Empirical Pseudopotential-Based Calculation of Electronic Structure and Transport in Nanostructures

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Preamble

- A changing environment
  - ❑ From "homogeneous" (mostly Si/SiO_2) to "heterogeneous" devices (SiGe, high-κ, Fins, III-Vs, graphene, dichalcogenides, phase/changing, spin/magnetic,…)
  - ❑ From "narrow" (logic&telecom) to "diverse" applications (sensing, optical, energy storage/harvesting, bio-sensing, low-power, wearable, …)
  - ❑ From big…
    - Cold electrons → mobility, effective mass
    - Bulk materials → known atomic and electronic structure
    - Big devices → semiclassical transport
  - ❑ … to small (UTBs, Fins, NWs, GNRs, CNTs,..):
    - Quasi-ballistic, hot electrons → full electronic structure
    - Nanostructures → unknown atomic and electronic structure, quantum confinement
    - Small devices → quantum transport (at least in principle…)
- Why empirical pseudopotentials?
  - ❑ "Tunable" to experimental data (as compared to "*ab initio*", self-consistent pseudopotentials)
  - ❑ Flexibility and physical accuracy of the plane-wave basis (as compared to LCAO/TB… wavefunctions!)
  - ❑ Electron transport more cumbersome than TBs, but still manageable compared to DFT

Outline

- Electronic structure
  - ☐ Born-Oppenheimer and single-electron approximations
  - ☐ The concept of pseudopotential (self-consistent and empirical)
  - ☐ DFT *vs*. EPs
  - ☐ EPs for nanostructures (supercells) and examples: thin films, hetero-layers, graphene, nanowires, nanotubes
- Scattering
  - ☐ Electron-phonon interaction
    - DFT *vs.* rigid-ion approximation (bulk Si, thin Si films, graphene)
    - Scattering rates
  - ☐ Interface and line-edge roughness (Si films, graphene nanoribbons)
- Transport
  - ☐ Semiclassical:
    - Low-field (mobility) and high-field (MC) properties (Si thin films, graphene, NWs, AGNRs)
  - ☐ Quantum-ballistic:
    - Transport equation
    - Open boundary conditions

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Electronic structure: Adiabatic approximation

- Full crystal Hamiltonian:

$$\mathrm{H} = \sum_i \frac{\mathrm{p}_i^2}{2m} + \frac{1}{2}\sum_{i,j} \frac{e^2}{4\pi\epsilon_0 |\mathrm{r}_i - \mathrm{r}_j|} + \sum_\alpha \frac{\mathrm{P}_\alpha^2}{2M_\alpha} + \frac{1}{2}\sum_{\alpha,\beta} U(\mathrm{R}_\alpha - \mathrm{R}_\beta) + \sum_{i,\alpha} V_{ion}(\mathrm{r}_i - \mathrm{R}_\alpha)$$

- Born-Oppenheimer (adiabatic) approximation:

$$\Psi_\mathrm{R}(\mathrm{r})\ \mathrm{H}_L\ \Phi(\mathrm{R})\ +\ \Phi(\mathrm{R})\ \mathrm{H}_{el}\ \Psi_\mathrm{R}(\mathrm{r})\ +\ \mathrm{H}'\ \Phi(\mathrm{R})\ \Psi_\mathrm{R}(\mathrm{r})\ =\ E\ \Phi(\mathrm{R})\ \Psi_\mathrm{R}(\mathrm{r})$$

with wavefunction $\Xi(\mathrm{R},\mathrm{r},t)\ \approx\ \Phi(\mathrm{R},t)\ \Psi_\mathrm{R}(\mathrm{r},t)$ and lattice and electron Hamiltonians:

$$\mathrm{H}_L\ =\ \sum_\alpha \frac{\mathrm{P}_\alpha^2}{2M_\alpha} + \frac{1}{2}\sum_{\alpha,\beta} U(\mathrm{R}_\alpha - \mathrm{R}_\beta)$$

$$\mathrm{H}_{el}\ =\ \sum_i \frac{\mathrm{p}_i^2}{2m} + \sum_{i,\alpha} V_{ion}(\mathrm{r}_i - \mathrm{R}_\alpha) + \frac{1}{2}\sum_{i,j} \frac{e^2}{4\pi\epsilon_0 |\mathrm{r}_i - \mathrm{r}_j|}$$

ignoring "coupling" term $\mathrm{H}'\ \Phi(\mathrm{R})\ \Psi_\mathrm{R}(\mathrm{r})\ =\ \Phi(\mathrm{R})\ \mathrm{H}_L\ \Psi_\mathrm{R}(\mathrm{r})\ \sim\ -\ \Phi(\mathrm{R}) \sum_\alpha \frac{\hbar^2}{2M_\alpha} \nabla^2 \Psi_\mathrm{R}(\mathrm{r})$

of negligible magnitude:

$$\nabla^2 \Psi_\mathrm{R}(\mathrm{r}) \sim \textstyle\sum_i k_i^2 \longrightarrow \quad \Phi(\mathrm{R})\ \mathrm{H}_L\ \Psi_\mathrm{R}(\mathrm{r})\ \sim\ m/M_\alpha$$

Electronic structure: Single-electron approximation

- Full electron wave equation:

$$\left[\sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_{i,\alpha} V_{ion}(\mathbf{r}_i - \mathbf{R}_\alpha^{(0)}) + \frac{1}{2}\sum_{i,j} \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_i - \mathbf{r}_j|}\right] \Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N_{el}}) = E\,\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N_{el}})$$

- Assume:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N_{el}}) = \frac{1}{\sqrt{N_{el}!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \cdots & \psi_1(\mathbf{r}_{N_{el}}) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \psi_{N_{el}}(\mathbf{r}_1) & \cdots & \cdots & \cdots \end{vmatrix}$$

- Take care of anti-symmetrization (exchange) in steps…

 1. Hartree: “mean field” due to all other electrons:

$$\mathbf{H}_i\psi_i(\mathbf{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V_{lat}(\mathbf{r}) + \sum_{j\neq i} \frac{e^2}{4\pi\epsilon_0} \int \frac{\psi_j^*(\mathbf{r}')\psi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'\right] \psi_i(\mathbf{r}) = w_i\psi_i(\mathbf{r})$$

 2. Hartree-Fock: Add exchange term to lower repulsive electron-electron energy:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{lat}(\mathbf{r}) + \sum_{j\neq i} \frac{e^2}{4\pi\epsilon_0} \int \frac{\psi_j^*(\mathbf{r}')\psi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'\right] \psi_i(\mathbf{r})$$

$$- \sum_{j\neq i} \frac{e^2}{4\pi\epsilon_0} \psi_j(\mathbf{r}) \int \frac{\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = w_i\psi_i(\mathbf{r}) .$$

Electronic structure: Kohn-Sham density functional

3. Local exchange & correlation $V_{xc}(\rho) \propto \rho^{1/3}$ (Kohn-Sham, LDA) as in homogeneous electron gas, good for ground state only (Hohenberg-Kohn and Kohn-Sham theorems):

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V_{lat}(\mathbf{r}) + V_{xc}[\rho(\mathbf{r})]\right\}\psi(\mathbf{r}) = w_i\psi(\mathbf{r})$$

($V_{lat}(\mathbf{r})$) includes also the Hartree term).

4. Additional schemes (GGA, meta-GGA, hybrid, DFT+U, GW corrections) to improve the “band-gap problem”

Electronic structure: Plane-wave methods and pseudopotentials

- Single-electron Schrödinger equation:

$$-\frac{\hbar^2\nabla^2}{2m}\psi(\mathbf{r}) + V_{lat}(\mathbf{r})\psi(\mathbf{r}) = E\,\psi(\mathbf{r})$$

with Bloch wavefunction $\psi(\mathbf{k},\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} u_{\mathbf{k}\mathbf{G}}\, e^{i\mathbf{G}\cdot\mathbf{r}}$

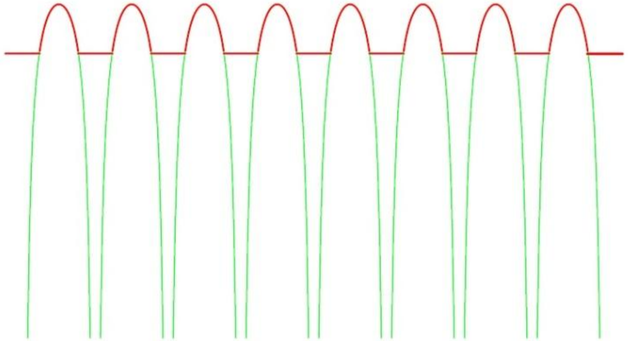
- Matrix form:

$$\left[\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2 - E(\mathbf{k})\right] u_{\mathbf{k}\mathbf{G}} + \sum_{\mathbf{G}'} V_{\mathbf{G}\mathbf{G}'}\, u_{\mathbf{k}\mathbf{G}'} = 0$$

with lattice potential:

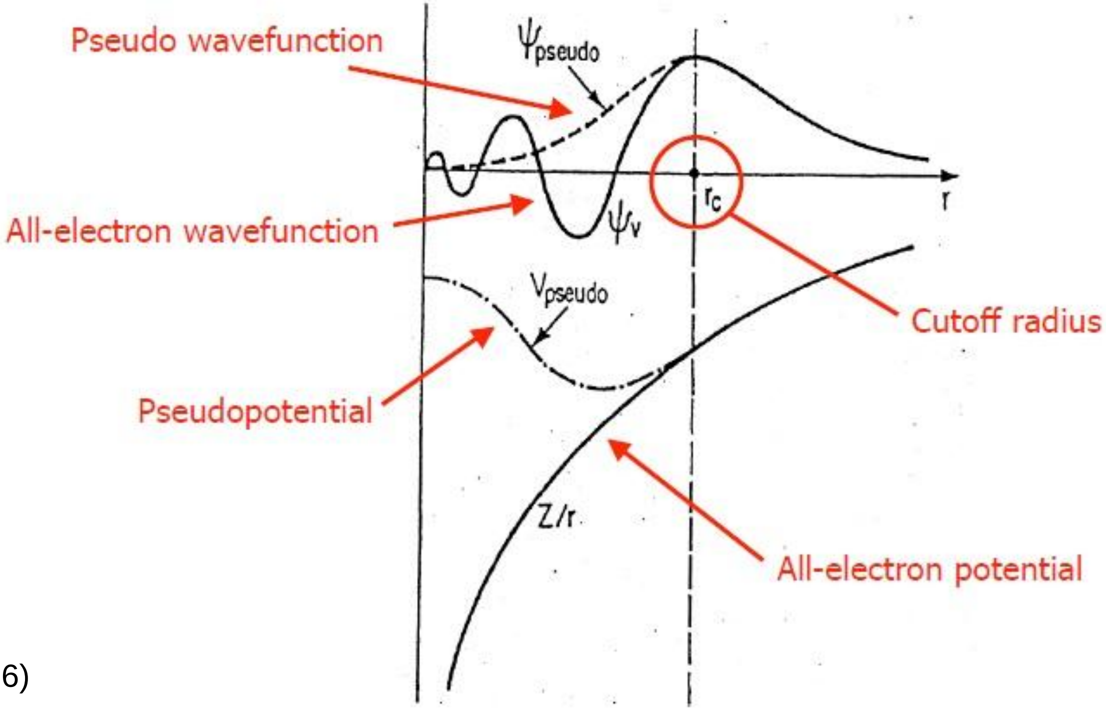
$$V_{\mathbf{G}\mathbf{G}'} = \sum_{\alpha} e^{-i(\mathbf{G}-\mathbf{G}')\cdot\tau_\alpha} \frac{1}{\Omega}\int_{\Omega} V_{ion}(\mathbf{r})\, e^{-i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}}\, d\mathbf{r} = S(\mathbf{G}-\mathbf{G}')\, V_{ion,\mathbf{G}-\mathbf{G}'}$$

- Eigen-system too large (≈10^6, ionic potential too “steep” in the core), replace lattice potential with ionic “pseudo”potentials



Self-consistent (“first-principles”, “*ab initio*”) pseudopotentials

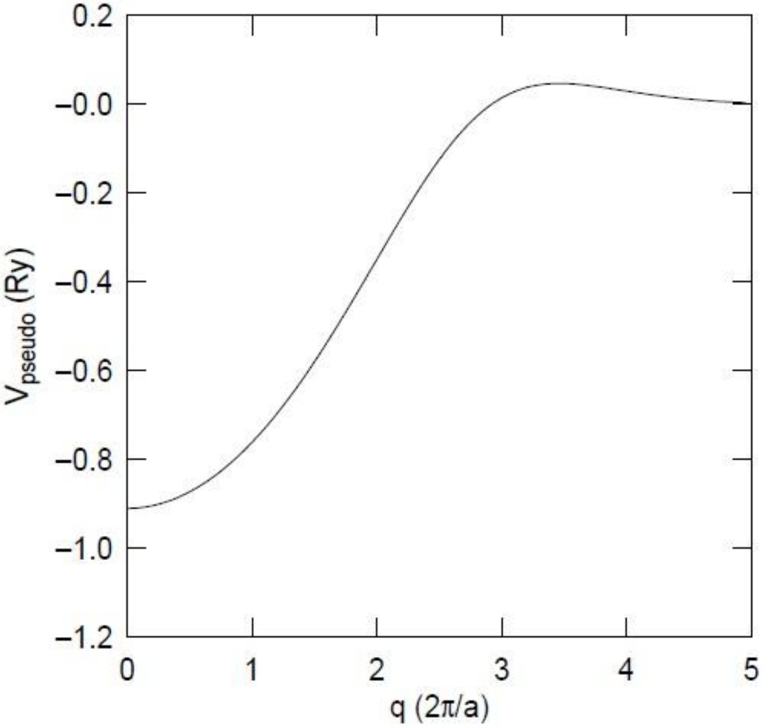
- “Exact” wavefunction and potential outside core
- “Node-less” wavefunction and singularity-free model/pseudo-potential inside core
- Match radial derivatives at cutoff radius
- Two approaches:
  - Orthogonalize valence wavefunction to core states, replace wavefunction with pseudo-wavefunction in the core (nonlocal pseudopotential from OPW, Harrison)
  - “Model” potentials (Animalu, Heine,…)
- Now a “zoo” of pseudopotentials: Norm-conserving (Hamann-Schlüter-Chiang), super-soft (Vanderbilt), PAW (Blöchl),… generated starting from Hartree-Fock or DFT for isolated atoms



From D. Vanderbilt (2006)

Empirical pseudopotentials

- Empirical forms fitted to experimental data (DoS via electron-reflectance, gaps and symmetry points, experimental information about bands, etc.)
- Various forms:
  - Si, Ge (Friedel, Hybertsen, Schlüter): $V_{Si,Ge}(q) = \frac{a_1(q^2 - a_2)}{e^{a_3(q^2-a_4)}+1} \frac{1}{2}\left[\tanh\left(\frac{a_5 - q^2}{a_6}\right)+1\right]$
  - III-V (Zunger et al.): $V_{III-V}(q) = \sum_{j=1}^{4} a_j e^{-b_j(q-c_j)^2}[1 - d_j e^{-f_j q^2}]$
  - Hydrogen (Zunger, Kurokawa): $V_H(q) = \begin{cases} b_0 + b_1 q + b_2 q^2 + b_3 q^3 & \text{for } (q \le 2) \\ b_{-1}/q + b_{-2}/q^2 + b_{-3}/q^3 + b_{-4}/q^4 & \text{for } (q > 2) \end{cases}$

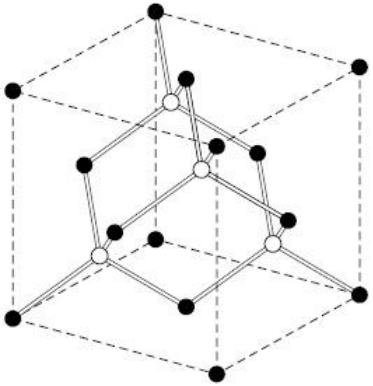


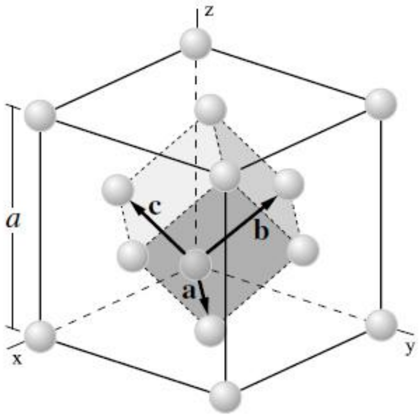
One possible form of an empirical pseudopotential for Si

DFT *vs.* Empirical pseudopotentials *vs.* ETB

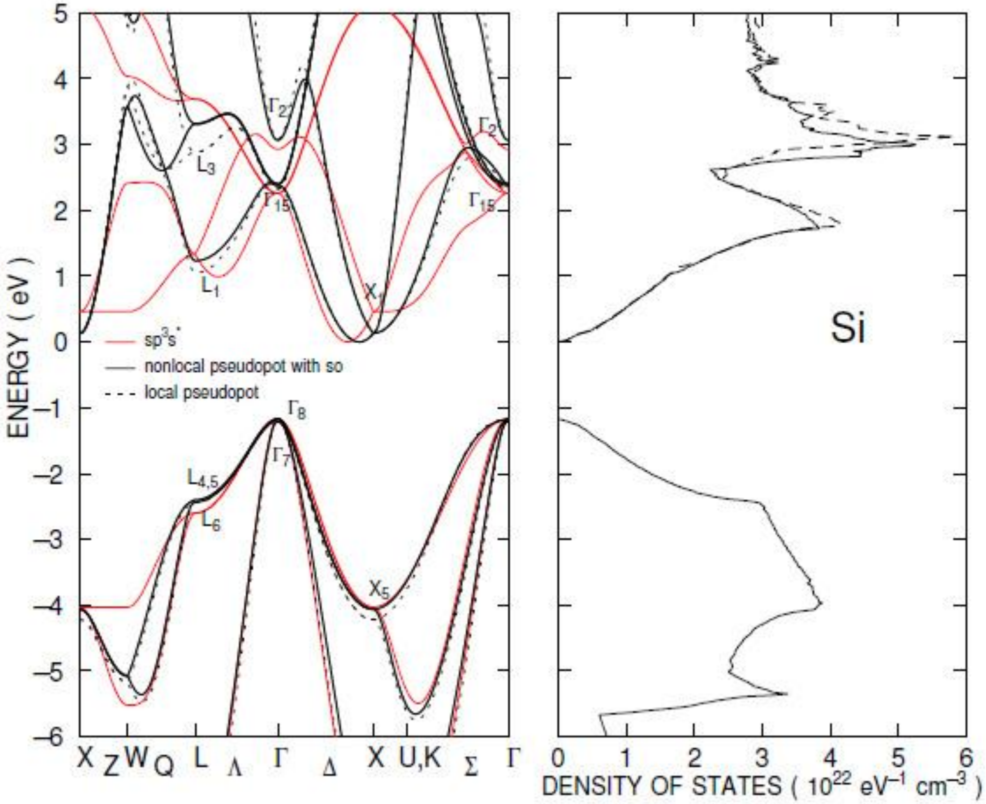
- DFT:
  - ❑ "Transferable" pseudopotentials: The valence charge shifts with changing atomic environment
  - ❑ Determination of the atomic structure now available and reliable
  - ❑ Phonon dispersion, stability (*ab initio* thermodynamics), reactivity
  - ❑ "Band-gap" problem (ground-state theory only)
  - ❑ Limited to 100-1000 atoms
  - ❑ Problems with long-range forces and strongly correlated systems
- EPs:
  - ❑ Calibrated to experimental information, gaps and masses reliable for transport 'by definition'
  - ❑ Million-atom systems (InAs pyramid-shape quantum dots with spectral-folding and FFT, Zunger)
  - ❑ Non transferable pseudopotentials
  - ❑ Not predictive, no atomic relaxation
- Empirical Tight-binding
  - ❑ Eigenvalue problem of a smaller rank
  - ❑ Scales with number of atoms, not cell size
  - ❑ No information about radial part of electron wavefunctions

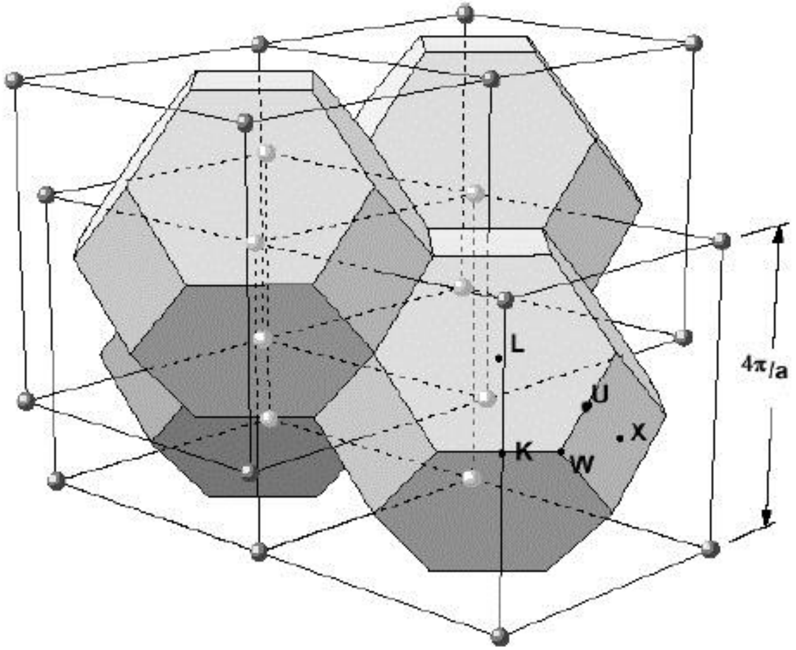
Empirical pseudopotentials: Bulk Si





← fcc unit and primitive cell

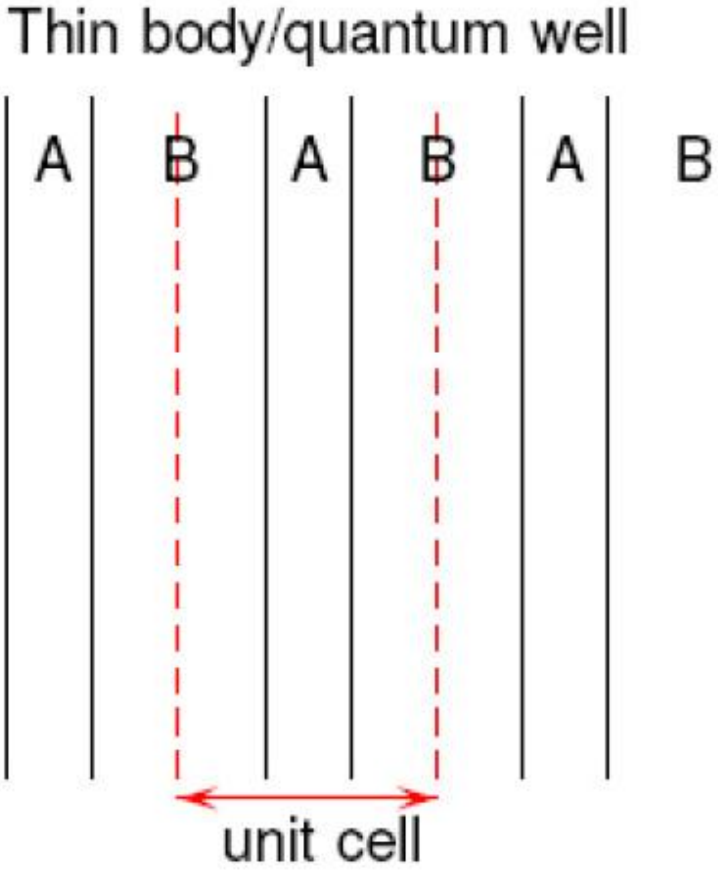


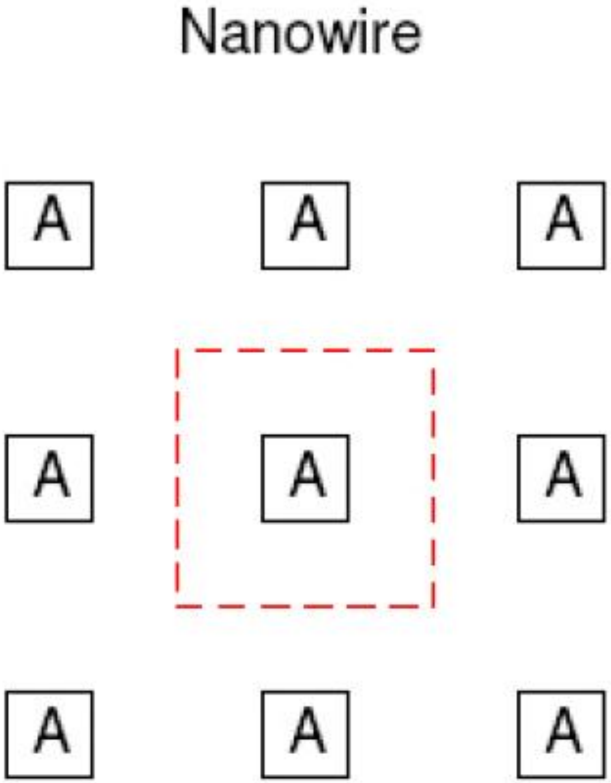


← fcc Brillouin Zones

EPs and nanostructures: Supercells

- Enlarge the cell beyond the WS primitive cell→ supercell
- Assume a `fake’ periodicity with supercells ‘sufficiently’ far apart
- Computational burden: Larger a, smaller π/a, more $\boldsymbol{G}$-vectors (*e.g.*, 14,000 for [111] Si NW)





EPs and nanostructures: Supercells

- Eigenvalue problem:

$$\sum_{\mathbf{G}'}\left[\frac{\hbar^2}{m}|\mathbf{k}+\mathbf{G}|^2\delta_{\mathbf{G}\mathbf{G}'}+V^{(lat)}_{\mathbf{G}-\mathbf{G}'}+\Phi_{\mathbf{G}-\mathbf{G}'}\right]\phi^{(n)}_{\mathbf{k}\mathbf{G}'} \;=\; E_n(\mathbf{k})\,\phi^{(n)}_{\mathbf{k}\mathbf{G}}$$

$$V^{(lat)}_{\mathbf{G}} \;=\; \frac{1}{\Omega}\sum_{\alpha} e^{i\mathbf{G}\cdot\boldsymbol{\tau}_\alpha}\,\Omega_\alpha\, V^{(\alpha)}_{\mathbf{G}}$$

Lattice (ions) potential

$$\Phi_{\mathbf{G}} = \frac{1}{\Omega}\int_{\Omega} d\mathbf{r}\;\Phi(\mathbf{r})\;e^{i\mathbf{G}\cdot\mathbf{r}}$$

External potential

- External potential for 2DEG and 1DEG:

$$\Phi_{\mathbf{G}} \;=\; \delta_{\mathbf{G}_\parallel}\,\Phi_{G_z} = \delta_{\mathbf{G}_\parallel}\,\frac{1}{L_z}\int_0^{L_z} dz\;\Phi(z)\;e^{iG_z z}$$

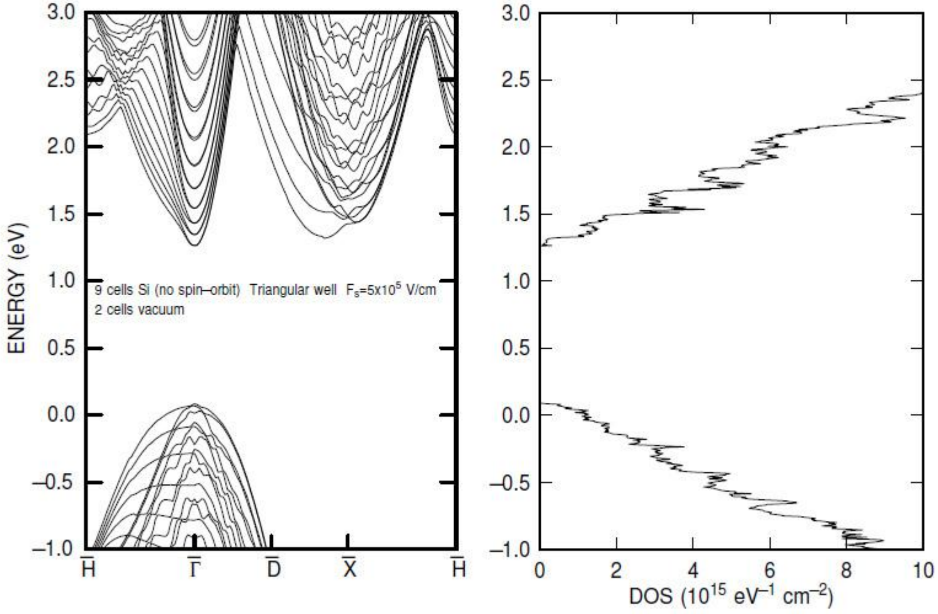
2DEG supercells (thin films, hetero-layers, graphene)

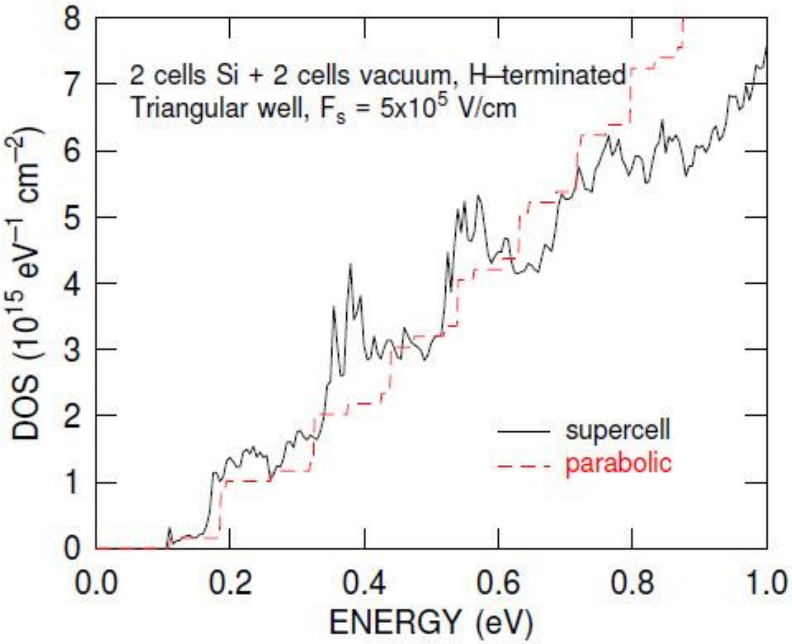
$$\Phi_{\mathbf{G}} \;=\; \delta_{G_z}\,\Phi_{\mathbf{G}_\parallel} = \delta_{G_z}\,\frac{1}{A}\int_{A} d\mathbf{R}\;\Phi(\mathbf{R})\;e^{i\mathbf{G}_\parallel\cdot\mathbf{R}}$$

1DEG supercells (NWs, GNRs, CNTs)

Note: So far structure periodic in all directions, extensions available (open bc)

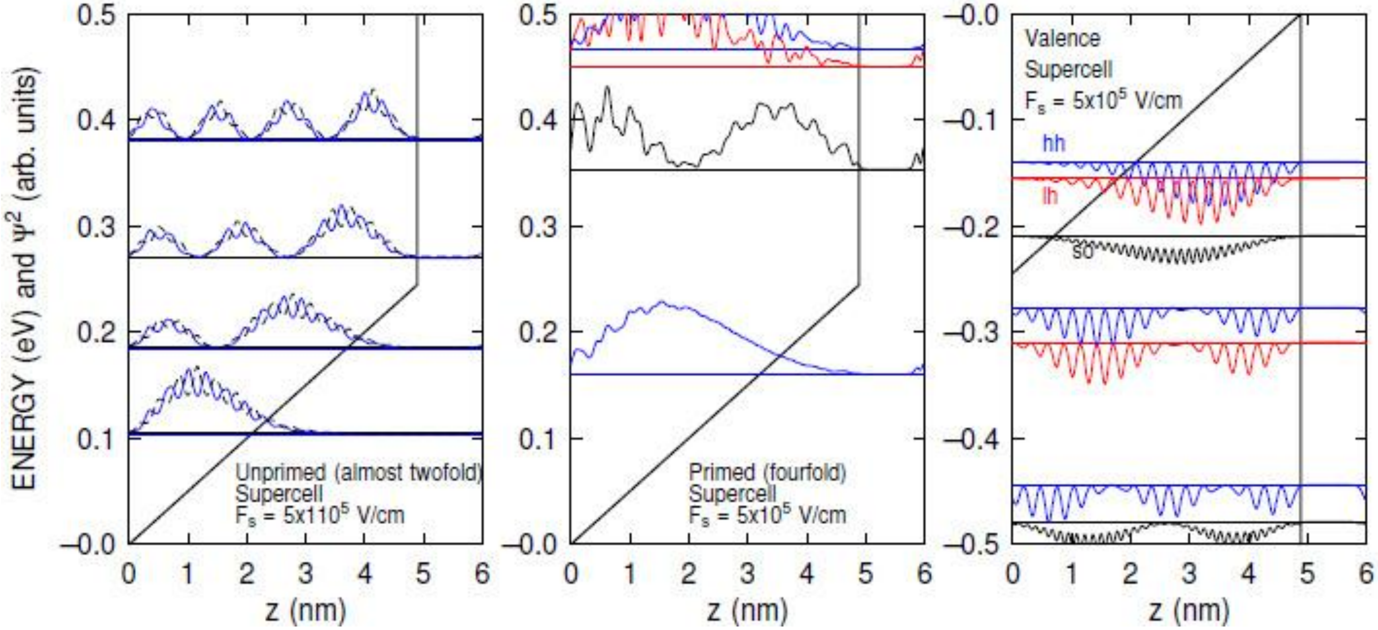
2DEG Supercell: Si thin films





↑

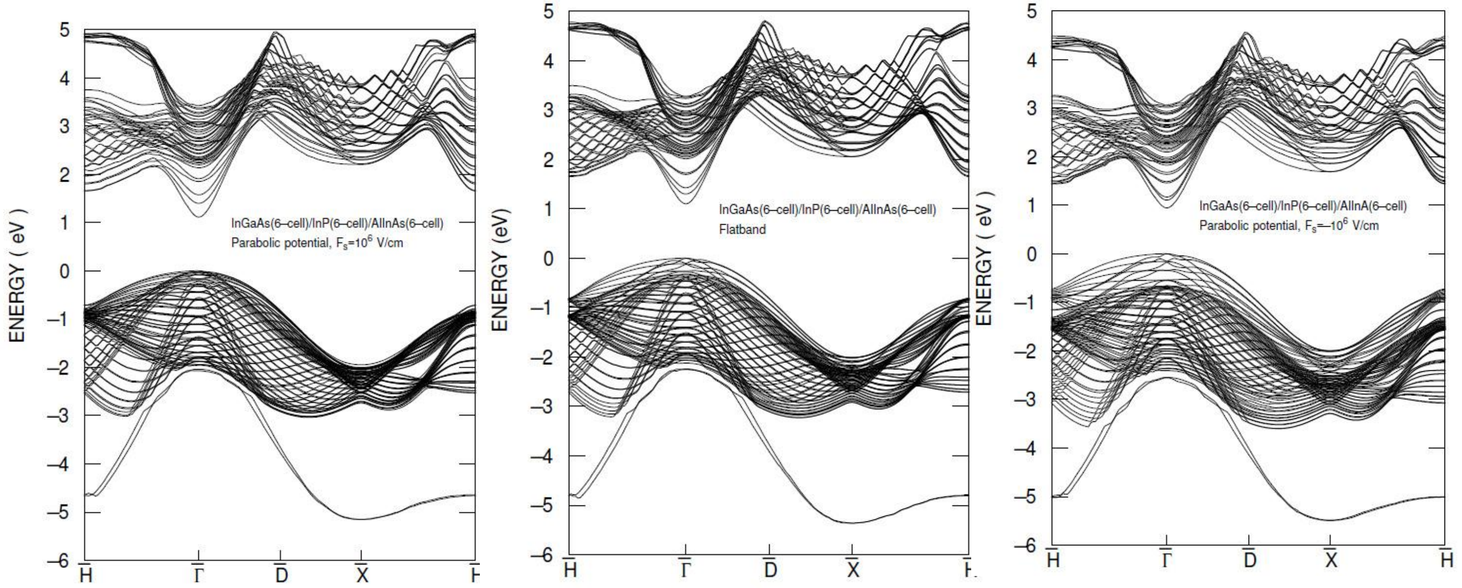
Band-structure and DOS



← Squared wavefunctions averaged over cell

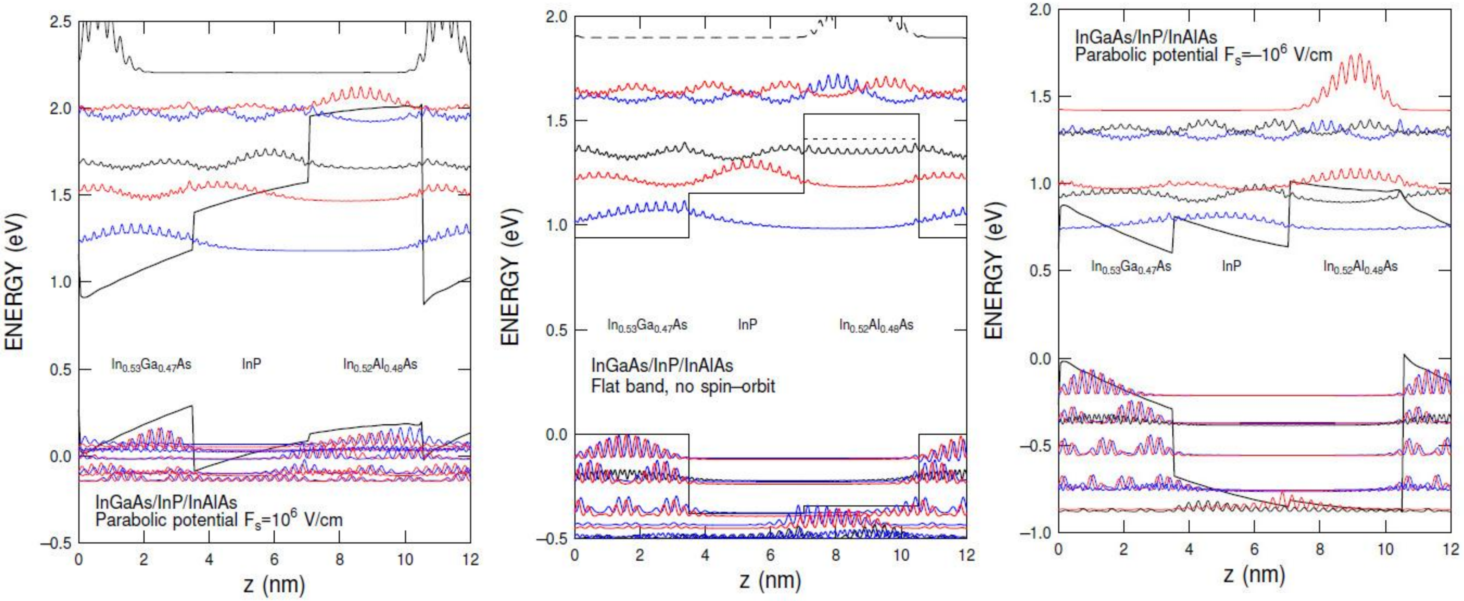
(Pseudopotentials from Zunger's group)

2DEG Supercell: III-V hetero-layers/channels



InGaAs/InP/AlInAs hetero-channel

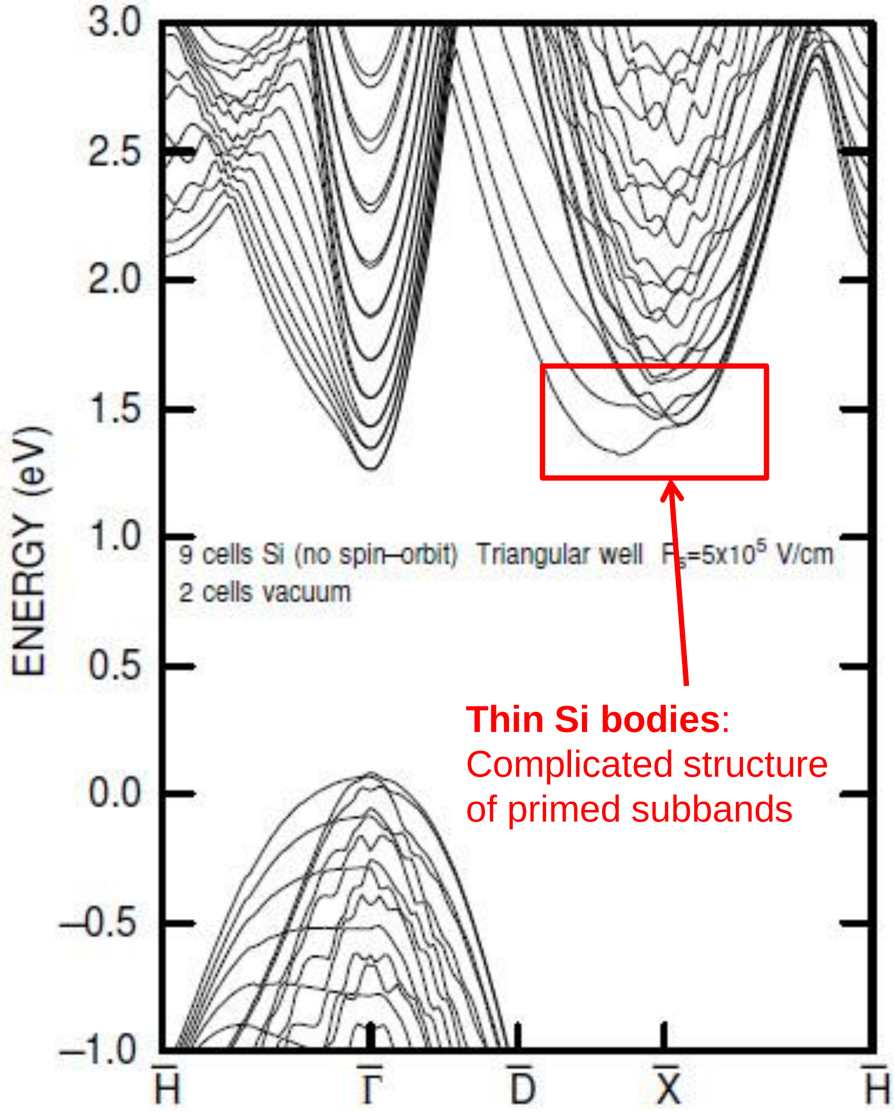
← Band structure:
Flat-band (center)
n-channel (left)
p-channel (right)



← Squared CB and VB wavefunctions:
Flat-band (center)
n-channel (left)
p-channel (right)

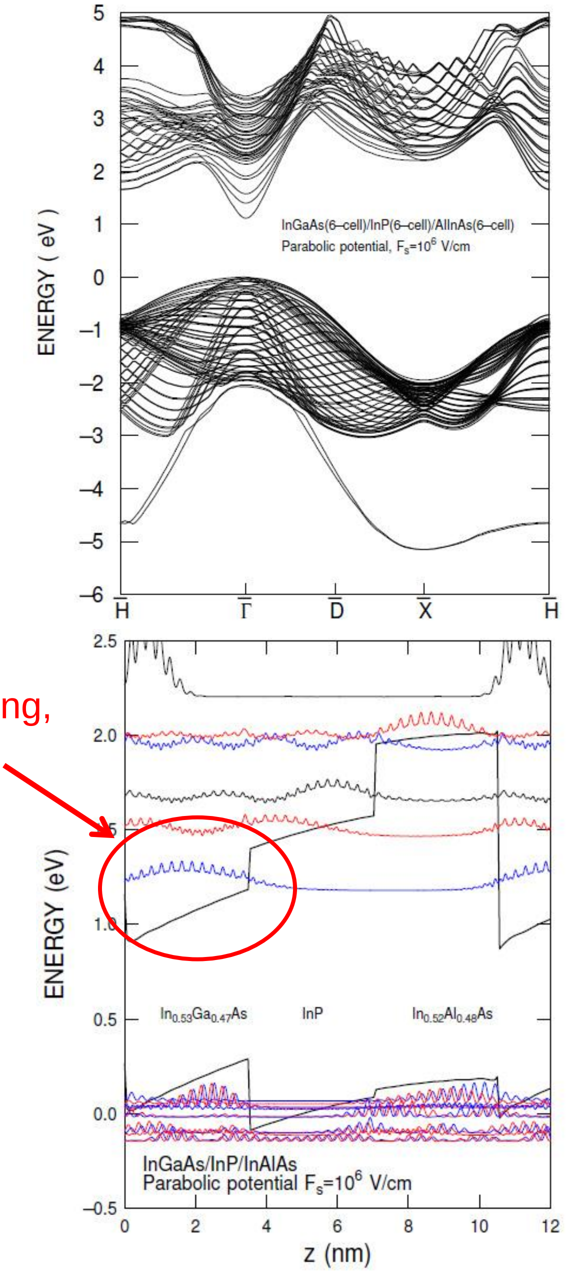
(Pseudopotentials from Zunger's group)

Si thin films/III-V hetero-layers: Some virtues of the EPs



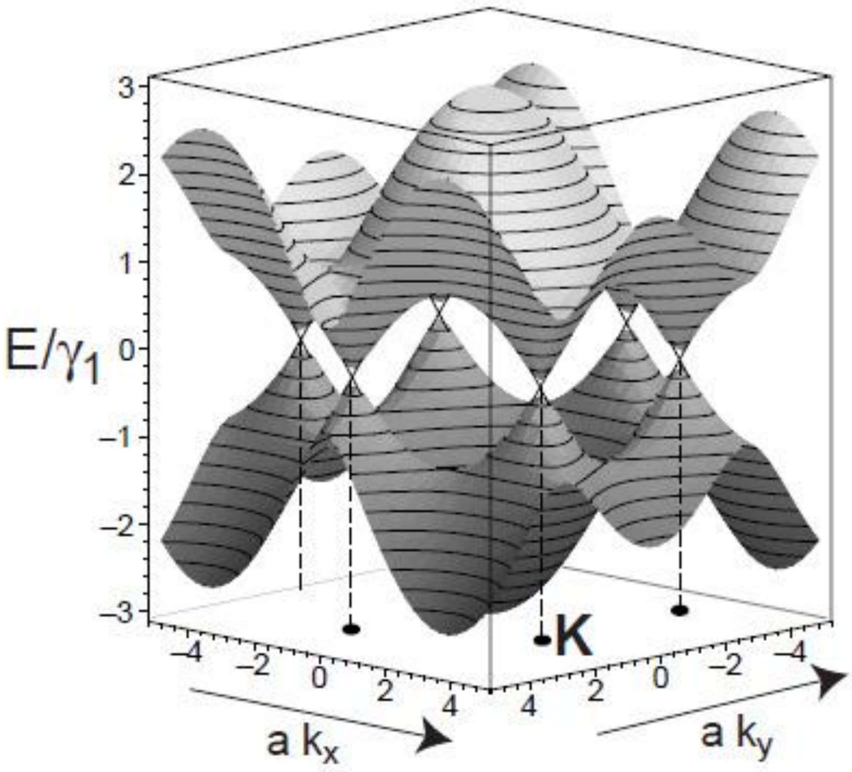
Thin Si bodies: Complicated structure of primed subbands

III-Vs: Wavefunction matching, effective mass in hetero-channels, etc.

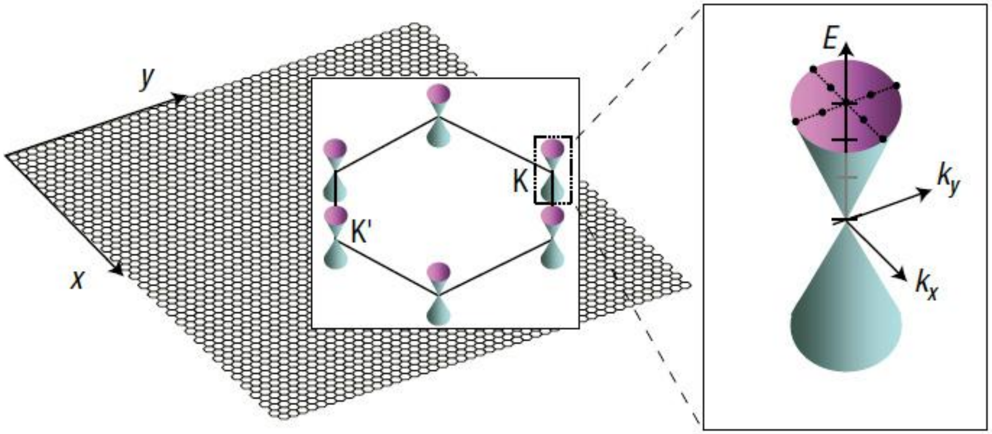


(Pseudopotentials from Zunger's group)

2DEG Supercell: Graphene and the Dirac points *K*, *K*’



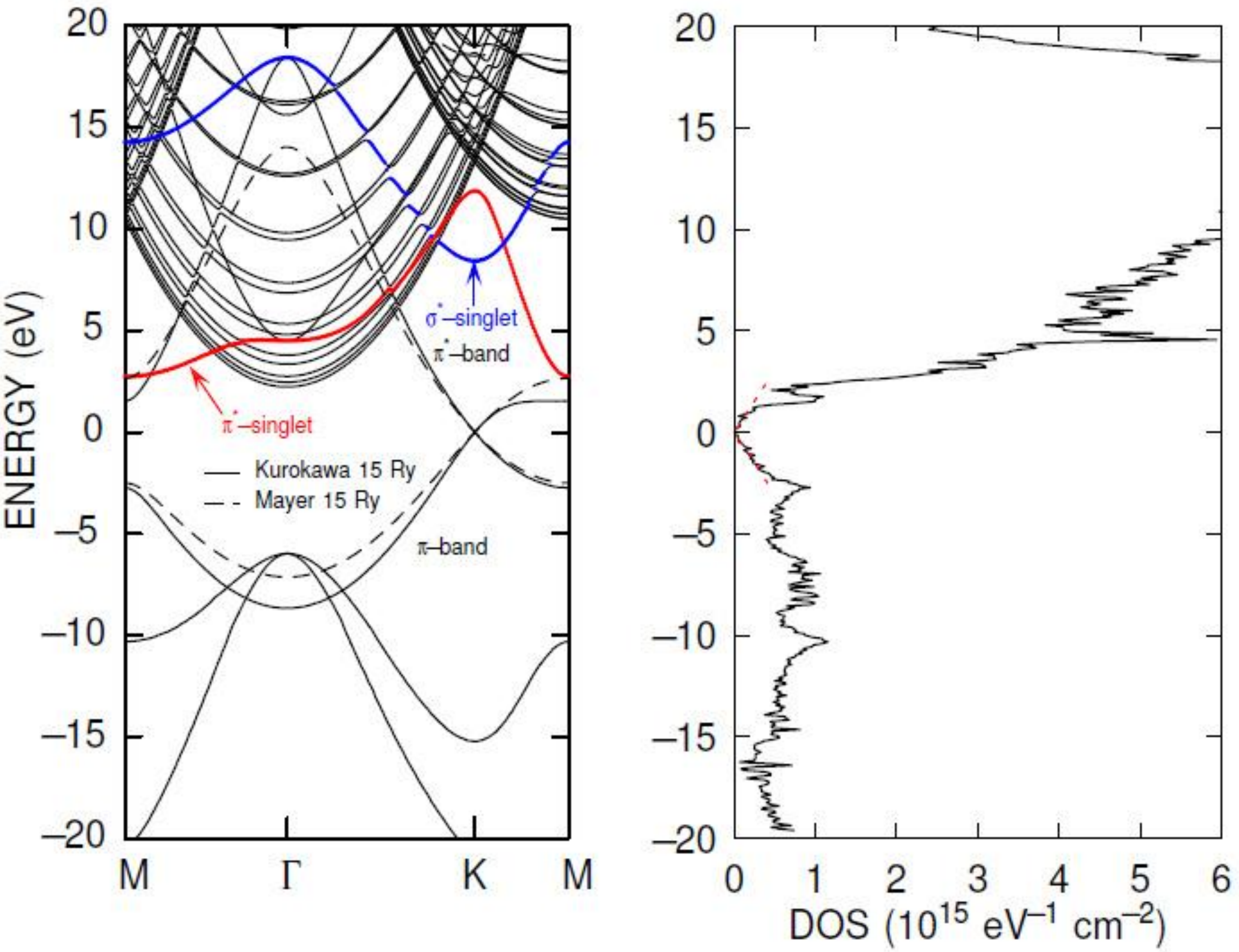
From C. Schönberg (2000)

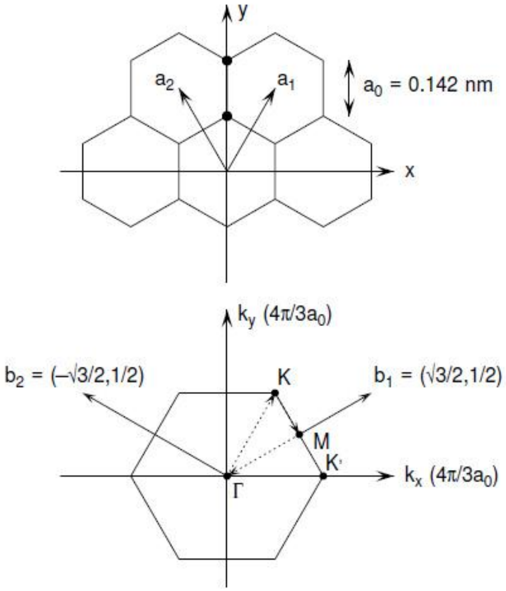


From C.-H. Park *et al*., Nature (2008)

2DEG Supercell: Graphene

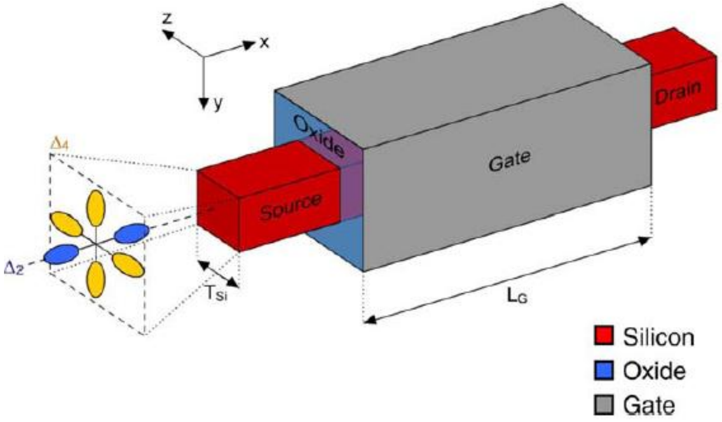
Local pseudopotentials from Kurokawa *et al*., PRB **61** 12616 (2000) (calibrated to diamond and trans-polyacetylene) and Mayer, Carbon **42**, 2057 (2004) (single-electron, calibrated to graphene)

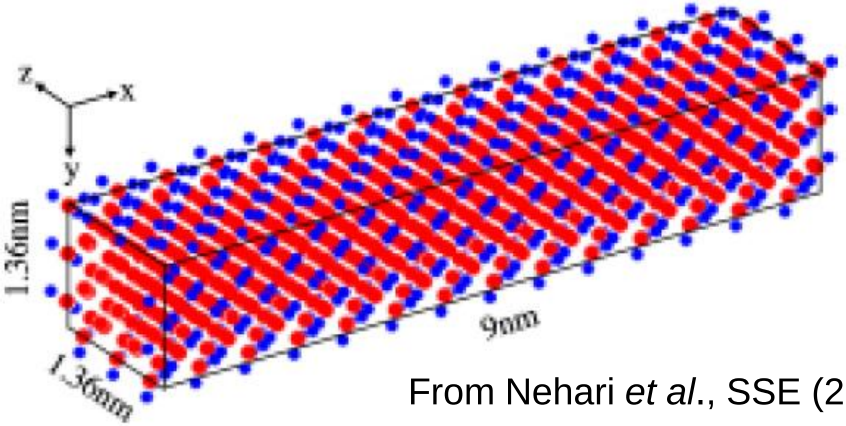




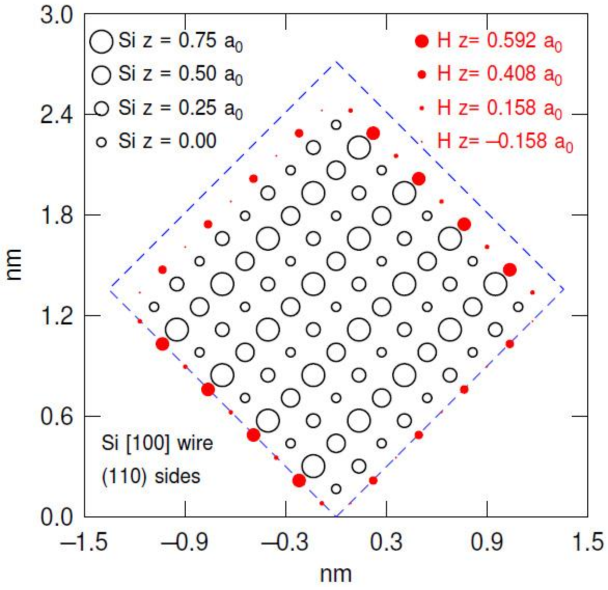
Problem(?): π^* and σ^* singlets at excessively low energy? It matters in CNTs.

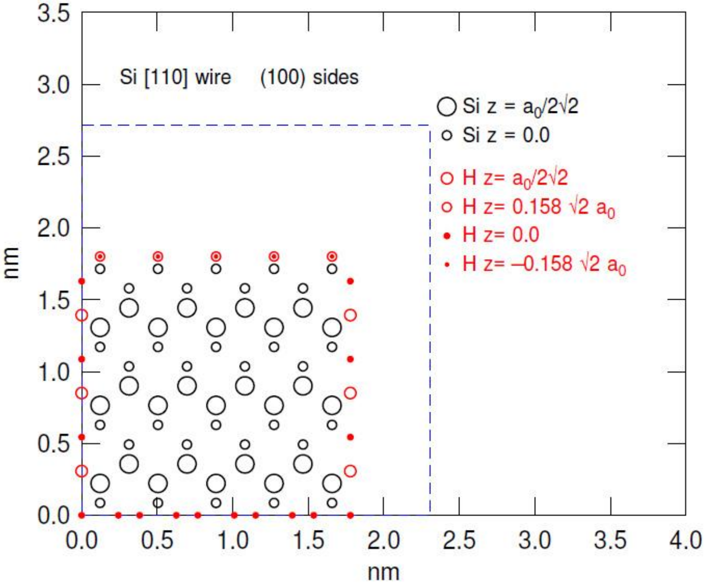
1DEG Supercell: Si Nanowires

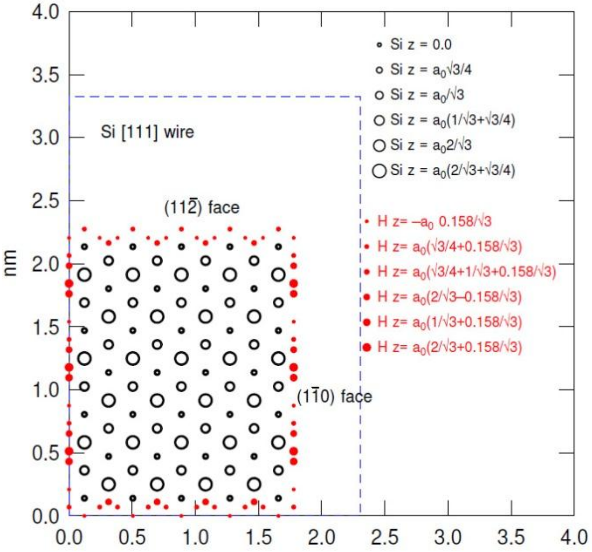




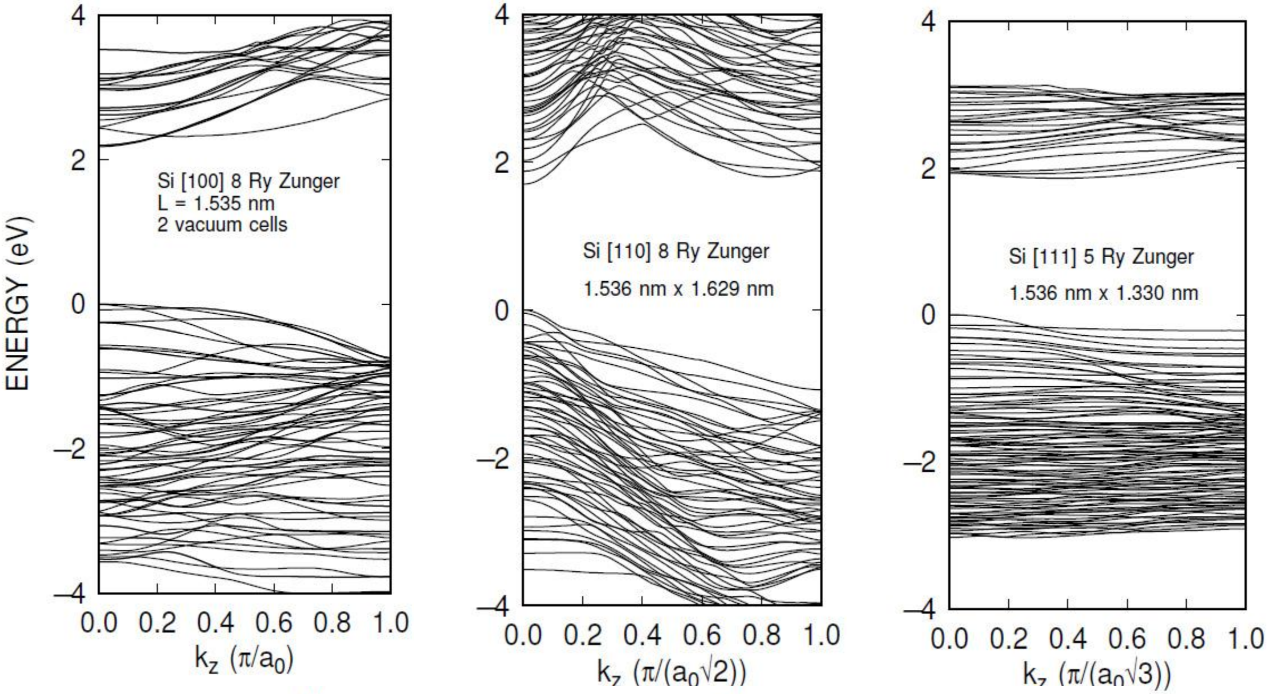
From Nehari *et al*., SSE (2006)



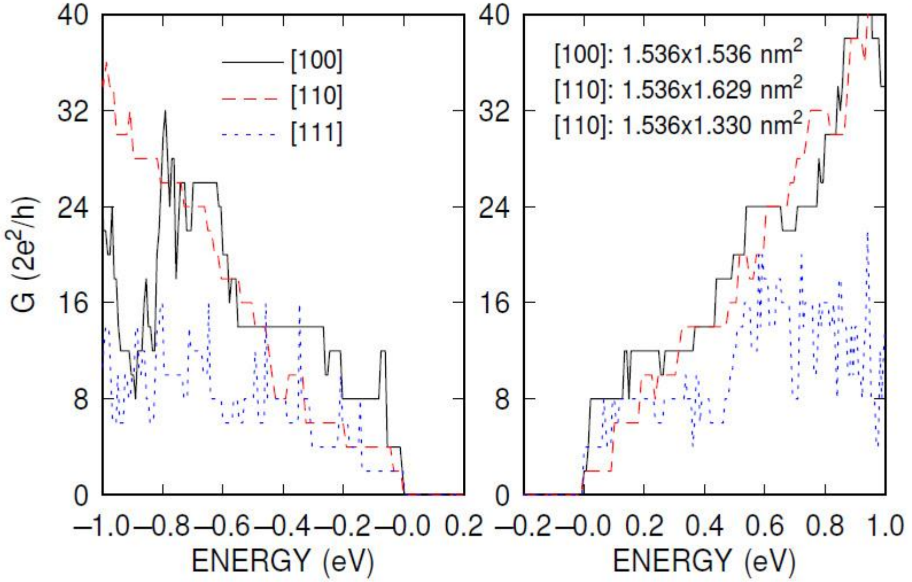




1DEG Supercell: Si nanowires

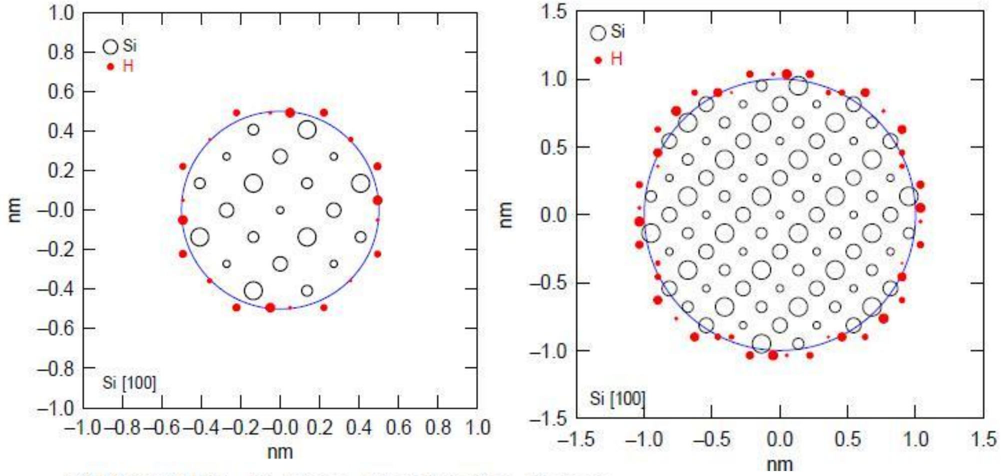


← Band structure of square-section 1.5 nm Si NWs: [111] indirect-gap (Scheel *et al.*, Phys. Stat. Sol. (2005))

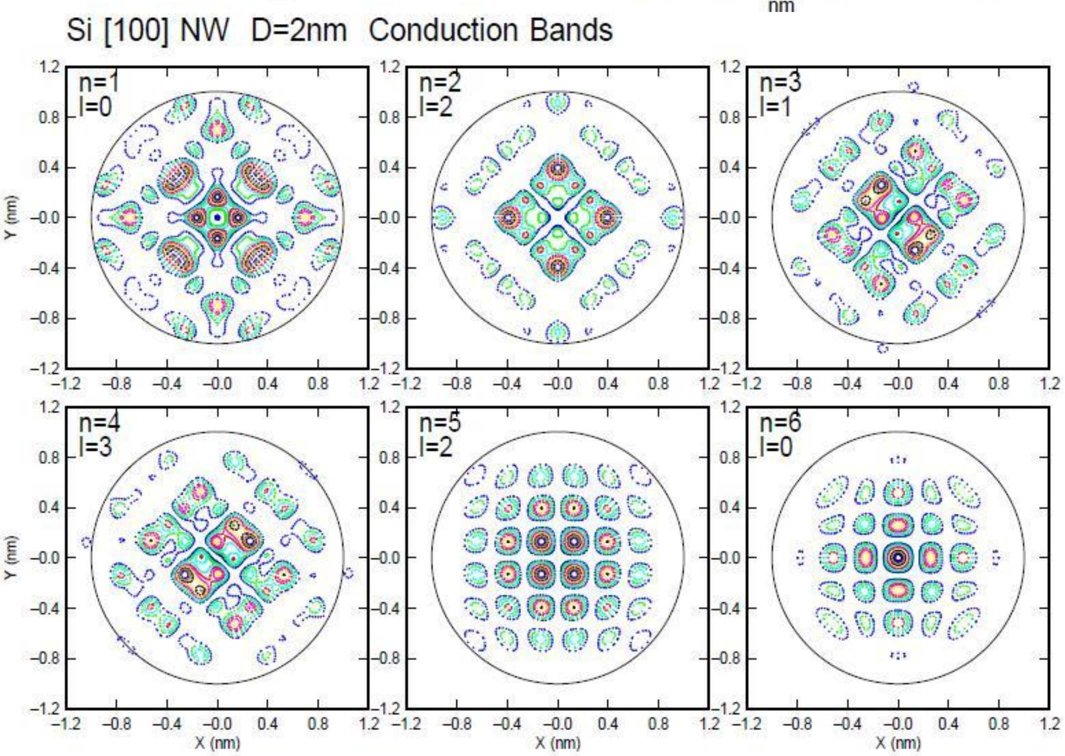


← Ballistic conductance in square-section 1.5 nm Si NWs: [100] best, [110]/[111] (e/h) worst

1DEG Supercell: Si nanowires



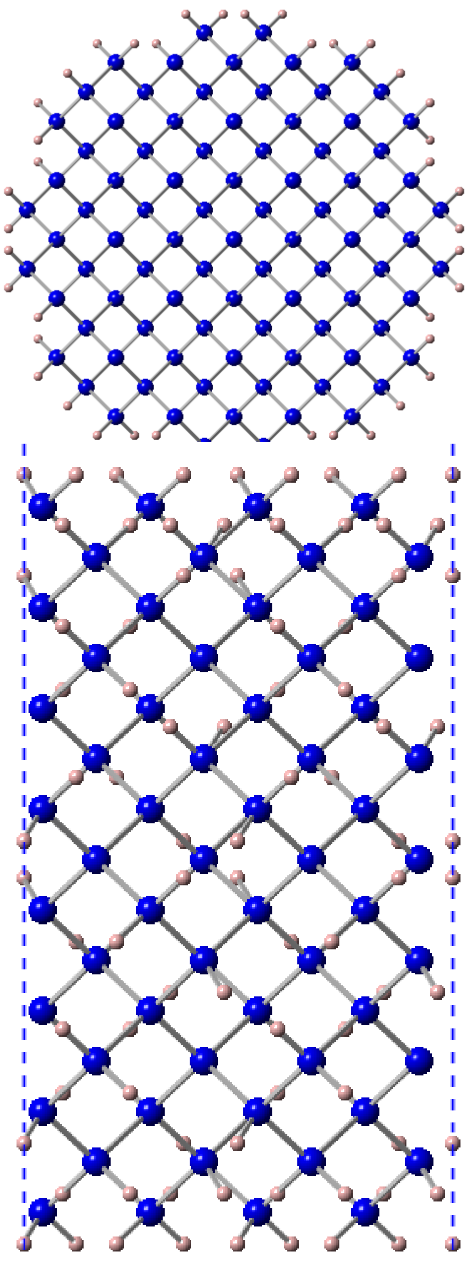
Atom position in 1 nm and 2nm diameter circular cross-section Si NW

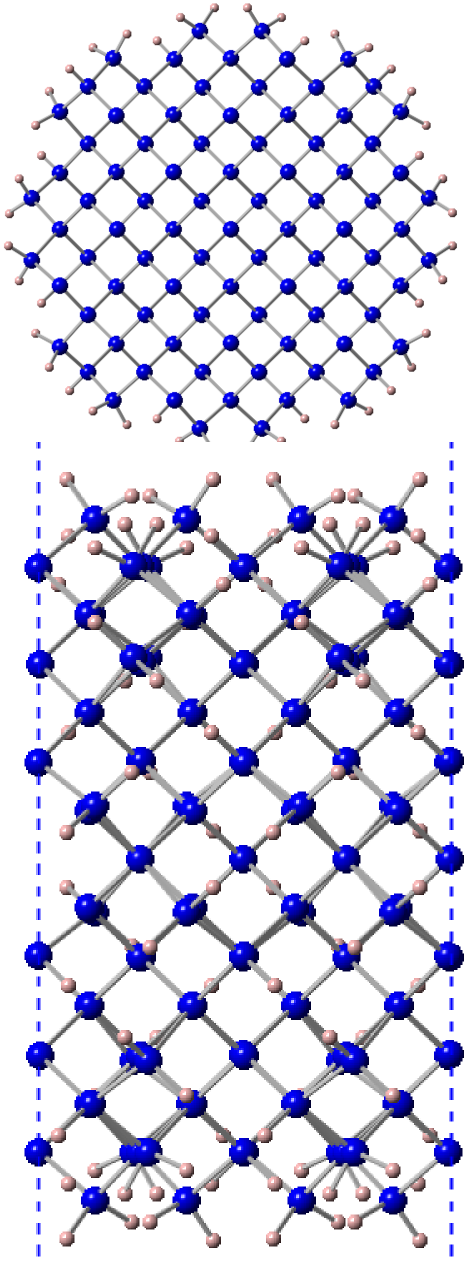

Si [100] NW D=2nm Conduction Bands

Conduction-band wavefunctions at Γ, 2 nm diameter circular cross-section Si NW

Atomic relaxation: 2 nm cylindrical [100] Si nanowires

Initial



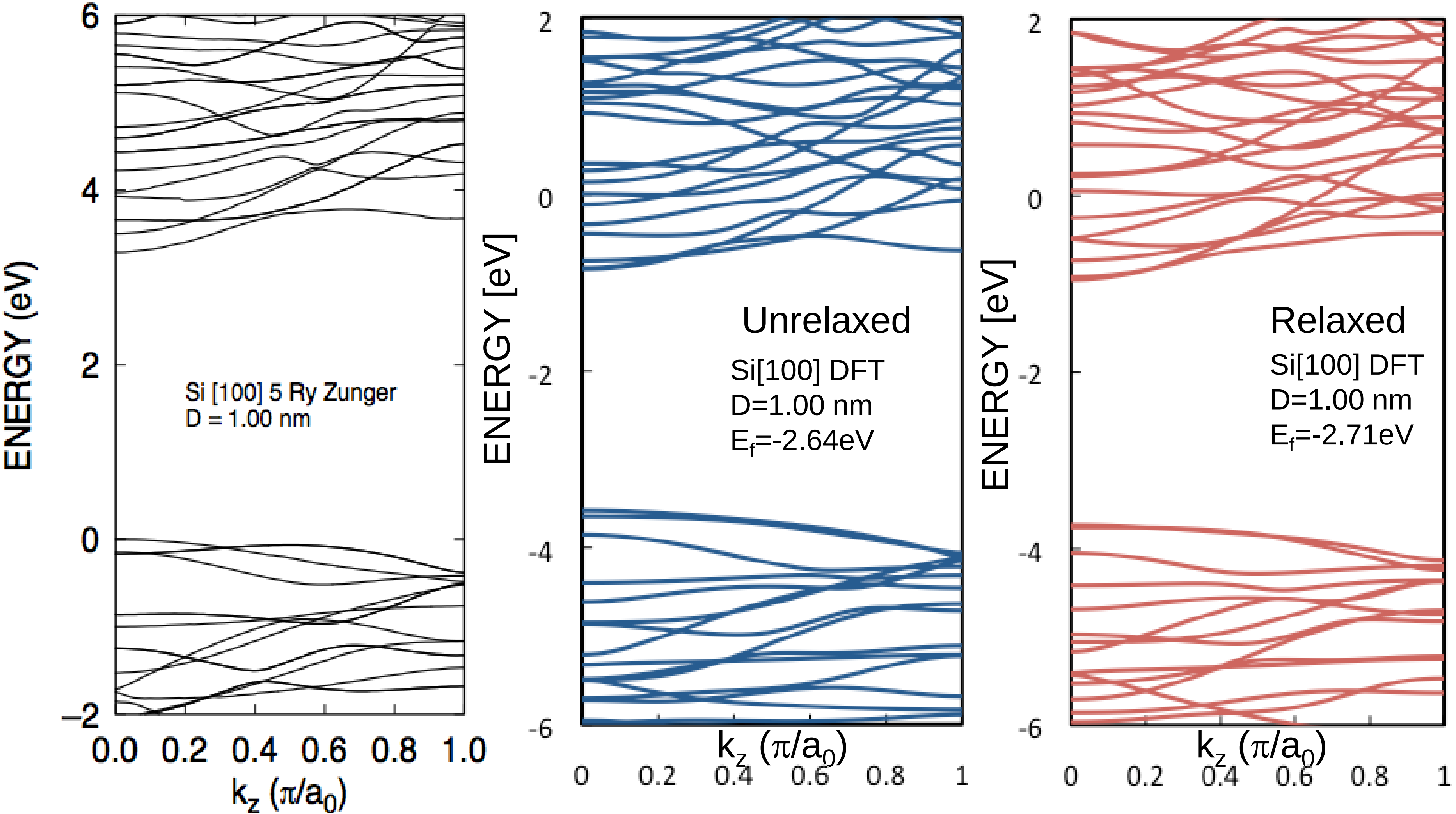


Final DFT (VASP) converged coordinates

Results by S. Aboud

1 nm Si NW: DFT *vs.* EPs, relaxed *vs.* unrelaxed

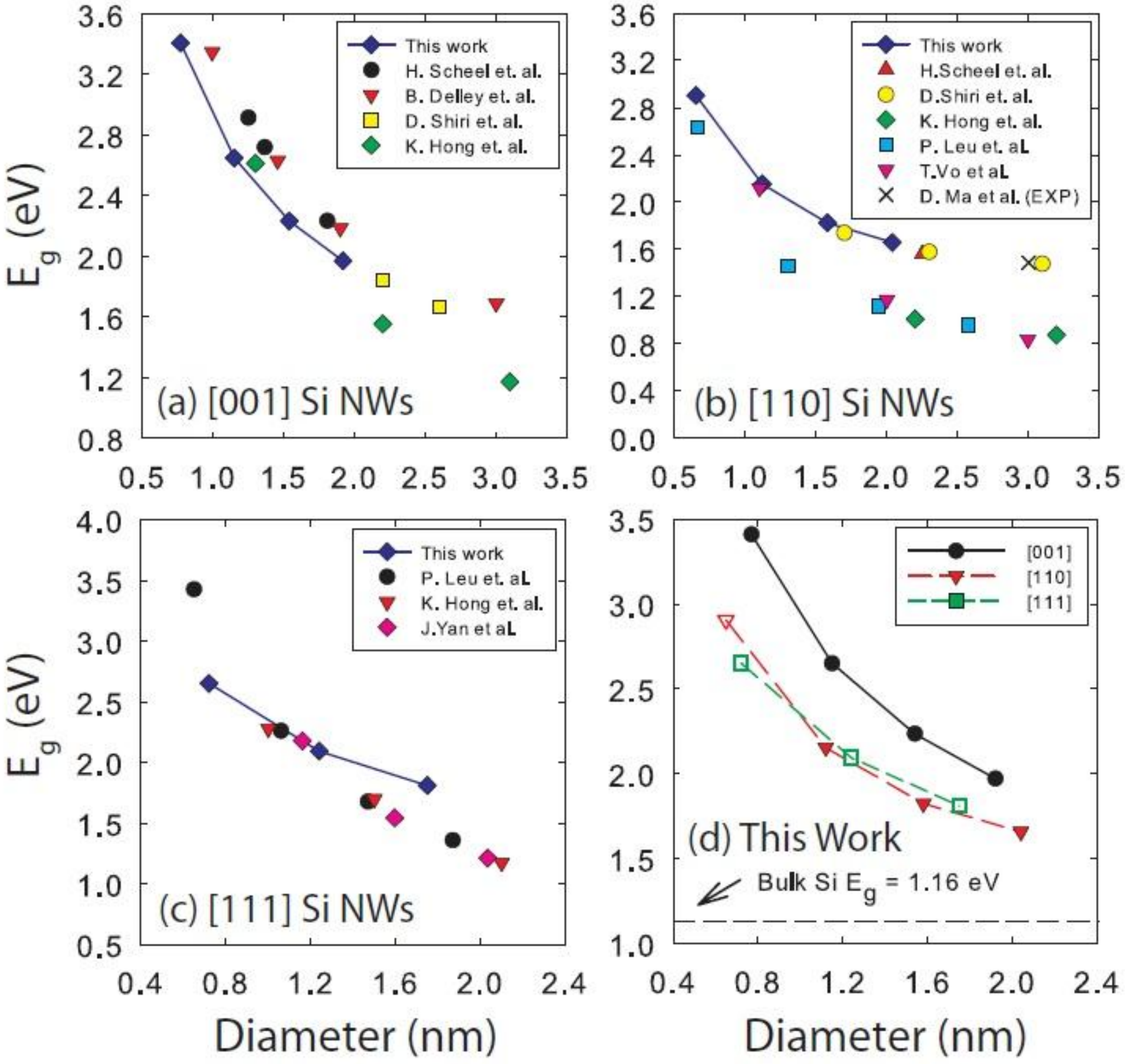
- Some differences due to atomic relaxation and pseudopotentials (~50-50)
- DFT gap not too different: Quantum confinement dominates

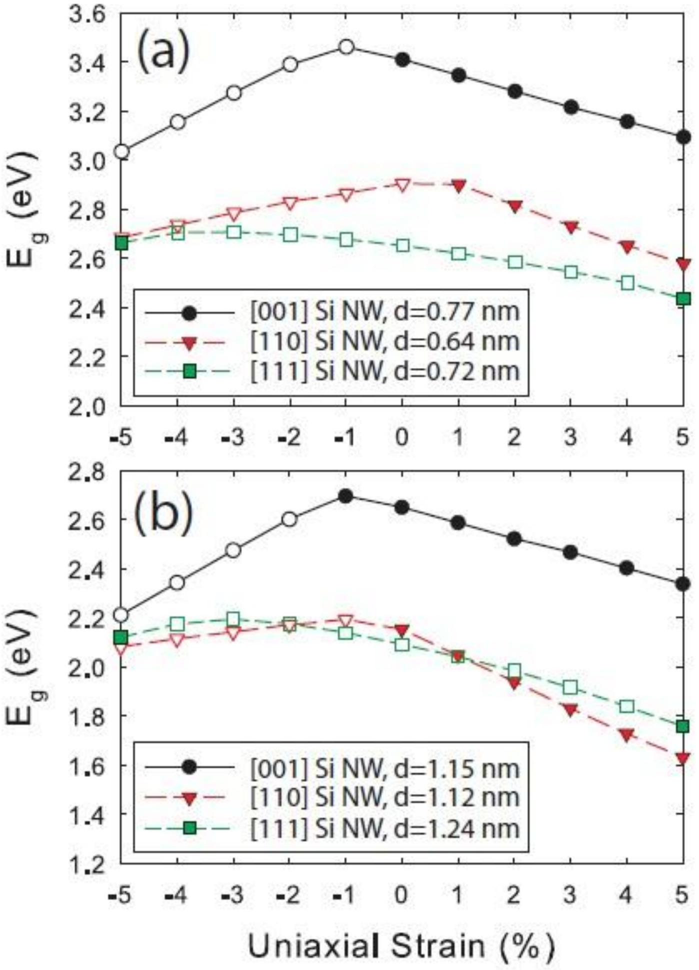


DFT results by S. Aboud

Si NW: Band-gap *vs*. diameter and strain

- Band-gap in good agreement with experiments
- Direct (solid symbols)/indirect (open symbols) transition with strain

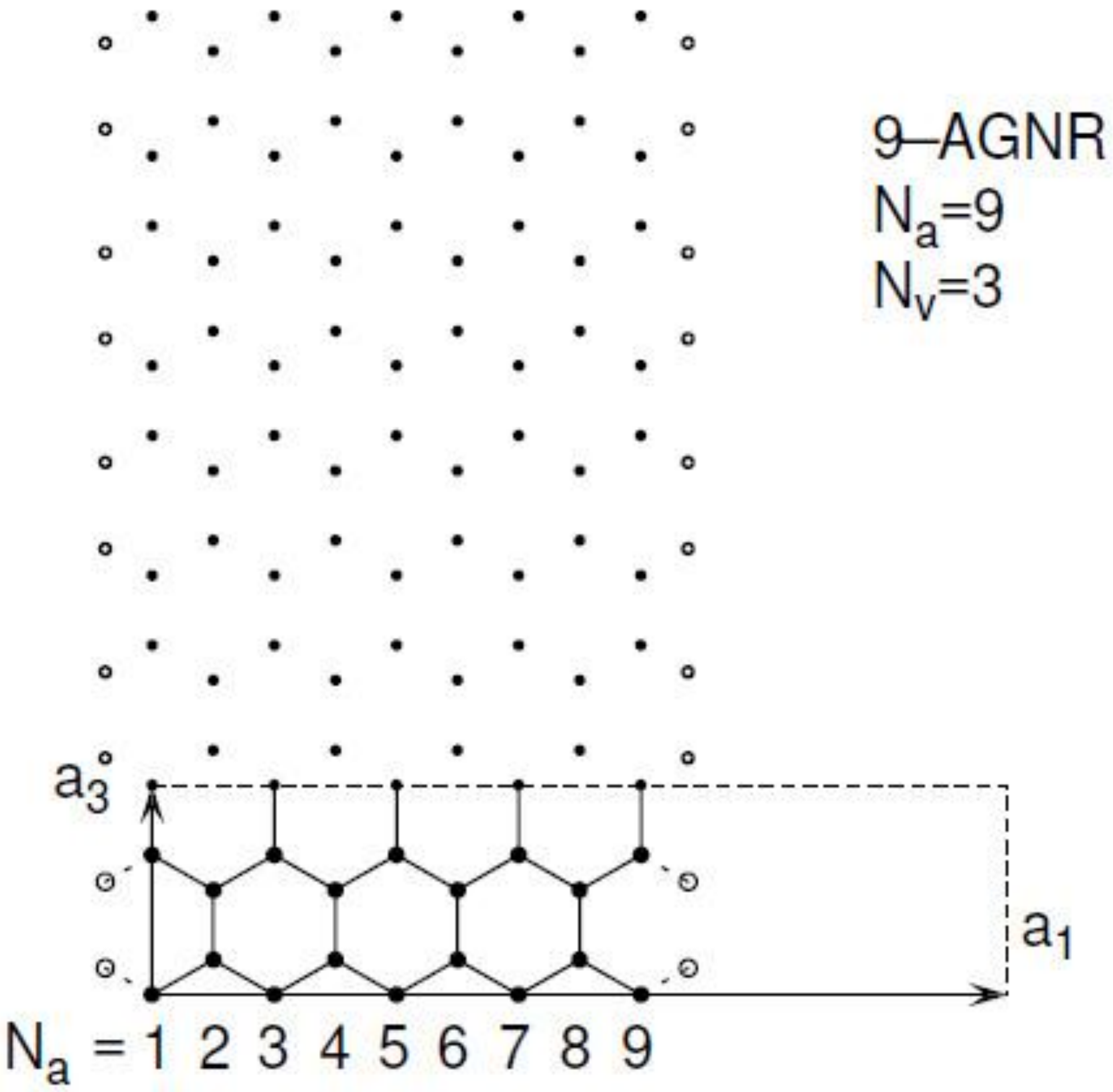




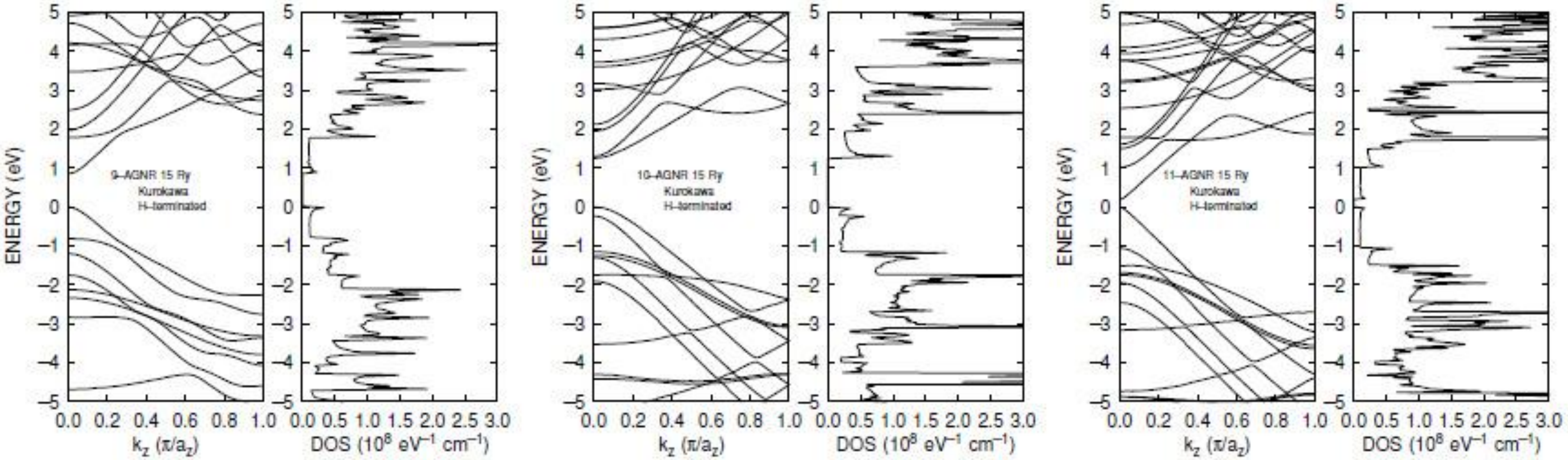
EP results by J. Kim

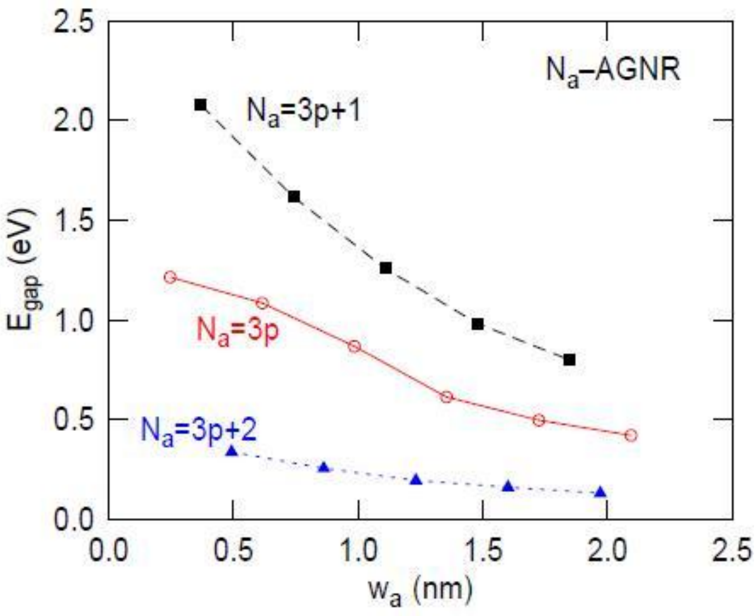
1DEG Supercell: Graphene nanoribbons

Band-gap depends on width N_a



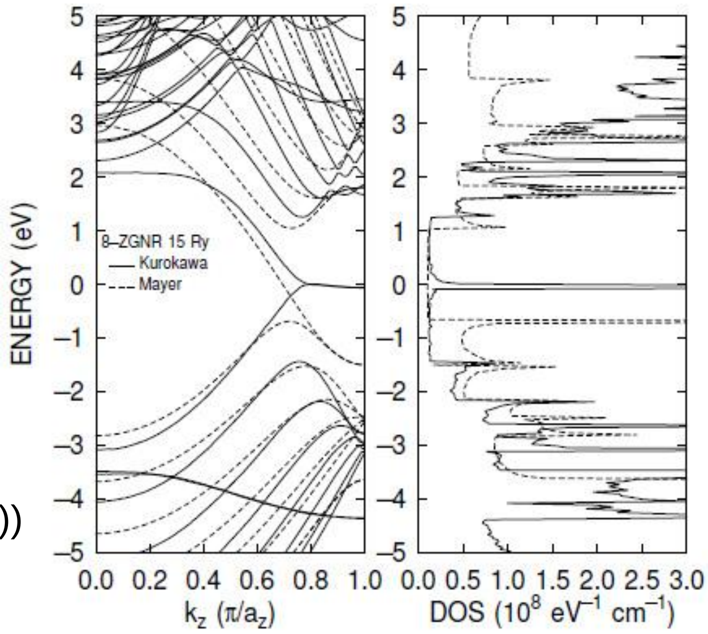
1DEG supercell: Graphene nanoribbons





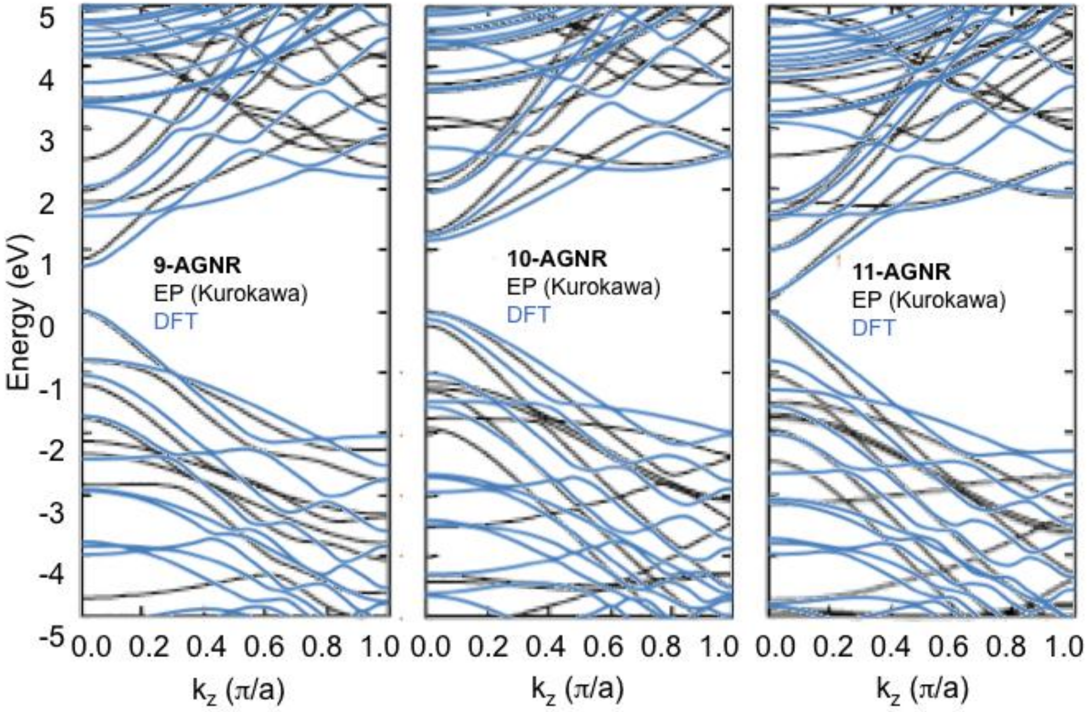
←Band-gap for AGNRs:
correct ordering (Son *et al.*, PRL (2006)), smaller than GGA-corrected DFT.
Due to aromaticity (Clar resonances), NOT edge-strain!

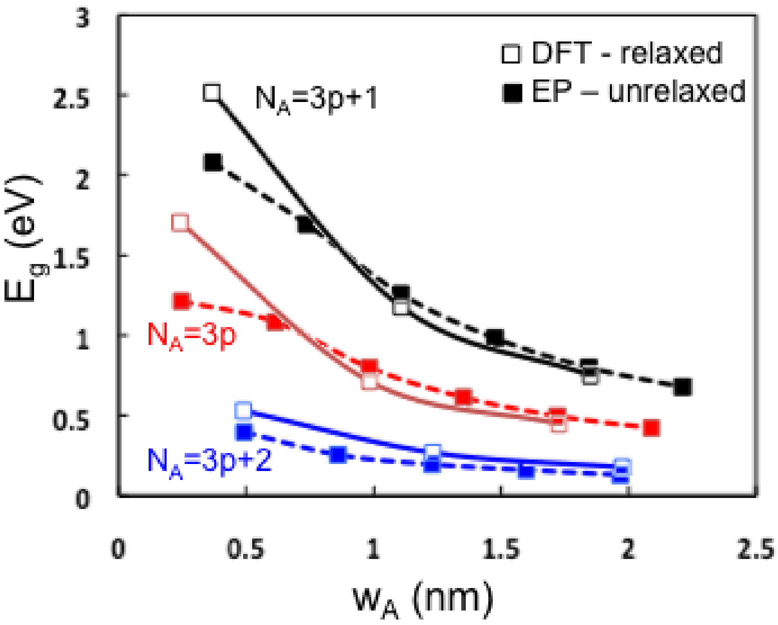
Problem: →
Non-magnetic state only, no gap for ZGNRs (Yang *et al.*, PRL (2007))



Band structure of AGNRs: DFT *vs.* EPs

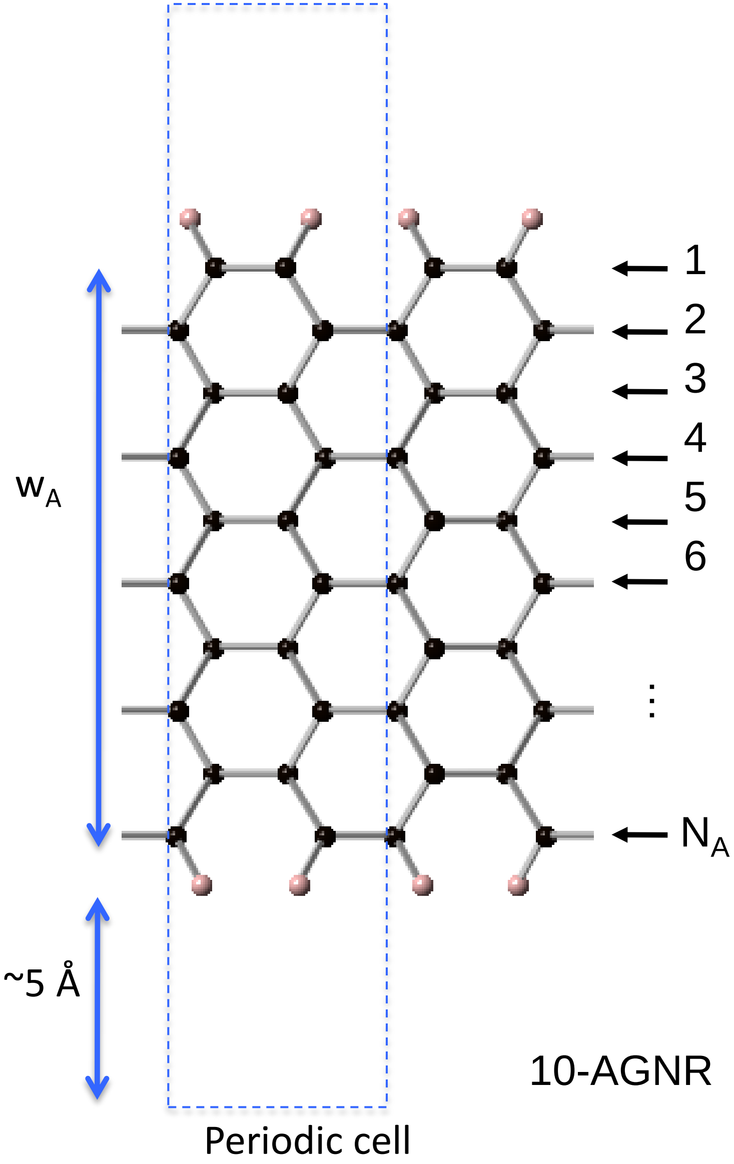
- Qualitatively similar, gap almost identical, similar masses
- Similar trend, same oscillatory behavior of gap, EPs fail (as also LDA) for the narrowest ribbons (DFT+GW yields 2x larger gaps – Yang *et al*., PRL 2007)



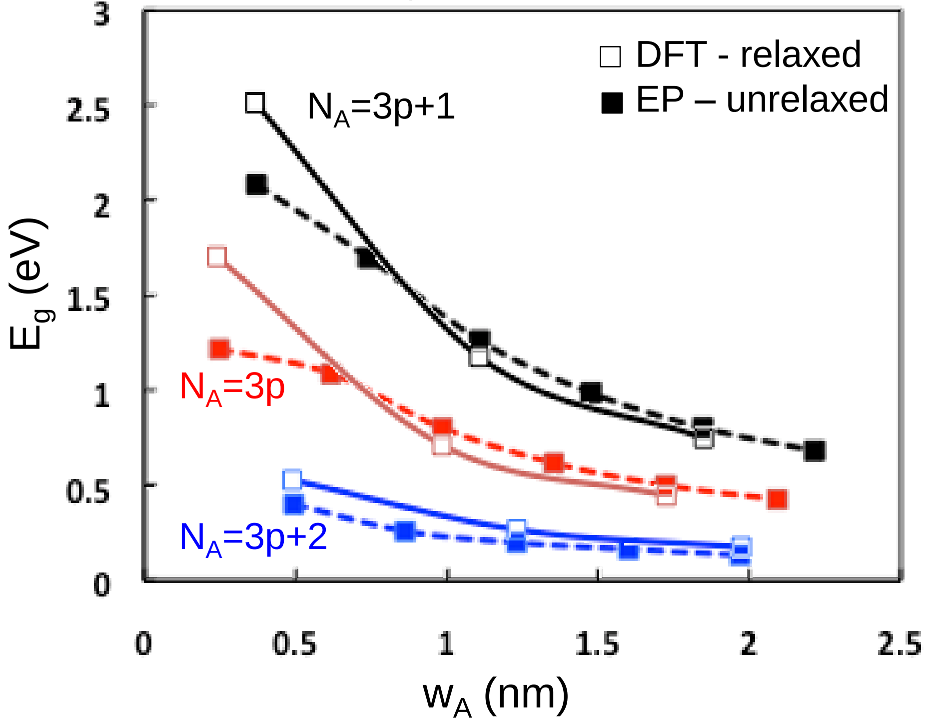


DFT results by S. Aboud

Armchair Nanoribbons (AGNRs)



“Claromaticity” Dependent Band Gap



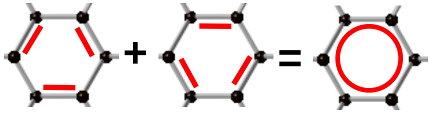
- Edges modify the aromaticity patterns (Clar sextets) which opens up a gap at the Dirac points

- Bandgap scales with inverse of width:
  $E_g(3p+1)>E_g(3p)>E_g(3p+2)$

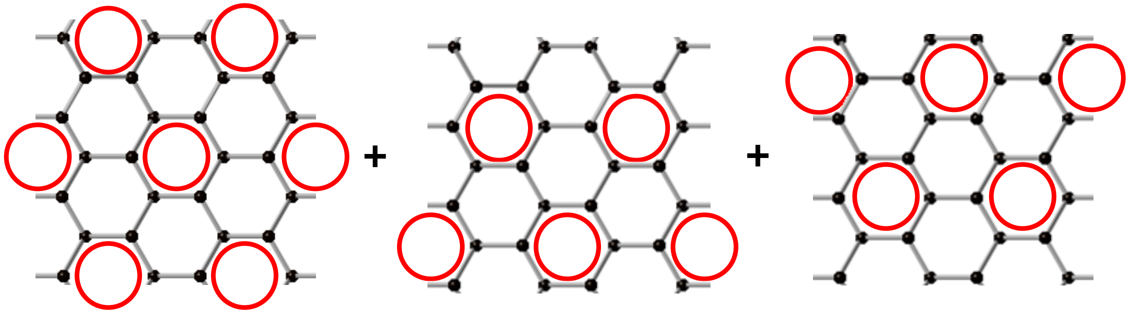
Courtesy S. Aboud

sp^2 Aromaticity - Clar Sextets

Clar Sextet

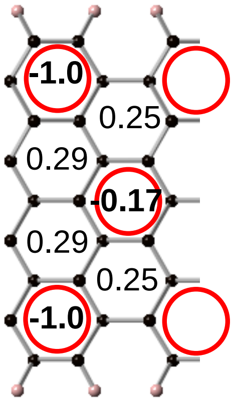


Infinite Graphene Sheet



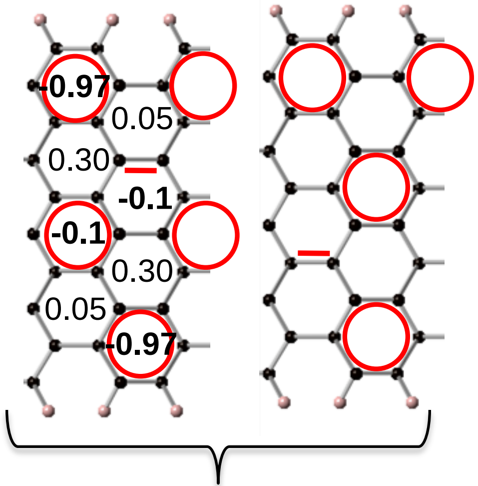
Nanoribbons

$N_A=3p$



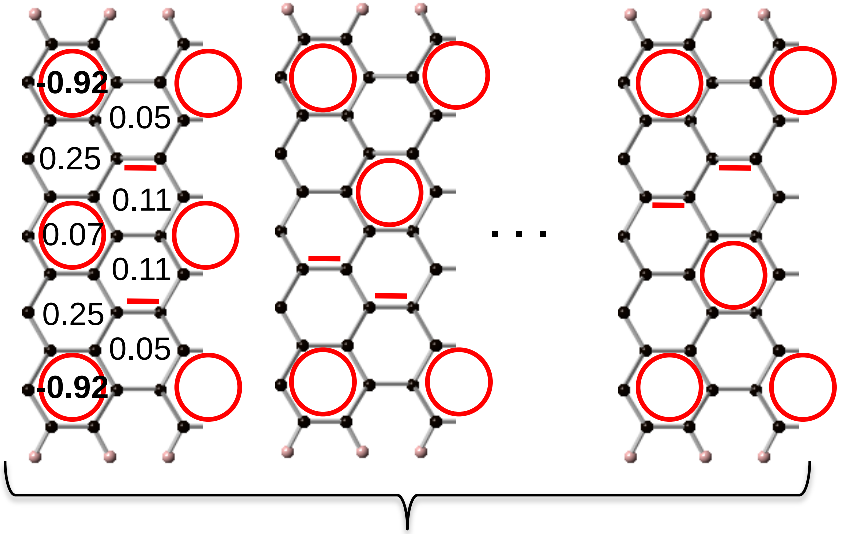
1 Clar Structure

$N_A=3p+1$



2 Clar Structure

$N_A=3p+2$

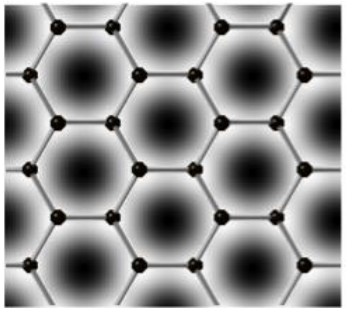


n Clar Structure

Courtesy S. Aboud

Spatial Electron Localization

Infinite Graphene Sheet

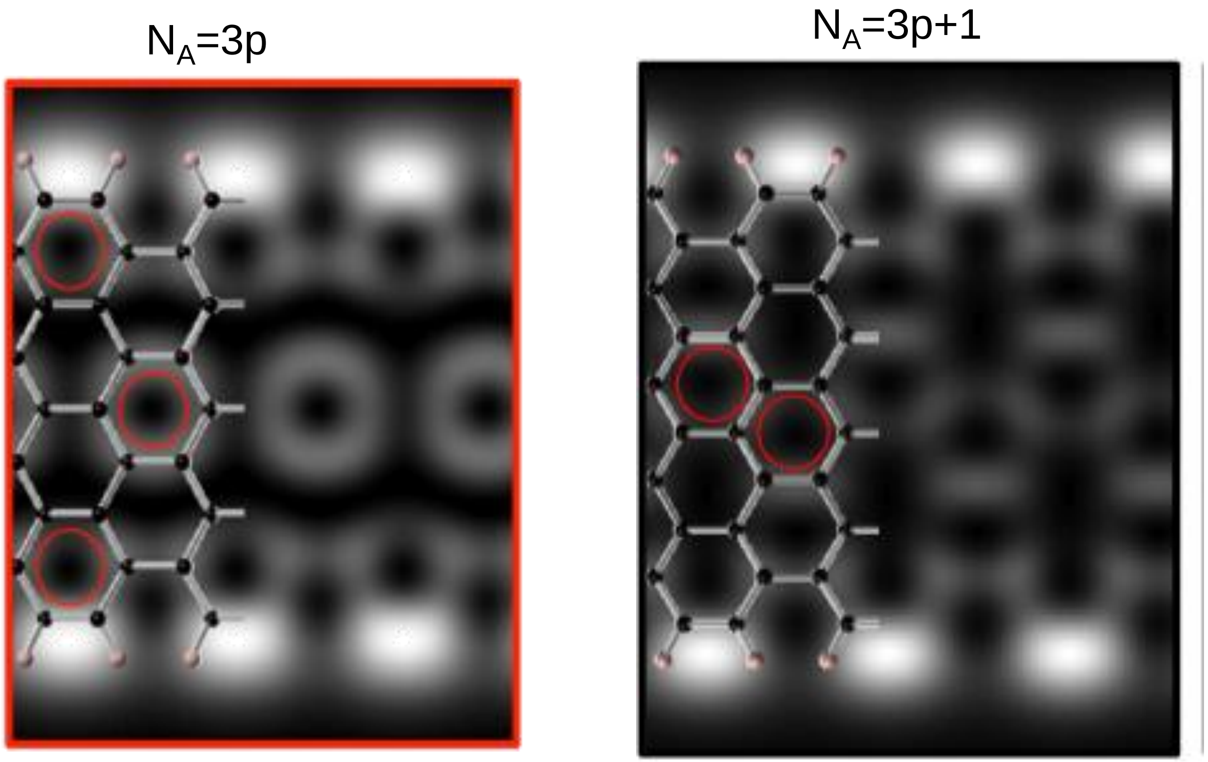


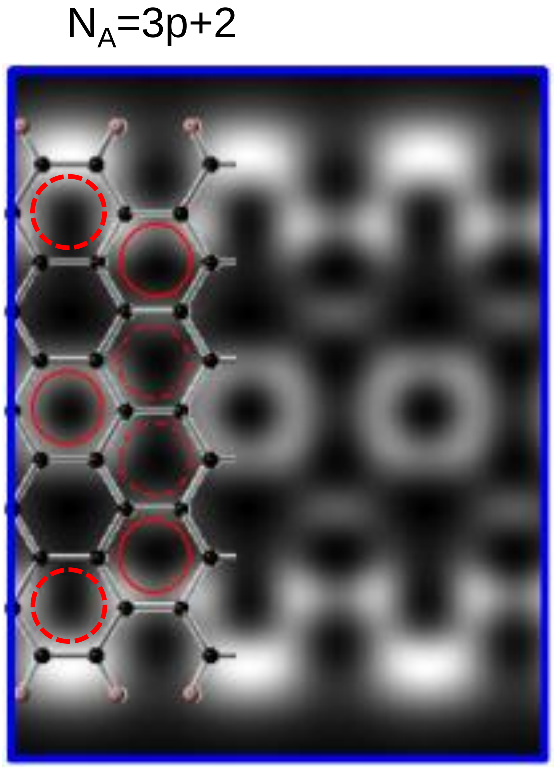
Tersoff-Hamann Approximation

$$I(x,y,z=0.2nm,U) \propto \sum_{\mu} \left|\Psi_{\mu}(x,y,z=0.2nm)\right|^{2} \left[f(\varepsilon_f-\varepsilon_{\mu})-f(\varepsilon_f+eU-\varepsilon_{\mu})\right]$$

J. Tersoff, D.R. Hamann, PRB 1985, 31, 805

Nanoribbons

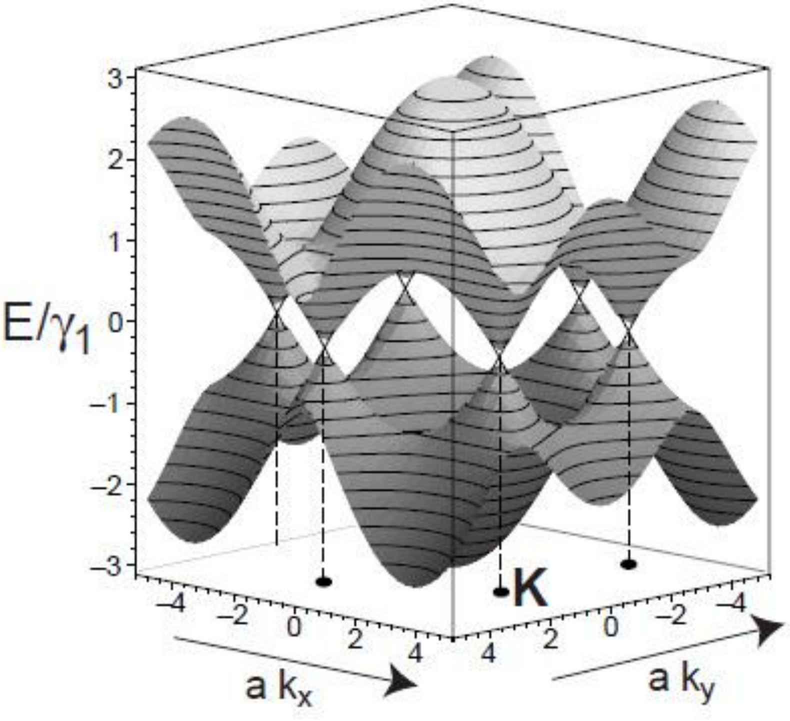




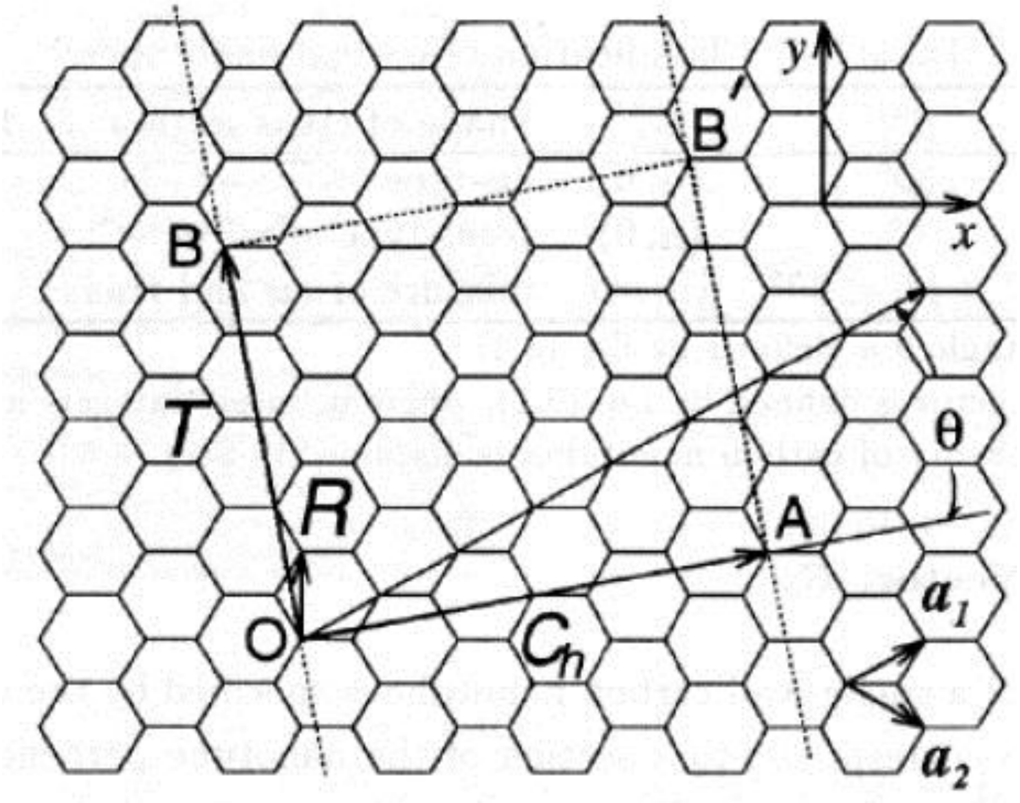
Courtesy S. Aboud

1DEG Supercell: Carbon nanotubes

- Zigzag/Armchair circumferences or general (n,m) chirality:
  - ❑ $C_n = na_1+ma_2$
- Metallic for n-m=$3p$

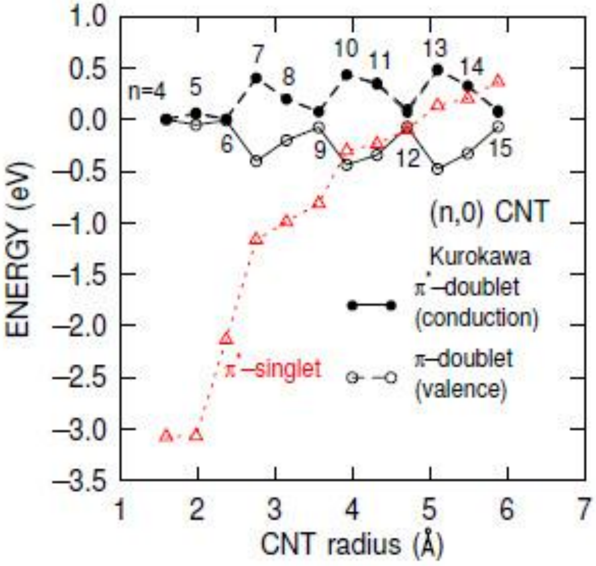


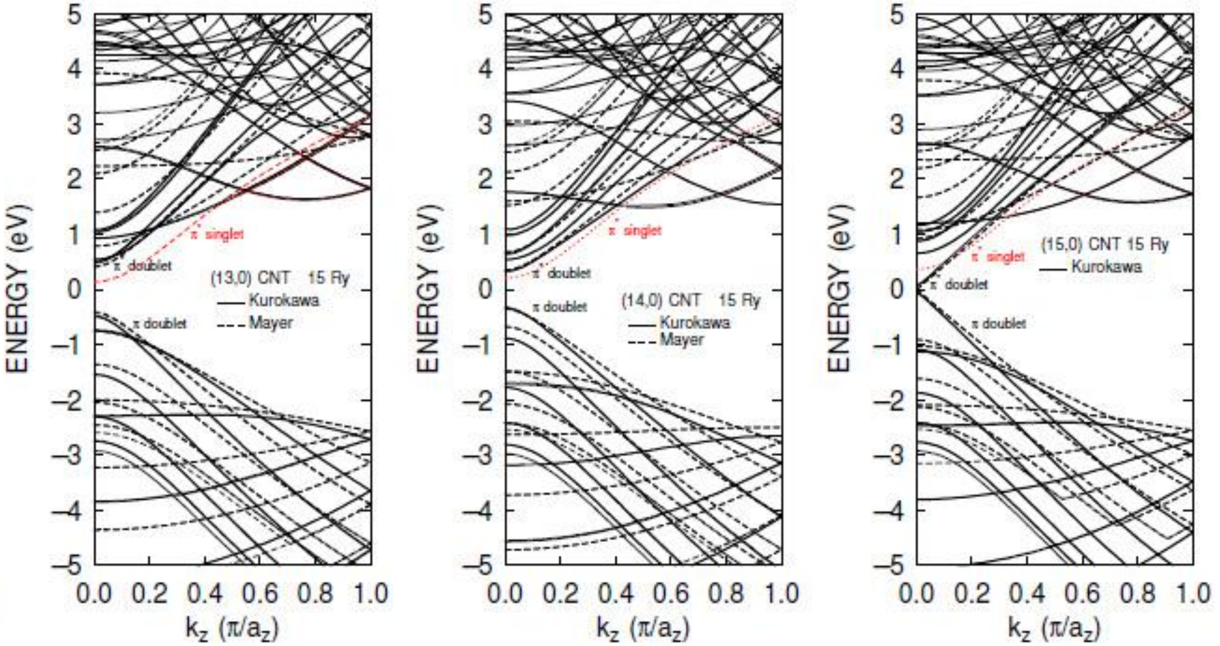
From C. Schönberg (2000)

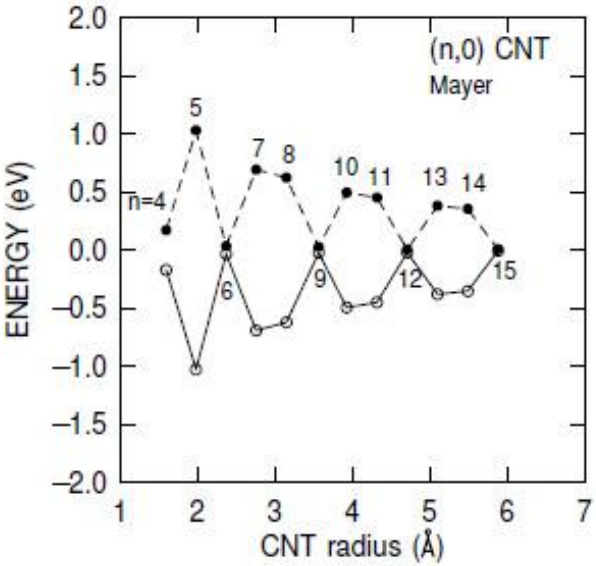


From K. Ghosh, Stanford (2005)

1DEG Supercell: Carbon nanotubes

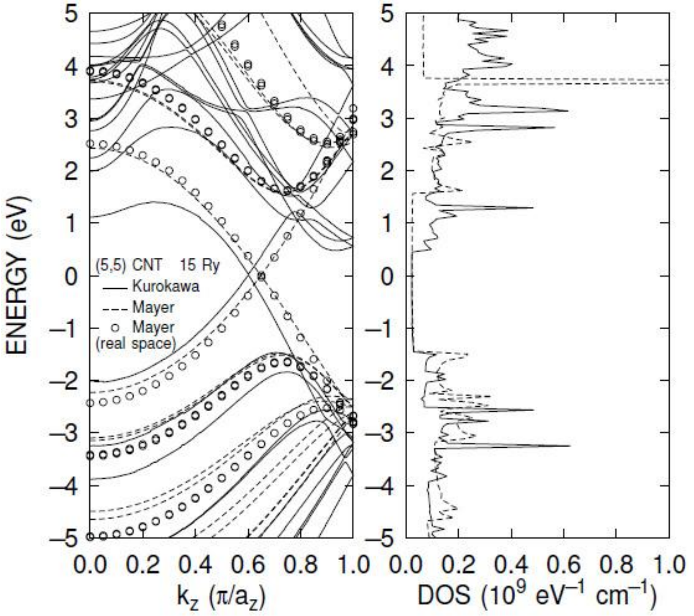




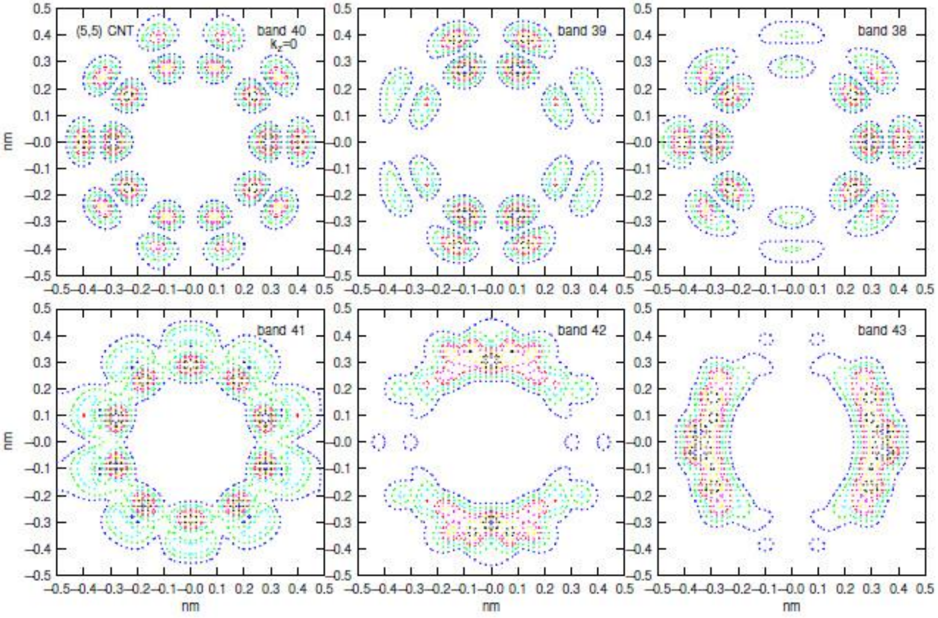


Problem(?): (n,0) CNTs metallic for n<10 due to π* and σ*-singlet curvature-Induced hybridization (Gulseren *et al*., PRB (2002))

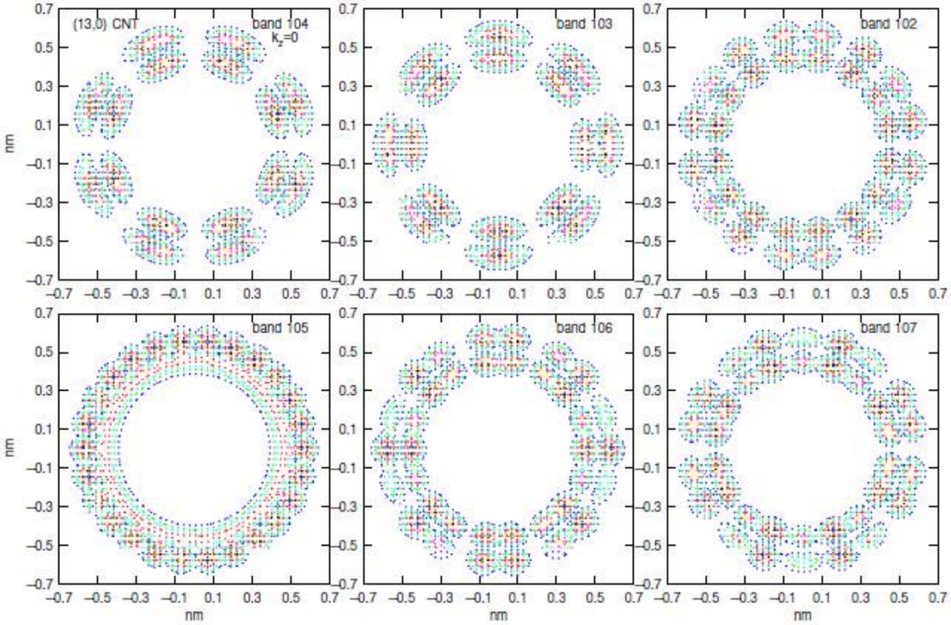
Real-space calculations by Zhang and Polizzi (SPIKE/FEAST) ⟶



2D Supercell: Carbon nanotubes



Conduction band wavefunctions at Γ,
metallic armchair (5,5) CNT



Conduction band wavefunctions at Γ,
semiconducting zigzag (13,0) CNT

Outline

- Electronic structure
  - ❑ Born-Oppenheimer and single-electron approximations
  - ❑ The concept of pseudopotential (self-consistent and empirical)
  - ❑ DFT *vs.* EPs
  - ❑ EPs for nanostructures (supercells) and examples: thin films, hetero-layers, graphene, nanowires, nanotubes
- Scattering
  - ❑ Electron-phonon interaction
    - DFT *vs.* rigid-ion approximation (bulk Si, thin Si films, graphene)
    - Scattering rates
  - ❑ Interface and line-edge roughness (Si films, graphene nanoribbons)
- Transport
  - ❑ Semiclassical:
    - Low-field (mobility) and high-field (MC) properties (Si thin films, graphene, NWs, AGNRs)
  - ❑ Quantum-ballistic:
    - Transport equation
    - Open boundary conditions

Electron-phonon Hamiltonian

- Interaction Hamiltonian:

$$\hat{H}_{ep}^{(\eta)} = \int d\mathbf{r}\; \rho(\mathbf{r},t)\; \delta V^{(\eta)}(\mathbf{r},t)$$

- Lattice (pseudo)potential can be self-consistent (DFT), empirical, model potential (TB),…

- Rigid-(pseudo)ion approximation:

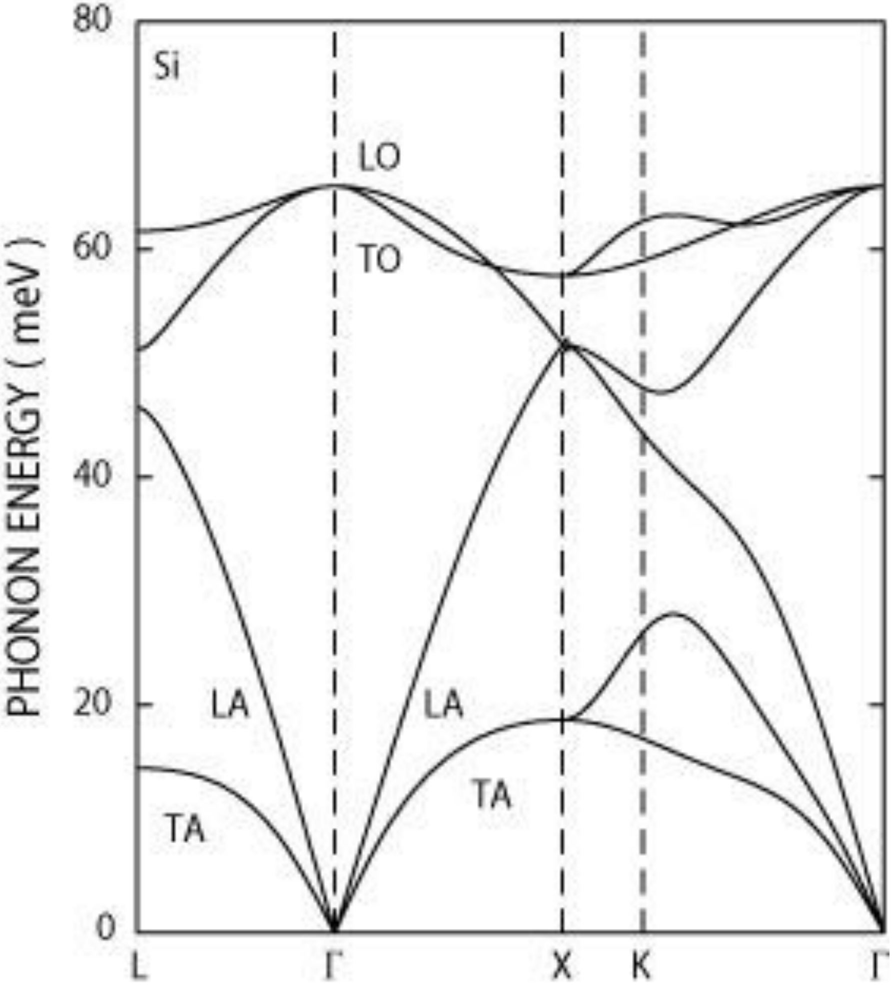
$$\delta V^{(\eta)}(\mathbf{r},t) = \frac{1}{N_c \Omega_c} \sum_{l,\gamma} \nabla V^{(\gamma)}(\mathbf{r} - \mathbf{r}_l - \boldsymbol{\tau}_\gamma) \cdot \boldsymbol{\Delta}_{l,\gamma}^{(\eta)}(t)$$

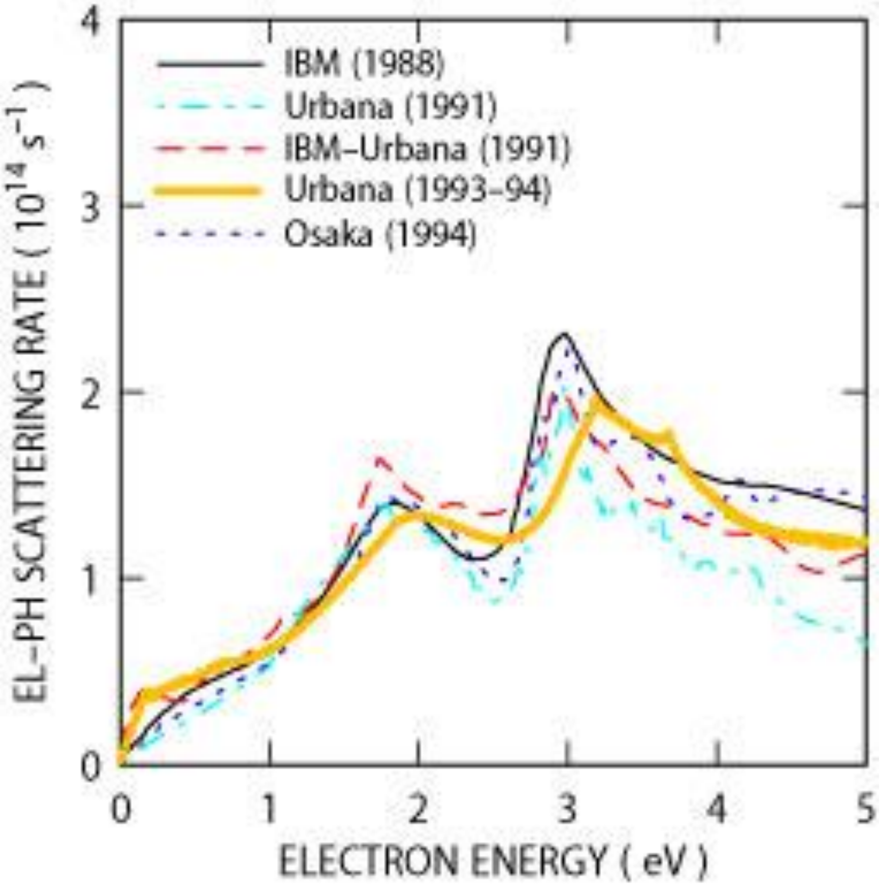
- Interaction Hamiltonian (rigid-pseudo-ion, Cardona’s group for III-Vs, Yoder for Si, …):

$$\hat{H}_{ep}^{(\eta)} = \sum_{n,n'} \sum_{\mathbf{Q},\mathbf{G}''_{\parallel}} i(\mathbf{q}+\mathbf{G}'') \cdot \sum_{\gamma} \mathbf{e}_{\mathbf{Q},\eta}^{(\gamma)} \frac{1}{\Omega_c} V_{\mathbf{q}+\mathbf{G}''}^{(\gamma)} e^{i(\mathbf{q}+\mathbf{G}'')\cdot\boldsymbol{\tau}_\gamma}$$

$$\left(\frac{\hbar}{2\rho_x \omega_{\mathbf{Q},\eta}}\right)^{1/2} e^{i(\mathbf{q}+\mathbf{G}")\cdot\mathbf{r}}\, e^{i\omega_{\mathbf{Q},\eta}t}\, c_{\mathbf{K}+\mathbf{Q},n'}^{\dagger} \left(b_{\mathbf{Q},\eta}^{\dagger} + b_{\mathbf{Q},\eta}\right) c_{\mathbf{K},n}$$

Electron-phonon scattering in bulk Si





MVF and Higman, 1991

Rigid-ion electron-phonon scattering in graphene: Matrix element

- Matrix element:

$$\langle \mathbf{K}'n'|\hat{H}_{ep}^{(\eta)}|\mathbf{K}n\rangle = \sum_{\mathbf{G}} \mathcal{D}^{(\eta)}_{\mathbf{K}'-\mathbf{K},\mathbf{G}} \int d\mathbf{r}\ \psi^{(n')*}_{\mathbf{K}'}(\mathbf{r})\ e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}\ \psi^{(n)}_{\mathbf{K}}(\mathbf{r})$$

with

$$\mathcal{D}^{(\eta)}_{\mathbf{Q},\mathbf{G}} = i(\mathbf{q}+\mathbf{G}) \cdot \sum_{\gamma} \mathbf{e}^{(\gamma)}_{\mathbf{Q},\eta}\ V^{(\gamma)}_{\mathbf{q}+\mathbf{G}}\ e^{i(\mathbf{q}+\mathbf{G})\cdot\boldsymbol{\tau}_\gamma}\ \mathcal{A}_{\mathbf{Q},\eta}$$

$$\mathcal{A}^2_{\mathbf{Q},\eta} = \left(\frac{\hbar}{2\rho_x\omega_{\mathbf{Q},\eta}}\right) \left\{ \begin{array}{c} N_{\mathbf{Q},\eta} \\ 1+N_{\mathbf{Q},\eta} \end{array} \right\}$$

- Exact expression (too time consuming):

$$\langle \mathbf{K}'n'|\hat{H}_{ep}^{(\eta)}|\mathbf{K}n\rangle = \sum_{\mathbf{G},\mathbf{G}'} \mathcal{D}^{(\eta)}_{\mathbf{K}'-\mathbf{K},\mathbf{G}'}\ u^{(n')*}_{\mathbf{K}',\mathbf{G}+\mathbf{G}'}\ u^{(n)}_{\mathbf{K},\mathbf{G}}$$

- *Normal* processes (no *Umklapp*) only:

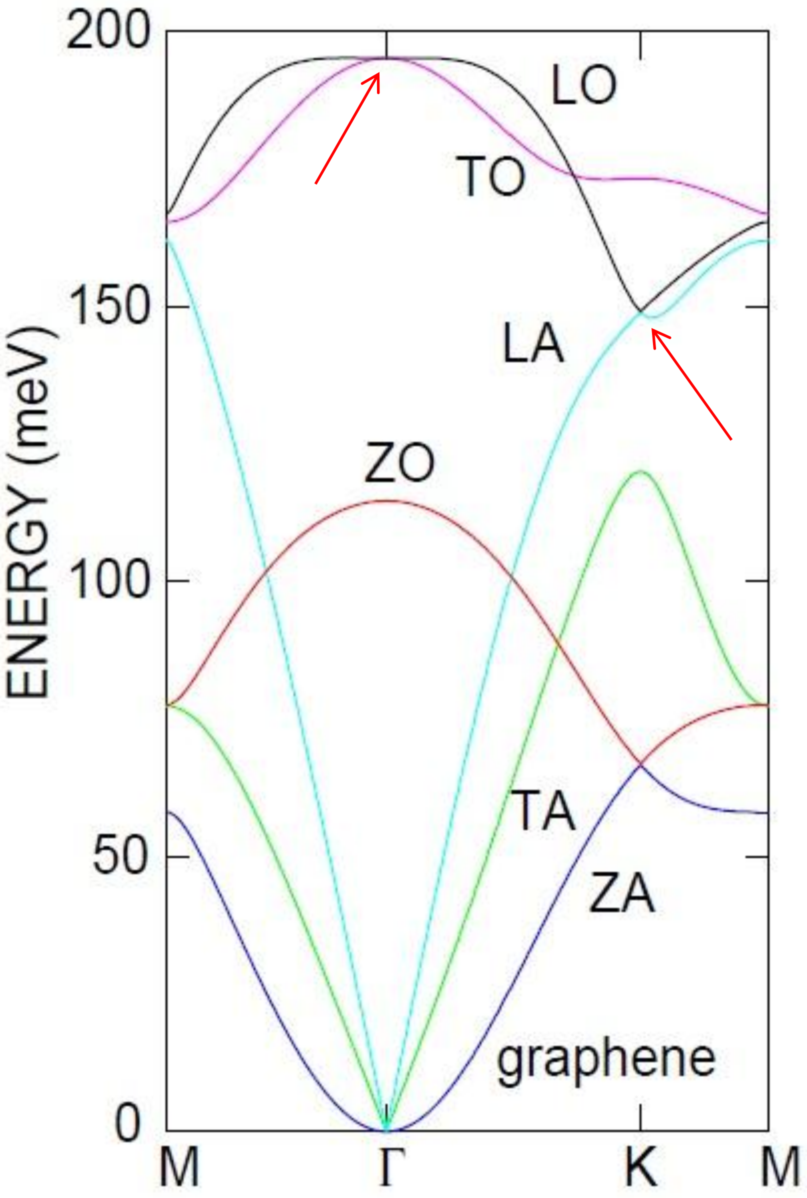
$$\langle \mathbf{K}'n'|\hat{H}_{ep}^{(\eta)}|\mathbf{K}n\rangle \approx \mathcal{D}^{(\eta)}_{\mathbf{K}'-\mathbf{K},\mathbf{0}} \sum_{\mathbf{G}} u^{(n')*}_{\mathbf{K}',\mathbf{G}}\ u^{(n)}_{\mathbf{K},\mathbf{G}}$$

- No in-plane *Umklapp*:

$$\langle \mathbf{K}'n'|\hat{H}_{ep}^{(\eta)}|\mathbf{K}n\rangle \approx \sum_{G_z} \mathcal{D}^{(\eta)}_{\mathbf{K}'-\mathbf{K},\mathbf{G}_{||}=0,G_z} \sum_{\mathbf{G}} u^{(n')*}_{\mathbf{K}',\mathbf{G}}\ u^{(n)}_{\mathbf{K},\mathbf{G}}$$

Electron-phonon scattering in graphene: Phonon spectra

- From “Born-van Kármán” method
  - ❑ Atomic force constants from fit to experiments **or** DFT (Falkovsky, Phys. Lett. A (2008); Zimmermann *et al*., PRB (2008)).
  - ❑ Include 4th nearest neighbor interactions

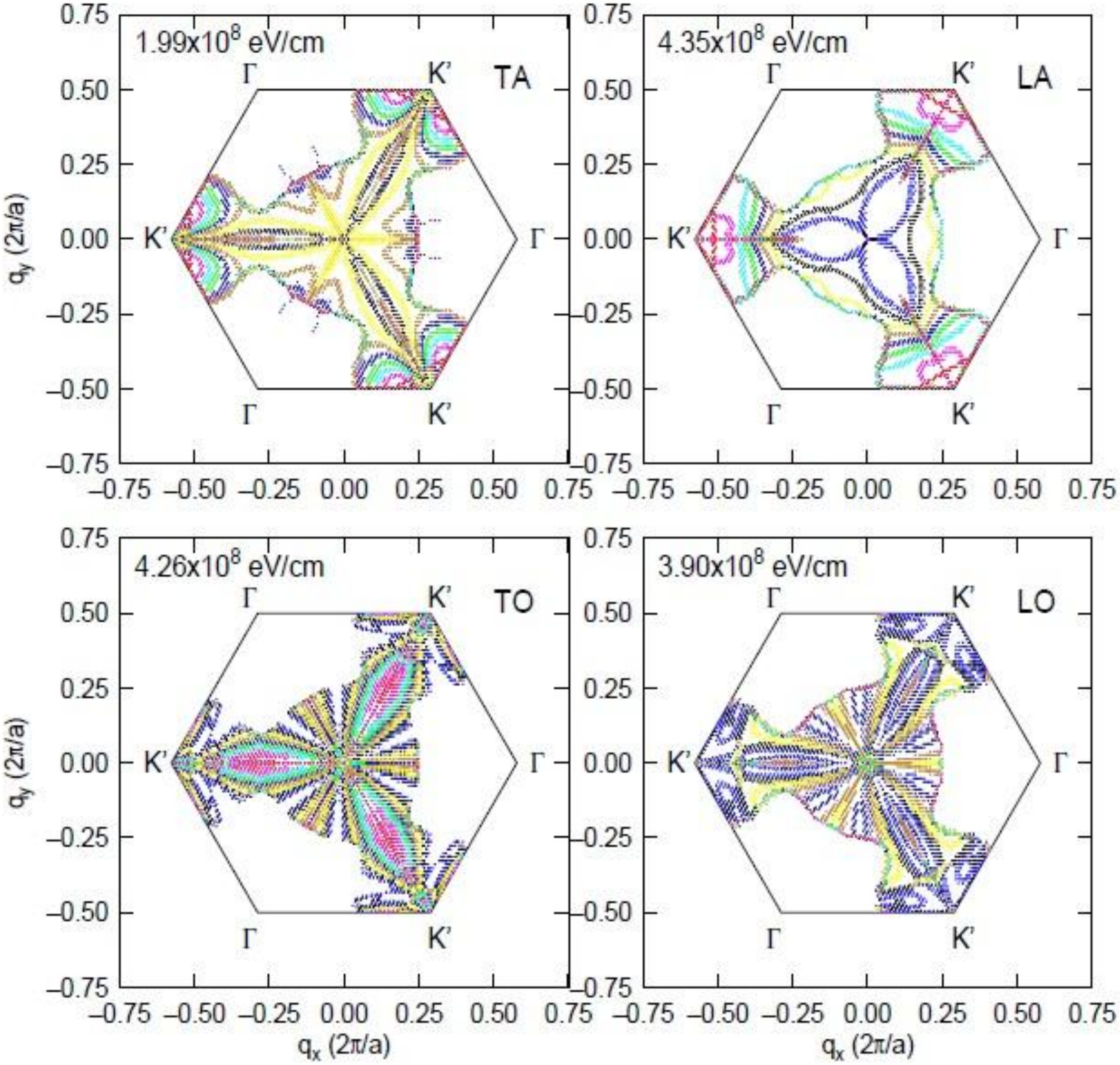


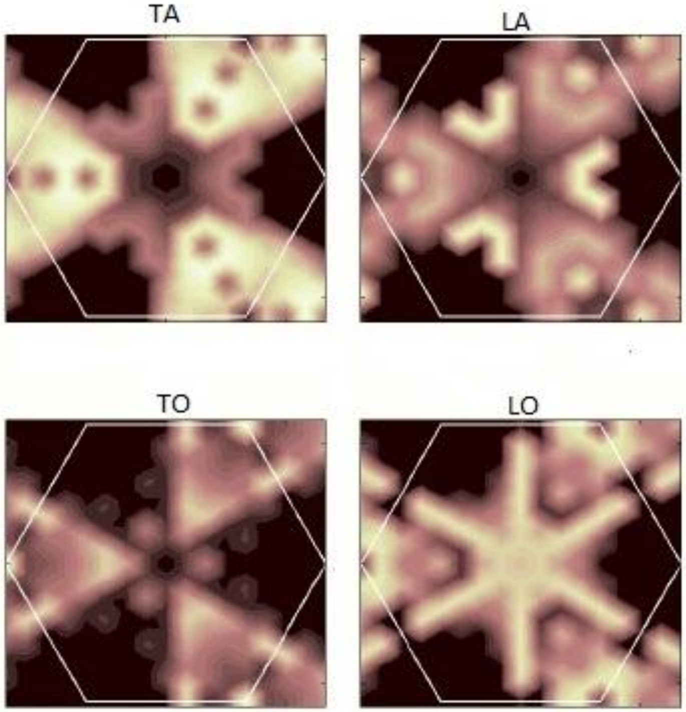
Courtesy C. Sachs

No Kohn anomalies! Cannot get them without self-consistency (Born-Oppenheimer also questionable)

Rigid-ion el-phonon scattering in graphene: Matrix elements

- Deformation potentials for initial state at the K-point as a function of phonon wavevector in the BZ (dynamic zero-T screening, Wunsch *et al*., New J. Phys., 2006)





Borysenko *et al*., Phys. Rev. (2010), DFT (Quantum Espresso) results for matrix elements

Rigid-ion el-phonon scattering in graphene: Matrix elements

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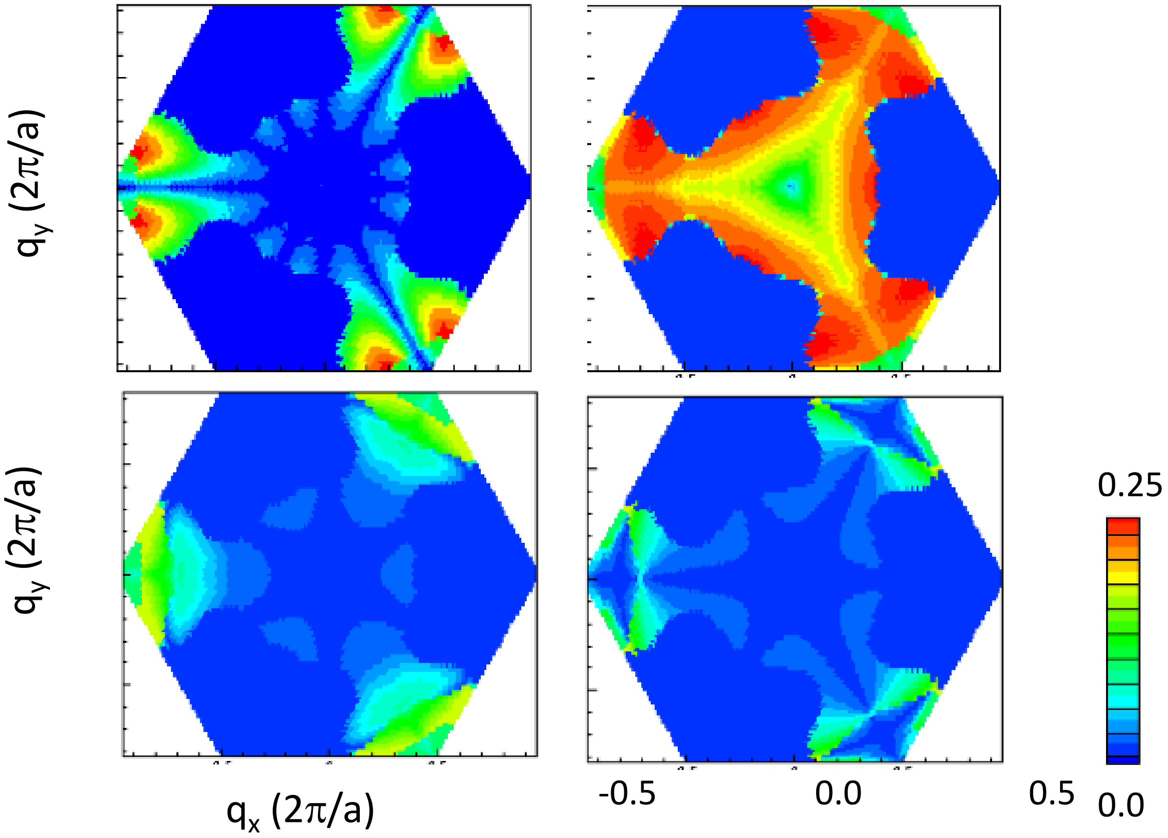
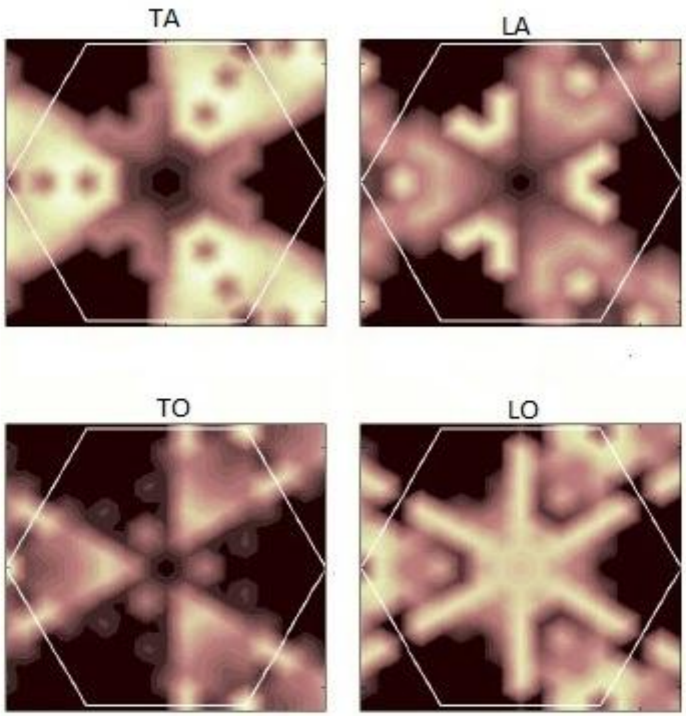
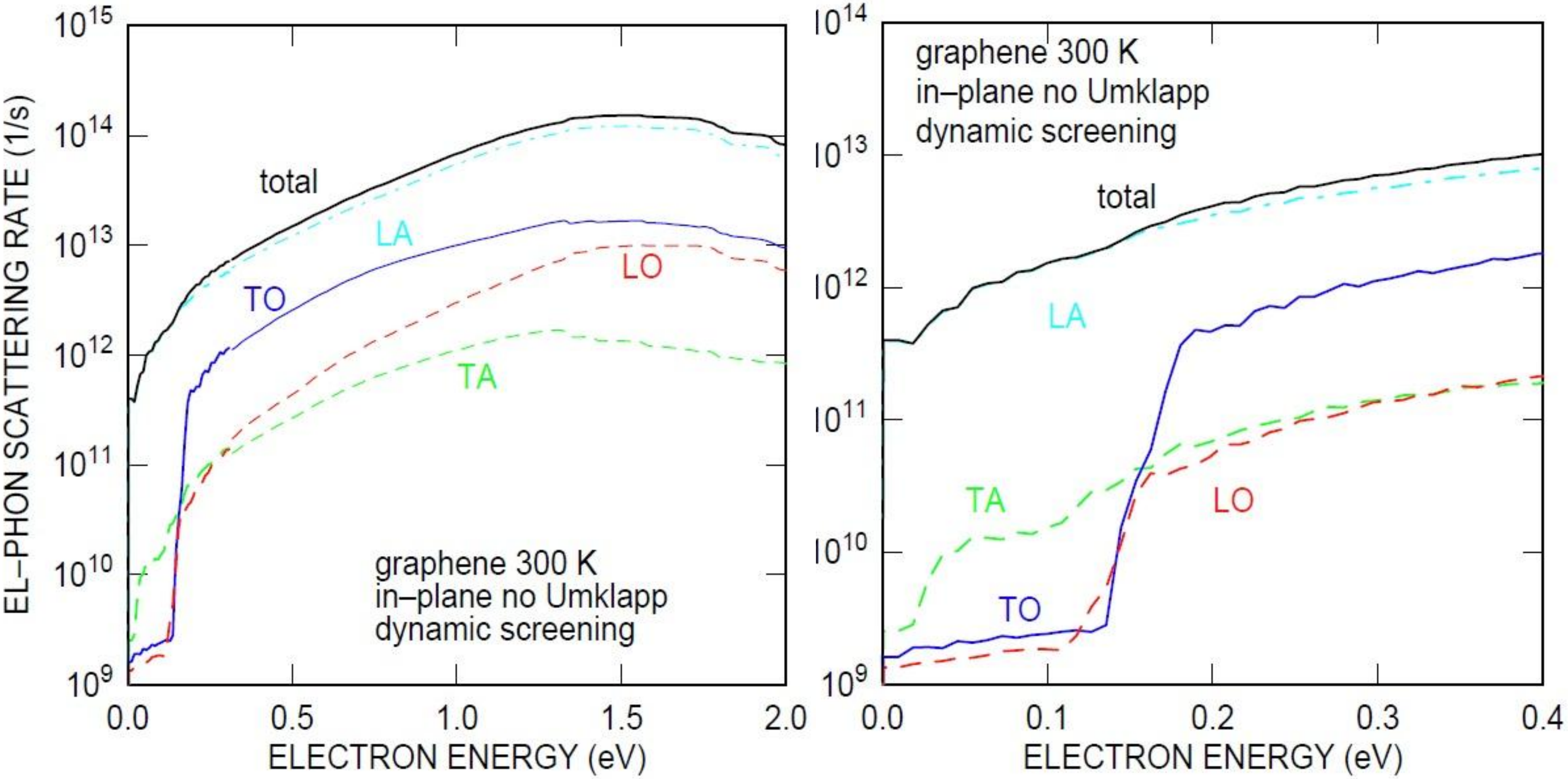




Borysenko *et al*., Phys. Rev. (2010), DFT (Quantum Espresso) results for matrix elements

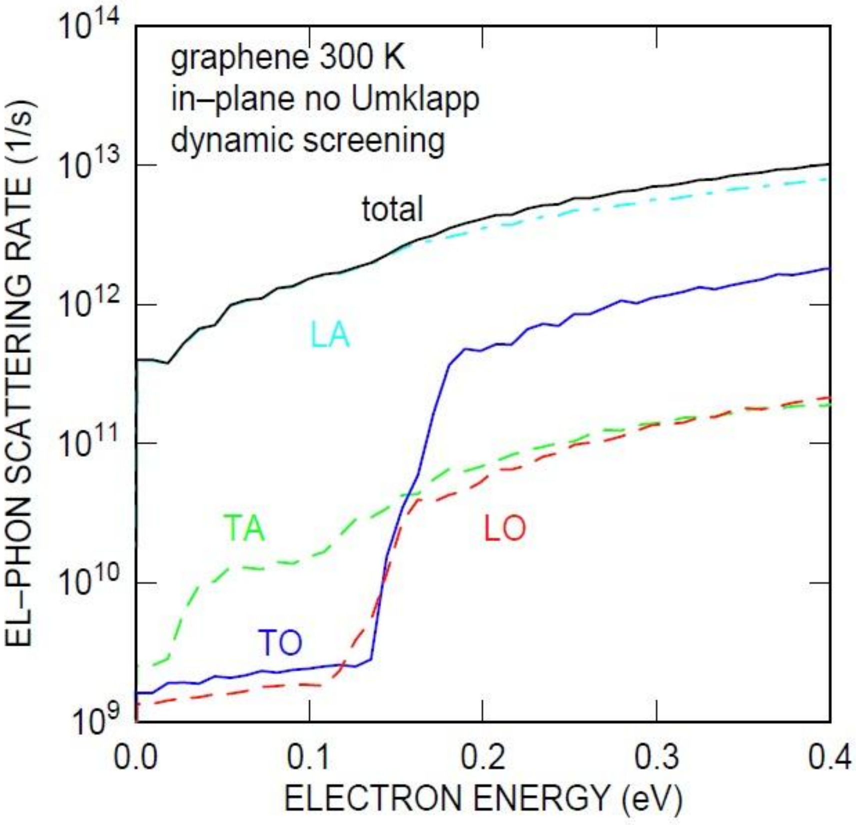
Rigid-ion el-phonon scattering in graphene: Scattering rates

- Total rates by mode (only in-plane *Umklapp* processes included):

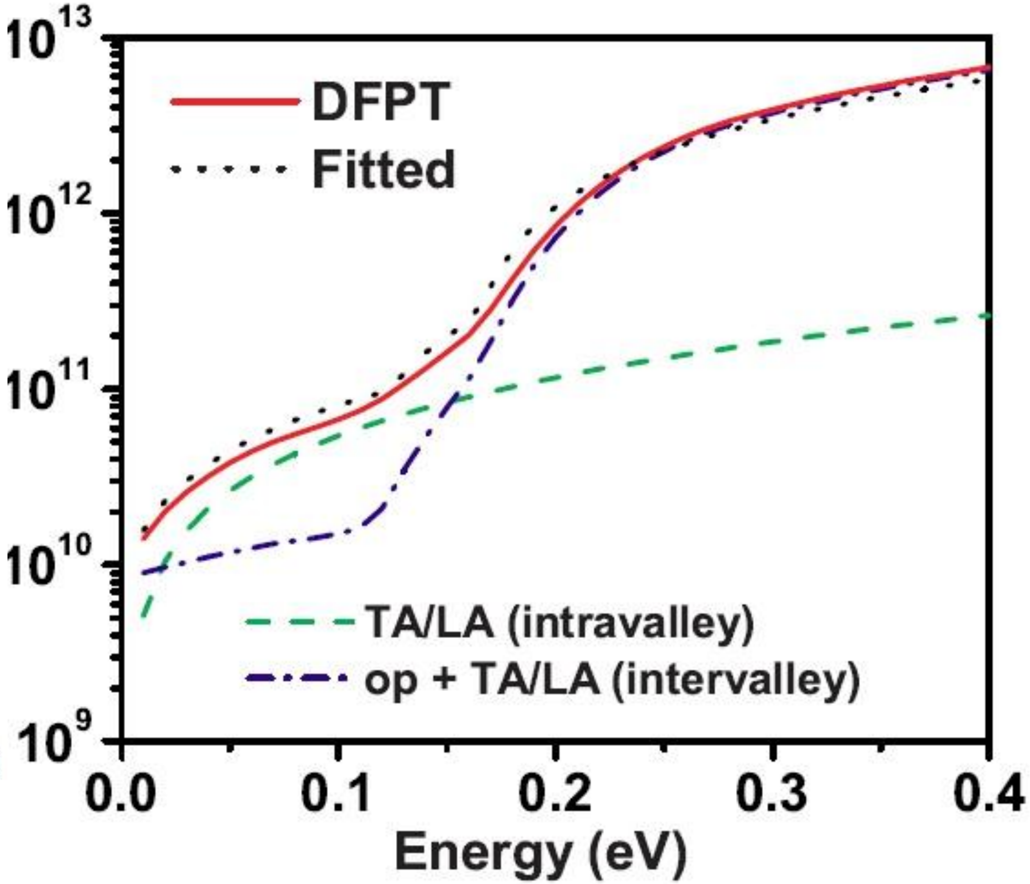


Rigid-ion el-phonon scattering in graphene: Scattering rates

- Overall comparison EP/rigid-(pseudo)ion *vs.* DFT:



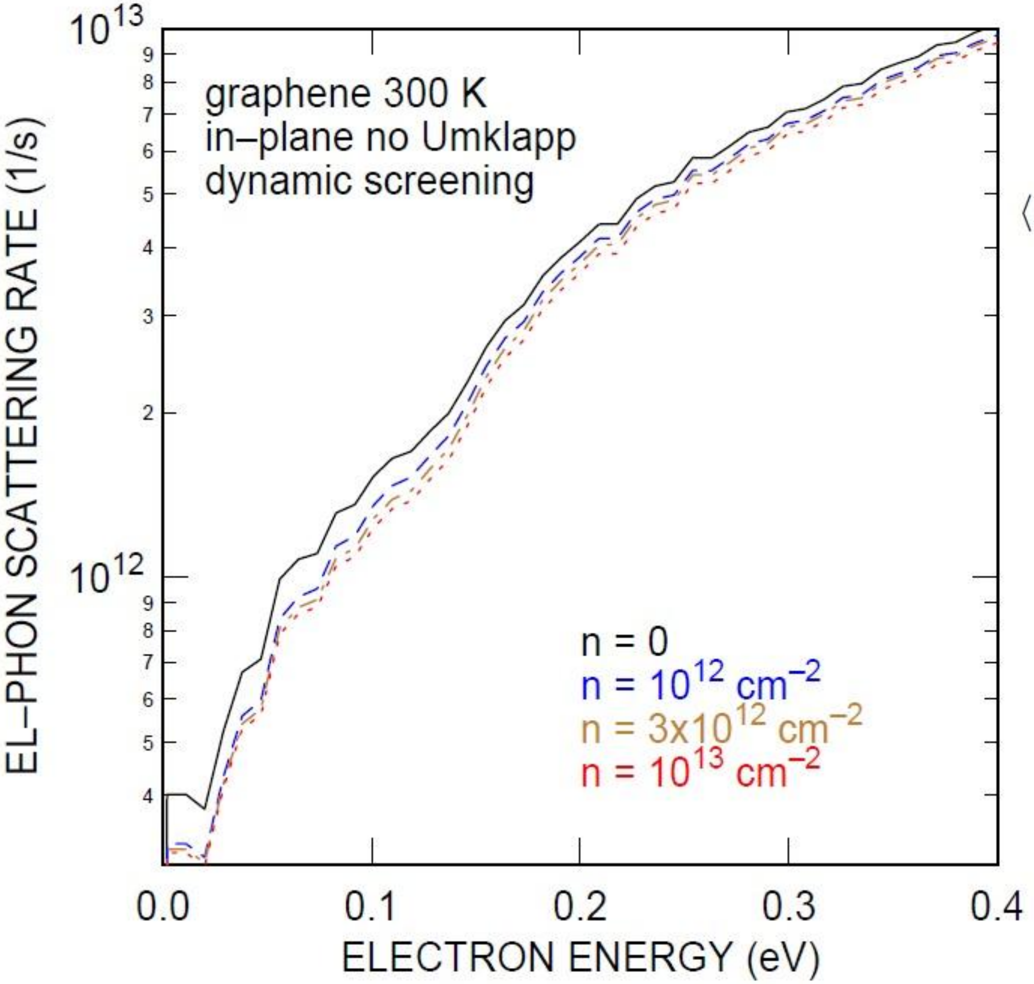
Rigid-ion



Borysenko *et al.*, Phys. Rev. B **81**, 121412 (2010): Full DFT from Quantum Espresso

Rigid-ion el-phonon scattering rates: Screening

- Effect of dynamic screening (Wunsch *et al*., New J. Phys. Rev. **8**, 318 (2006))



Screened matrix element (T=0 K):

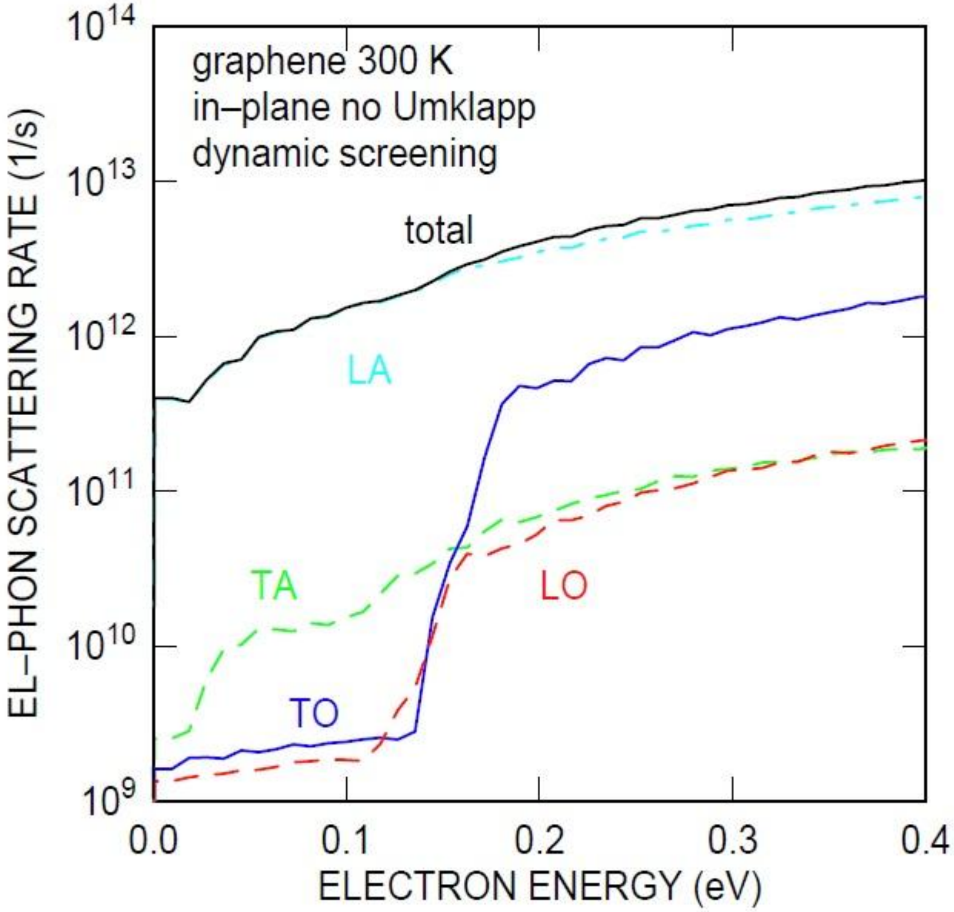
$$\langle \mathbf{K}'n'|\hat{H}_{ep}^{(\eta)}|\mathbf{K}n\rangle \;\rightarrow\; \frac{\langle \mathbf{K}'n'|\hat{H}_{ep}^{(\eta)}|\mathbf{K}n\rangle}{1 \;-\; [e^2/(2\kappa_0 Q)]\Pi_{RPA}(Q,\omega_{Q\eta})}$$

RPA polarizability:

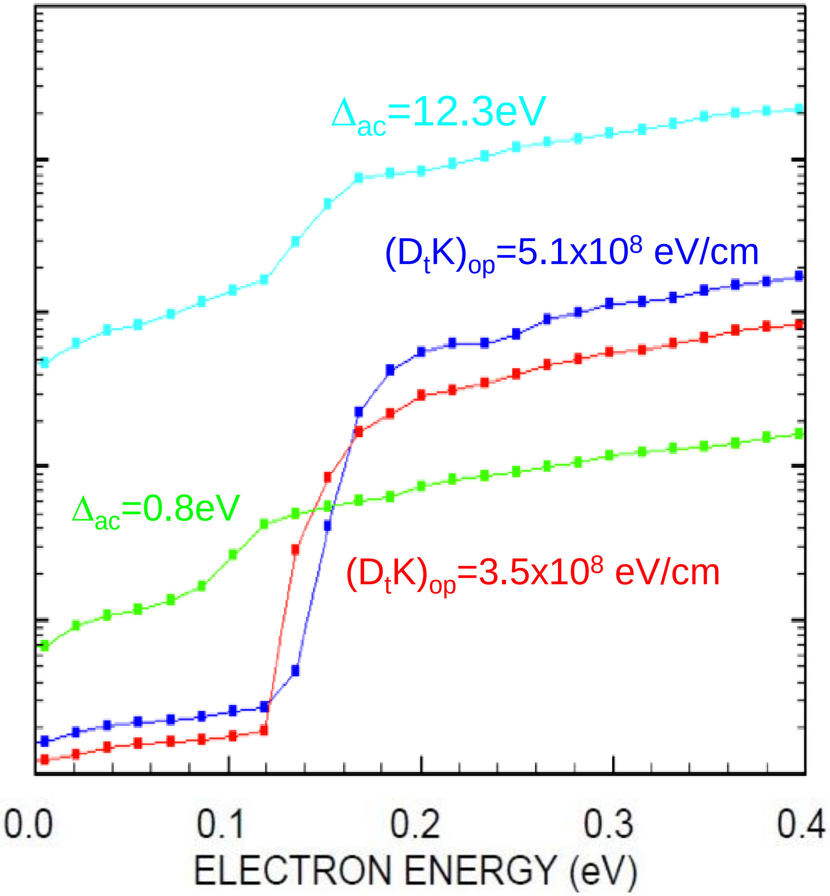
$$\Pi_{RPA}(Q,\omega) \;=\; \frac{\Pi(Q,\omega)}{1-[e^2/(2\kappa_0 Q)]\Pi(Q,\omega)}$$

Deformation Potential Scattering

Rigid-Ion



Fitted Deformation Potentials



Courtesy S. Aboud

Roughness-induced scattering

- Two approaches to roughness scattering:
  - Macroscopic (Ando): Assume “barrier potential’, perturb wavefunctions
    - Pros: Ensemble average ‘on the fly’, qualitatively correct
    - Cons: Effective mass, a bit *ad hoc*
  - Microscopic/atomistic: Add/remove atoms/assume a particular geometric configuration
    - Pros: Microscopically/geometrically correct
    - Cons: Need “expensive” ensemble average over many configurations
- New approach: Merge the two perspectives:
  - Use EPs to shift/add/remove atoms and obtain “scattering” (pseudo)potential
  - Normalize the scattering potential by actual “displacement”
  - Calculate scattering rate with a statistically averaged roughness power spectrum

Note: Prange-Nee terms only, no Coulomb effects… yet…

MVF and S. Narayanan, JAP 2011

Pseudopotential-based SR/LER Scattering

- Combine atomistic/configurational approach with macroscopic (Ando's barrier potential) approach:
  - ❑ SR Hamiltonian for (pseudo)atomic shift : $\mathcal{H}^{(SR)}(\mathbf{r}) = i \sum_{\mathbf{QG}} \Delta_{\mathbf{Q}} V_{\mathbf{G}}^{(lat)} G_z e^{i(\mathbf{G}\cdot\mathbf{r}+\mathbf{Q}\cdot\mathbf{R})}$
  - ❑ SR Hamiltonian for insertion/deletion of atomic lines:

$$\mathcal{H}^{(SR)}(\mathbf{r}) = \sum_{\mathbf{GQ}} e^{i(\mathbf{G}\cdot\mathbf{r}+\mathbf{Q}\cdot\mathbf{R})} \left[\sum_{\alpha} e^{-i\mathbf{G}\cdot\boldsymbol{\tau}_\alpha} V_{\mathbf{G}}^{(\alpha)} - \sum_{\alpha'} e^{-i\mathbf{G}\cdot\boldsymbol{\tau}'_\alpha} V_{\mathbf{G}}^{(\alpha')} \right]$$

  - ❑ Matrix elements for UTBs, cylindrical NWs, AGNRs:

$$V^{(SR)(ac)}_{\mathbf{K}',\mathbf{K},n',n} \approx \Delta_{\mathbf{K}-\mathbf{K}'} \left[\int dz\ \zeta^{(n')*}_{\mathbf{K}'}(z) \frac{d\langle V^{(t)}(z)\rangle}{dz} \zeta^{(n)}_{\mathbf{K}}(z) + \int dz\ \zeta^{(n')*}_{\mathbf{K}'}(z) \frac{d\langle V^{(b)}(z)\rangle}{dz} \zeta^{(n)}_{\mathbf{K}}(z) \right]$$

$$|V^{(SR)}_{k'_z,k_z,n,n'}|^2 = \langle |V^{(SR)}_{k'_z,k_z,n,n'}|^2 \rangle \approx \frac{1}{2\pi} \sum_{ll'l''} \langle |\Delta_{l-l'+l'',k_z-k'_z}|^2 \rangle \left| \int dR\ R\ \rho^{(n')*}_{k'_z,l'}(R) \frac{dv^{(lat)}_{l''}(R)}{dR} \rho^{(n)}_{k_z,l}(R) \right|^2$$

$$\left| V^{ER)(ac)}_{k'_z,k_z,n',n} \right|^2 = \frac{1}{4} \left\{ \langle |\Delta^{(left)}_{k_z-k'_z}|^2 \rangle \left[\left| \mathcal{I}^{(ER,left,+)}_{k'_z,k_z,n',n} \right|^2 + \left| \mathcal{I}^{(ER,left,-)}_{k'_z,k_z,n',n} \right|^2 \right] \right.$$

$$\left. + \langle |\Delta^{(right)}_{k_z-k'_z}|^2 \rangle \left[\left| \mathcal{I}^{(ER,right,+)}_{k'_z,k_z,n',n} \right|^2 + \left| \mathcal{I}^{(ER,right,-)}_{k'_z,k_z,n',n} \right|^2 \right] \right\}$$

- Expected results for Si UTBs and cylindrical NWs
- **Huge LER scattering rate for AGNRs** due to chirality-dependence of the gap

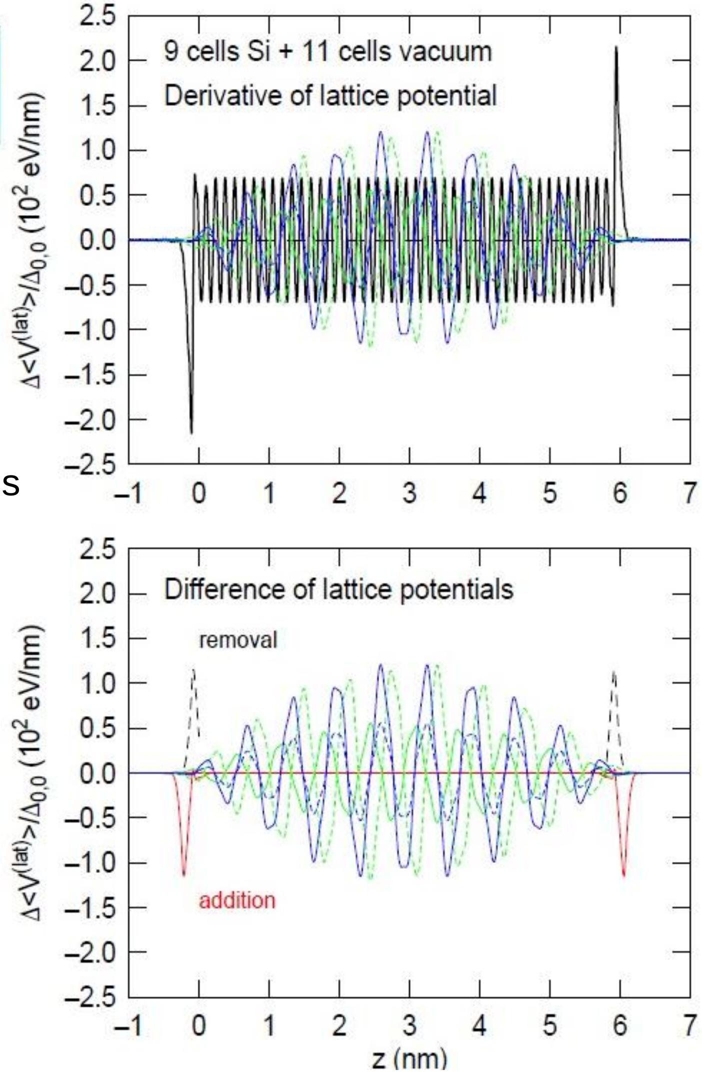
SR Scattering: Si UTBs

1. Uniform atomic shift (correlated): $\mathcal{H}^{(SR)}(\mathbf{r}) = i \sum_{\mathbf{QG}} \Delta_{\mathbf{Q}} V_{\mathbf{G}}^{(lat)} G_z e^{i(\mathbf{G}\cdot\mathbf{r}+\mathbf{Q}\cdot\mathbf{R})}$
2. Add/delete atoms (un- and anti-correlated)

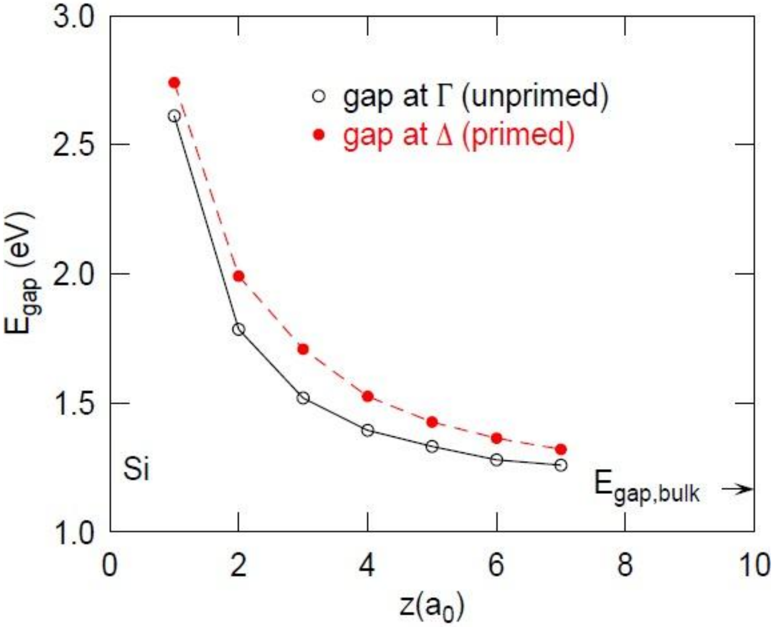
$$\mathcal{H}^{(SR)}(\mathbf{r}) = \sum_{\mathbf{GQ}} e^{i(\mathbf{G}\cdot\mathbf{r}+\mathbf{Q}\cdot\mathbf{R})} \left[\sum_{\alpha} e^{-i\mathbf{G}\cdot\boldsymbol{\tau}_\alpha} V_{\mathbf{G}}^{(\alpha)} - \sum_{\alpha'} e^{-i\mathbf{G}\cdot\boldsymbol{\tau}'_\alpha} V_{\mathbf{G}}^{(\alpha')} \right]$$

3. *rms* roughness:

$$\langle|\Delta_{\mathbf{Q}}|^2\rangle = \pi\Delta^2\Lambda^2(1+Q^2\Lambda^2/2)^{-n-1}$$



Squared wavefunctions and SR potential →

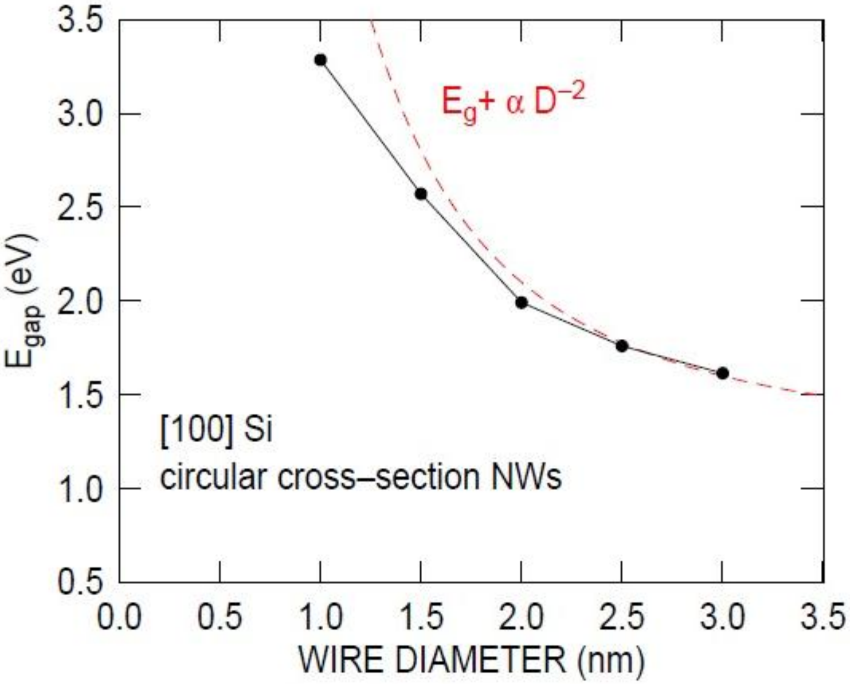


Gap *vs.* thickness ←

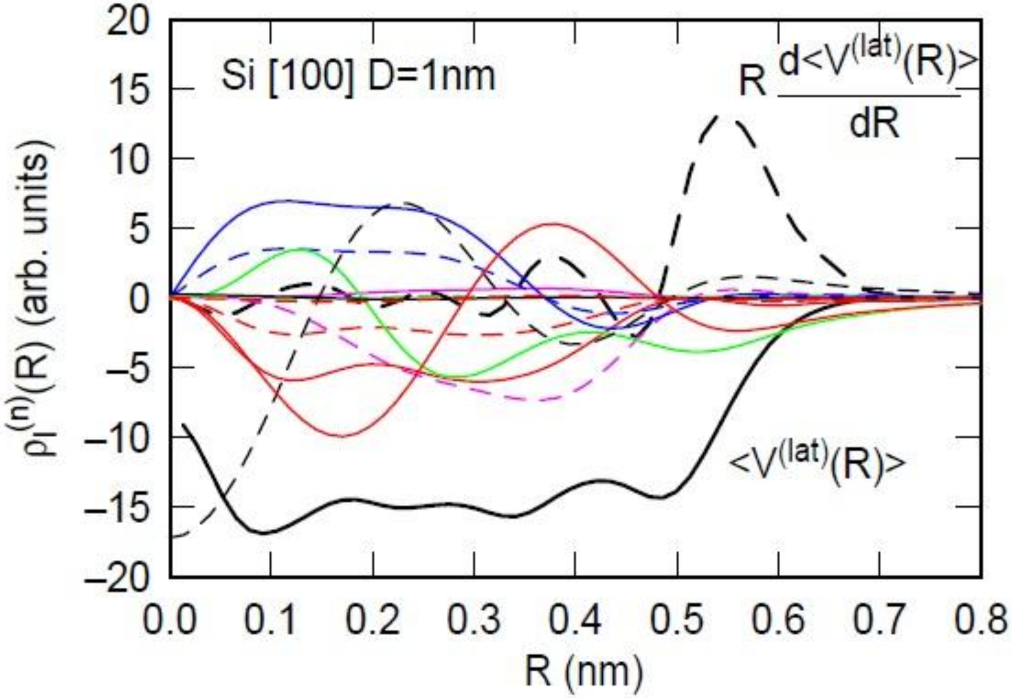
SR Scattering: cylindrical Si NWs

1. Atomic shift in radial direction
2. Decompose scattering potential and wavefunctions into angular-momentum components
3. *rms* roughness:

$$\langle|\Delta_{l,q}|^2\rangle = \frac{\Delta^2\Lambda^2}{2r_s}\left[1 + \frac{\Lambda^2}{2}\left(\frac{l^2}{r_s^2} + q^2\right)\right]^{-3/2}$$



Gap *vs.* thickness

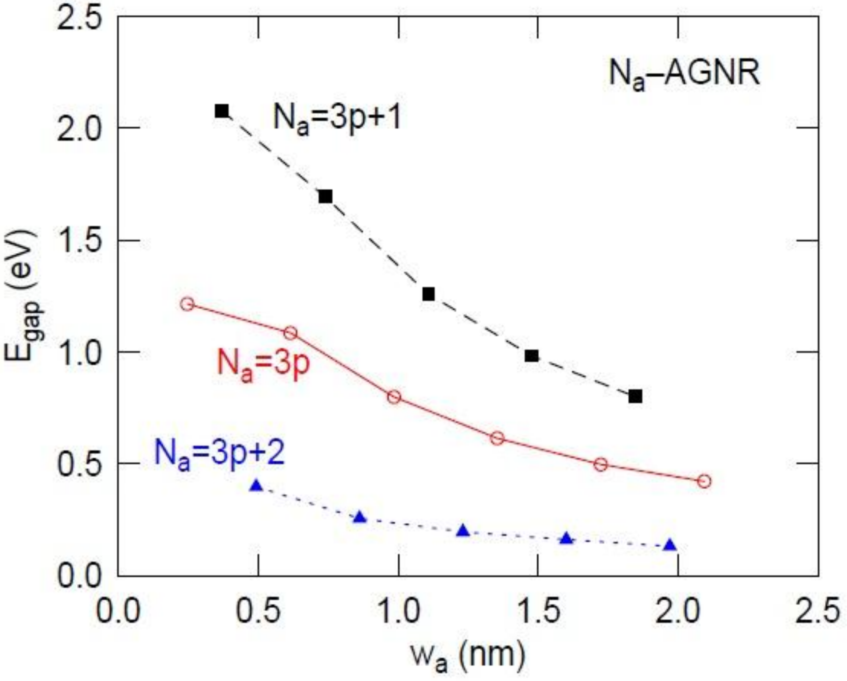


Radial wavefunctions of various angular momentum, radial pseudopotential and SR potential

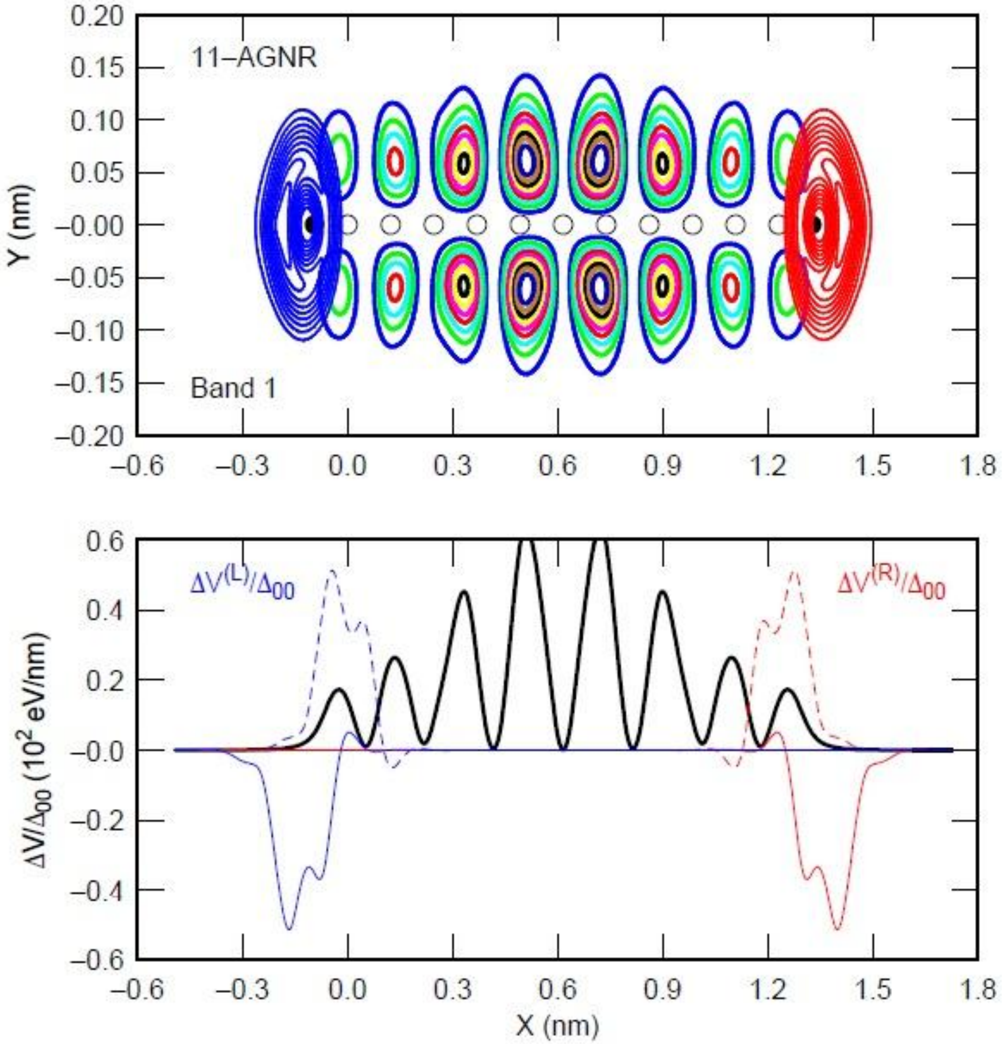
LER Scattering: AGNRs

1. Add/delete atomic lines at left/right edges
2. *rms* roughness:

$$\langle|\Delta_q|^2\rangle = \sqrt{2}\Delta^2\Lambda(1+q^2\Lambda^2/2)^{-1}$$



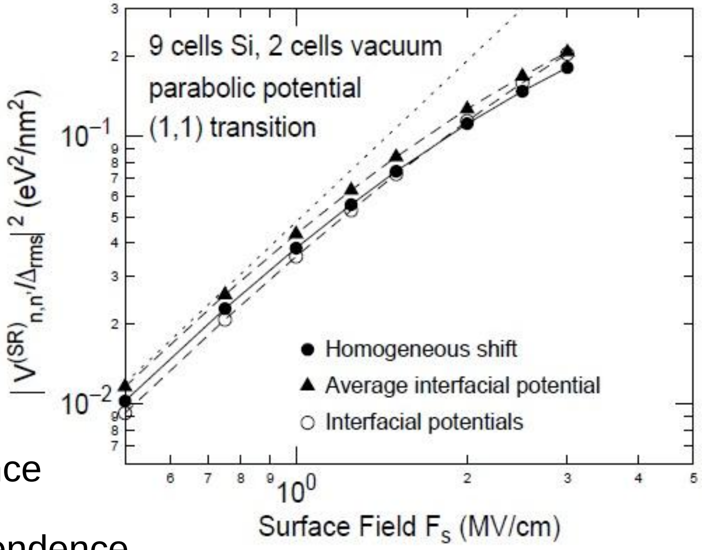
Gap *vs.* thickness



Squared wavefunctions and SR potential

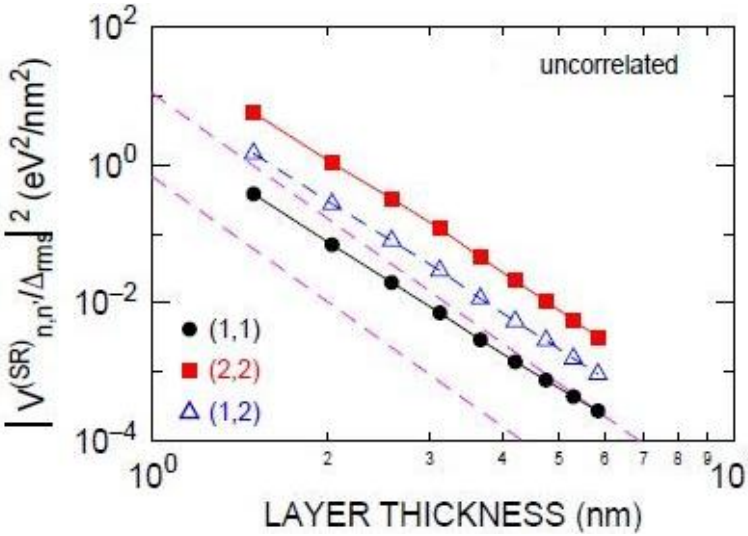
SR and LER Scattering: Matrix elements

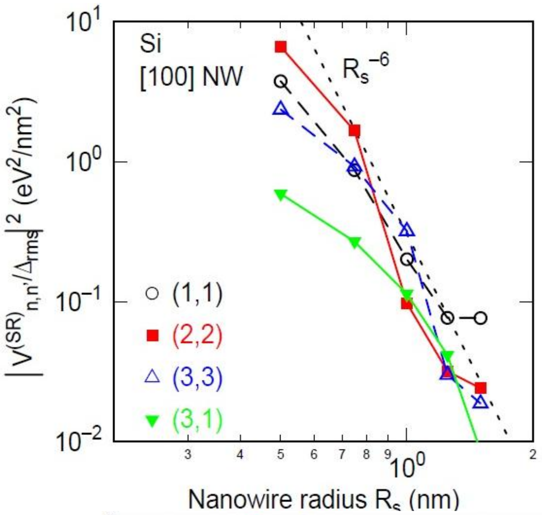
Si UTB →



Field dependence

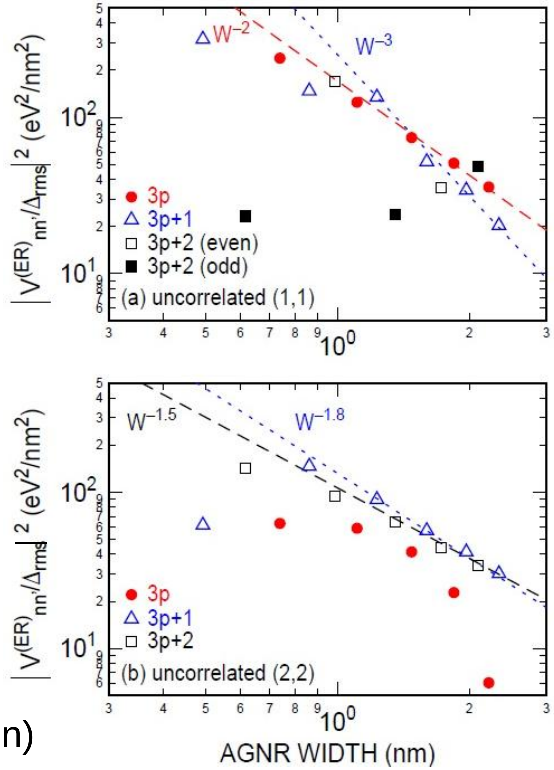
Thickness dependence





← Si NWs

Radius dependence



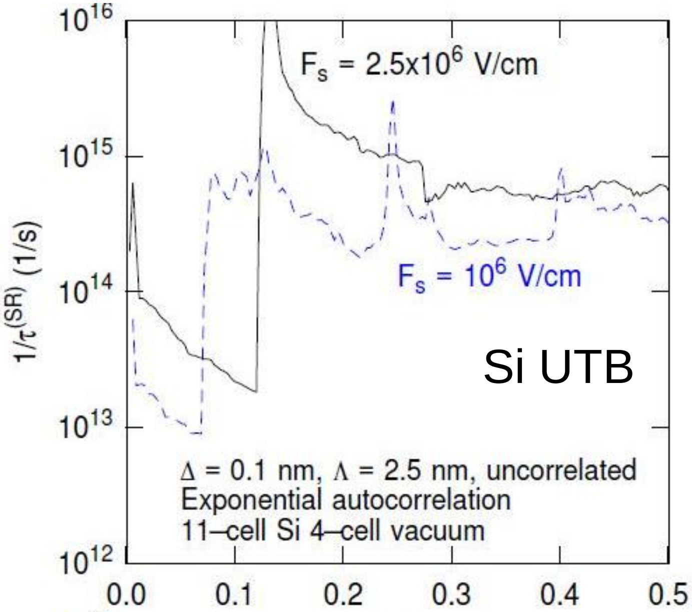
← AGNRs

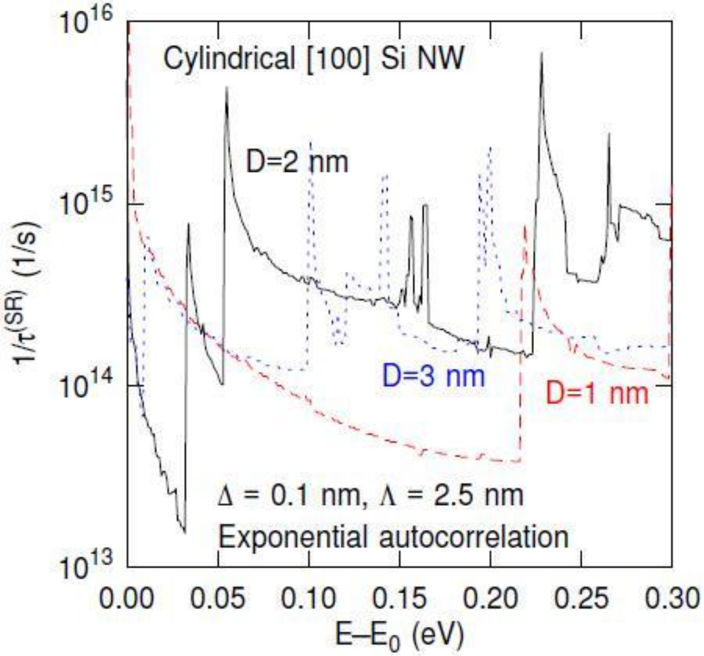
Width/chirality dependence

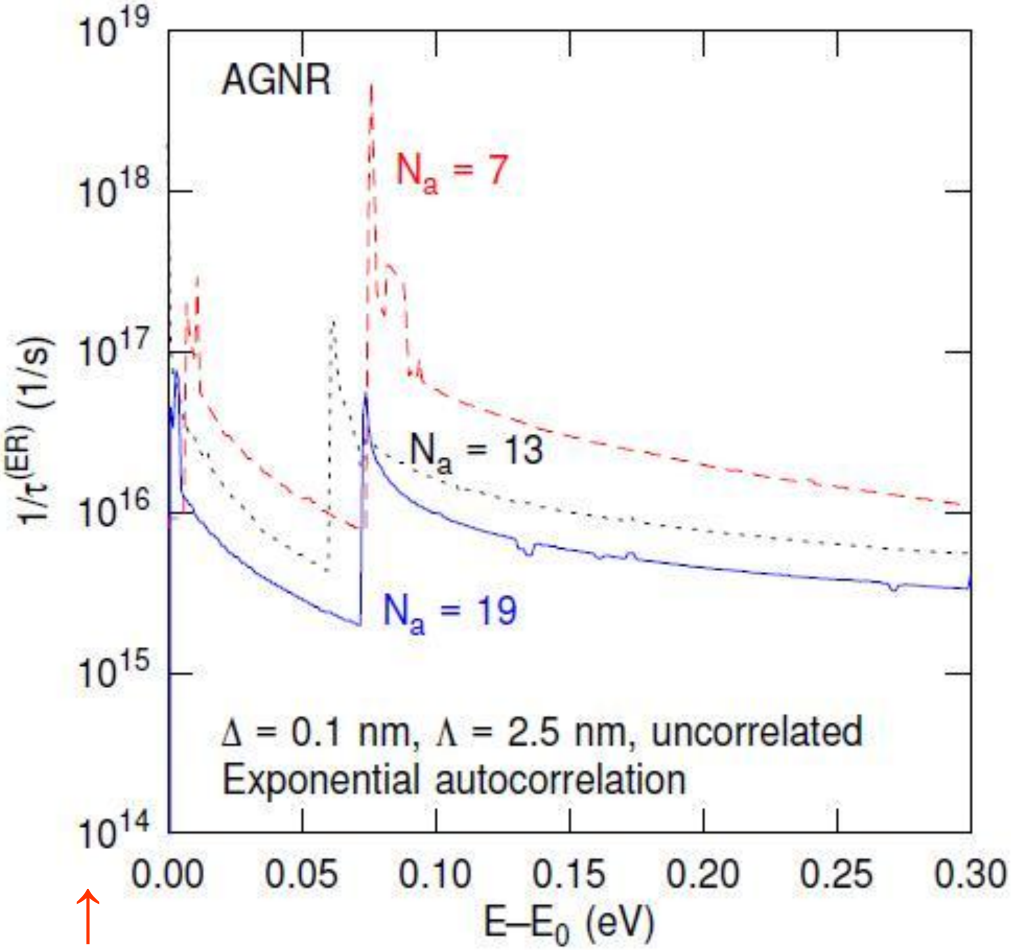
Note scale! →

- ❑ Due to chirality dependence of the gap
- ❑ Beyond perturbation theory (1st Born approximation)

SR/LER Scattering: Huge for AGNRs!







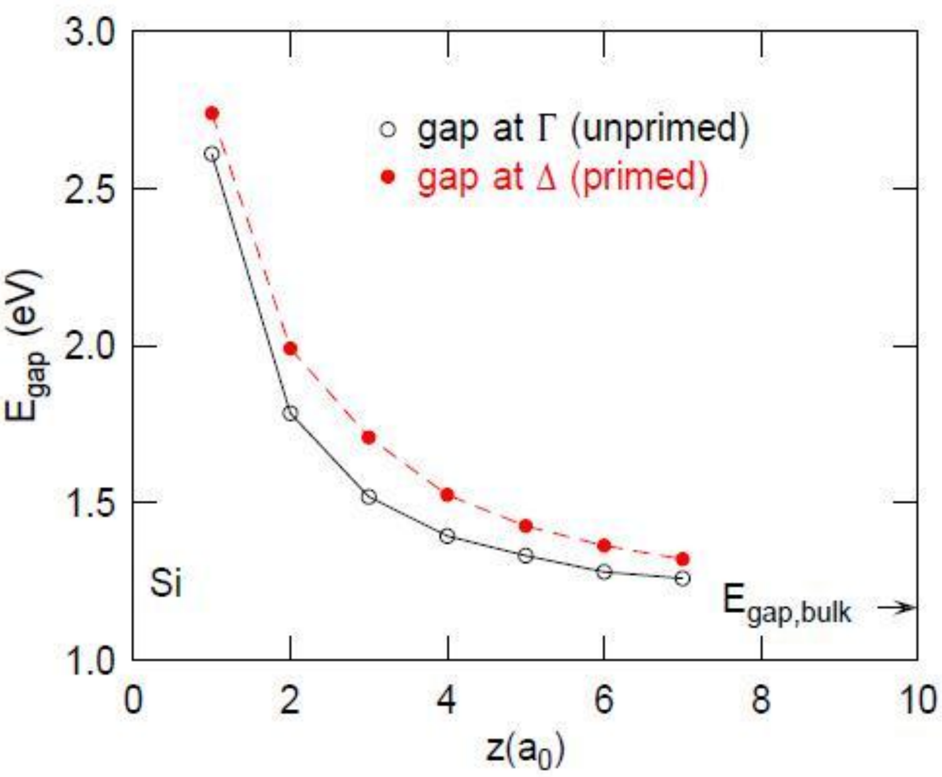
↑

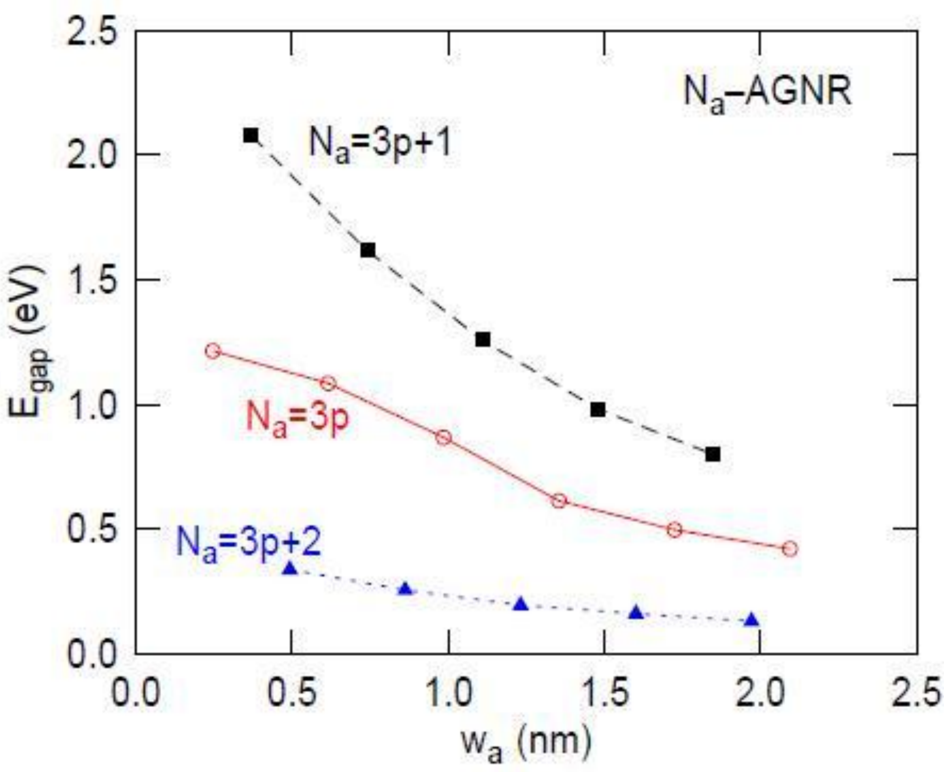
Note scale!

- Due to chirality dependence of the gap
- Beyond perturbation theory (Born but mainly transport!)
- **Low LER-limited mobility (~ 1-10 cm^2/Vs) expected**

LER scattering in AGNRs: “Aromaticity” dependence and magnitude

- Smooth bandgap dependence on thickness of Si films (left) and NWs (not shown)
- Chirality-dependent gap for AGNRs (DFT, EP) → large and aromaticity-dependent dE/dW





Outline

- Electronic structure
  - ❑ Born-Oppenheimer and single-electron approximations
  - ❑ The concept of pseudopotential (self-consistent and empirical)
  - ❑ DFT *vs*. EPs
  - ❑ EPs for nanostructures (supercells) and examples: thin films, hetero-layers, graphene, nanowires, nanotubes
- Scattering
  - ❑ Electron-phonon interaction
    - DFT *vs.* rigid-ion approximation (bulk Si, thin Si films, graphene)
    - Scattering rates
  - ❑ Interface and line-edge roughness (Si films, graphene nanoribbons)
- Transport
  - ❑ Semiclassical:
    - Low-field (mobility) and high-field (MC) properties (Si thin films, graphene, NWs, AGNRs)
  - ❑ Quantum-ballistic:
    - Transport equation
    - Open boundary conditions

Semiclassical Transport: Mobility and MC

- A very interesting trip (Kohn&Luttinger; Argyres; Price): From Liouville-von Neumann to Boltzmann:

$$[\mathbf{H}, \hat{\rho}] = i\hbar\frac{\partial \hat{\rho}}{\partial t} \longrightarrow \frac{\partial f(\mathbf{r},\mathbf{k},t)}{\partial t} = -\frac{1}{\hbar}\nabla_{\mathbf{k}}E(\mathbf{k})\cdot\nabla_{\mathbf{r}}f(\mathbf{r},\mathbf{k},t) + e\nabla_{\mathbf{r}}\varphi(\mathbf{r},t)\cdot\nabla_{\mathbf{k}}f(\mathbf{r},\mathbf{k},t) + \\ + \sum_{\mathbf{k}'}\left[\,W(\mathbf{k},\mathbf{k}')f(\mathbf{r},\mathbf{k}',t) - W(\mathbf{k}',\mathbf{k})f(\mathbf{r},\mathbf{k},t)\,\right]$$

- Low-field mobility (from a linearization of the Boltzmann transport equation):

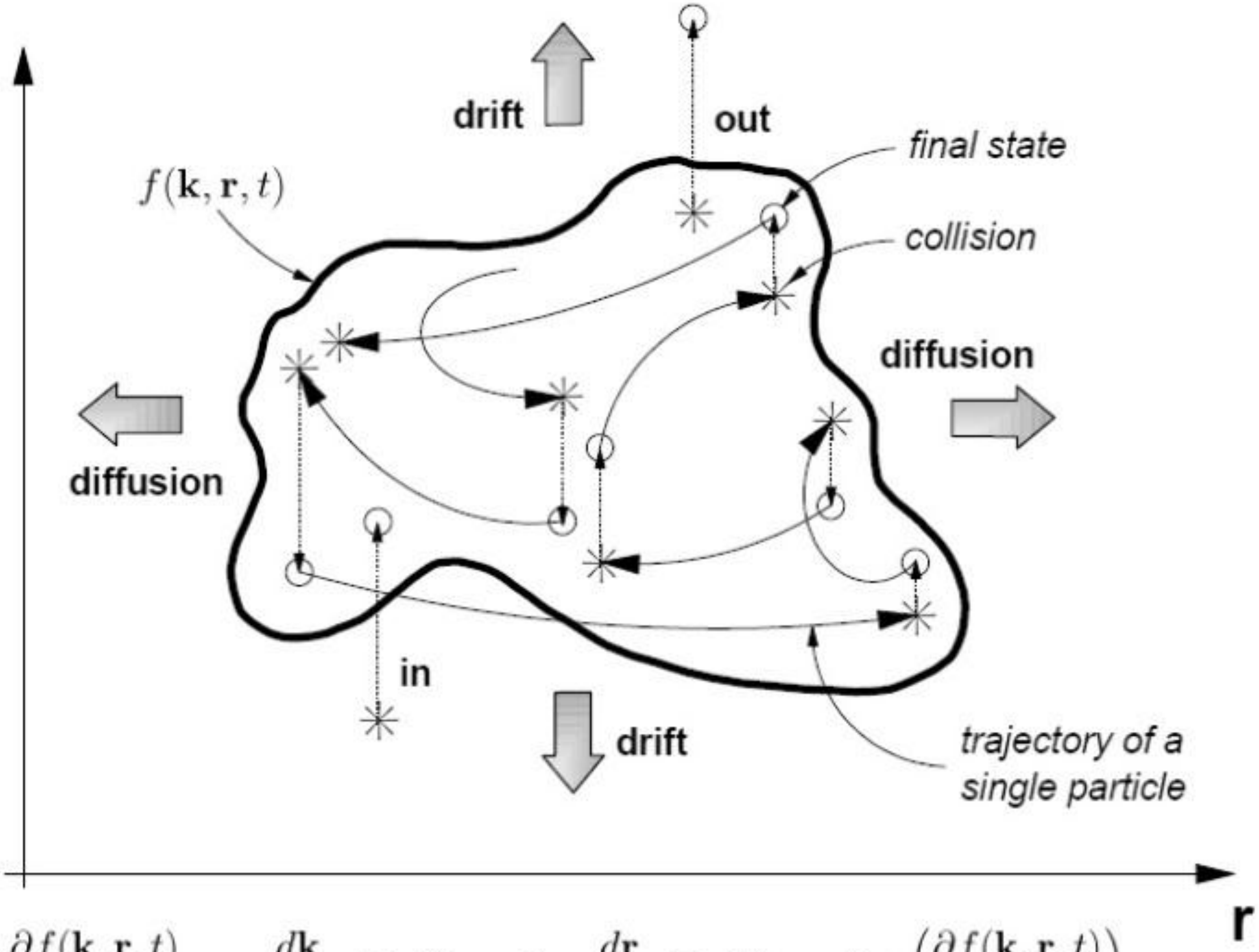
$$\mu_{ij} = -\frac{e}{\hbar}\left\langle \tau_{p,i}v_i\left(\frac{\partial f}{\partial K_j}\frac{1}{f}\right)\right\rangle_{th}$$

with momentum relaxation rate (2DEG):

$$\frac{1}{\tau_{\mu\nu}(\mathbf{K})} = \frac{2\pi}{\hbar}\int\frac{d\mathbf{K}'}{(2\pi)^2}|M_{\mu\mathbf{K}',\nu\mathbf{K}}|^2\delta[E_\mu(\mathbf{K}) - E_\nu(\mathbf{K}') \pm \hbar\omega_{\mathbf{K}'-\mathbf{K}}]\times\frac{1-f(E')}{1-f(E)}\left\{1 - \frac{v_x^{(\nu)(\mathbf{K}')}\tau_x^{(\nu)(\mathbf{K}')}f_x^{(\nu)(\mathbf{K}')}}{v_x^{(\mu)(\mathbf{K})}\tau_x^{(\mu)(\mathbf{K})}f_x^{(\mu)(\mathbf{K})}}\right\}$$

- High-field (Monte Carlo or direct solution)

Semiclassical (MC) Transport: The Boltzmann equation



$$\frac{\partial f(\mathbf{k},\mathbf{r},t)}{\partial t} = -\underbrace{\frac{d\mathbf{k}}{dt}\cdot\nabla_{\mathbf{k}} f(\mathbf{k},\mathbf{r},t)}_{\text{"drift"}} - \underbrace{\frac{d\mathbf{r}}{dt}\cdot\nabla_{\mathbf{r}} f(\mathbf{k},\mathbf{r},t)}_{\text{"diffusion"}} + \underbrace{\left(\frac{\partial f(\mathbf{k},\mathbf{r},t)}{\partial t}\right)_{coll}}_{\text{"in" - "out"}}$$

Courtesy S. Laux

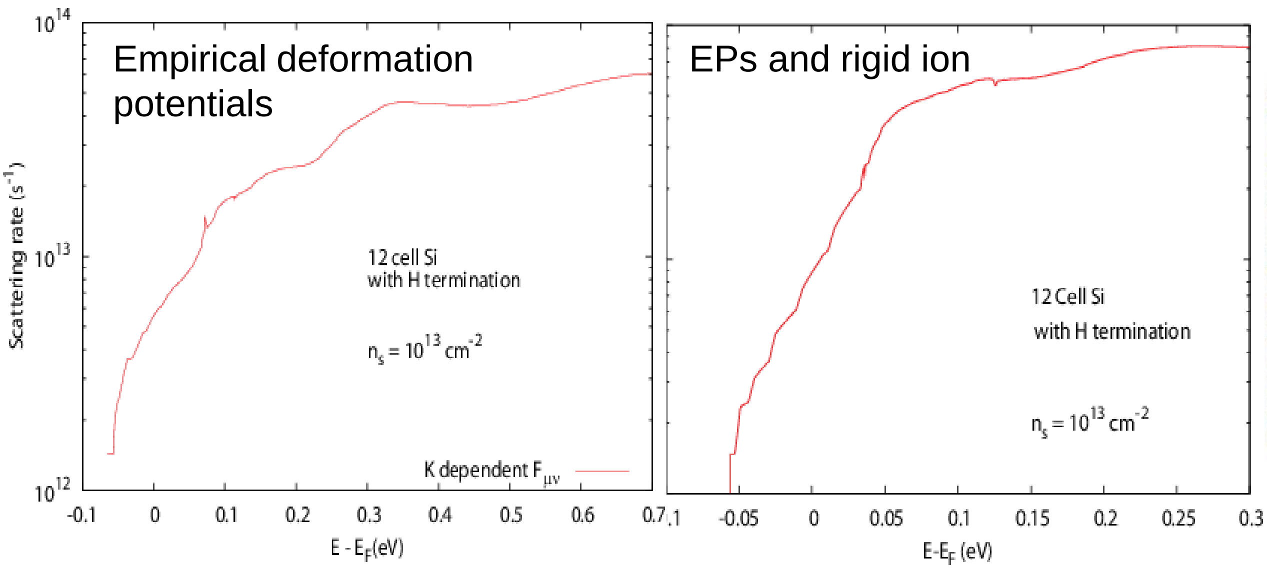
Semiclassical (MC) Transport in Si UTBs

$$\frac{1}{\tau_n^{(\eta)}(\mathbf{K})} \approx \frac{2\pi}{\hbar} \sum_{jn'}^{*} \int \frac{dq_z}{2\pi} \left| V^{(\eta)}_{\mathbf{K}-\mathbf{K}_j,q_z} \mathcal{I}^{(2D)}_{\mathbf{K},\mathbf{K}_j,n,n'}(q_z) \right|^2 \frac{L(w_j)}{|\nabla_{2D} E_j|}$$

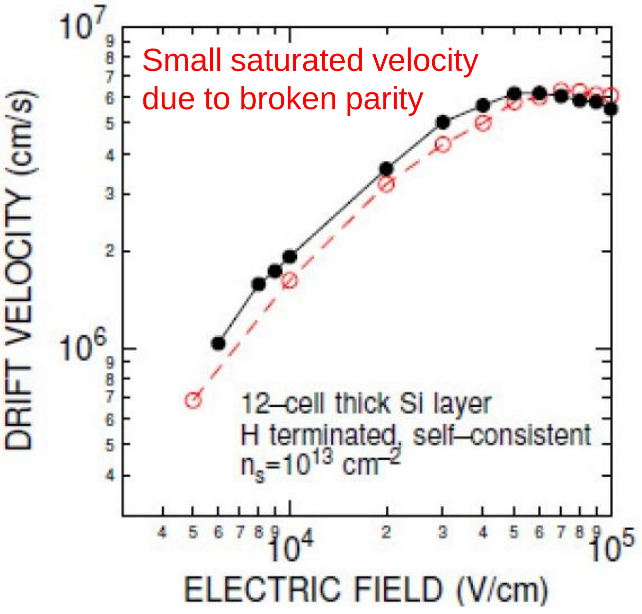
← Scattering rates for 1D supercells. Overlap factors main numerical issue. ↓

$$\mathcal{I}^{(2D)}_{\mathbf{K},\mathbf{K}',n,n'}(q_z) = \sum_{\mathbf{G}_\parallel} \int dz\, \xi^{(n')*}_{\mathbf{G}_\parallel,\mathbf{K}'}(z)\, e^{iq_z z}\, \xi^{(n)}_{\mathbf{G}_\parallel,\mathbf{K}}(z)$$

- **Low saturated velocity (6×10^6cm/s) unexplained so far**
- **Due to dispersion in primed valleys**



El-phonon scattering rate, self-consistent potential

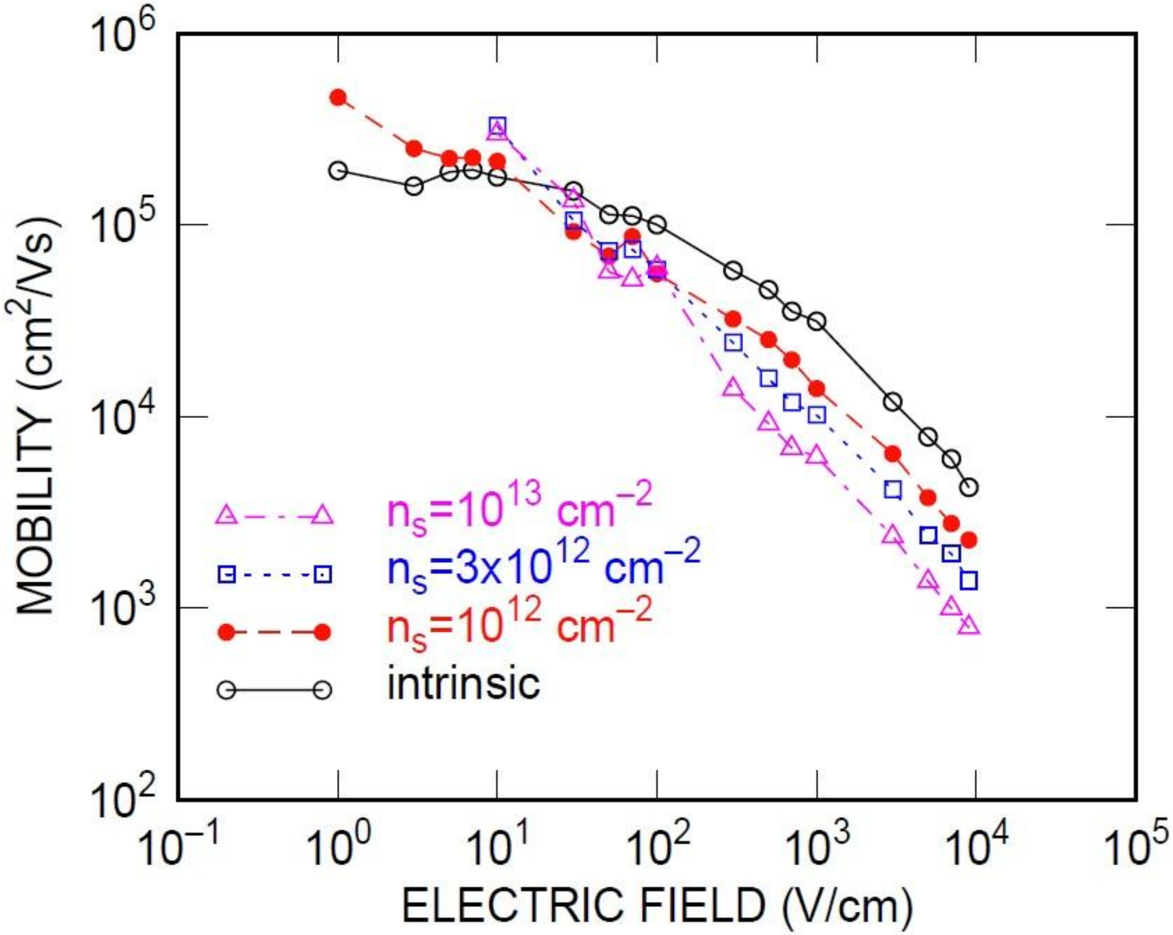


Velocity-field characteristics (***K***-dependent or independent wavefunctions)

Courtesy S. Narayanan

Electron mobility graphene

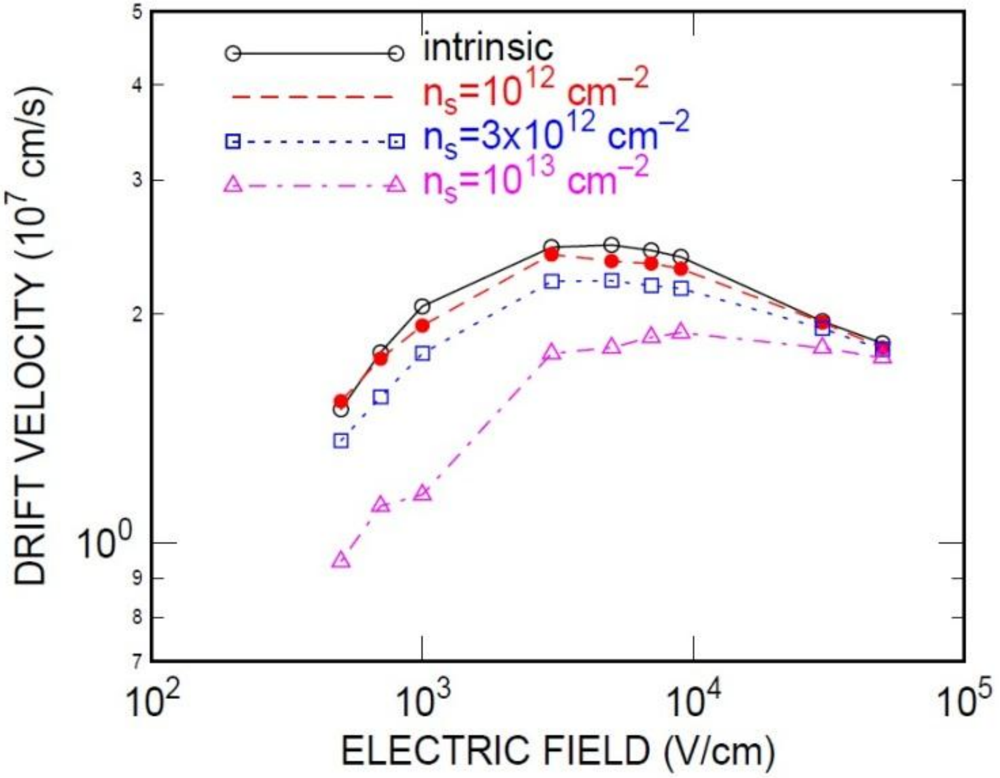
- From MC evaluation of diffusion constant D and $\mu=(\mathrm{d}n/\mathrm{d}E_F)(e/n)D$ (Zebrev, Intech 2011)
- Density and field dependence: Stronger n_s-dependence than total scattering rates, screening of momentum-relaxation time more effective for zone-edge modes (~100-120 meV ~ $\hbar\omega_P$)



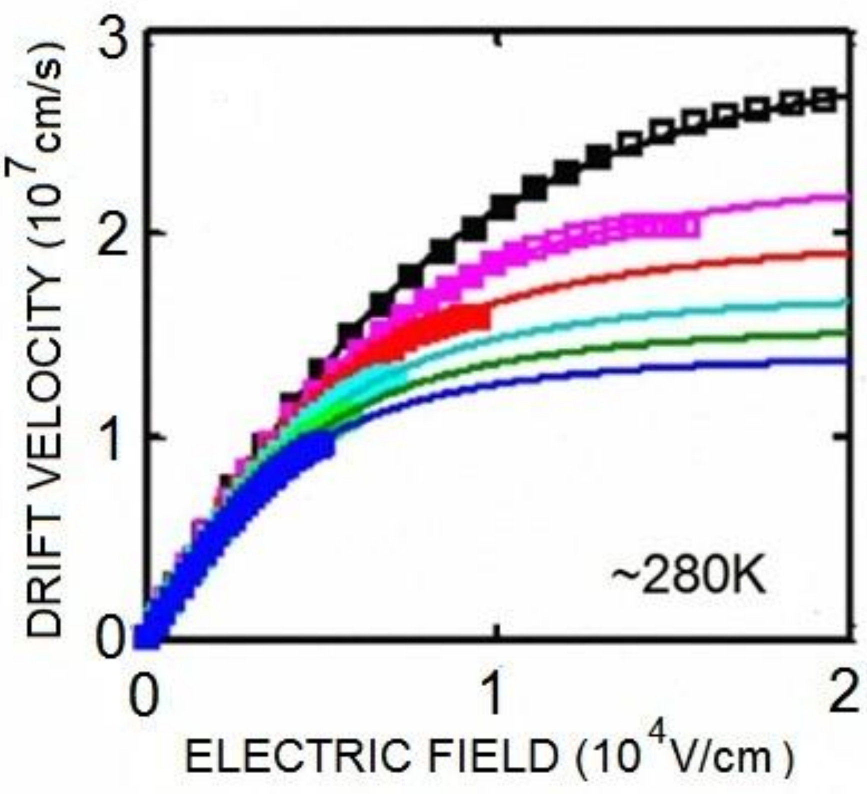
Courtesy S. Narayanan

Drift-velocity vs. field

- Negative differential mobility? Deviation from linear *E*-**k** dispersion?
  - ❑ Some do (full-band: Betti, Pisa; Akturk, Maryland), some don't (Shishir, ASU; Bresciani, Udine)
- Density dependence: Crossover at small fields (~10^1-to-10^2 V/cm), screening *vs.* nonlinearity of *E*-**k** dispersion

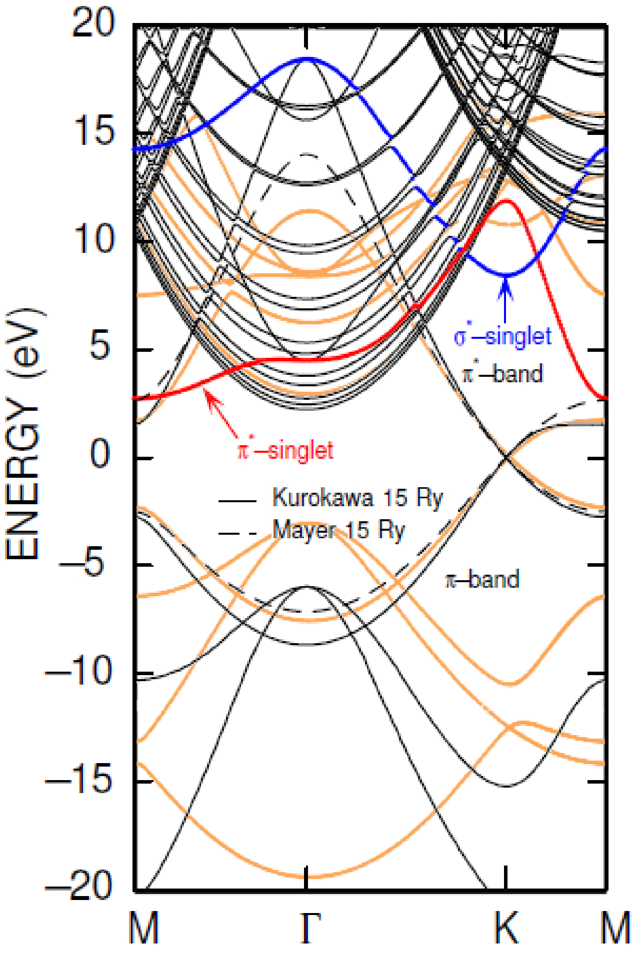


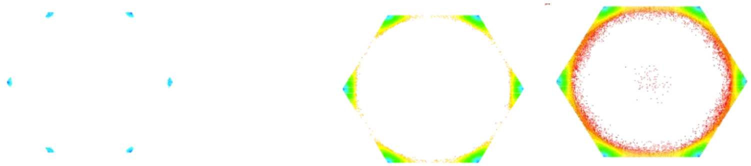
Theoretical results by Sudarshan Narayanan (UT-Dallas PhD Thesis)

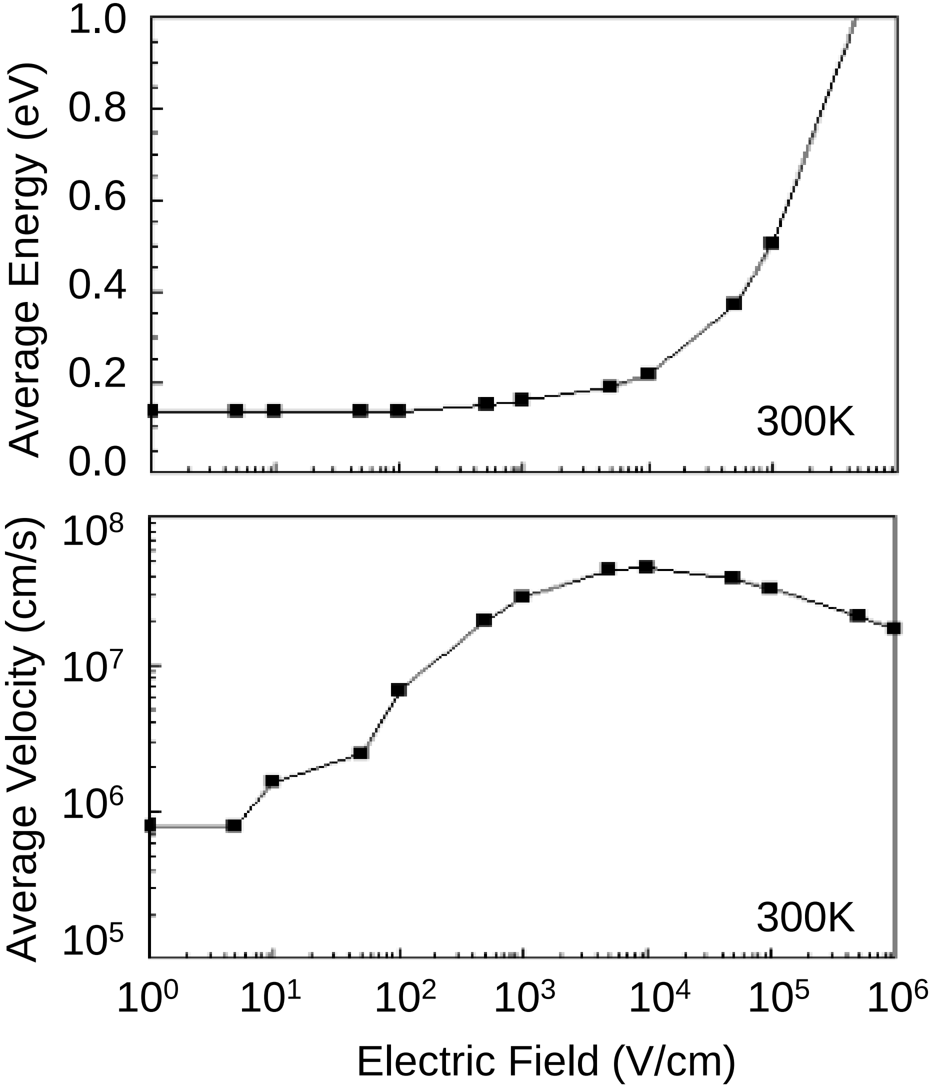


Experimental results by Dorgan *et al.*, APL 2010, graphene-on-SiO_2

Importance of the Band Structure





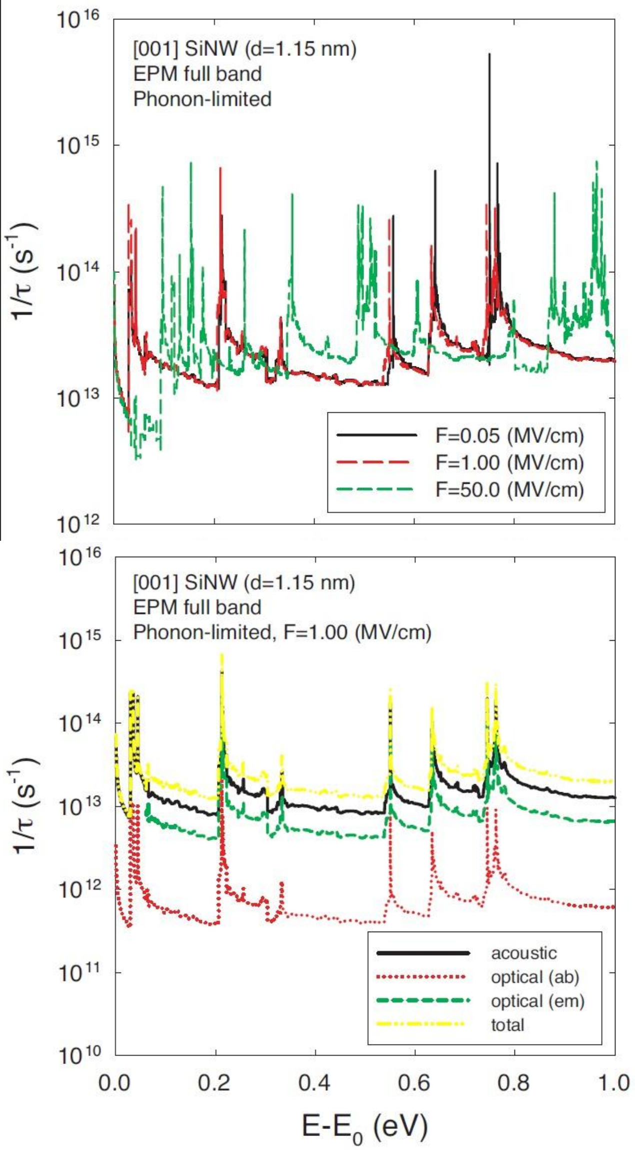


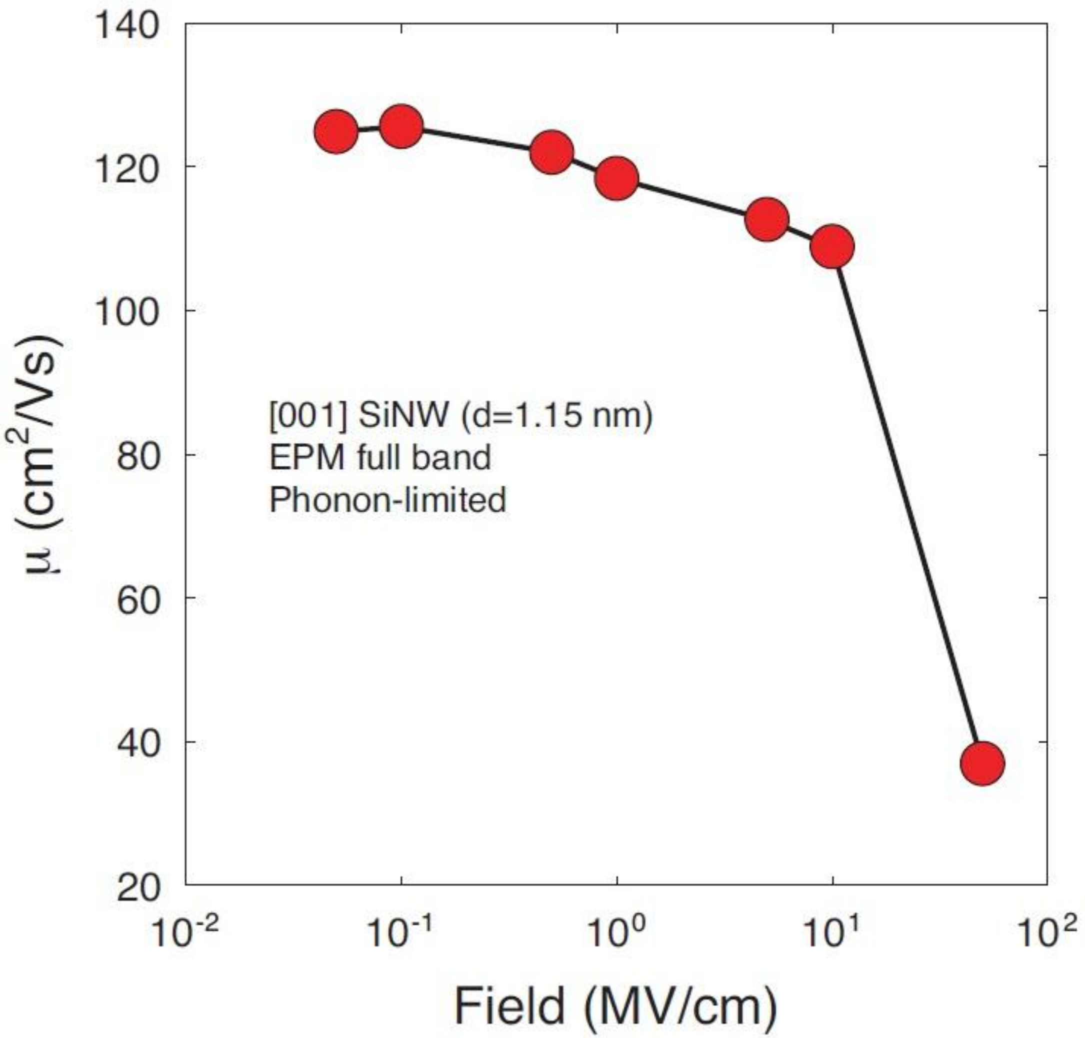
Courtesy S. Aboud

3x3 Si NW: Electron-phonon interaction and mobility

Momentum relaxation rate calculated from full bands (EPM) and deformation potentials.

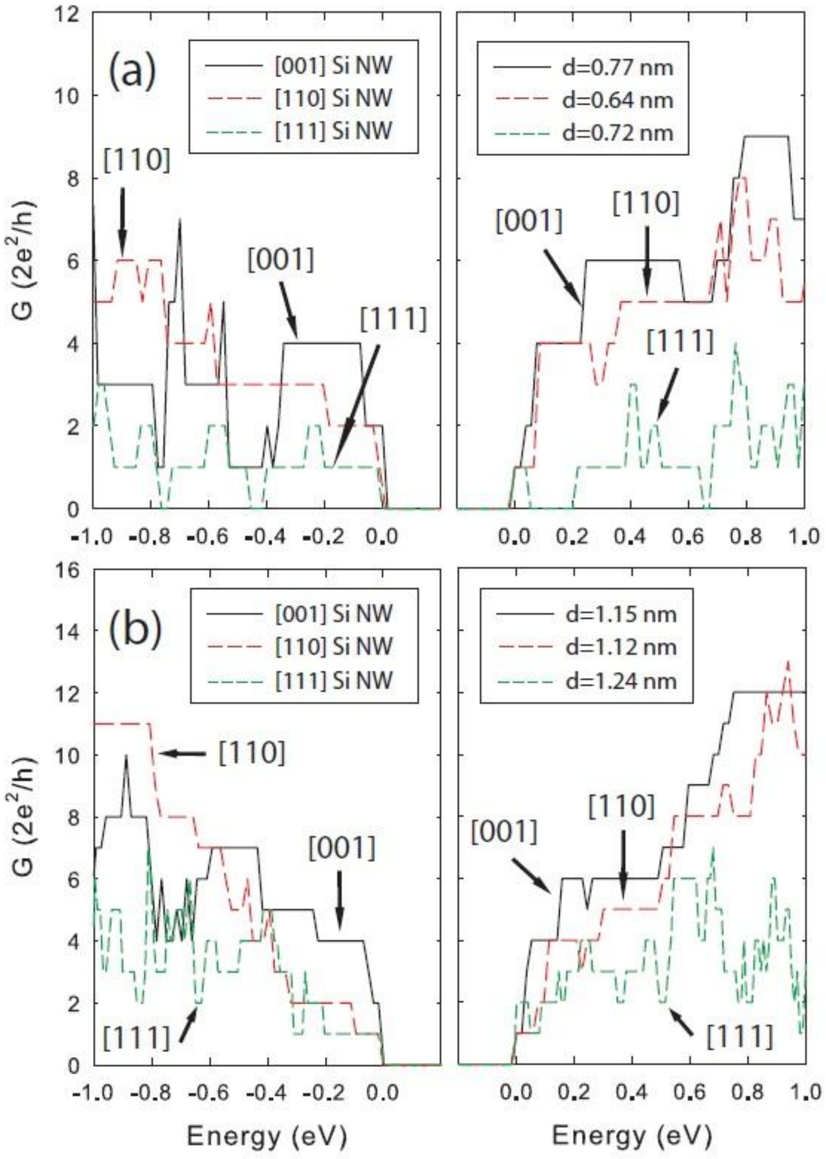
Electron mobility as a function of applied field (non self-consistent… yet…).

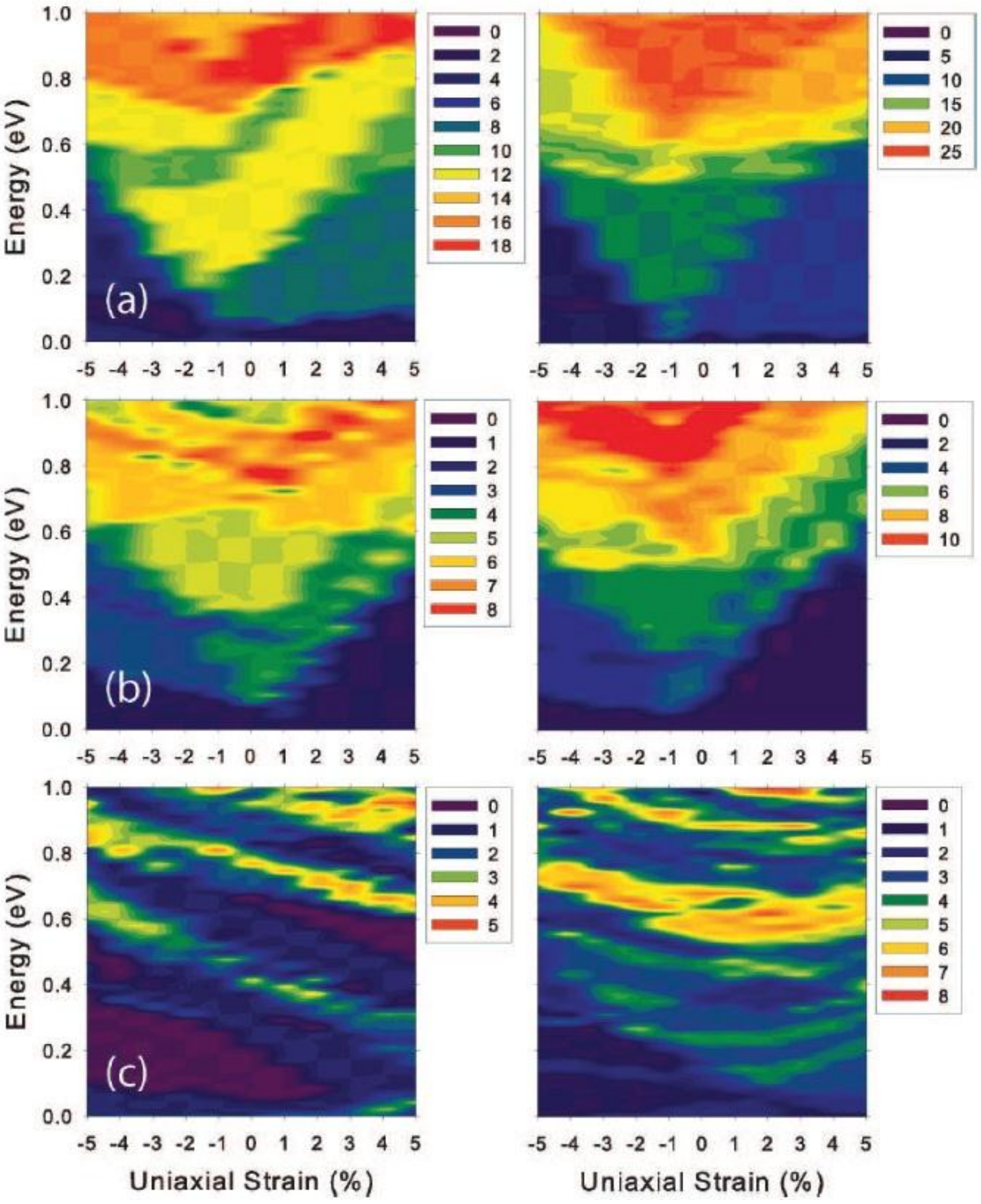




EP results by J. Kim

Si NW: Ballistic conductance *vs*. diameter and strain

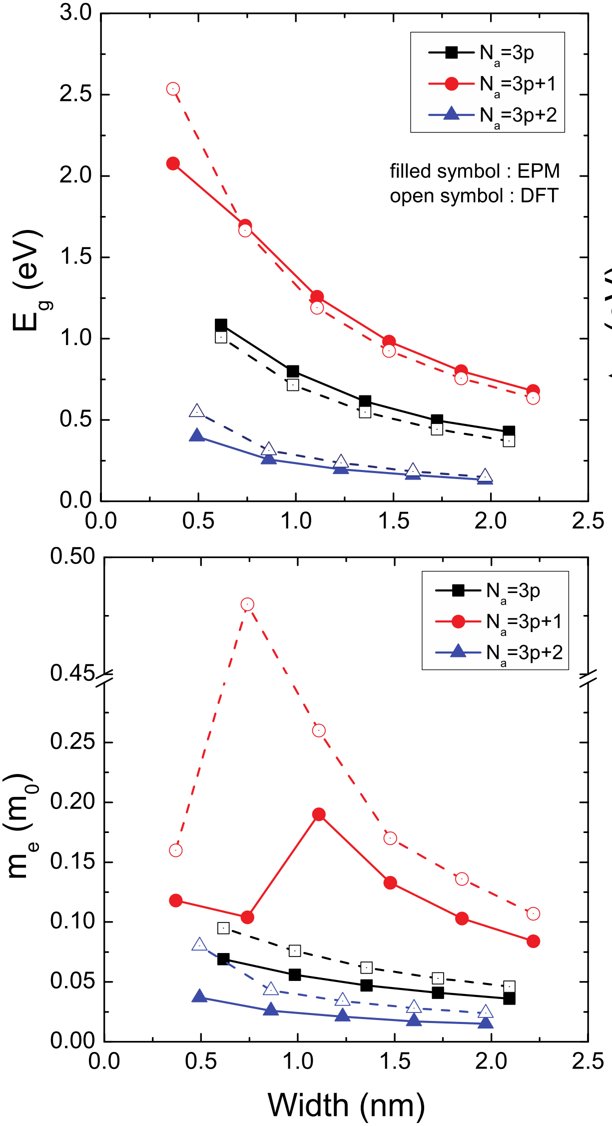




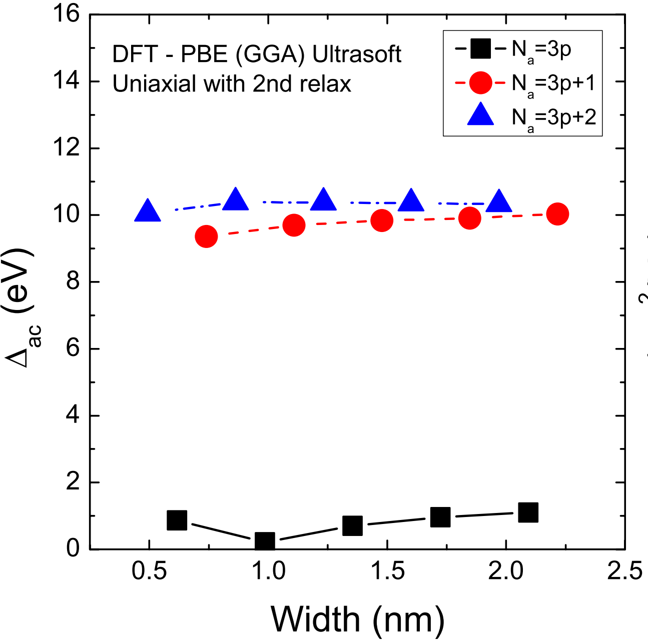
EP results by J. Kim

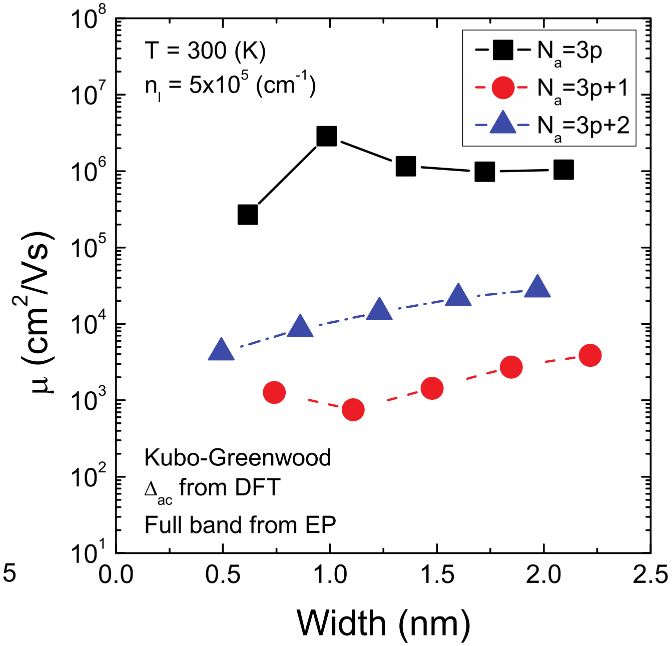
AGNRs: Electron mobility vs. width

- “Claromatic” dependence of mobility*



Results by Jiseok Kim (unpublished, 2013)





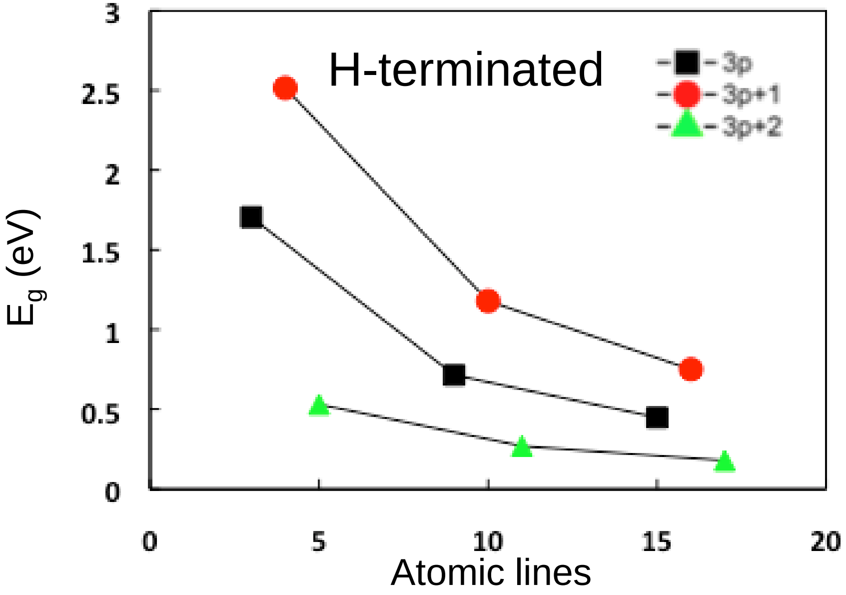
- Uniaxial deformation potentials extracted from DFT, EP bands
- Aromatic dependent deformation potentials :

Δ_{ac} (3p+2) > Δ_{ac} (3p+1) >> Δ_{ac} (3p)

(see also Wang, Chem. Phys. Lett. **533**, 74 (2012) and Long *et al*., J. Am. Chem. Soc. **131**, 17728 (2009))

*see Aboud’s talk

Edge termination of AGNRs and LER scattering



H-terminated AGNR

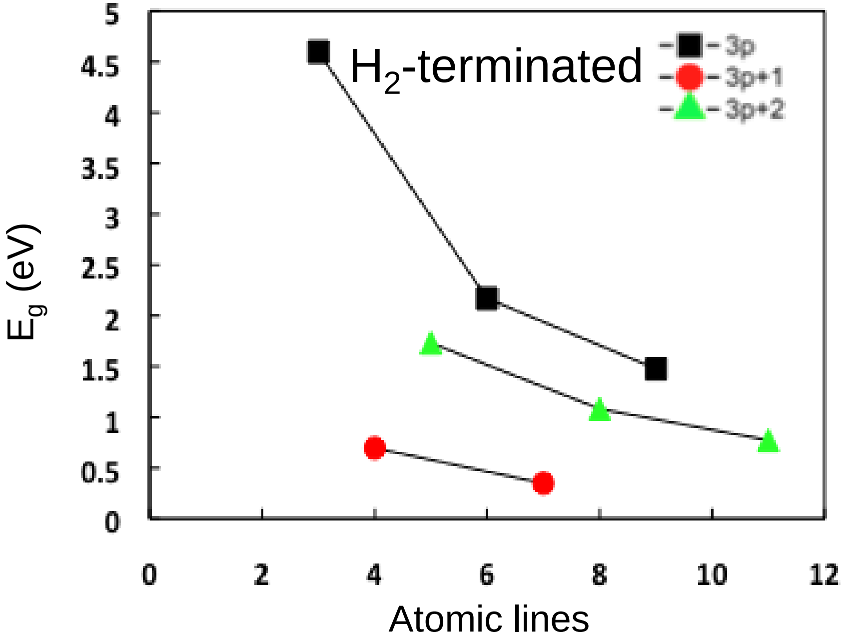
E_g(3p+1)>E_g(3p)>E_g(3p+2)

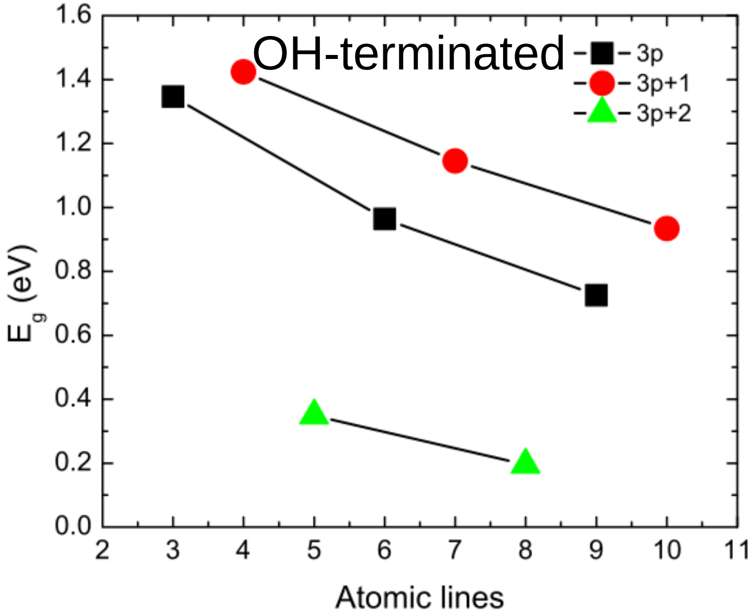
H2-terminated AGNR

E_g(3p)>E_g(3p+2)>E_g(3p+1)

OH-terminated AGNR

E_g(3p+1)>E_g(3p)>E_g(3p+2)

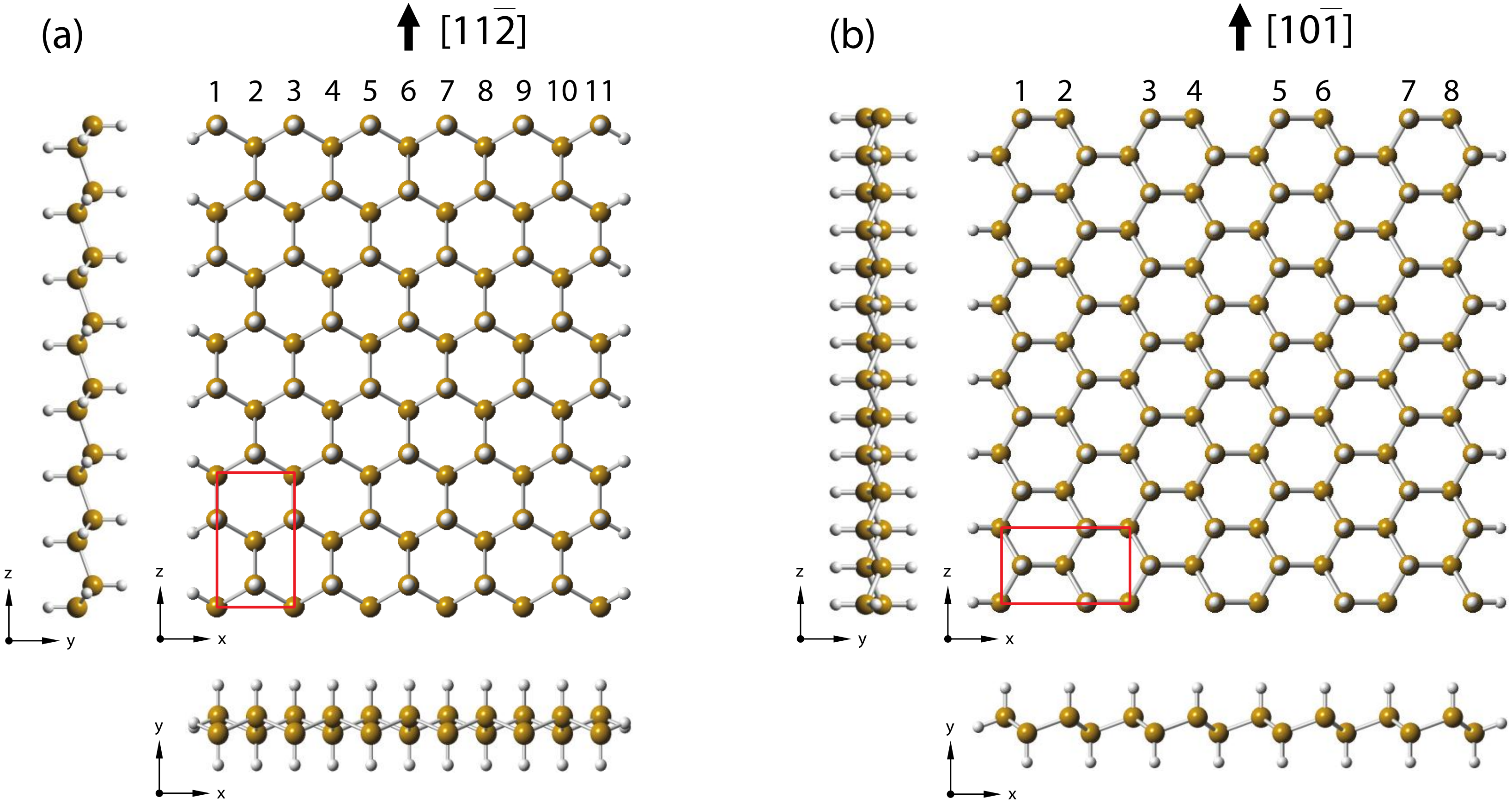




DFT results by S. Aboud and J. Kim

Silicane nanoribbons

- Need sp^3 bonding configuration to minimize edge-effects:
  - ❑ Graphane, silicane, germanane… NRs
  - ❑ DFT and *ab initio* thermodynamics needed to assess stability

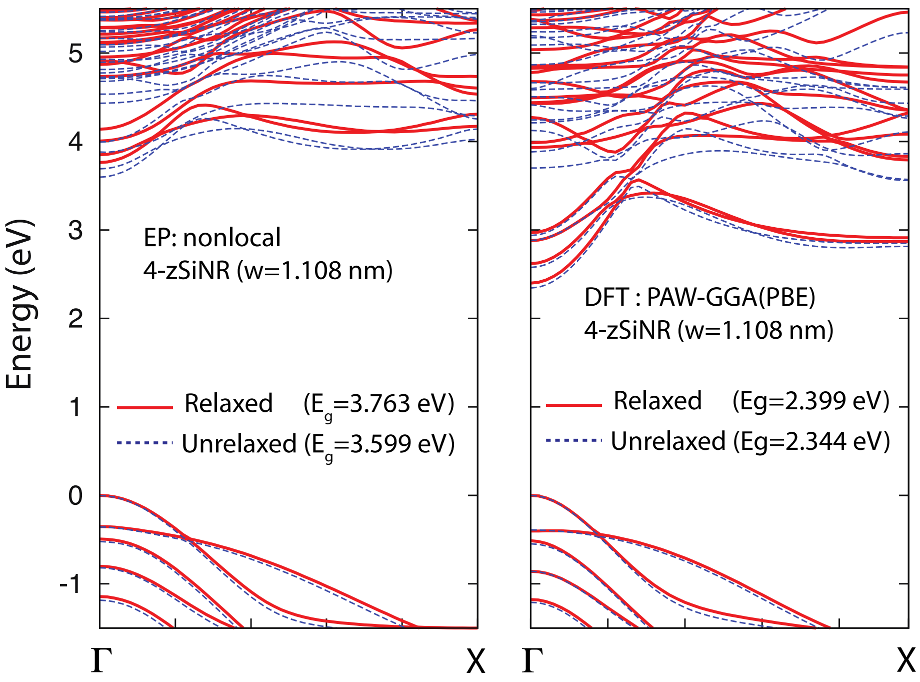


11 aSiNR

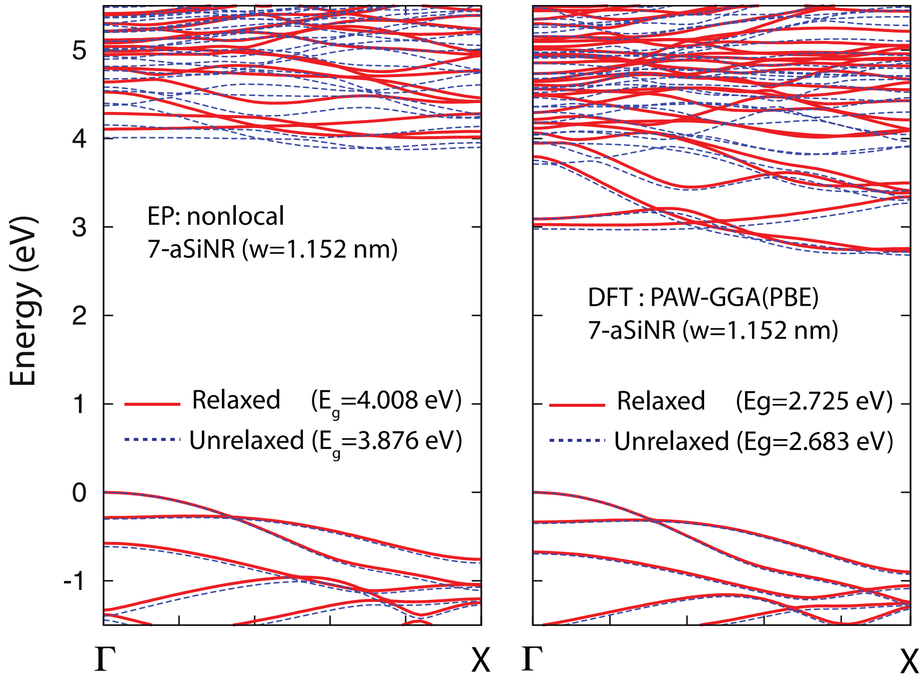
8 zSiNR

Silicane NRs: EP *vs.* DFT and atomic relaxation

4-zSiNR (1.108 nm)



7-aSiNR (1.152nm)

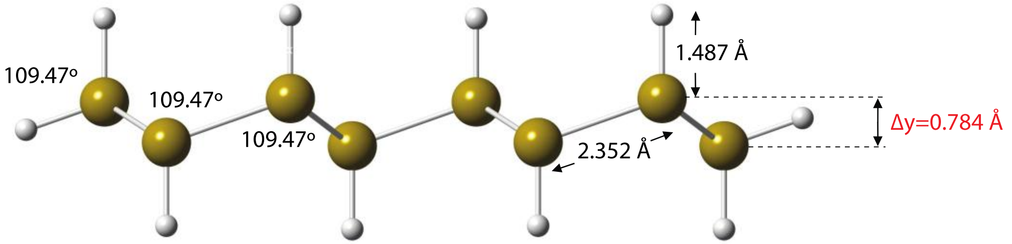


- EPM comparable to DFT except the smaller band-gap in DFT → due to band-gap underestimation of GGA
- No significant effect of atomic relaxation

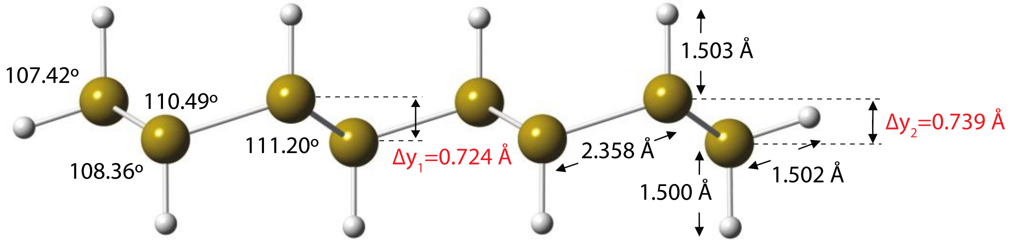
DFT results (VASP) by J. Kim

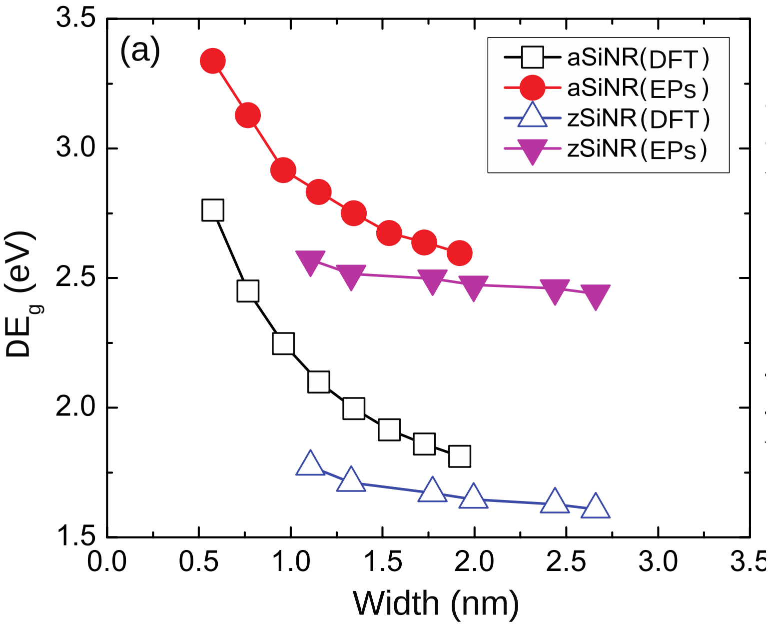
Silicane NRs: Relaxation, band-gap and ballistic conductance

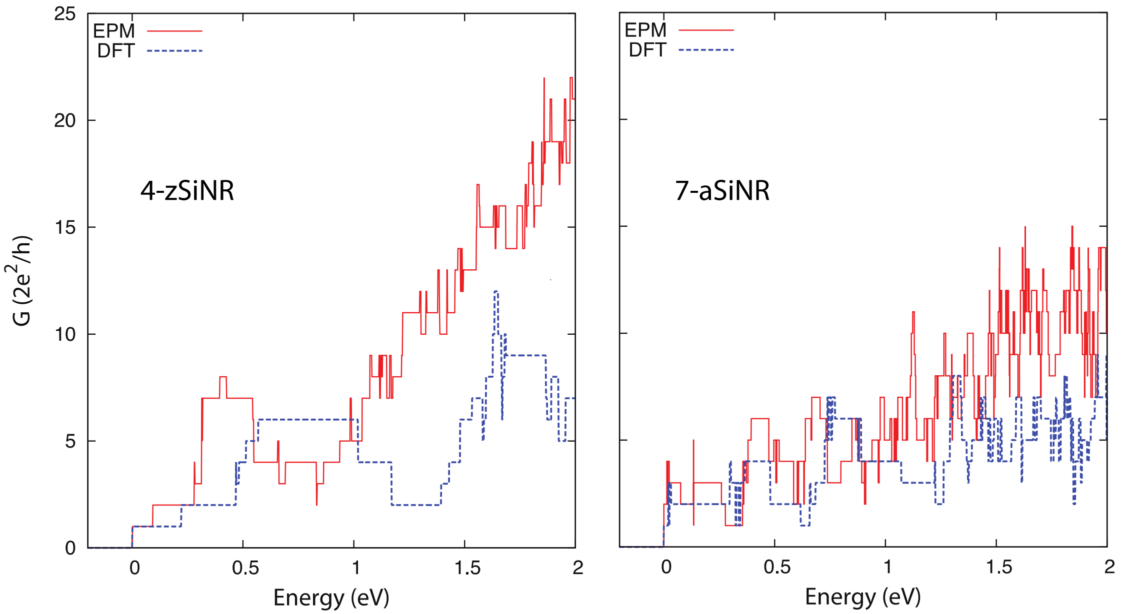
(a) EPM (UNRELAXED)



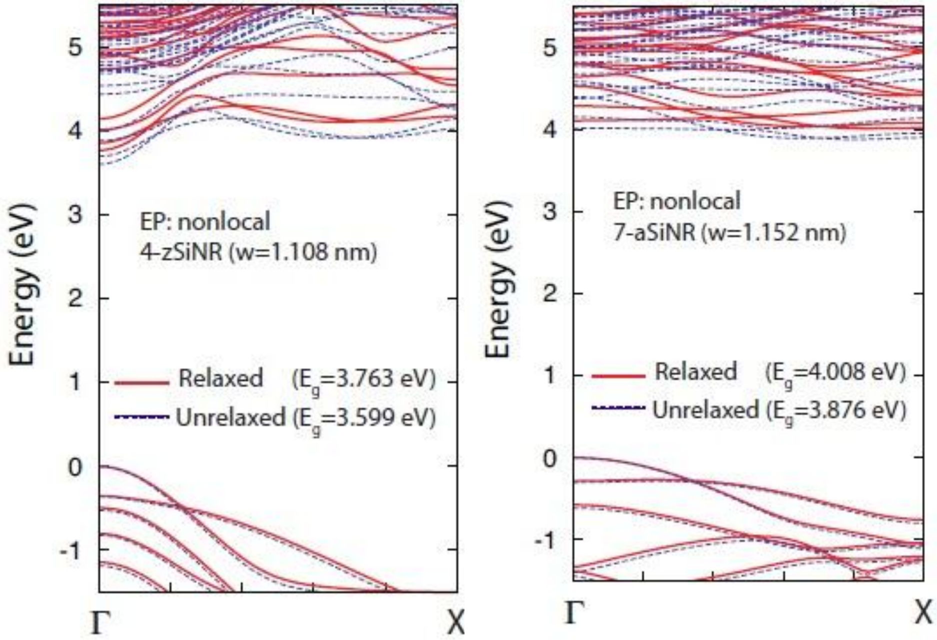
(B) DFT (RELAXED)

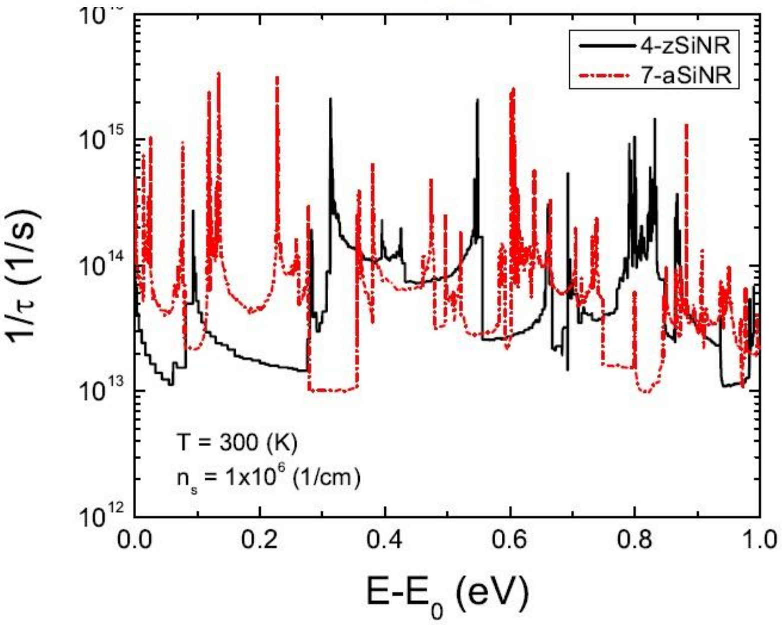




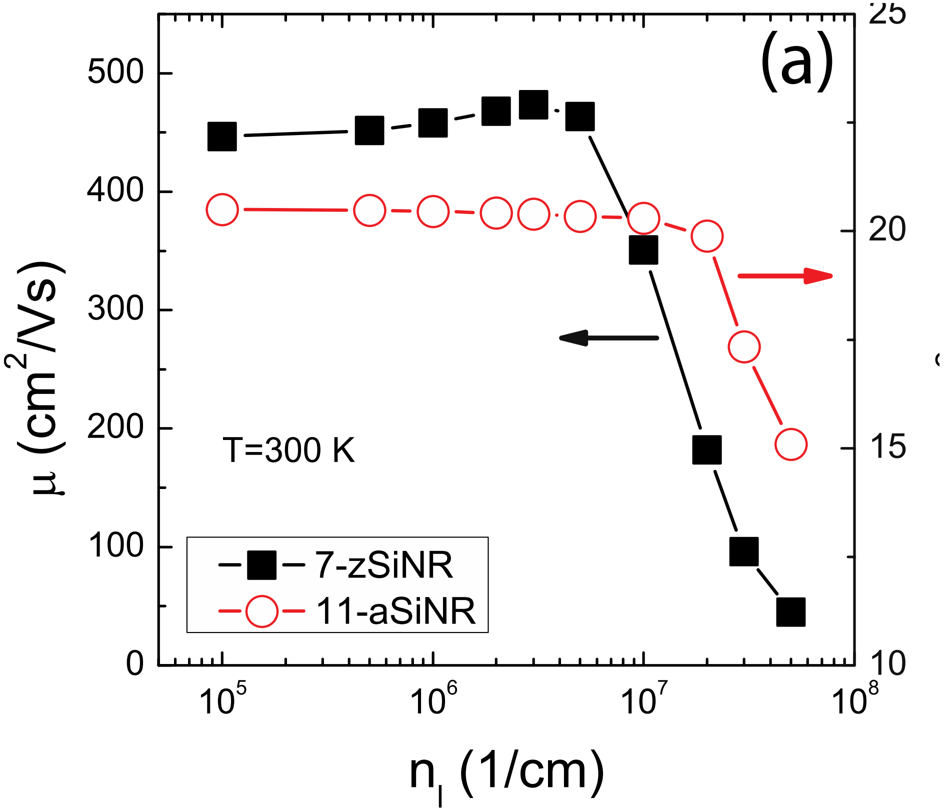


Silicane NRs: Electron-phonon interaction and mobility





Electron mobility as a function of applied field (non self-consistent… yet…).



Mobility in zSiNRs >> aSiNR (orientation effect)

Results by J. Kim

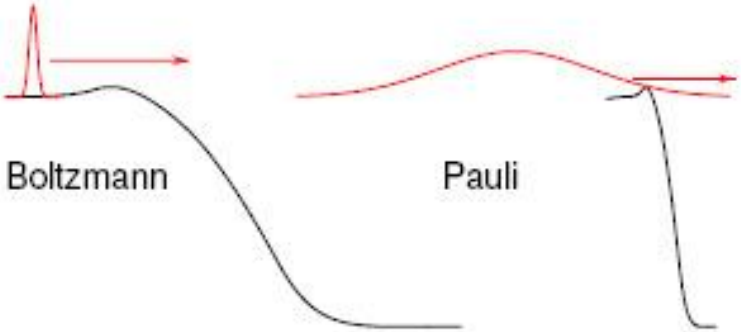
Quantum Transport

- Boltzmann Transport Equation:

1. Device length $L >> \lambda_\phi$, coherence length (packet size) of injected electrons → describe electrons with their 'central position' $\mathbf{r}$
2. Weak scattering → energetic broadening of injected electrons $\delta E_{th} \sim \hbar v_{th}/\lambda_\phi << E_{ch}$, some characteristic energy (e.g., k_BT, eV_D, E_{ave}) → describe electrons with their 'central (crystal) momentum' $\mathbf{k}$
3. 'Self-averaging' collisions (tricky tricky, revisit below): Boltzmann-like collision term
4. Thus, semiclassical description of distribution function $f(\mathbf{r}, \mathbf{k}, t)$

$$\frac{\partial f}{\partial t} + \frac{1}{\hbar}\nabla_{\mathbf{k}} E(\mathbf{k}) \cdot \nabla_{\mathbf{r}} f + e\nabla_{\mathbf{r}} V(\mathbf{r}) \cdot \nabla_{\mathbf{k}} f = \int \frac{d\mathbf{k}'}{(2\pi)^3} \left[S(\mathbf{k}, \mathbf{k}') f(\mathbf{r}, \mathbf{k}', t) - S(\mathbf{k}', \mathbf{k}) f(\mathbf{r}, \mathbf{k}, t) \right]$$

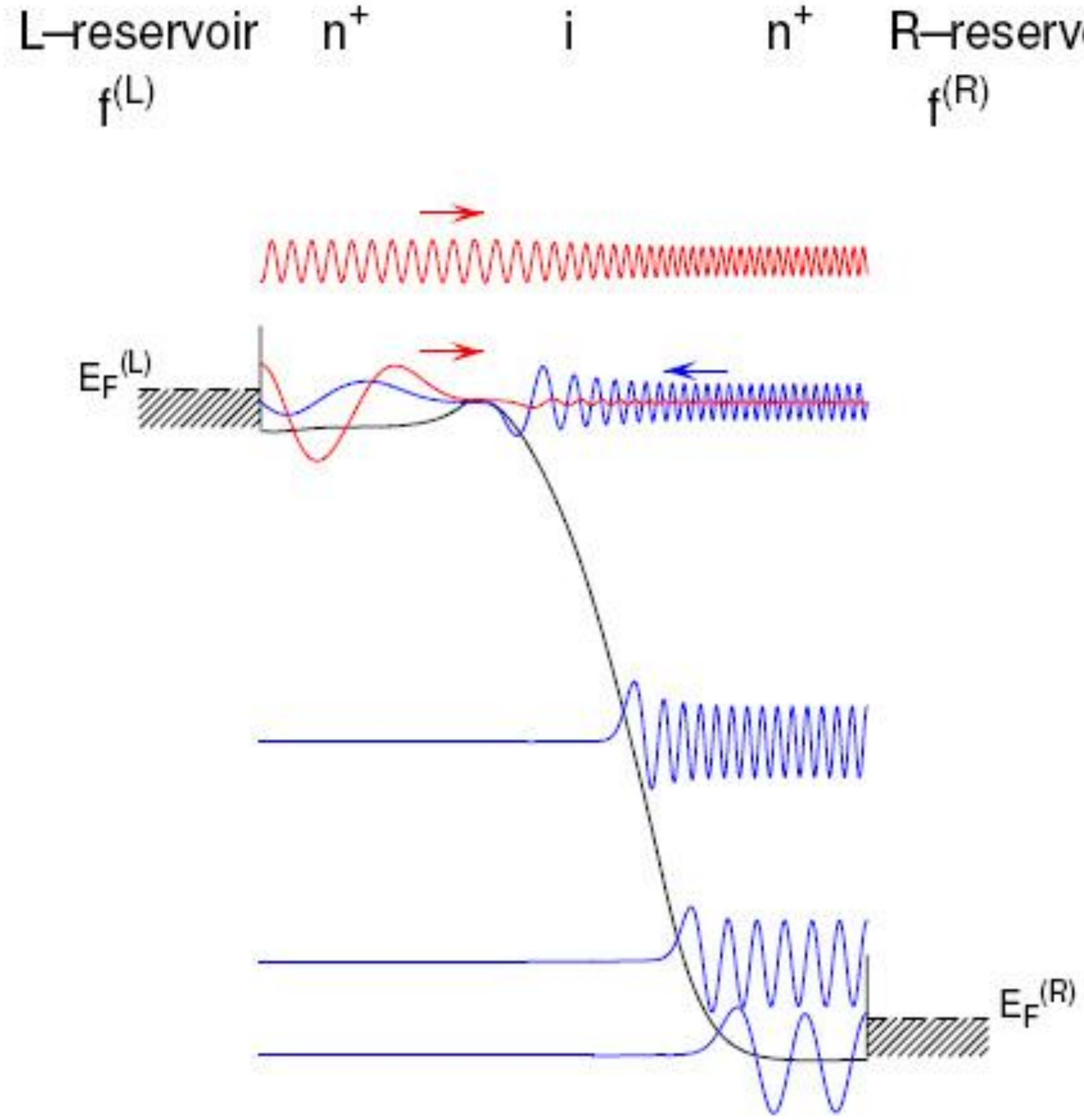
- Pauli Master Equation: retain assumptions 2 and 3, but drop 1



Quantum Transport

- Approaches to handle quantum transport:
    - Ballistic, all equivalent (NEGF with DFT, EPs, TB, *etc*,), just different basis
    - Dissipative:
        - NEGF: Unsolvable in practice (…the Dyson equation… Gordon Baym, ISANN 2011)
        - Wigner function: Serious issues with boundary conditions (F. Rossi *et al*.)
        - Density-matrix (Master eqns., Semiconductor Bloch Equations): Same-time Green's function… How much information do we lose?
- Open boundary conditions:
    - Quantum Transmitting Boundary Method (QTBM, Lent and Kirkner 1990)
    - Rarely implemented with plane waves and pseudopotentials (Ihm-Choi 1999, DFT)

An open system

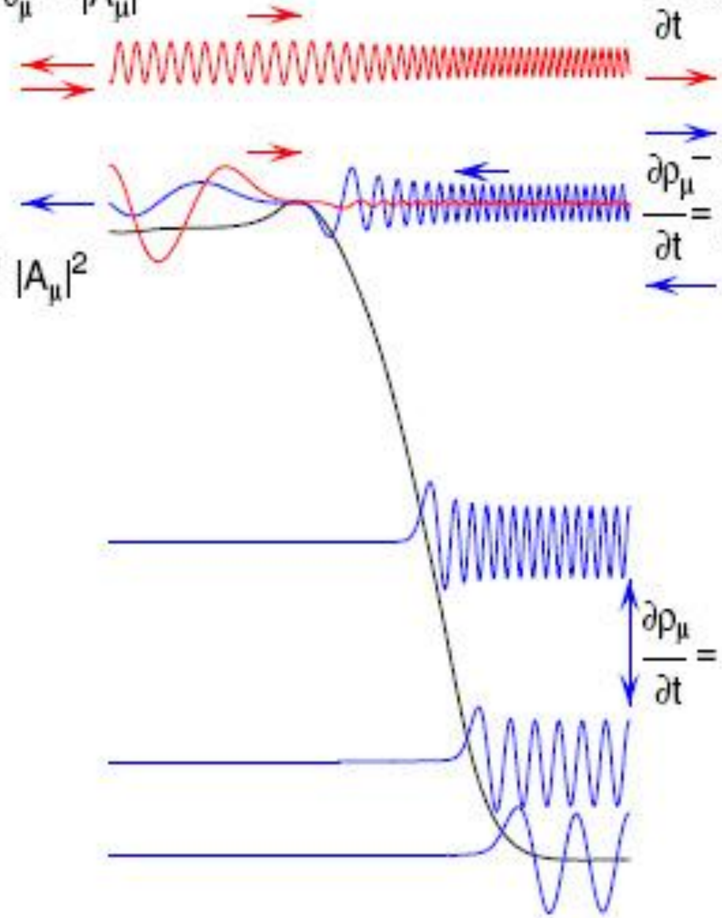


Ballistic transport in an open system

$$\frac{\partial \rho_\mu^{s}}{\partial t} = \text{reservoirs} = 0$$

$$\frac{\partial \rho_\mu^{+}}{\partial t} = [f^{(L)} - |r_\mu|^2 \rho_\mu^{+}]\, \upsilon_\mu^{(L)} |A_\mu|^2$$

$$\frac{\partial \rho_\mu^{+}}{\partial t} = -\rho_\mu^{+} |t_\mu^{+}|^2 \upsilon_\mu^{(R)} |A_\mu|^2$$



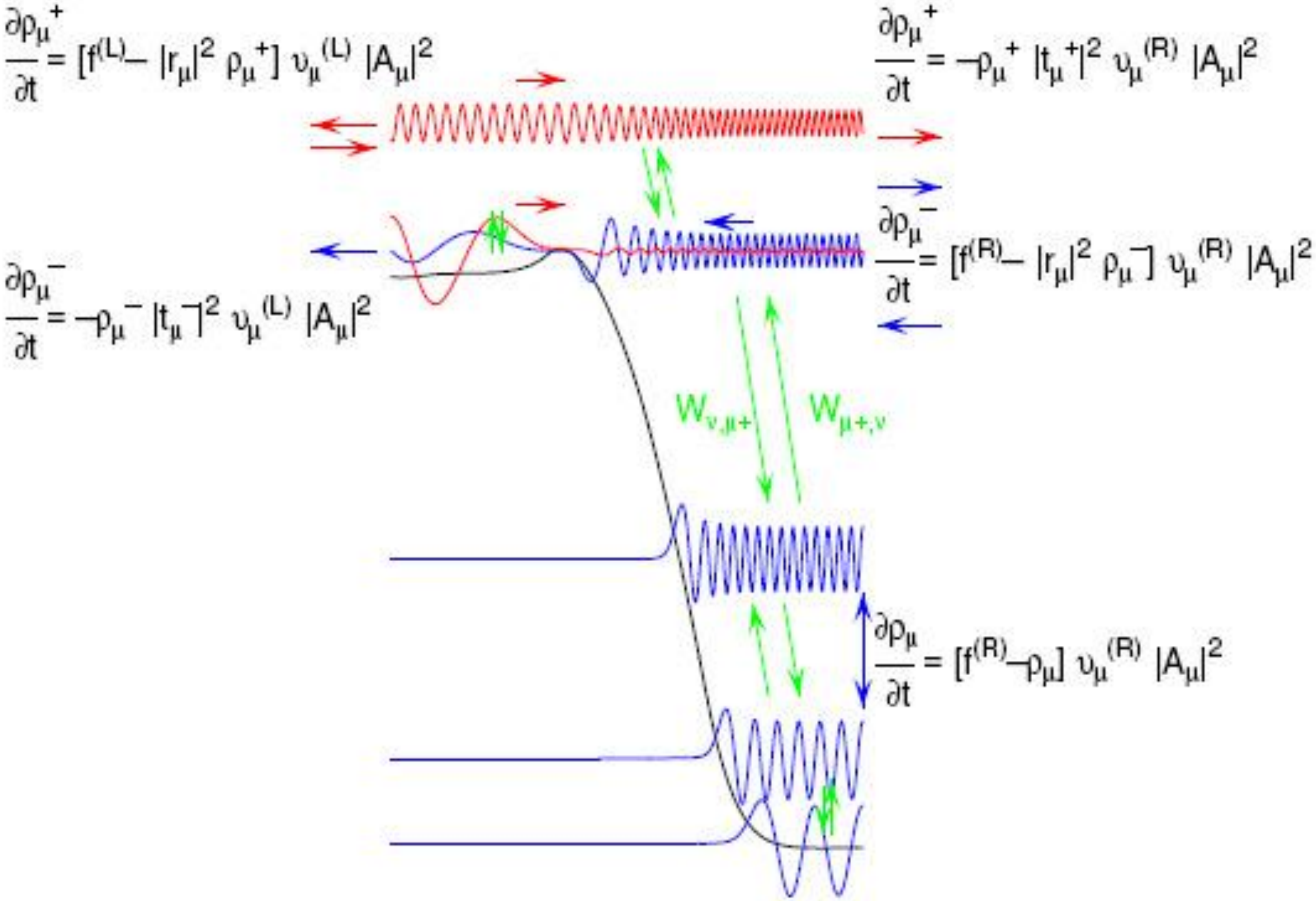
$$\frac{\partial \rho_\mu^{-}}{\partial t} = [f^{(R)} - |r_\mu|^2 \rho_\mu^{-}]\, \upsilon_\mu^{(R)} |A_\mu|^2$$

$$\frac{\partial \rho_\mu^{-}}{\partial t} = -\rho_\mu^{-} |t_\mu^{-}|^2 \upsilon_\mu^{(L)} |A_\mu|^2$$

$$\frac{\partial \rho_\mu}{\partial t} = [f^{(R)} - \rho_\mu]\, \upsilon_\mu^{(R)} |A_\mu|^2$$

A dissipative open system

$$\frac{\partial \rho_\mu{}^s}{\partial t} = \Sigma_{\nu r} \left[W_{\mu s,\nu r}\, \rho_\nu{}^r - W_{\nu r,\mu s}\, \rho_\mu{}^s \right] + \text{reservoirs} = 0$$



$$\frac{\partial \rho_\mu{}^+}{\partial t} = [f^{(L)} - |r_\mu|^2 \rho_\mu{}^+]\, \upsilon_\mu{}^{(L)}\, |A_\mu|^2$$

$$\frac{\partial \rho_\mu{}^-}{\partial t} = -\rho_\mu{}^- \, |t_\mu{}^-|^2\, \upsilon_\mu{}^{(L)}\, |A_\mu|^2$$

$$\frac{\partial \rho_\mu{}^+}{\partial t} = -\rho_\mu{}^+ \, |t_\mu{}^+|^2\, \upsilon_\mu{}^{(R)}\, |A_\mu|^2$$

$$\frac{\partial \rho_\mu{}^-}{\partial t} = [f^{(R)} - |r_\mu|^2 \rho_\mu{}^-]\, \upsilon_\mu{}^{(R)}\, |A_\mu|^2$$

$$\frac{\partial \rho_\mu}{\partial t} = [f^{(R)} - \rho_\mu]\, \upsilon_\mu{}^{(R)}\, |A_\mu|^2$$

Scattering: A Monte Carlo Solution

- Like Boltzmann, but no field (already included 'exactly' in the $|\mu>$ eigenstates)
- Start from ballistic solution, divide total charge into 'particles', place them in states according to equilibrium distribution at the contacts, stochastically re-distribute them among states (scattering), extract/inject them into/from contacts, solve 2D Poisson, solve 2D Schrödinger, iterate...
- Scattering processes included:
  - Intravalley acoustic:

$$\frac{1}{\tau_{\mu}^{(ac\ \eta\pm)}(k)} = \sum_{\mu'} W_{\mu'\mu}^{(ac)} = = \sum_{\mu'} \frac{m_{\mu' z}^{1/2}\Delta_{\eta}^{2} k_B T}{2^{3/2} E'^{1/2} \hbar^2 c_{\eta}^{2} \rho_x} \mathcal{F}_{\mu'\mu}\, \theta(E') \ ,$$

$$(E' = E_\mu + \hbar^2 k^2/(2 m_{\mu z}) - E_{\mu'})$$

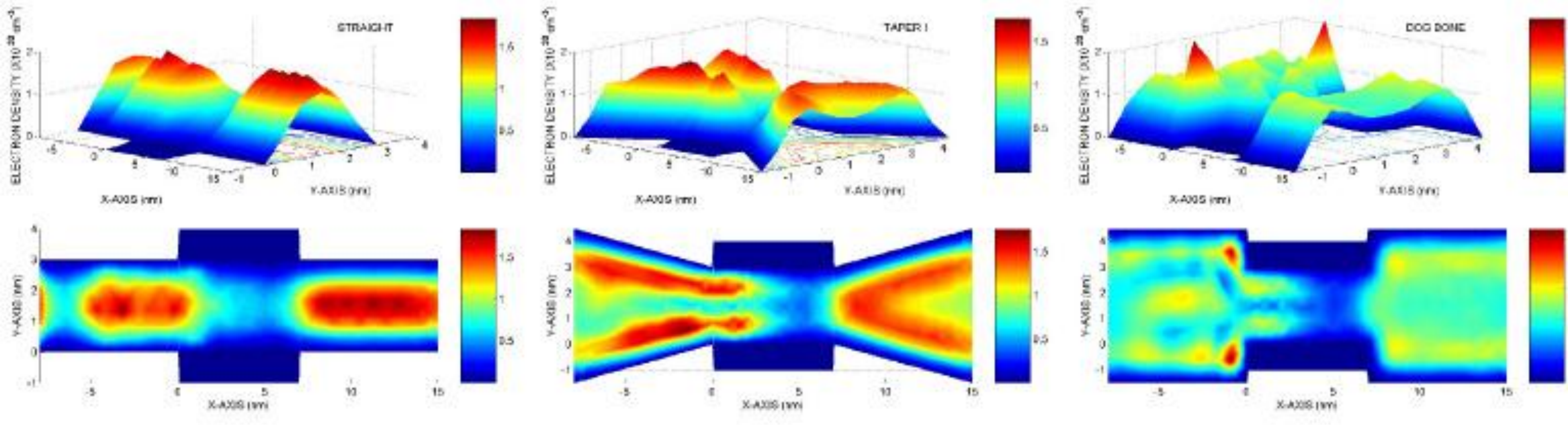
  - Intervalley (6 phonons):

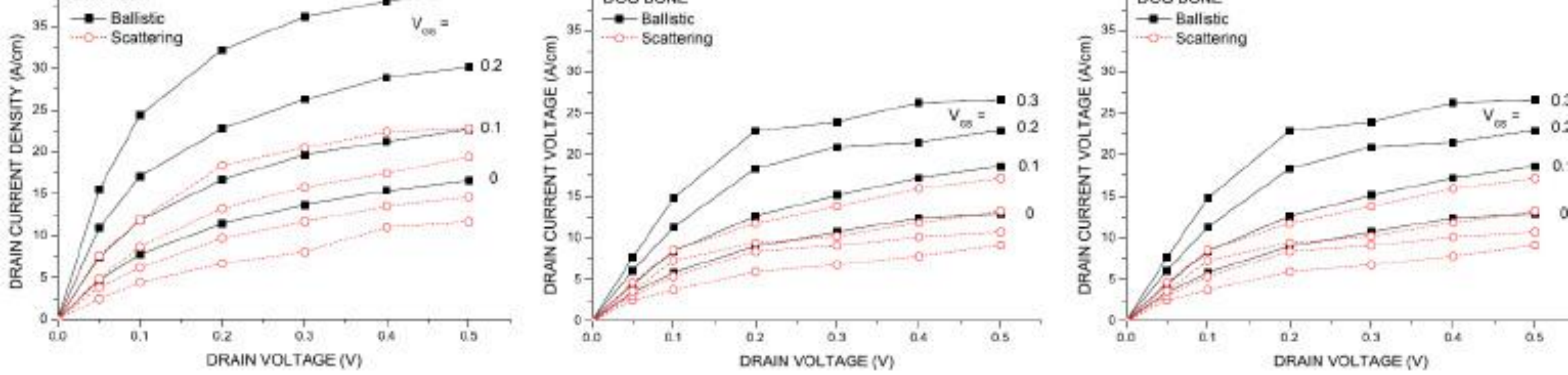
$$\frac{1}{\tau_{\mu}^{(iv\ \pm)}(k)} = \sum_{\mu'} W_{\mu'\mu}^{(iv)} = = \sum_{\mu'} \frac{m_{\mu' z}^{1/2}(DK)_{iv}^{2}}{2^{3/2} E'^{1/2} \hbar \rho_x \omega_{iv}} \left(\frac{1}{2} \pm \frac{1}{2} + n_{iv}\right) \mathcal{F}_{\mu'\mu}\, \theta(E') \ ,$$

$$(E' = E_\mu + \hbar^2 k^2/(2 m_{\mu z}) \mp \hbar\omega_{iv} - E_{\mu'}).$$

A straight/tapered/dog-bone DG (pseudo)Si FET

- Quantum access resistance matters as much as phonon scattering…
- Will impurity-scattering change the picture (more reflection/diffraction at dopants)?





Bo Fu-MVF, IWCE (2009)

Impurity scattering: Phase-breaking or not?

- Electron-electron interactions are "self-averaging" (RPA), provided there are "many" electrons.
- Scattering with ionized impurities:
  - Non-phase-breaking in 3D beyond Born: Just many Coulomb-potential "wells" affecting the transmission amplitude of each propagating state.
    Dissipation (*i.e.*, decoherence) only after ensemble-averaging
  - In 2D: Either "unaveraged" Born (including coherence over multiple collisions)

$$W_{\mu\nu}^{(imp)} \propto \frac{2\pi}{\hbar}\,\delta(E_\mu - E_\nu)\left|\sum_{\alpha=1}^{N_{imp}} \int_\Omega d\mathbf{R}\ \psi_\mu^\dagger(\mathbf{R})\ V_{imp}(\mathbf{R}-\mathbf{R}_\alpha)\ \psi_\nu(\mathbf{R})\right|^2 ,$$

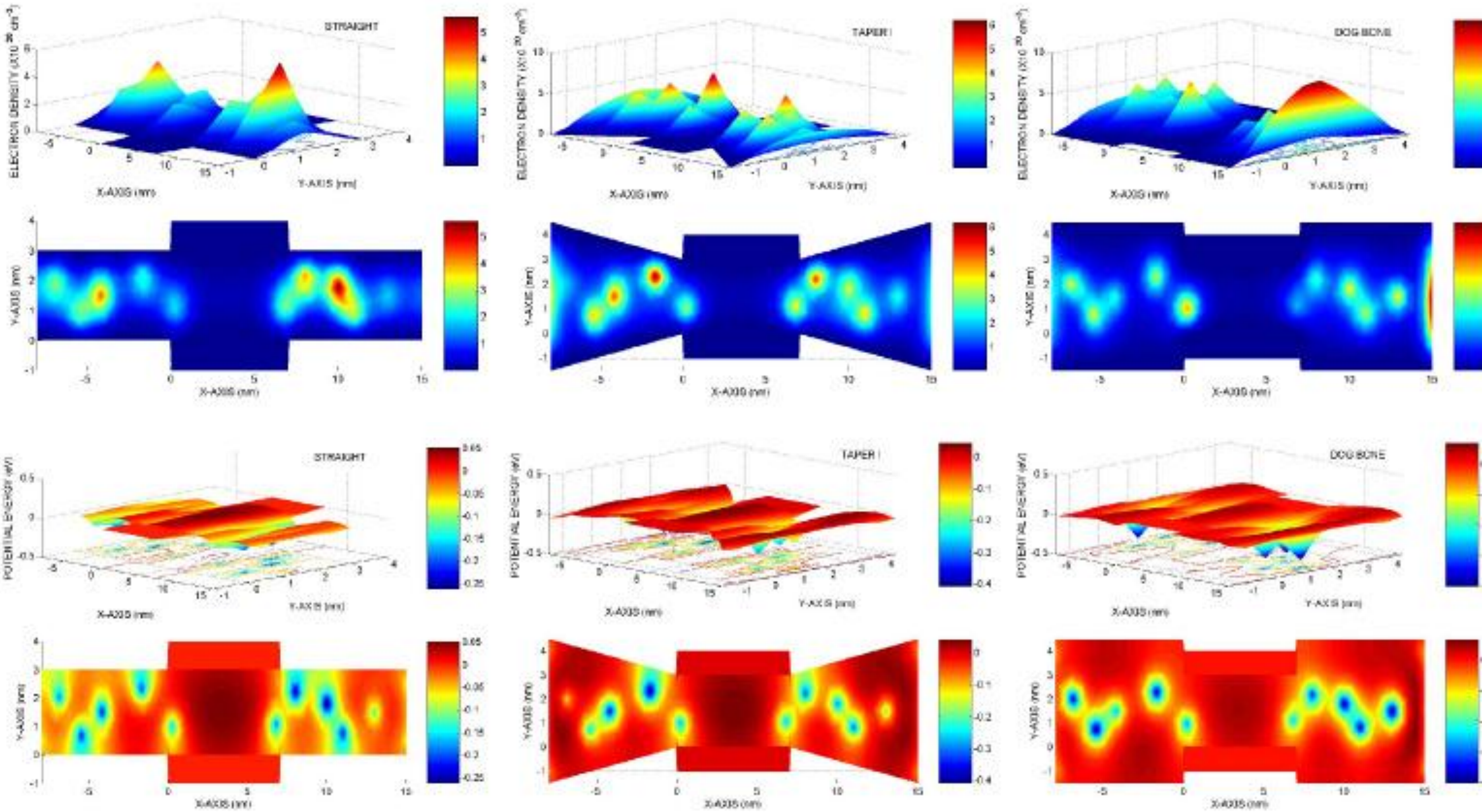
followed by explicit (time-consuming) ensemble average over configurations $\{\mathbf{R}_\alpha\}$, or go back to Van Hove (and Kohn-Luttinger):

$$\sum_{\{\mathrm{r}\alpha\}} \sum_{\lambda} \sum_{\alpha\beta} <\mu|\ \mathbf{H}_{ei}^{(I)(\alpha)}(t)\ |\lambda><\lambda|\mathbf{H}_{ei}^{(I)(\beta)}(t')\ |\mu> ,$$

employing "self-averaging" directly:

$$W_{\mu\nu}^{(imp)} \propto \frac{2\pi}{\hbar}\,\delta(E_\mu - E_\nu)\sum_{\alpha=1}^{N_{imp}}\left|\int_\Omega d\mathbf{R}\ \psi_\mu^\dagger(\mathbf{R})\ V_{imp}(\mathbf{R}-\mathbf{R}_\alpha)\ \psi_\nu(\mathbf{R})\right|^2 .$$

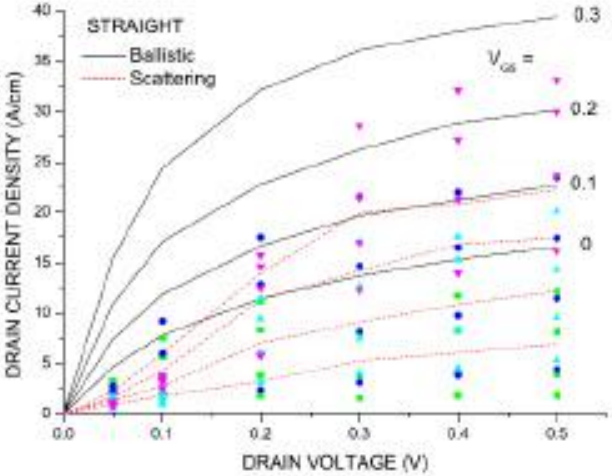
DGFET with dopants: Density and potential

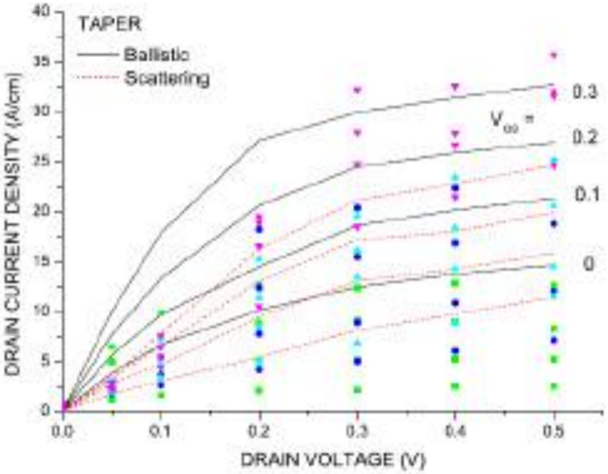


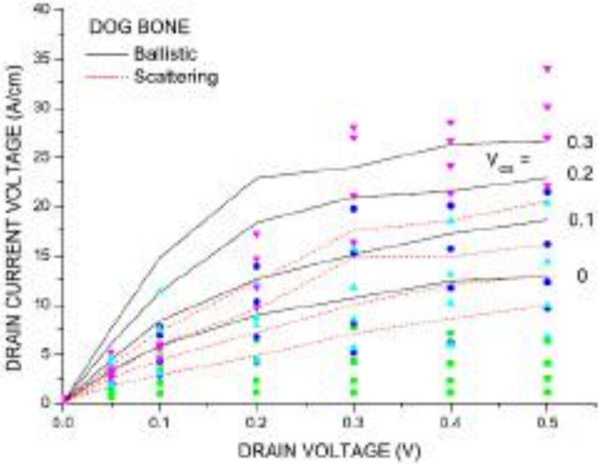
Bo Fu-MVF, IWCE (2009)

DGFET with dopants: Current-voltage characteristics

- Impurity scattering (**purple lines**) reduces the effect of ballistic (**black lines**) access resistance… as expected(?)







Bo Fu-MVF, IWCE (2009)

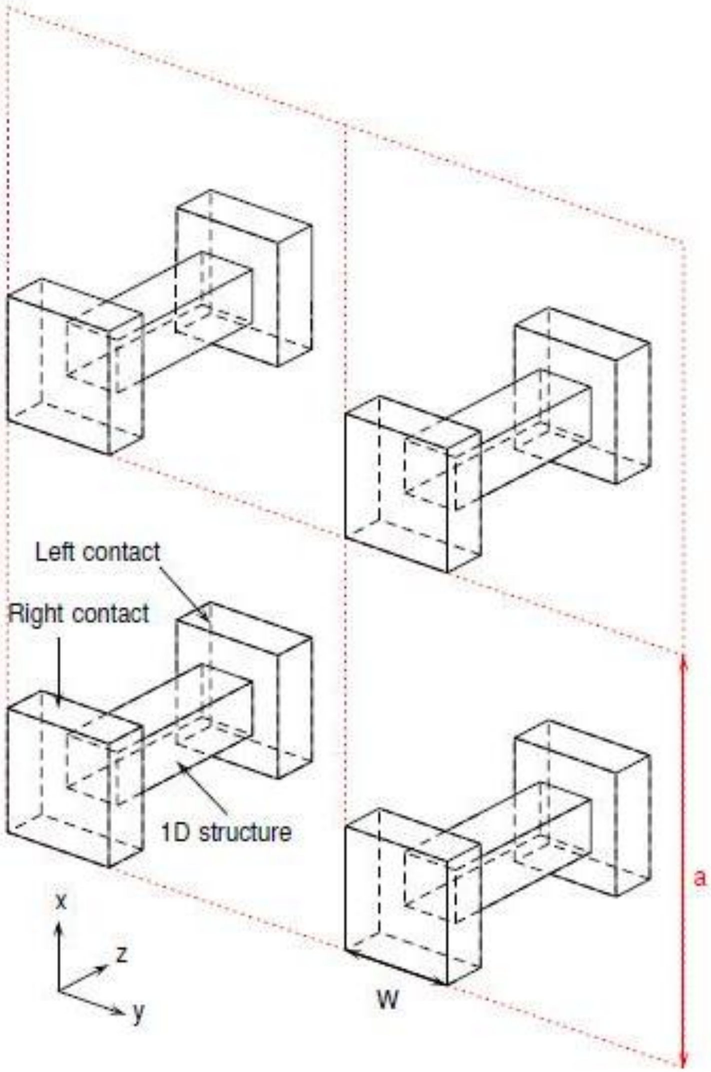
Supercell + EPs: Open boundary conditions

- Wave equation for arbitrary potential and atomic structure:

$$\sum_{\mathbf{g}'} \left\{ \frac{\hbar^2}{2m} \left(|\mathbf{g}+\mathbf{K}|^2 - \frac{d^2}{dz^2} \right) \delta_{\mathbf{g},\mathbf{g}'} + V_{\mathbf{g}-\mathbf{g}'}(z) \right\} \phi_{\mathbf{g}',\mathbf{K}}(z) = E(\mathbf{K})\, \phi_{\mathbf{g},\mathbf{K}}(z)$$

- Wavefunction:

$$\psi_{\mathbf{K}}(\mathbf{r}) = \psi_{\mathbf{K}}(\mathbf{R},z) = \frac{1}{A^{1/2}} \sum_{\mathbf{g}} \phi_{\mathbf{g},\mathbf{K}}(z)\, e^{i(\mathbf{K}+\mathbf{g})\cdot\mathbf{R}}$$



- Main problem: Resolve variations of lattice (pseudo)potential with *z*-discretization
  - Choi and Ihm, Phys. Rev. B **59**, 2267 (1999): transfer-matrix-like method.
  - For atomically periodic structures assume slow variation of the external potential (‘**envelope**’)

Supercell + Envelope: Open boundary conditions

- Supercell+Envelope differential equation for atomically periodic structure:

$$\sum_{\mathbf{G}'}\left\{\left[-\frac{\hbar^2}{2m}\frac{d^2}{dz^2}-i\frac{\hbar^2}{m}G_z\frac{d}{dz}\right]\delta_{\mathbf{G},\mathbf{G}'}+W^{(1D)}_{\mathbf{G},\mathbf{G}'}(z)\right\}\phi_{\mathbf{G}'}(z)=E\phi_{\mathbf{G}}(z)$$

$$W^{(1D)}_{\mathbf{G}\mathbf{G}'}(z) \;=\; V^{(lat)}_{\mathbf{G}-\mathbf{G}'}+\Phi_{\mathbf{G}_{\|}-\mathbf{G}'_{\|}}(z)\;\delta_{G_z,G'_z}\;+\;\frac{\hbar^2G^2}{2m}\;\delta_{\mathbf{G},\mathbf{G}'}$$

- Wavefunction:

$$\psi_{\mathbf{K}n}(\mathbf{r}) \;=\; \frac{e^{i\mathbf{K}\cdot\mathbf{R}}}{A^{1/2}L_c^{1/2}}\sum_{\mathbf{G}}\phi^{(n)}_{\mathbf{G},\mathbf{K}}(z)\;e^{i\mathbf{G}\cdot\mathbf{r}}$$

- Huge (N_zxN_G)x (N_zxN_G) block-tridiagonal linear system (Polizzi's FEAST/SPIKE)

$$\begin{bmatrix}
\widehat{\mathbf{D}}^{(1)}+\Sigma^{(L)} & \widehat{\mathbf{T}}^{(+)} & . & . & . & . & . & . & . \\
\widehat{\mathbf{T}}^{(-)} & . & . & . & . & . & . & . & . \\
. & . & \widehat{\mathbf{T}}^{(-)} & \widehat{\mathbf{D}}^{(l-1)} & \widehat{\mathbf{T}}^{(+)} & 0 & 0 & . & . \\
. & . & 0 & \widehat{\mathbf{T}}^{(-)} & \widehat{\mathbf{D}}^{(l)} & \widehat{\mathbf{T}}^{(+)} & 0 & . & . \\
. & . & 0 & 0 & \widehat{\mathbf{T}}^{(-)} & \widehat{\mathbf{D}}^{(l+1)} & \widehat{\mathbf{T}}^{(+)} & . & . \\
. & . & . & . & . & . & . & . & \widehat{\mathbf{T}}^{(+)} \\
. & . & . & . & . & . & . & \widehat{\mathbf{T}}^{(-)} & \widehat{\mathbf{D}}^{(N)}+\Sigma^{(R)}
\end{bmatrix}
\begin{bmatrix}
\phi^{(1)} \\ . \\ \phi^{(l-1)} \\ \phi^{(l)} \\ \phi^{(l+1)} \\ . \\ \phi^{(N)}
\end{bmatrix}
=
\begin{bmatrix}
(A\mathbf{I}+\Sigma^{(L)})\;\phi^{(Ln)}_{k_L} \\ . \\ 0 \\ 0 \\ 0 \\ . \\ 0
\end{bmatrix}$$

- The 'usual' finite-difference discretized Schrödinger equation, but with 'scalars' D, $T \rightarrow N_G$ x N_G blocks

Supercell + Envelope: Boundary conditions

- Effective mass (one band, no evanescent waves): The “Frensley” approach:

  $\psi_1 = 1+\boldsymbol{r}$, $\qquad\qquad \psi_\mathbf{N} = t$

  $\psi_0 = e^{-\mathbf{i}k\boldsymbol{\Delta}} + (\psi_{\mathbf{1}}\text{-}1)\, e^{\mathbf{i}k\boldsymbol{\Delta}}$, $\qquad\qquad \psi_\mathbf{N} = \psi_\mathbf{N+1}\, e^{\mathbf{i}k'\boldsymbol{\Delta}}$

  $\Sigma^{(\mathbf{L})} = [(\hbar^2/(2m\,\Delta^2)]\,(e^{-\mathbf{i}k\boldsymbol{\Delta}} - e^{\mathbf{i}k\boldsymbol{\Delta}})$ $\qquad\qquad \Sigma^{(\mathbf{R})} = [(\hbar^2/(2m\,\Delta^2)]\, e^{\mathbf{i}k'\boldsymbol{\Delta}}$

  - ❑ One coefficient (“*r*”) sufficient to link wavefunction inside to wavefunction in contact
- Full-bands need $N_\mathbf{G}$ coefficients “r_G”…. *i.e*., the full complex band-structure of the ‘contacts’, *in principle*…
  - ❑ $\Sigma^{(L)}$ and $\Sigma^{(R)}$**:** Left(right)-reservoir/device interaction (*i.e*., b.c., self-energies)

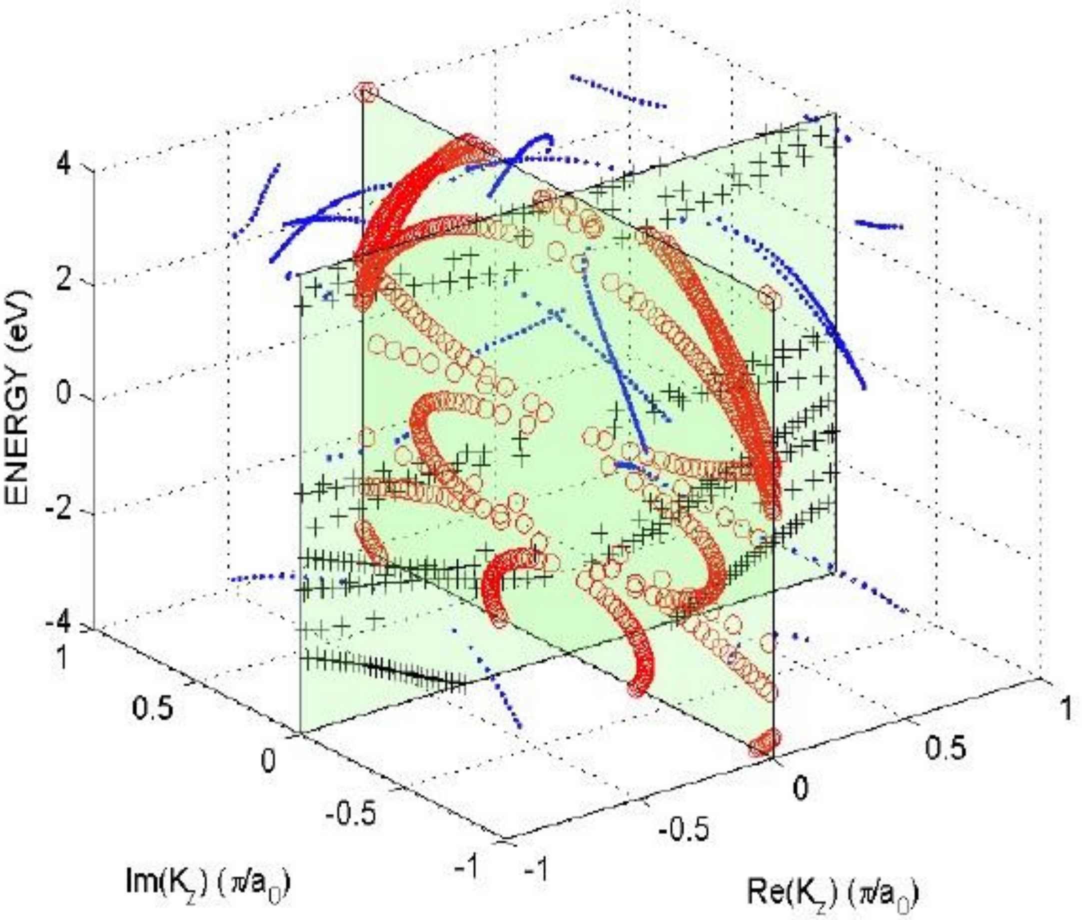
$$\Sigma^{(L)}_{\mathbf{GG}'} = -\left(\frac{\hbar^2}{2m\Delta^2} - i\frac{\hbar^2}{2m\Delta}G_z\right)\sum_p \mathcal{M}^{(L)}_{\mathbf{G}p}\mathcal{M}^{(L)-1}_{p\mathbf{G}'}\; e^{ik_{Lp}\Delta} \qquad \mathcal{M}^{(L)} = \begin{bmatrix} \phi^{(L,1)}_{\mathbf{G}_1} & \phi^{(L,2)}_{\mathbf{G}_1} & \dots & \phi^{(L,M_p)}_{\mathbf{G}_1} \\ \phi^{(L,1)}_{\mathbf{G}_2} & \phi^{(L,2)}_{\mathbf{G}_2} & \dots & \phi^{(L,M_p)}_{\mathbf{G}_2} \\ \dots & \dots & .. & \dots \\ \phi^{(L,1)}_{\mathbf{G}_{N_G}} & \phi^{(L,2)}_{\mathbf{G}_{N_G}} & \dots & \phi^{(L,M_p)}_{\mathbf{G}_{N_G}} \end{bmatrix}$$

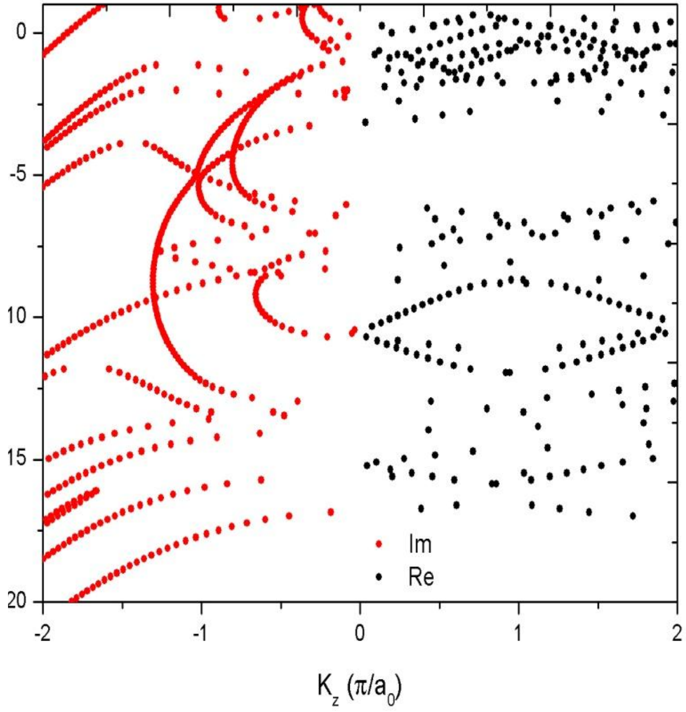
  - ❑ Must solve an eigenvalue problem of double the rank and non-Hermitian!

$$\begin{bmatrix} 0 & \mathbf{I} \\ -\mathbf{H}^{(L,R)(0)}(E) & -\mathbf{H}^{(L,R)(1)} \end{bmatrix}\begin{bmatrix} \phi^{(L,R)} \\ k_z\phi^{(L,R)} \end{bmatrix} = k_z \begin{bmatrix} \phi^{(L,R)} \\ k_z\phi^{(L,R)} \end{bmatrix}$$

  - ❑ …and must invert dense $N_\mathbf{G}$x$N_\mathbf{G}$ matrix to obtain the coefficient r_G!
  - ❑ Since ‘far-away’ bands matter exponentially less, invert, instead, ‘rectangular’ matrix relative to ‘near’ bands (Moore-Penrose pseudo-inverse’)

Quantum transport: Complex bands of a Si NW

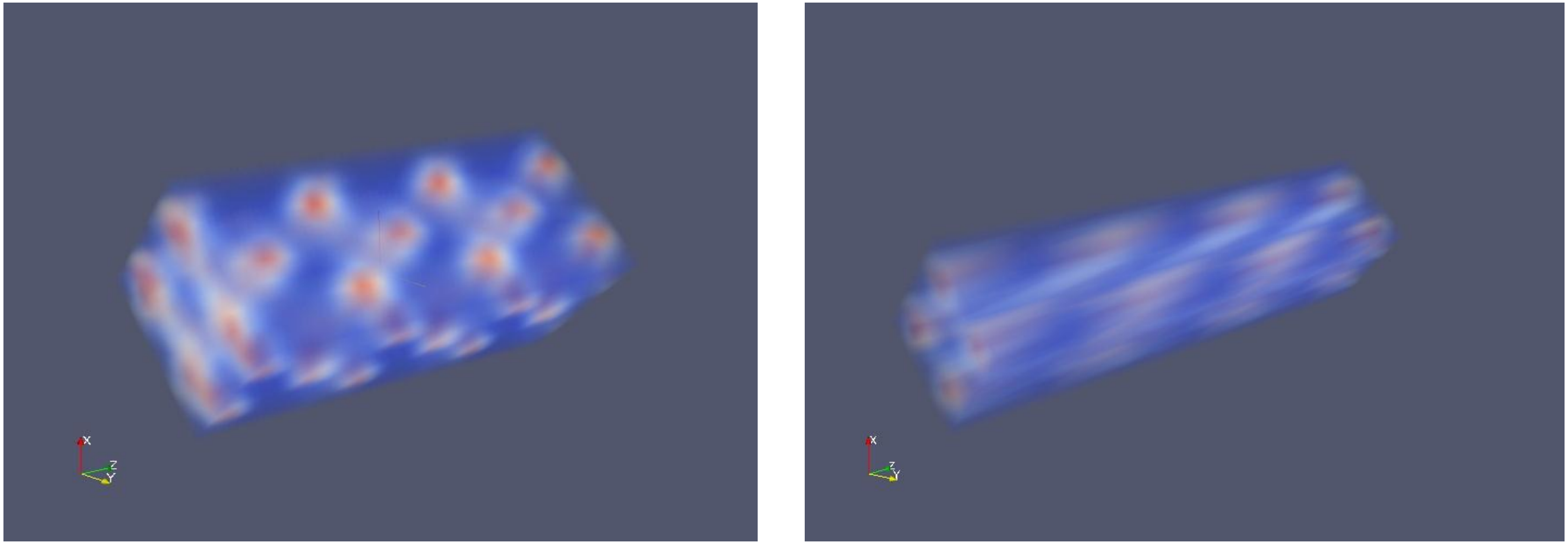




Complex Band Structure for Si [100] NW, (110) sides, (1x1) Si, 1 cell vacuum padding

Courtesy Bo Fu (2013)

Quantum transport: A Si NW



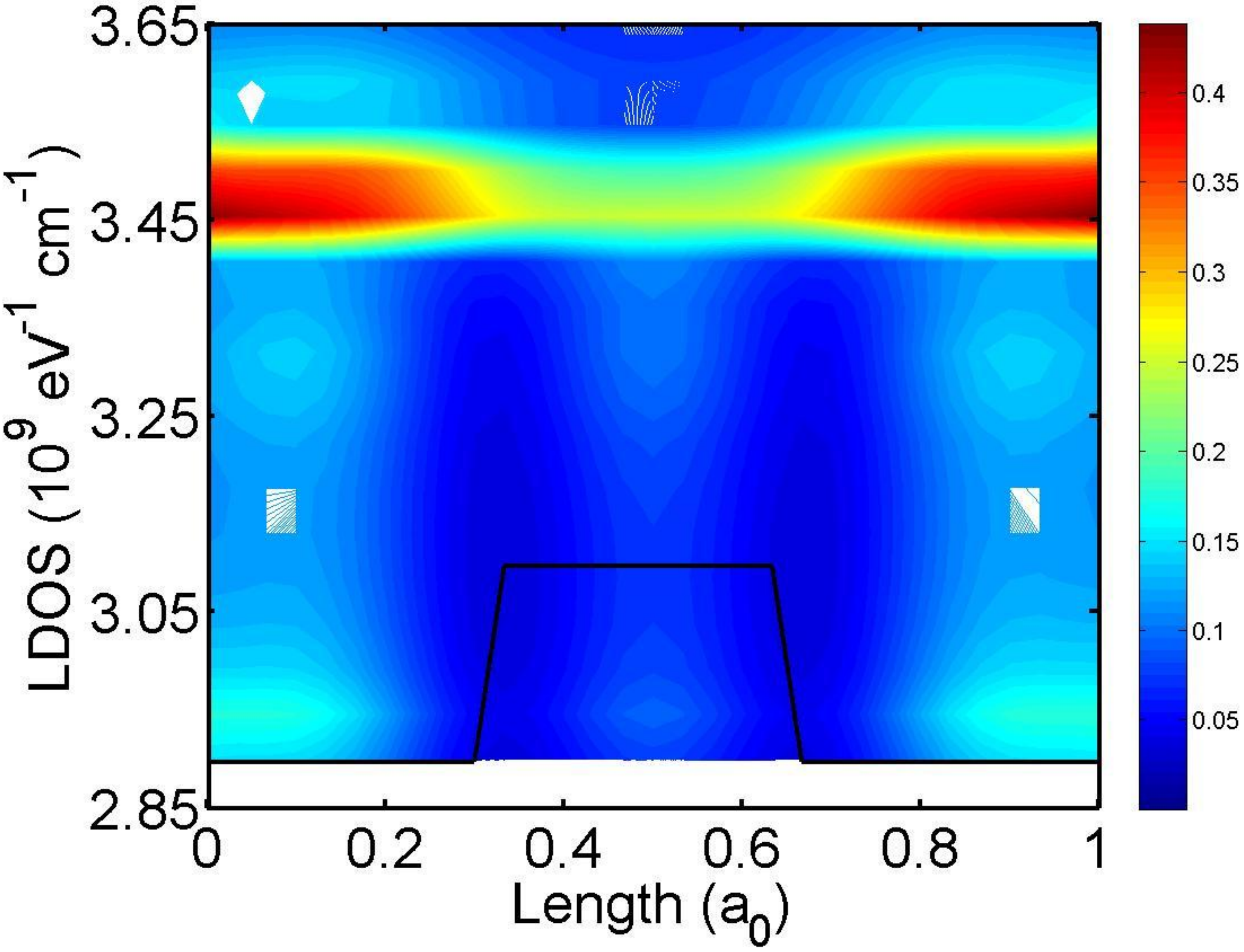
Closed system ($|\Psi|^2$ of a certain energy state)

Open system (zero bias)

Electron Density in Si [100] nanowire (110) sides,
(1x1x3) Si, 1 "cell" of vacuum padding

Courtesy Bo Fu (2013)

Quantum transport: A Si NW with a potential barrier



Courtesy Bo Fu (2013)

Outline

- Electronic structure
  - Born-Oppenheimer and single-electron approximations
  - The concept of pseudopotential (self-consistent and empirical)
  - DFT *vs*. EPs
  - EPs for nanostructures (supercells) and examples: thin films, hetero-layers, graphene, nanowires, nanotubes
- Scattering
  - Electron-phonon interaction
    - DFT *vs.* rigid-ion approximation (bulk Si, thin Si films, graphene)
    - Scattering rates
  - Interface and line-edge roughness (Si films, graphene nanoribbons)
- Transport
  - Semiclassical:
    - Low-field (mobility) and high-field (MC) properties (Si thin films, graphene, NWs, AGNRs)
  - Quantum-ballistic:
    - Transport equation
    - Open boundary conditions

Additional material

Exchange-Correlation Energy

Exchange-Correlation Energy

$$E_{xc}[\rho] = \left(T[\rho] - T_s[\rho]\right) + \left(V_{ee}[\rho] - V_H[\rho]\right)$$

Error from using a non-interacting kinetic energy

Error in using a classical description of the electron-electron interaction

Local Density Approximation (LDA)

$$E_{xc}[\rho] = \int \rho(\mathbf{r})\varepsilon_{xc}(\rho)d\mathbf{r}$$

Generalized Gradient Approximation (GGA)

$$E_{xc}[\rho] = \int \rho(\mathbf{r})\varepsilon_{xc}(\rho, \nabla\rho)d\mathbf{r}$$

Other flavors:

DFT+U
Meta-GGA Functionals
Hybrid Exchange Functionals
GW Corrections
…

Courtesy S. Aboud

Density Functional Theory

Electron density: $\rho(\mathbf{r}) = \sum_{i=1}^{N_{el}} \left|\psi_i(\mathbf{r})\right|^2$

Use electron densities instead of the wavefunctions to determine all the physical properties (Thomas and Fermi 1927).

Hohenberg-Kohn Theorems (1964):

1. The ground state energy of a many-particles system is a unique functional of the particle density.
2. The energy functional has a minimum relative to variations in the particle density at the ground state density.

Kohn-Sham Equations (1965):

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V_{lat}(\mathbf{r}) + \mathrm{V_H}[\rho(\mathbf{r})] + \mathrm{V_{XC}}[\rho(\mathbf{r})]\right\}\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

$$E[\rho(\mathbf{r})] = \underbrace{\mathrm{T_S}[\rho(\mathbf{r})]}_{} + \int d\mathbf{r}\, \underbrace{V_{lat}(\mathbf{r})}_{}\rho(\mathbf{r}) + \underbrace{\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}}_{} + \underbrace{E_{XC}[\rho(\mathbf{r})]}_{}$$

KE noninteracting electrons

PE between electrons and nuclei

Hartree PE

Everything else!

Courtesy S. Aboud

DFT: The Good and The Bad

What DFT can do:

- Geometric and electronic structure
- Phonon dispersion – dynamical matrix method, linear response
- Stability - *ab initio* thermodynamics
- Adsorption/Absorption/Bonding – electron localization function, density of states, *ab initio* thermodynamics
- Reactivity
  - Brønsted Acidity/Basicity (hydrogen donator/acceptor) – bond valence
  - Lewis Acidity/Basicity (electron-pair acceptor/donator) – workfunction, Bader charge, density of states

When DFT can fail:

- Over estimates binding energies
- Underestimates band gaps
- Difficulties with long-range interactions
- Ground-state theory – no excited states
- Problems with strongly correlated systems (*e.g.*, late transition metal oxides, sulfides)

Courtesy S. Aboud

Phonon Dispersion Calculations

Small Displacement Method

$$F_{ls} = \frac{\partial U}{\partial u_{ls}} = -\sum_{l's'} \Phi_{ls,l's'} u_{l's'}$$

u_{ls} : Displacement of ion *s* in the unit cell *l*

Force-Constant Matrix

$$\Phi_{ls,l's'} = \frac{\partial^2 U}{\partial u_{ls} \partial u_{l's'}}$$

Dynamical Matrix

$$D_{ss'}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{l} \Phi_{ls,0s'} \exp[-i\mathbf{q} \cdot \mathbf{R}_l]$$

$$\sum_{s'} [D_{ss'}(\mathbf{q}) - \omega^2 \delta_{ss'}] u_{s0} = 0$$

$$|D_{ss'}(\mathbf{q}) - \omega^2 \delta_{ss'}| = 0$$

1. Calculate the force constant matrix with VASP with the atoms in their equilibrium position
2. Diagonalization of the dynamical matrix done with PHON[1] – generates vibrational frequencies and amplitudes

[1] D. Alfe , PHON: A program to calculate phonons using the small displacement method, Computer Physics Communication, 2009.

Courtesy S. Aboud

SiNRs: *Ab initio* thermodynamics: Stability analysis

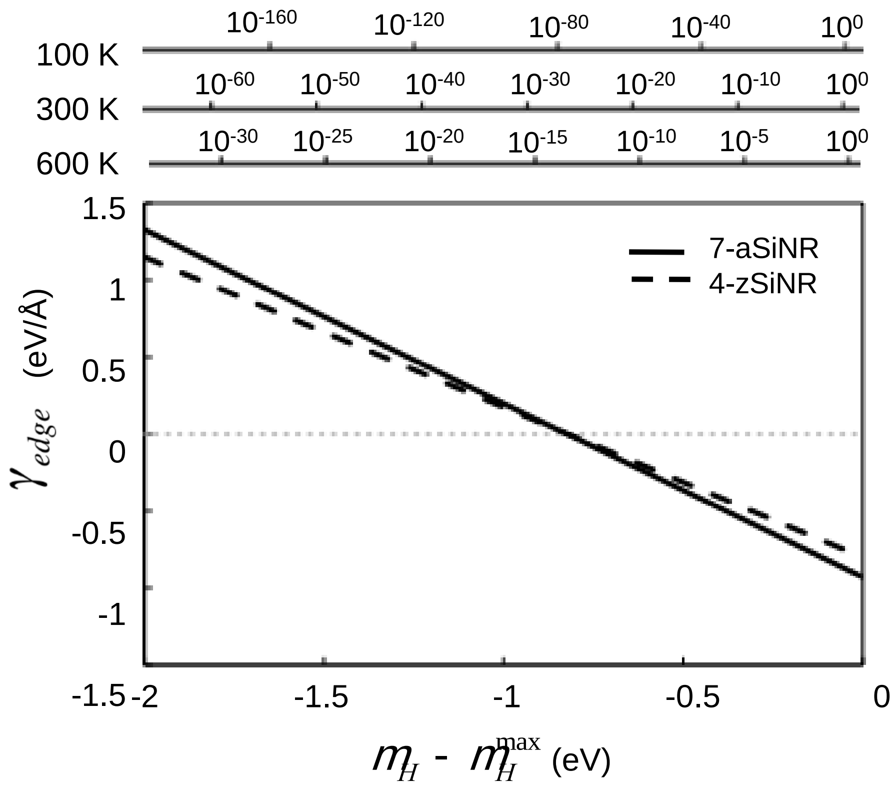
- Zigzag and Armchair edge free energy:

$$\gamma_{edge} = \frac{1}{2L}\left[G_{SNR} - N_{Si}\mu_{Si} - N_H\mu_H\right]$$

$$\gamma_{edge} = \frac{1}{2L}\left[G_{SNR} - N_{Si}g_{SiH}^{sheet} + \frac{(N_{Si}-N_H)}{2}\mu_{H_2}\right]$$

Neglecting the contributions due to the vibration frequency:

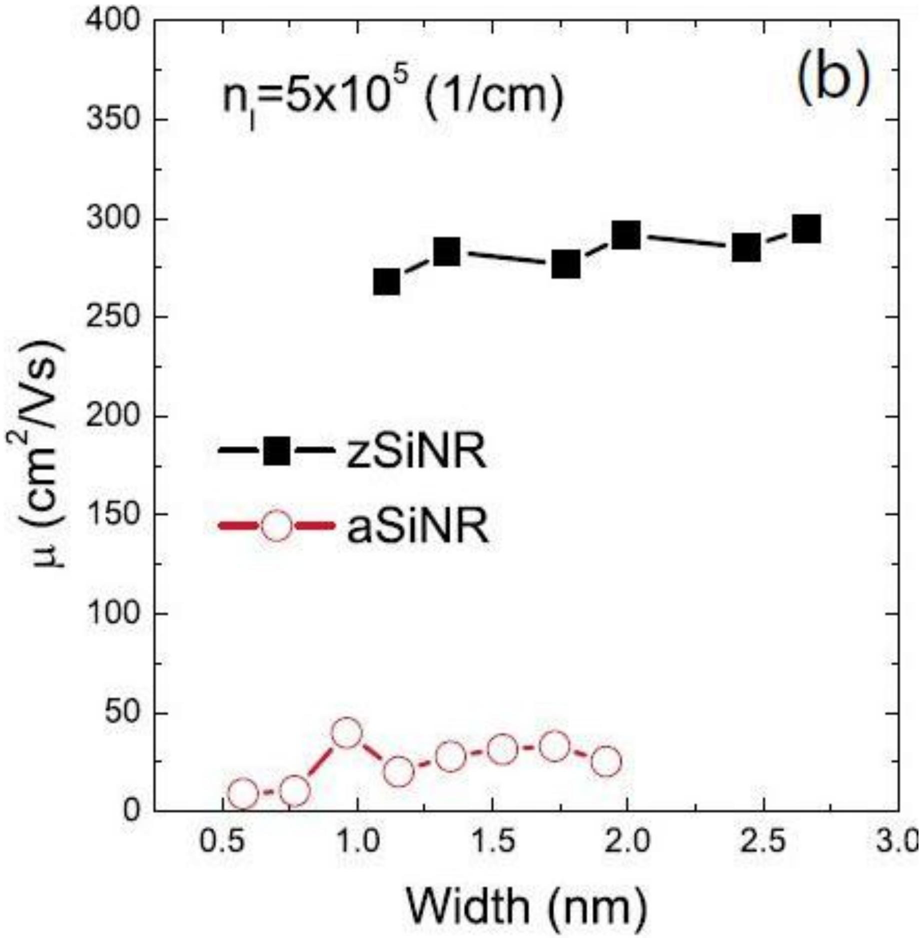
$$\mu_H(T,p) = \frac{1}{2}\mu_H(T,p) = \frac{1}{2}E_{H_2} + \underbrace{\mu_H(T,p^0) + \frac{k_BT}{2}\ln\left(\frac{p}{p^0}\right)}_{\text{JANAF Tables}}$$



- Silicane sheets stable only at very low partial pressures of hydrogen, predicted to break into ribbons under ambient conditions
- Edge free-energy not significantly influenced by the ribbon width
- Armchair edge ribbons only slightly more favorable (compared to graphene in which zigzag edges are significantly more unstable)

DFT results (VASP) by J. Kim and S. Aboud
See Aboud's talk

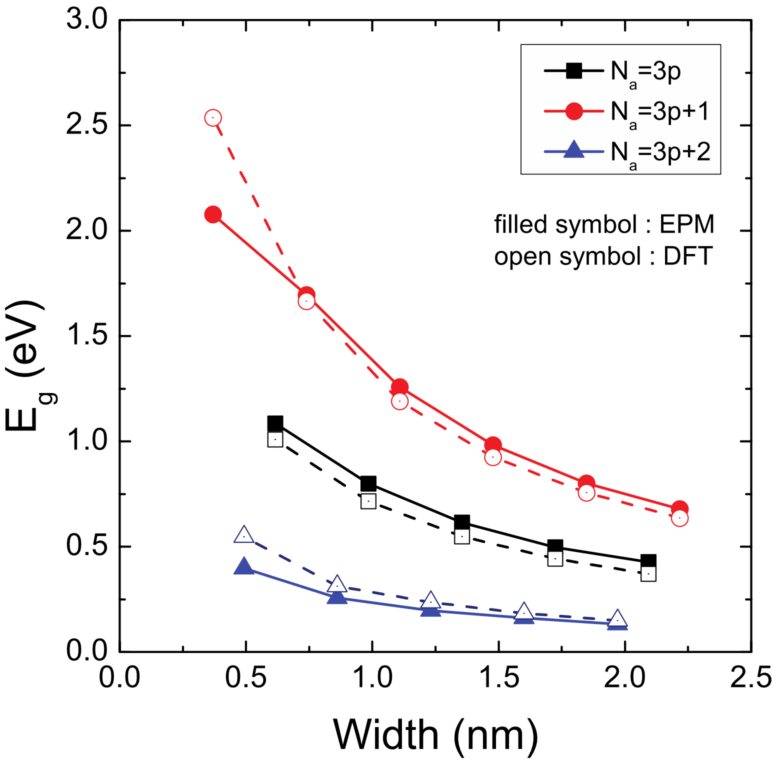
Si NRs: Electron mobility *vs.* width

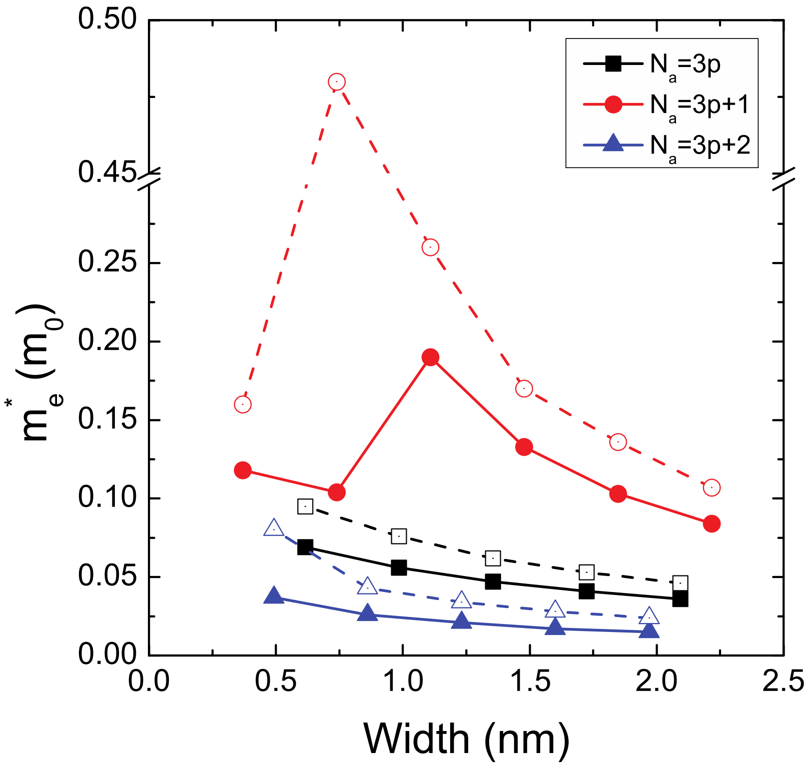


Mobility in zSiNRs >> aSiNR (orientation effect)

Results by J. Kim

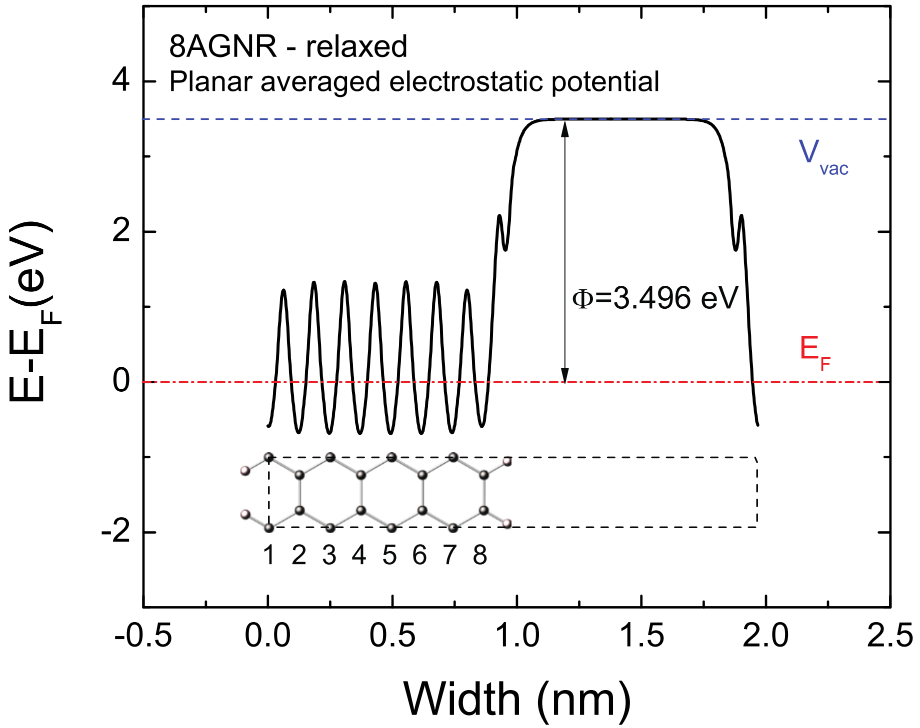
EPM vs DFT

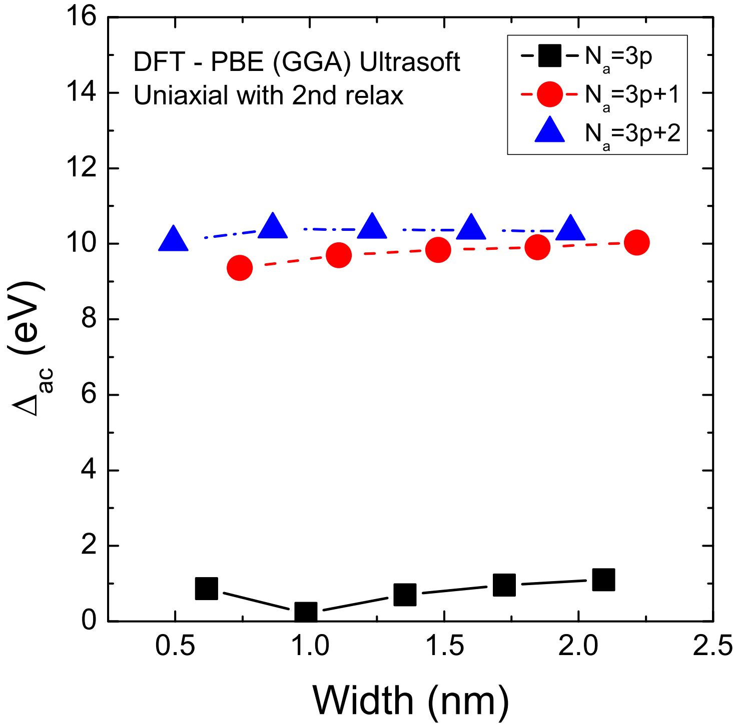




- Good agreement between EPM and DFT
  - ❑ EPM : empirical pseudopotential from Kurokawa
  - ❑ DFT : PBE (GGA), Ultrasoft pseudopotential
- Sudden jump in effective mass due to the band crossing as the width increases.

Deformation potential





- Uniaxial deformation potentials extracted from DFT.
- Vacuum level when equilibrium as an absolute energy reference.
- Aromatic dependent deformation potentials :
  - ☐ Δ_{ac} (3p+2) > Δ_{ac} (3p+1) >> Δ_{ac} (3p)

Mobility

- Kubo-Greenwood
  - Full band from EPM (exact subband energies and wavefunctions).
  - Explicitly calculating the overlap integral.

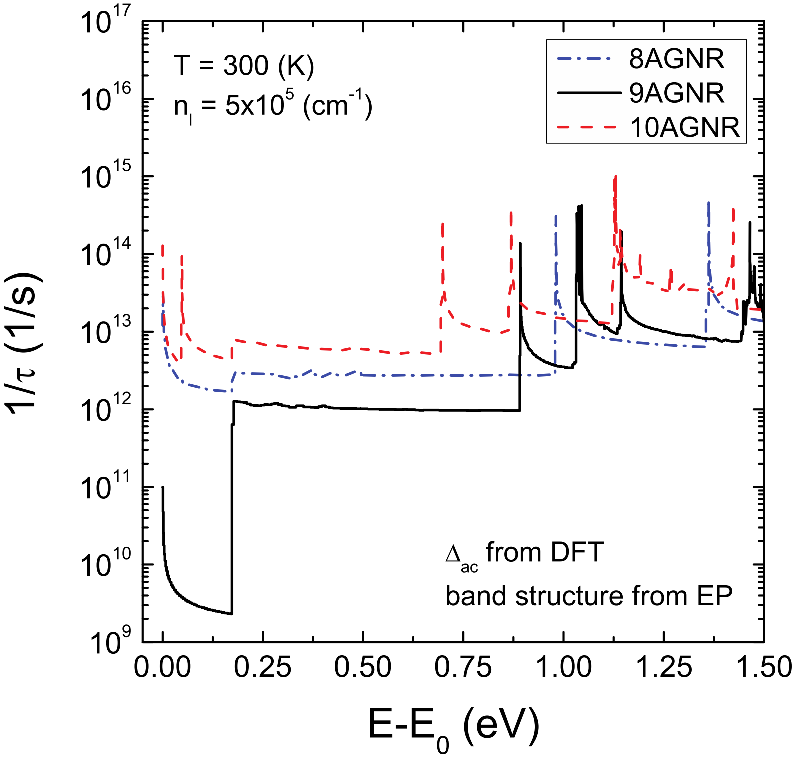
- Effective mass
  - Effective mass obtained from EPM and DFT (parabolic band approximation)
  - No overlap integral.
  - No subband effect.

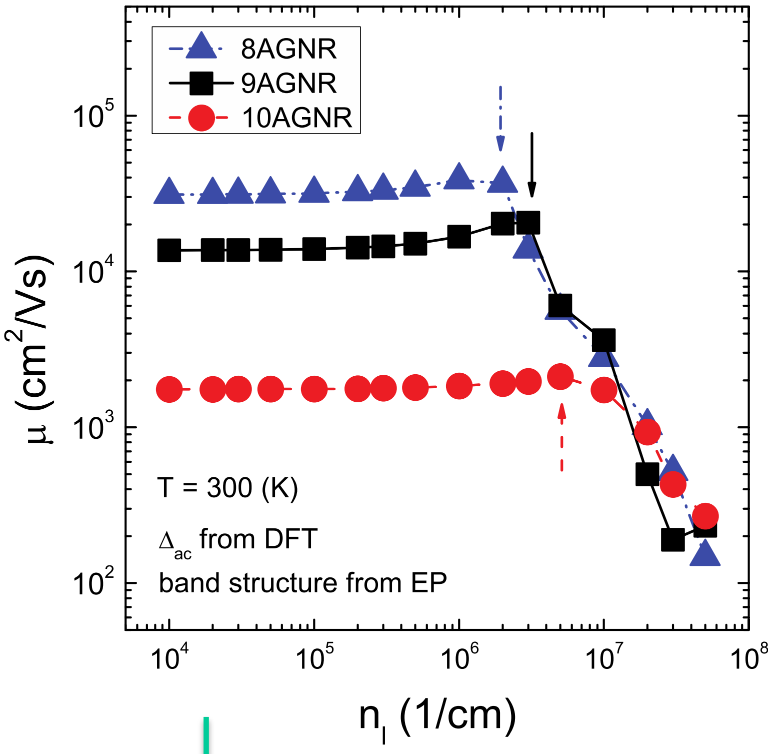
Electron-phonon scattering using the deformation potentials

$$\mu_{zz} = \frac{1}{n_l} \sum_{\alpha} n^{(\alpha)} \mu_{zz}^{(\alpha)} \quad \text{vs} \quad \mu_{zz} = \frac{e\hbar C}{(2\pi k_B T)^{1/2} \left| m_e^* \right|^{3/2} \Delta_{ac}^2}$$

Momentum relaxation rate

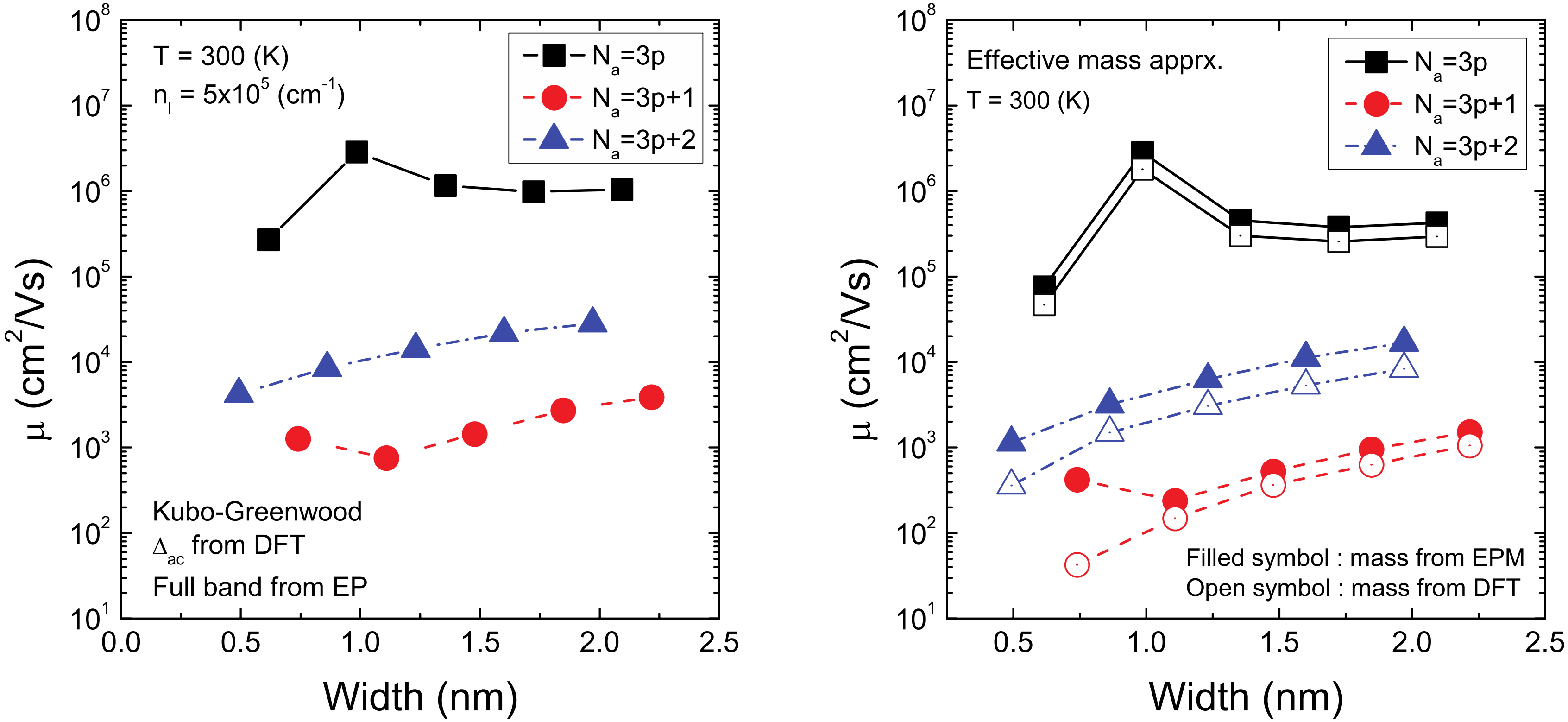
$$\frac{1}{\tau^{(\alpha)}_{ac,z}(k_z)} = \frac{2\pi}{\hbar}|V|^2 \sum_{k'_z,\alpha'} F_{k_z,k'_z,\alpha,\alpha'}\,\delta\left[E^{(\alpha)}(k_z) - E^{(\alpha')}(k'_z)\right]$$





need to be replaced by new plot

Aromatic dependence



- Aromatic dependent deformation potentials :
  - ☐ μ (3p) > μ (3p+2) > μ (3p+1)
- Same aromaticity from Kubo-Greenwood and effective mass approximation.
- No significant different between EPM and DFT in effective mass approximation.
- Electron mobility mostly dominated by the deformation potentials but some contribution from effective mass.