onida, L. Reining, A. Rubio
Rev. Mod. Phys., 74, 601, (2002)]

DFT packages:
VASP, CASTEP
Abinit
WIEN2K
LMTO
SIESTA
LASTO
Linearized Slater-type orbital (LASTO) method


• Inside MTs: exact numerical solution ($u$) & $du/dE$

• Outside MTs: Slater-type orbitals, $r^{n-1} e^{-br} Y_{lm}(\Omega)$

• Match boundary conditions for each spherical harmonics
Symmetry-adapted basis

[Y.-C. Chang, R. B. James, and J. W. Davenport, PRB 73, 035211 (2006)]

Use of symmetry can reduce the computation effort significantly

- Symmetry-adapted basis was not commonly adopted in DFT calculations
- (For general $k$, point symmetry is lost)
- For large supercell calculations, only $k=0$ is needed, the use of symmetry-adapted basis can be very beneficial
- Examples:
  1. Defects in solids with high point symmetry
  2. High-symmetry nanoparticles like C60.
  3. Optical excitations of nanoclusters
  4. Excitonic excitation of solids with high symmetry
Optically allowed transitions for $T_d$ group

Only the following 6 (and exchange) out of 100 possible configurations are allowed:

\[
\langle \Gamma_1 | p_x | \Gamma_{5x} \rangle, \langle \Gamma_{3u} | p_x | \Gamma_{5x} \rangle, \langle \Gamma_{4y} | p_x | \Gamma_{5z} \rangle, \langle \Gamma_{5y} | p_x | \Gamma_{5z} \rangle, \langle \Gamma_2 | p_x | \Gamma_{5x} \rangle, \langle \Gamma_{3u} | p_x | \Gamma_{5x} \rangle
\]

Polarization matrix in RPA:

\[
P_{G,G'}^0(\omega) = \sum_{i \text{ occ}} \sum_{j \text{ unocc}} \zeta_{ij}(G)\zeta_{ij}^*(G') \cdot \left[ \frac{1}{\omega - \omega_{ij}} - \frac{1}{\omega + \omega_{ij}} \right]
\]

Polarization matrix in symmetry-adapted basis:

\[
\zeta_{ij}(G) = \int dr e^{iG \cdot r} \phi_i(r)\phi_j^*(r)
\]

[Use FFT]

Using Wigner-Eckart theorem:

\[
\zeta_{ij}(\Gamma \nu, s) = \zeta_{i, l_j}(\Gamma, s) V(\gamma_i, \gamma_j, \Gamma; \nu_i, \nu_j, \nu),
\]
Optical spectra calculated by Bathe-Salpeter Eq. in LASTO basis

- Results similar to LAPW results:
  - [Puschnig* and C. Ambrosch-Draxl, PRB 66, 165105 (2002)]
Optical spectra of GaAs, AlAs & SLs

Supercell method in plane-wave basis
Symmetrized Plane-wave basis

- The star of $G_s$

$$\Psi = \sum_s C(G_s)|G_s>$$

- $G_s$

- (001)

- (010)

- (001)
1) Comparison of our result to publication

<table>
<thead>
<tr>
<th>Method</th>
<th>HOMO</th>
<th>LUMO</th>
<th>$E_{\text{Singlet}}$</th>
<th>$E_{\text{Triplet}}$</th>
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<td>LDA</td>
<td>-8.0</td>
<td>-0.1</td>
<td>7.9</td>
<td>7.9</td>
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<tr>
<td>HFA</td>
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<td>1.5</td>
<td>8.3</td>
<td>6.9</td>
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<tr>
<td>GW-BSE (diag. $\Sigma$)</td>
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<td>Exp$^5$</td>
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2) The HFA calculation shows our successful inclusion of long-range tail in self-energy.
3) Our converged planewave calculation gives right screening on electron and exciton screening.
Table 2: Energies of $Si_{29}H_{24}$ and $Si_{29}H_{36}$

<table>
<thead>
<tr>
<th>Method</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_{QP}$ (eV)</th>
<th>$E_{Singlet}$ (eV)</th>
<th>$E_{Triplet}$ (eV)</th>
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<tbody>
<tr>
<td>LDA($Si_{29}H_{24}$)</td>
<td>-0.8</td>
<td>1.7</td>
<td>2.5</td>
<td>5.0</td>
<td>4.8</td>
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<tr>
<td>HFA</td>
<td>-3.3</td>
<td>5.6</td>
<td>8.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GW-BSE</td>
<td>-2.3</td>
<td>4.7</td>
<td>7.0</td>
<td>3.3</td>
<td>3.2</td>
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<tr>
<td>LDA($Si_{29}H_{36}$)</td>
<td>-0.8</td>
<td>2.5</td>
<td>3.3</td>
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<tr>
<td>GW-BSE</td>
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<td>5.4</td>
<td>7.4</td>
<td>4.9</td>
<td>4.7</td>
</tr>
</tbody>
</table>

- The $Si_{29}H_{24}$ has the 3.3eV peak as observed in experiment.
- The first excitation of $Si_{29}H_{36}$ is 4.9eV.
- Extra peaks can be found at 4.5eV and 5.3eV, which is corresponding to the Monte Carlo 4.8eV and 5.5eV.
The meta-Generalized Gradient Approximation

mGGA (TB09) [F. Tran and P. Blaha, Phys. Rev. Lett. 102, 226401 (2009)]

In TB09, the exchange-correlation energy is

$$E_{XC}(r) = \int \epsilon_{XC}[n(r), \nabla n(r), \tau(r)] ,$$

$$v_{TB}^{BR}(r) = c \nu_{BR}(r) + (3c - 2) \frac{1}{\pi} \sqrt{\frac{5}{12}} \sqrt{\frac{\tau(r)}{n_{\sigma}(r)}} ,$$

$$\nu_{BR}(r) = -\frac{1}{b_{\sigma}(r)} \left[ 1 - \epsilon_{x\sigma}(r) - \frac{1}{2} \epsilon_{x\sigma}(r)e^{x\sigma}(r) \right] ,$$

TDDFT with mGGA :

$$f_{G,G'}^{xc} \approx -\frac{\partial \epsilon_{xc}}{\partial \tau} \chi^{-1}_{K_S,s}(G, G') ,$$

$$\chi_{K_S}(r, r') = \sum_{\alpha, \beta, \sigma} \frac{f_{\alpha} - f_{\beta}}{\omega - \epsilon_{\beta} + \epsilon_{\alpha} + i\eta} \psi_{\alpha, \sigma}(r) \psi_{\beta, \sigma}(r') \psi_{\beta, \sigma}^{*}(r') \psi_{\alpha, \sigma}^{*}(r) ,$$


[V.U. Nazarov & G. Vignale, PRL 107, 216402(2011)]
Band structure comparison

- GaAs
- InGaAs$_2$
- In$_2$AsP
Comparison between LASTO & WIEN2k

Figure 4.10: Plot the kinetic energy density of Si in the interstitial region
Excitation spectra

Si

GaAs
Dielectric functions of InGaAs & InAsP alloys obtained by TDDFT based on mGGA

[F. Tran and P. Blaha, PRL 102, 226401 (2009)]
[V.U. Nazarov and G. Vignale, PRL 107, 216402(2011)]
Bond-orbital model

[S. Sun, Y. C. Chang, PRB 62, 13631 (2000)]

\[ H_{\alpha,\alpha'}(k) = E_p \delta_{\alpha,\alpha'} + \sum_{\tau} e^{i k \cdot \tau} \left\{ E_{xy} \tau_\alpha \tau_{\alpha'} + \left[ (E_{xx} - E_{xy}) \tau_\alpha^2 + E_{zz} (1 - \tau_\alpha^2) \right] \delta_{\alpha,\alpha'} \right\} \]

**Strain Hamiltonian**

\[
H_{st} = \begin{pmatrix}
-\Delta V_H + D_1 & \sqrt{3}d e_{xy} & \sqrt{3}d e_{xz} \\
\sqrt{3}d e_{xy} & -\Delta V_H + D_2 & \sqrt{3}d e_{yz} \\
\sqrt{3}d e_{xz} & \sqrt{3}d e_{yz} & -\Delta V_H + D_3
\end{pmatrix}
\]

\[
e_{ij} = (\varepsilon_{ij} + \varepsilon_{ji})/2
\]

\[
\Delta V_H = (a_1 + a_2)(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz})
\]

\[
D_1 = b(2\varepsilon_{xx} - \varepsilon_{yy} - \varepsilon_{zz})
\]

\[
D_2 = b(2\varepsilon_{yy} - \varepsilon_{xx} - \varepsilon_{zz})
\]

\[
D_3 = b(2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy})
\]

\[ a_1, a_2, b, d = \text{deformation potentials.} \]
InAs/GaAs Self assembled quantum dots

- InAs
- GaAs
- Wetting layer
- Lattice mismatch 7%
- Incident light
- Infrared detector
- Laser
- Area density $10^{11} \text{ / } cm^2$
Bond-orbital model

[S. Sun, Y. C. Chang, PRB 62, 13631 (2000)]
Valence force field (VFF) Model

\[ V = \frac{1}{4} \sum_{ij} \frac{3}{4} \alpha_{ij} \left( d_{ij}^2 - d_{0,ij}^2 \right)^2 / d_{0,ij}^2 \]

\[ + \frac{1}{4} \sum_i \sum_{j \neq k} \frac{3}{4} \beta_{ijk} \left( \vec{d}_{ij} \cdot \vec{d}_{ik} + d_{0,ij} d_{0,ik} / 3 \right)^2 / d_{0,ij} d_{0,ii} \]

i labels atom positions
j, k label nearest-neighbors of i
d_{ij} = bond length joining sites i and j
d_{0,ij} is the corresponding equilibrium length
\( \alpha_{ij} = \) bond stretching constants
\( d_{ijk} = \) bond bending constants
We take \( d_{ijk}^2 = d_{ij} d_{ik} \)
FIG. 3. (Color online) The strains on OZ axes: (a) the radial strain $\varepsilon_{rr}$, (b) the strain $\varepsilon_{zz}$, (c) the hydrostatic $\varepsilon_{\text{hyd}}$, and (d) the biaxial strain $\varepsilon_{\text{biax}}$ on the OZ axis, for the ratios $R/H=10/3.9$, 10/4.9, 10/5.9, 10/6.9, 10/7.9, with $R=100$ Å. The dots are for the VFF model and the continuum lines for CM.
Ground Transition Energy Varying With Dot Height (comparing to Experiment)

Dot base length 200Å

![Graph showing the comparison of theory and experiment for ground transition energy varying with dot height. The x-axis represents island height in Å, and the y-axis represents energy in eV. The graph shows a decreasing trend.]
PL/PLE Characterization: Electronic Structure

Ground state at 1.062 eV
Excited states:
Strongest at 1.147 eV and 1.229 eV
Weaker at 1.121 eV and 1.197 eV

[Data from A. Madhkar (USC)]
Intra-band Transitions

Data from A. Madhkar (USC)
### Intra-band Transitions

**Table 4**  
Inter-sub band transition matrix elements of ground electron state to upper three electron states, \( \left| \langle \phi_{1,c} | \mathbf{r} | \phi_{i,c} \rangle \right|^2 \).  
B=200A, h=80A.

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<th>Symmetry</th>
<th>state i</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
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<td>A1</td>
<td>#2 (0.111)</td>
<td>0</td>
<td>0</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>#3 (0.123)</td>
<td>0</td>
<td>0</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>#4 (0.197)</td>
<td>0</td>
<td>0</td>
<td>201</td>
</tr>
</tbody>
</table>

|          | #2 (0.106) | 0      | 0      | 28.5   |
|          | #3 (0.114) | 0      | 0      | 0      |

|          | #2 (0.109) | 0      | 0      | 15     |
|          | #3 (0.138) | 0      | 0      | 42     |
|          | #4 (0.201) | 0      | 0      | 14     |

| A1-B1n   | #1 (0.062) | 446    | 446    | 0      |
|          | #2 (0.162) | 0.2    | 0.2    | 0      |
|          | #3 (0.218) | 0.4    | 0.4    | 0      |

| B1-A1n   | #2(0.049)  | 536    | 536    | 0      |
|          | #3(0.061)  | 659    | 659    | 0      |
|          | #4(0.135)  | 376    | 376    | 0      |
|          | #5(0.161)  | 10.2   | 10.2   | 0      |
Effective bond-orbital model for QWRs

Wave Vector, k (nm$^{-1}$)  

InAs NW VB  

$E$ (eV)  

InAs NW CB  

d = 5nm  

InAs NW CB  

d = 7nm  

• (a)  

• (b)  

• (c)  

• (d)
Excitation spectra of colloidal QDs

[8-band or (6+2)-band $k.p$ model]

Figure 1. Schematic bulk band-offset for ZnTe/ZnSe CSQD.

Absorption coefficient for ZnTe/ZnSe CSQDs

(a) $r_0 = 1.8\text{nm}$, shell=2ML

(b) $r_0 = 1.8\text{nm}$, shell=3ML

(c) $r_0 = 1.8\text{nm}$, shell=4ML

(d) Comparison of theory and experiment for different shell thicknesses.
Transport through nanostructure junctions

Macroscopic electrode S (quantum hydrodynamic eq.)

Macroscopic electrode D (quantum hydrodynamic eq.)

Nano-component (NEGF)

\[ \text{Trace}[\Gamma_S A] f_S / 2\pi \]

\[ \text{Trace}[\Gamma_D A] f_D / 2\pi \]

\[ \text{Trace}[\Gamma_S G^n] f_S / 2\pi \]

\[ \text{Trace}[\Gamma_D G^n] f_D / 2\pi \]
Green function approach for GMR


A. Fert & P. Grunberg
2007 Nobel Prize (GMR)

Fe$_4$/Cr$_3$/Fe$_4$

trilayer junction

(Fe$_2$/Cr$_M$/Fe$_2$)$_N$
multiilayer junction

\[ G_L^0 = (Eo_L - H_L + i\eta)^{-1} \]

\[ G_R^0 = (Eo_R - H_R + i\eta)^{-1} \]

\[ G_S = (Eo_S - H_S - \Sigma_L(E) - \Sigma_R(E))^{-1}, \]

\[ \Sigma_L = (V_{SL}-Eo_{SL}) G_L^{0} (V_{LS}-Eo_{LS}) \]
DFT to Tight-binding conversion

Ag by 3NN (orthogonal) vs. Ag by 7NN (non-orthogonal)

BS of Fe–up by 3NN vs. BS of Fe–up by 7NN

BS of Fe–dn by 3NN vs. BS of Fe–dn by 7NN

Energy levels for Ag and Fe atoms at different k points.
GaAs zineblende/wurtzite heterostructure

H. Shtrikman et al., Nano Lett., 9, 215 (2009);
Transport characteristics of GaAs ZB/WZ junctions

Normal-incidence conductance

Total potentials of Ga and As atoms by lasto64
Tunneling current spectroscopy of a nanostructure junction involving multiple energy levels

$E_s, E_{p_z}, E_d$

Energy diagram for STM-QD junction

(a) No bias

(b) Forward bias

(c) Reverse bias
Theory vs. Experiment for STM-QD tunneling spectra

[Data from L. Jdira et al., Phys. Rev. B 73, 115305 (2006)]

Reverse bias

Forward bias

M-level case

\[ a^j \equiv 1 - (N_{j,\sigma} + N_{j,-\sigma}) + \langle n_{j,\sigma} n_{j,-\sigma} \rangle \]

\[ b^j \equiv N_{j,\sigma} + N_{j,-\sigma} - 2\langle n_{j,\sigma} n_{j,-\sigma} \rangle \]

\[ c^j \equiv \langle n_{j,\sigma} n_{j,-\sigma} \rangle \]

\[ \ell \neq j \neq j' \]

\[ a^{j'} \equiv 1 - (N_{j',\sigma} + N_{j',-\sigma}) + \langle n_{j',\sigma} n_{j',-\sigma} \rangle \]

\[ b^{j'} \equiv N_{j',\sigma} + N_{j',-\sigma} - 2\langle n_{j',\sigma} n_{j',-\sigma} \rangle \]

\[ c^{j'} \equiv \langle n_{j',\sigma} n_{j',-\sigma} \rangle \]

\[ p_1 = a^j a^{j'}, \, p_2 = b^j a^{j'}, \, p_3 = a^j b^{j'}, \, p_4 = c^j a^{j'}, \, p_5 = c^{j'} a^j, \ldots \]

\[ \Pi_1 = 0, \, \Pi_2 = U_{\ell j}, \, \Pi_3 = U_{\ell j'}, \, \Pi_4 = 2U_{\ell j}, \, \Pi_5 = 2U_{\ell j}. \]
単光子発射器 (Single-Photon generator)


M. T. Kuo, Y. C. Chang, PRB
Quantum interference in triple-QD junction


Thermal rectification properties of QD junctions

\[ ZT = S^2 G T / k \]
\[ S = dV / dT \]


FIG. 3. (Color online) Figure of merit $ZT$ as a function of temperature for various quantum dot configurations.

FIG. 6. (Color online) Electrical conductance $G$, thermal power $S$, and electron thermal conductance $\kappa_e$ as a function of temperature for various quantum dot configurations.
Thermoelectric properties of TQD junctions


Fig. 1  (a) Electrical conductance ($G_0$) and (b) Seebeck coefficient ($S$) of TQDMs as a function of central QD energy ($\Delta E = E_C - E_F$) for different $t_{IR}$ strengths at $E_L = E_R = E_F$, $t_{LC} = t_{CR} = t_c = 3T_0$ and $K_0 = 1T_0$. We assume $U_{LC} = U_{CR} = 30T_0$, $U_{LR} = 10T_0$, $U_R = U_0 = 100T_0$ and $\Gamma_L = \Gamma_R = \Gamma = 0.3T_0$.

Fig. 2  (a) Electrical conductance ($G_0$) and (b) Seebeck coefficient ($S$) of TQDMs as a function of central QD energy ($\Delta E = E_C - E_F$) for different $t_{IR}$ strengths at $E_L = E_R = E_F$, $t_{LC} = t_{CR} = t_c = 3T_0$ and $K_0 = 1T_0$. We assume $U_{LC} = U_{CR} = 30T_0$, $U_{LR} = 10T_0$, $U_R = U_0 = 100T_0$ and $\Gamma_L = \Gamma_R = \Gamma = 0.3T_0$.

Fig. 3  The curves of Fig. 3 are one to one corresponding to those of Fig. 2. The calculation of Fig. 3 only considers the single particle assumption.

Fig. 4  (a) Electron thermal conductance ($k_0$), and (b) Lorenz number ($\kappa_0/G_0$) as a function of central QD energy for different temperatures. The curves of Fig. 4 correspond to those of Fig. 2. $k_0 = k_B T$.
TE behavior of QD array

[M. T. Kuo, Y. C. Chang, Nanotechnology 24 175403 (2013) ]

\[
\kappa_{ph} = \frac{\pi^2 k_B^2 T}{3h} F_s
\]

\[(F_s = 0.01)\]

\[
G_e(2e^2/h) (a)
\]

\[
S (k_B/e) (b)
\]

\[
\kappa_e (k_B T_0 / h) (c)
\]

\[
ZT (d)
\]
Enhancement in TE efficiency of QD junctions due to increase of level degeneracy


Single QD

\[ \kappa_{ph} = \frac{\pi^2 k_B^2 T}{3\hbar} F_s \]  \( (F_s = 0.1) \)

DQD

\[ \kappa_{E} = \frac{e^2 G_0}{h} S \]

\[ ZT = \frac{\kappa_{E}}{\kappa_{ph}} \]
Summary

• Computation codes were implemented for electronic and optical excitation calculations by using symmetry adapted PW & LASTO basis.
• Electronic states and optical linear response of nanoclusters (with high symmetry) by including the quasi-particle self-energy correction (GW approximation) and the excitonic effects can be calculated efficiently.
• For high-symmetry (Oh,Td,C3v,D2d) systems, our method improves the computation efficiency by two-three orders of magnitude.
• Self-assembled or colloidal QDs can be suitably modeled by VFF model for strain distribution+EBOM for electronic states
• Intra-level and inter-level Coulomb interactions play keys roles in the optical properties
• Non-equilibrium transport and correlation are important in the analysis of nanostructure junction devices
• Computation codes were implemented for electronic and optical excitation calculations of 1D and 2D materials by using PW-B spline mixed basis.
DFT with LASTO basis

A LASTO basis function at a given site (taken as the origin) is defined as

$$\psi_N(r) = r^{n-1} e^{-\zeta_{nl} r} Y_{lm}(\hat{r})$$

for $r$ outside muffin-tin (MT) spheres and

$$\psi_N(r) = \sum_{\tilde{N}} [\beta_{N\tilde{N}} g_i(r_i) + \alpha_{N\tilde{N}} \dot{g}_i(r_i)] Y_{lm}(\hat{r}_i)$$

for $r$ inside MTs sphere, where $N$ is a composite index for the LASTO orbitals, which includes the site index $i$ and orbital index $\{nlm\}$, while $\tilde{N}$ is a composite index for $\{\tilde{i}, \tilde{l}, \tilde{m}\}$, which labels the spherical harmonics expansion of the basis function at site $\tilde{i}$. $\zeta_{nl}$ denotes the exponents.
Optical spectra of SiH₄ cluster

- Peaks at 8.8, 9.5, 9.8, 10.8, 11.7 eV
Optical spectra of 1nm Si clusters
Effect of asymmetric tunneling

\[ \Gamma_{out} = 1 \text{meV} \]

\[ \Gamma_{in} = 0.1 \text{meV} \]

Shell-tunneling

Shell-filling

\[ \Gamma_{in} = 10 \text{meV} \]
Comparison with continuum Model


using Green’s function method one obtains (see Refs. 8–10)

$$u(r) = \frac{C}{\pi} \int \frac{1}{|r - r_0|} dS(r_0),$$

where $C = \varepsilon_d (1 + \nu) / [4(1 - \nu)]$, $\nu$ is Poisson’s ratio, $\varepsilon_d$ is the interface dilation defined as $\varepsilon_d = (a_{\text{int}} - a_{\text{ext}}) / a_{\text{ext}}$ ($a_{\text{ext}}$, $a_{\text{int}}$ are the lattice constant of the external, internal (inclusion) material, respectively) and it coincides with the compression

FIG. 1. The schematic representation of the QD-WL system (in gray) in a plan containing OZ axes. The specific regions $I_{\text{int}}$, $I_{\text{out}}$, $II_{\text{int}}$, $II_{\text{out}}$, and III are shown.
The diagrams show absorption coefficients for different materials:

- **p-type InAs NW**: Absorption coefficients for two different diameters, 5nm and 7nm.
- **p-type GaSb NW**: Absorption coefficients for two different diameters, 5nm and 7nm.

Each graph plots the absorption coefficient (in units of $10^4$ cm$^{-1}$) against photon energy (in eV). The graphs illustrate how the absorption properties change with different diameters and materials.
Modeling of Quantum Wires
Potential for zine-blende (ZB)/wurtzite (WZ) heterostructure

By Abinit

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<th>ZB</th>
<th>WZ</th>
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<td></td>
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<td>$m_e/m_0$</td>
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<td>0.310232</td>
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</table>
Total potentials of Ga and As atoms by lasto64

- **Ga1** to **Ga7** in ZB (total potential of Ga atoms)
- **As1** to **As7** in WZ (total potential of As atoms)
Emission spectrum of QD transistor
Symmetry-adapted basis for large supercells
Coupled-wave transfer method

• Energy and wave functions computed using a stabilized transfer matrix technique by dividing the system into many slices along growth direction.

• Envelope function approximation with energy-dependent effective mass is used.

• Effective-mass Hamiltonian in $k$-space:

\[
\frac{(k_x^2 + k_y^2)}{m_t(E)} + \frac{\partial_z^2}{m_l(E) - E} \mathcal{F}(k) + \sum_{k'} [V(k, k') + V_{imp}(k, k')] \mathcal{F}(k') = 0
\]

is solved via plane-wave expansion in each slice.

• 14-band $k \cdot p$ effects included perturbatively in optical matrix elements calculation

• Dopant effects incorporated as screened Coulomb potential

• The technique applies to quantum wells and quantum dots (or any 2D periodic nanostructures)
Charge densities of low-lying states in lens-shaped QD

s-like

d-like

$p_x/p_y$ like

$p_z$ like
Quantum well intrasubband photodetector (QWISP) for far infrared and terahertz radiation detection

[Ting et al., APPLIED PHYSICS LETTERS 91, 073510 (2007)]

Fig. 4 A schematic illustration of the laterally repeating supercell geometry used in our simulations. Note that the supercell also repeats in the x direction with periodicity of $L_x$ (not drawn). The example shown in this figure illustrates a quantum well containing several randomly placed dopant impurities.
Quantum well intrasubband photodetector (QWISP) for far infrared and terahertz radiation detection

FIG. 1. (Color online) Schematic illustrations of the energy dispersions and energy band diagrams of (a) FIR/terahertz QWIP; (b) QWISP showing intersubband and impurity scattering assisted intrasubband optical absorption and carrier extraction mechanisms.

FIG. 3. (Color online) Low-temperature FIR/terahertz QWIP (set P) side-incidence responsivity and QWISP (set S) normal-incidence responsivity. Modeling parameters are listed in Table I.
Quantum well intrasubband photodetector (QWISP) for far infrared and terahertz radiation detection

Fig. 5: The zero-bias wave functions of a pair of states involved in an intra-subband transition in a QWISP structure. The energy of the lower state is slightly below the Fermi level, and the energy of the upper state is just above the barrier band edge. The left panel shows the in-plane averaged probability densities as functions of z (growth direction). The random dopant distribution induced in-plane fluctuations of the wave functions are displayed in the right panel, which shows the translucent probability density isosurfaces, overlaid on top of probability density color contour plane located at the middle of the quantum well.
Submonolayer QD infrared photodetector

[Ting et al., APPLIED PHYSICS LETTERS 94, 1 (2009)]

FIG. 2. (Color online) Measured normal and 45° incidence spectral responsivity curves for two SML QDIP samples.

FIG. 1. (Color online) The left panel illustrates a conventional DWell structure where a SK QD, consisting of pyramidal shape QD resting on a wetting layer, is embedded in a QW structure. The right panel show two stacks of SML QDs embedded in a QW.

FIG. 4. (Color online) 80 K images taken with a 1024×1024 pixel SML QDIP FPA with f/2 optics.
Optical absorption spectra of Si

![Graph showing optical absorption spectra of Si](image)
Comparison in CPU time

The algorithm is tested on $SiH_4$ with a XEON 3GHz/4GB PC.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Memory</th>
<th>CPU Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straight PW</td>
<td>3GB</td>
<td>24hrs</td>
</tr>
<tr>
<td>Fully symmetrized</td>
<td>50MB</td>
<td>5mins</td>
</tr>
</tbody>
</table>

Memory reduced to 2%, CPU reduced to 0.3%.
The coding is much more complicated.
• GW approximation for Quasi-particle energy

\[ E_n^{QP} \equiv \epsilon_n + \langle \phi_n | \Sigma(E_n^{QP}) - V_{xc} | \phi_n \rangle \]
\[ \approx \epsilon_n + Z_n \langle \phi_n | \Sigma(\epsilon_n) - V_{xc} | \phi_n \rangle \]  \hspace{1cm} (2)

with \( Z_n^{-1} = 1 - \langle \phi_n | d\Sigma/d\epsilon | \epsilon_n | \phi_n \rangle \).

In real space and energy domain, we have,

\[ \Sigma(r, r'; \omega) = \frac{i}{2\pi} \int_{-\infty}^{\infty} d\omega' \ W(r, r'; \omega') \ G(r, r'; \omega - \omega') e^{i\omega' \delta}, \]  \hspace{1cm} (13)

where the screened Coulomb interaction \( W \) is expressed as,

\[ W(r, r'; \omega) = \int d^3r'' v(r - r'') \ e^{-1}(r'', r'; \omega) \]  \hspace{1cm} (14)

where \( v(r - r'') \) is the Coulomb interaction \( 1/|r - r''| \) and \( G \) is the one-particle Green’s function. \( G \) itself depends on \( \Sigma \) through the Dyson equation and should arguably be determined self-consistently. In practice, however, in calculations for real systems, \( G \) can approximated by the non-interacting LDA Green’s function, i.e.,

\[ G^{LDA}(r, r'; \omega) = \sum_n \frac{\Psi_{nk}(r) \Psi_{nk}^*(r')}{\omega - \epsilon_n - i\eta_n} \]  \hspace{1cm} (15)

\[ \Delta_n(E_n) \equiv \langle \phi_n | \Sigma(E_n) - V_{xc} \delta(r - r') | \phi_n \rangle \]
\[ = \int dr dr' \phi_n^*(r) \Sigma(r, r'; \epsilon_n) \phi_n(r') \]
\[ - \int dr \phi_n^*(r) V_{xc}(r) \phi_n(r') \]  \hspace{1cm} (18)

In our scheme, we first workout \( W \) in reciprocal space. We define the matrix element \( \langle \Sigma \rangle \)

\[ W_{GG'}(\omega) \equiv \langle G | W(\omega) | G' \rangle = \frac{1}{V_{cell}} v_G e^{-1}_{GG'}(\omega), \]  \hspace{1cm} (19)

where \( V_{cell} \) is the volume of the supercell and \( v_G \) is the Fourier transform of the Coulomb interaction.

In real space, we have,

\[ W(r, r'; \omega) = \sum_{G, G'} e^{-iGr} W_{G, G'}(\omega) e^{iG'r'} \]  \hspace{1cm} (20)
• $\omega$ Integration & plasma pole approximation

$$
\Sigma_n(E_n) = \sum_{mG'G} \zeta^*_{nm}(G)\zeta_{nm}(G') \cdot \frac{i}{2\pi} \int d\omega' \frac{W_{GG'}(\omega')}{\omega' - \omega_{mn} - i\eta_m}
$$

$$
= \sum_m \frac{i}{2\pi} \int d\omega' \frac{\tilde{W}_{nm}(\omega')}{\omega' - \omega_{mn} - i\eta_m}
$$

(24)

where

$$
\tilde{W}_{nm}(\omega) = \sum_{G,G'} \zeta^*_{nm}(G)W_{GG'}(\omega')\zeta_{nm}(G')
$$

(25)

and $\eta_m$ is a small imaginary part depending on $m$,

$$
\eta_m = \begin{cases} 
-\delta & \text{for } m = \text{unocc}, \\
+\delta & \text{for } m = \text{occ}
\end{cases}
$$

(26)

Note that $\epsilon^{-1}(\omega) - 1$ is an analytic function, which decays to zero as $|\omega| \to \infty$ and has no pole in the upper half of the complex $\omega$ plane for retarded screening. So is the function $\tilde{W}_{nm}(\omega) - \nu_{nm}$. These properties allow us to perform the $\omega'$ integral in Equ.(24) analytically.

For retarded screening, the polarization and dielectric function have poles in the lower half of the complex plane. This means that, in time domain, $t \to 0^-$.}

$$
\Sigma_n(E_n) = -\sum_{m} \tilde{W}_{nm}(\omega_{mn}) - \sum_{m} \sum_{j} \frac{z_{j}(nm)}{\omega_{mn} + \omega_j}.
$$

(27)

In the above equation, the first term is due to the screened exchange while the second term the Coulomb-hole (COH) contribution, which is a result beyond RPA.
•How to obtain symmetrization coefficients

To obtain the symmetrization coefficients, $C(i, l m)$, we first construct the lattice harmonics at each site $j$. The lattice harmonics is the linear combination of spherical harmonics of the same $l$ that transforms like a basis function (labelled $\nu$) associated with an irreducible representation (labelled $\Gamma$) of a point group. We define

$$K_l^{\Gamma \nu}(G) = \sum_m C_{l m}^{\Gamma \nu} Y_{l m}(G).$$ (1)

In general, these coefficients can be obtained via the use of projection operator. We have

$$C_{l m}^{\Gamma \nu} = \frac{n(\Gamma)}{h} \sum_{\Lambda} \Gamma_{\nu, \nu}(\Lambda) D_{m, m'}^{(l)}(\Lambda),$$ (2)

where $n(\Gamma)$ is the dimension of irreducible representation, $\Gamma$, $h$ is the order of the point group, $\Lambda$ denotes a group operation, and $D_{m, m'}^{(l)}(\Lambda) \equiv \int d\Omega Y_{l m}^*(\Omega) Y_{l m'}(\Lambda^{-1} \Omega)$, which can be evaluated efficiently via the Gaussian quadrature method.

Next we construct the symmetrized site functions for each shell, $s$ defined as

$$S_s^{\Gamma \nu} = \sum_m C_s^{\Gamma \nu}(j) e^{iG \cdot r_j}.$$ (3)

using the projection operator, we obtain

$$C_s^{\Gamma \nu}(j) = \frac{n(\Gamma)}{h} \sum_{\Lambda} \Gamma_{\nu, \nu}(\Lambda) D_{j, j'}^{(s)}(\Lambda),$$ (4)

where $D_{j, j'}^{(s)}(\Lambda) \equiv \sum_G e^{iG \cdot (r_j - \Lambda^{-1} r_j)}$ which is 1 if $(r_j - \Lambda^{-1} r_j)$ is a lattice vector of the "superlattice" and zero otherwise. Finally, we use the direct products of cubic harmonics and the symmetrized site functions to obtain the fully symmetrized states. We have

$$\psi_s^{\Gamma \mu} = \sum_{\gamma \nu, \gamma' \nu'} V^{\Gamma}(\gamma \nu, \gamma' \nu') K_l^{\Gamma \nu} S_s^{\gamma' \nu'},$$ (5)

where $V^{\Gamma}(\gamma \nu, \gamma' \nu')$ are the vector coupling coefficients, which are readily available in Ref.

Evaluating matrix elements

The most time consuming part of the LASTO code is the evaluation of the structure coefficients ($\alpha$ and $\beta$) and the overlap ($S$) and hamiltonian ($H$) matrices, which involve double summation over the reciprocal lattice vectors $G$ and $G'$. [14] For $k = 0$ these matrices are given by

$$S_{N,N'} = \sum_{\tilde{N}} (\beta^*_{N\tilde{N}} \beta_{N'\tilde{N}} + \alpha^*_{N\tilde{N}} \alpha_{N'\tilde{N}} \langle \hat{g}_i | \hat{g}_{i'} \rangle)$$

$$+ \frac{1}{v_s} \sum_{G} \psi^*_N(G) \psi_{N'}(G)$$

$$- \frac{1}{v_s^2} \sum_{G,G'} \psi^*_N(G) \psi_{N'}(G') \sum_{\tilde{N}} e^{i(\mathbf{G}' - \mathbf{G}) \cdot \mathbf{R}_i} f(|\mathbf{G}' - \mathbf{G}|)$$

$$H_{N,N'} = \epsilon \sum_{\tilde{N}} (\beta^*_{N\tilde{N}} \beta_{N'\tilde{N}} + \alpha^*_{N\tilde{N}} \alpha_{N'\tilde{N}} \langle \hat{g}_i | \hat{g}_{i'} \rangle)$$

$$+ \frac{1}{v_s} \sum_{G} \psi^*_N(G)(|G|^2 + V_0) \psi_{N'}(G)$$

$$+ \frac{1}{2} R_s \sum_{\tilde{N}} g_i^* \hat{g}_{i'} (\beta^*_{N\tilde{N}} \alpha_{N'\tilde{N}} + \alpha^*_{N\tilde{N}} \beta_{N'\tilde{N}}) + \hat{g}_i g_{i'}^* \beta_{N\tilde{N}} \beta_{N'\tilde{N}}$$

$$+ \frac{1}{2} R_s \sum_{G,G'} \psi^*_N(G) \psi_{N'}(G') \sum_{\tilde{N}} e^{i(\mathbf{G}' - \mathbf{G}) \cdot \mathbf{R}_i} f(|\mathbf{G}' - \mathbf{G}|),$$

where $f(|\mathbf{G}|)$ is the Fourier transform of the cut-off function $\theta(r_s - |r'|)$, $v_s$ is the supercell volume, and $\psi_N(G)$ is the Fourier transform of the LASTO orbital, $\psi_N(r - r_i)$. 

Symmetry reduction factor $\sim n_h^2$
Optical spectra of 1nm Si clusters
GaSb NW CB
\[ d = 5\text{nm} \]

GaSb NW CB
\[ d = 7\text{nm} \]

GaSb NW VB
\[ d = 5\text{nm} \]

GaSb NW VB
\[ d = 7\text{nm} \]
GaAs NW CB
\( d = 5\text{nm} \)

GaAs NW CB
\( d = 7\text{nm} \)

GaAs NW VB
\( d = 5\text{nm} \)

GaAs NW VB
\( d = 7\text{nm} \)
CdTe NW VB

CdTe NW CB

CdTe NW CB

CdTe NW VB

\( d = 5\text{nm} \)

\( d = 7\text{nm} \)

Wave Vector, \( k \) (nm\(^{-1}\))

E (eV)
\begin{enumerate}
\item \textbf{a})
\item \textbf{b})
\item \textbf{c})
\item \textbf{d})
\end{enumerate}
Wave vector, $k$ (cm$^{-1}$)

Energy, $E$ (eV)

Si NW VB

- $d=5$nm

- $d=7$nm

Ge NW VB

- $d=5$nm

- $d=7$nm

- $a$

- $b$

- $c$

- $d$
Absorption Coefficient $\times 10^4 \text{ cm}^{-1}$ vs. Photon Energy (eV) for different NW materials and diameters:

- **ZnSe NW**
  - $d = 7\text{ nm}$
  - $d = 5\text{ nm}$

- **CdTe NW**
  - $d = 7\text{ nm}$
  - $d = 5\text{ nm}$
Application to optical excitation of solids & superlattices

• Use time-reversal symmetry

\[ \Psi_{cv-k}(r_h, r_e) = \Psi_{cvk}^*(r_h, r_e) \]

\[ \langle \Psi_{cvk}^\pm | K | \Psi_{c'v'k'}^\mp \rangle = \text{Re} \langle \Psi_{cvk}^\pm | K | \Psi_{c'v'k'}^\mp \rangle = \pm \text{Im} \langle \Psi_{cvk}^\pm | K | \Psi_{c'v'k'}^\mp \rangle = \langle \Psi_{cvk}^\pm | K | \Psi_{c'v'k'}^\mp \rangle \]

\[ G(E) = G_0(E) + G_0(E)K G(E) \]

\[ \langle \Psi_{cvk}^\pm | G_0(E)p_\alpha | 0 \rangle = \langle \Psi_{cvk}^\pm | p | 0 \rangle / [E - E_c(k) + E_v(k) + i\delta] \]

\[ \langle \Psi_{cv\Lambda k}^\pm | Gp_\alpha | 0 \rangle = \langle \Psi_{cv\Lambda k}^\pm | Gp_\Lambda | 0 \rangle \]

\[ -\text{Im} \sum_{cvk} < 0 | p_\alpha | \Psi_{cv\Lambda k}^S > < \Psi_{cv\Lambda k}^S | Gp_\alpha | 0 > \]

[Puschnig* and C. Ambrosch-Draxl, PRB 66, 165105 (2002)]
FIG. 5. (Color online) The piezoelectric potential $V_p$: (a) in the horizontal plane, $z=0$ containing the top of the cone; (b) in the horizontal plane $z=H/3$; (c) in the horizontal plane $z=H$. The left side figures are the three-dimensional plots and the right side figures are the contour plots. The red circles in these plots represent the cross sections of the QD with the horizontal planes. (d) Equipotential surfaces of piezoelectric potential $V_p$ for 0.065 V (red), −0.065 V (dark blue), 0.04 V (orange), and −0.04 V (blue). In the left side figure only the positive equipotential surfaces are plotted. In the right side figure are plots with a top view.
Supercell calculations in symmetry-adapted LASTO basis

[Y.-C. Chang, R. B. James, and J. W. Davenport, PRB 73, 035211 (2006)]

FIG. 1. (a) Wigner-Seitz cell of a 128-atom supercell. The solid squares indicate the positions of cations in the irreducible segment of the Wigner-Seitz cell. The coordinates are in units of $a/4$. (b) Wigner-Seitz cell of a 54-atom supercell. The solid circles indicate the positions of anions in the irreducible segment of the Wigner-Seitz cell. The open circles indicate the positions of anions outside the irreducible segment of the 54-atom supercell but within the irreducible segment of the 128-atom supercell.