SAND2011-2535C

Nanoscale Effects in Heterostructure Nanowires and Carbon Nanotubes

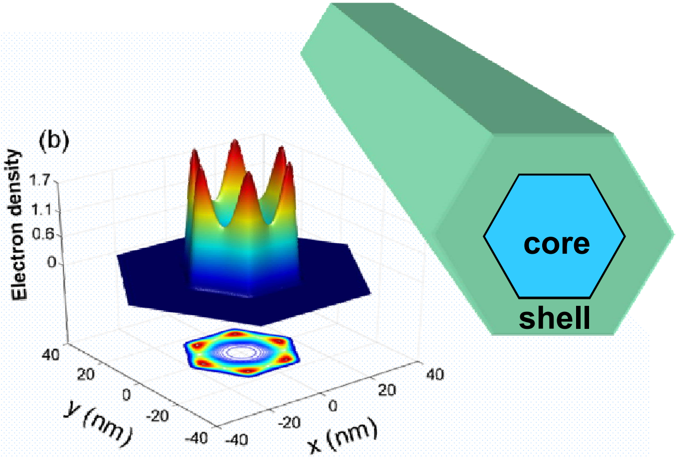
Bryan M. Wong

Materials Chemistry Department
Nanoelectronics and Nanophotonics Group
Sandia National Laboratories, Livermore, California

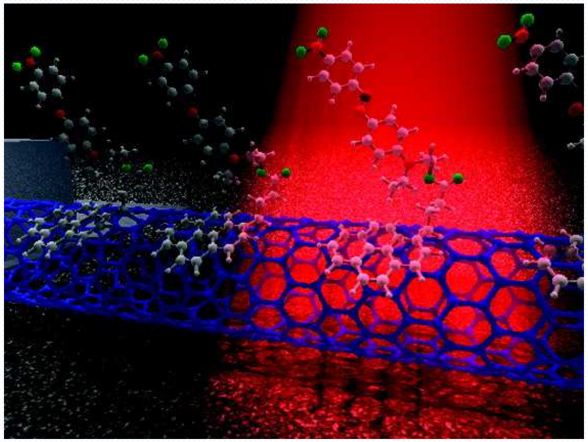
Bradley University Physics Department – April 15, 2011

Road map

- ***Heterostructure Nanowires***
  - Why are electronic properties in 1D nanowires so unique?



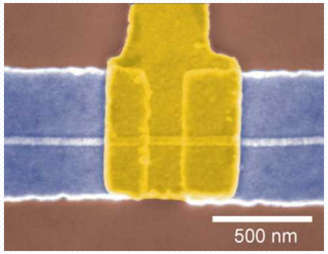
- ***Carbon Nanotubes***
  - Can we control optoelectronic properties in carbon nanotubes?



- Overall theme: theory to *complement* experiment

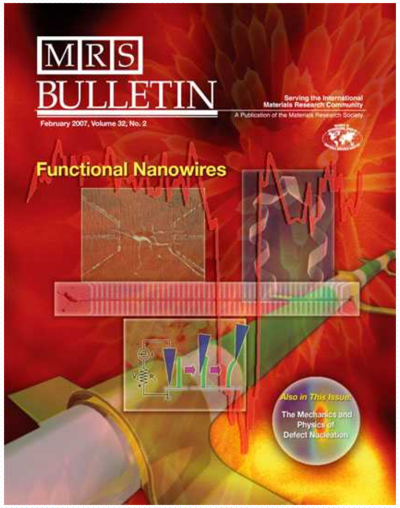
Nanowires

- Immense interest in nanowires for transistors, circuits, devices



nanowire field-effect transistor

(Lieber group, Harvard)



MRS BULLETIN

Serving the International Materials Research Community

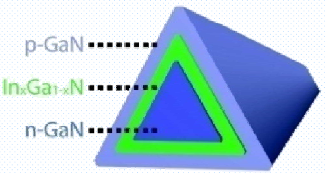
A Publication of the Materials Research Society

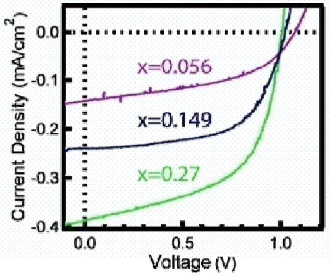
February 2007, Volume 32, No. 2

Functional Nanowires

Also in This Issue: The Mechanics and Physics of Defect Nucleation

- *Reduction in dimensionality* yields novel nanoscale properties
  - Ballistic transport, conductance quantization
- Can you control electron gas formation?

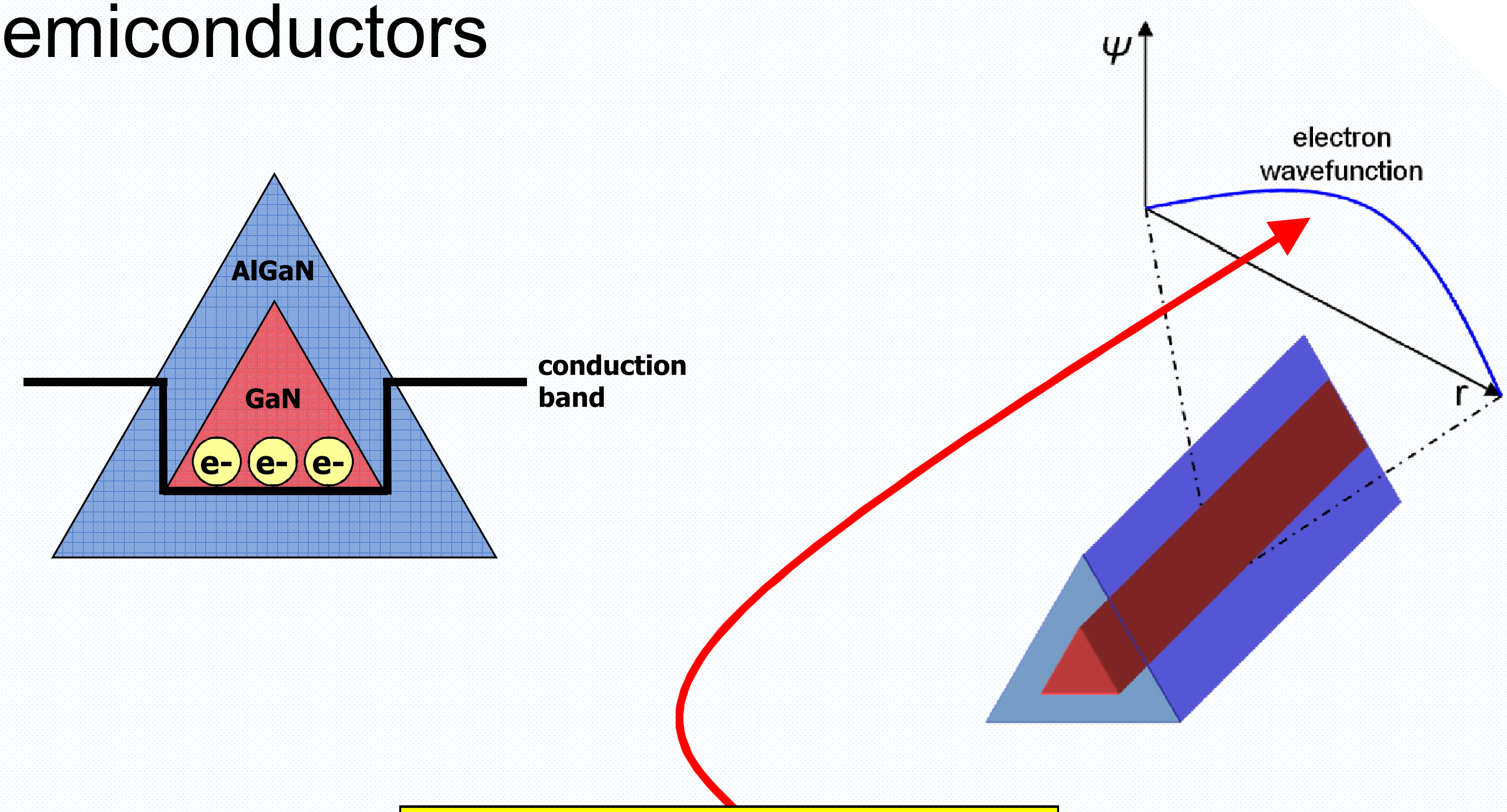




(Lieber group, Harvard)

Core-shell nanowires

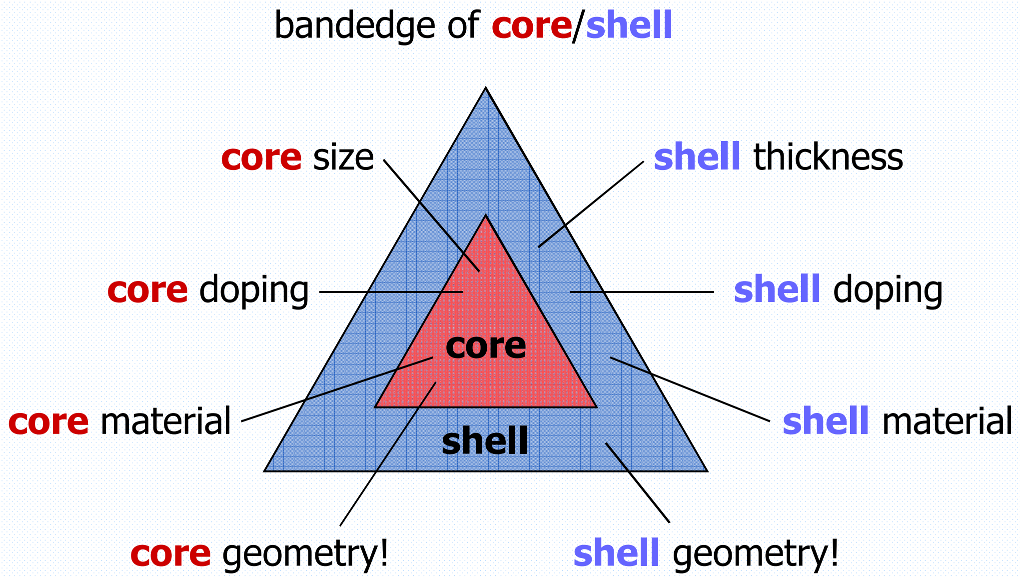
- *Core-shell*: heterostructure made with 2 different semiconductors



What are the properties of this confined electron gas?

Core-shell nanowires

- ***Huge*** parameter space (both experimental and computational)



bandedge of **core**/**shell**

core size

shell thickness

core doping

shell doping

core

core material

shell material

shell

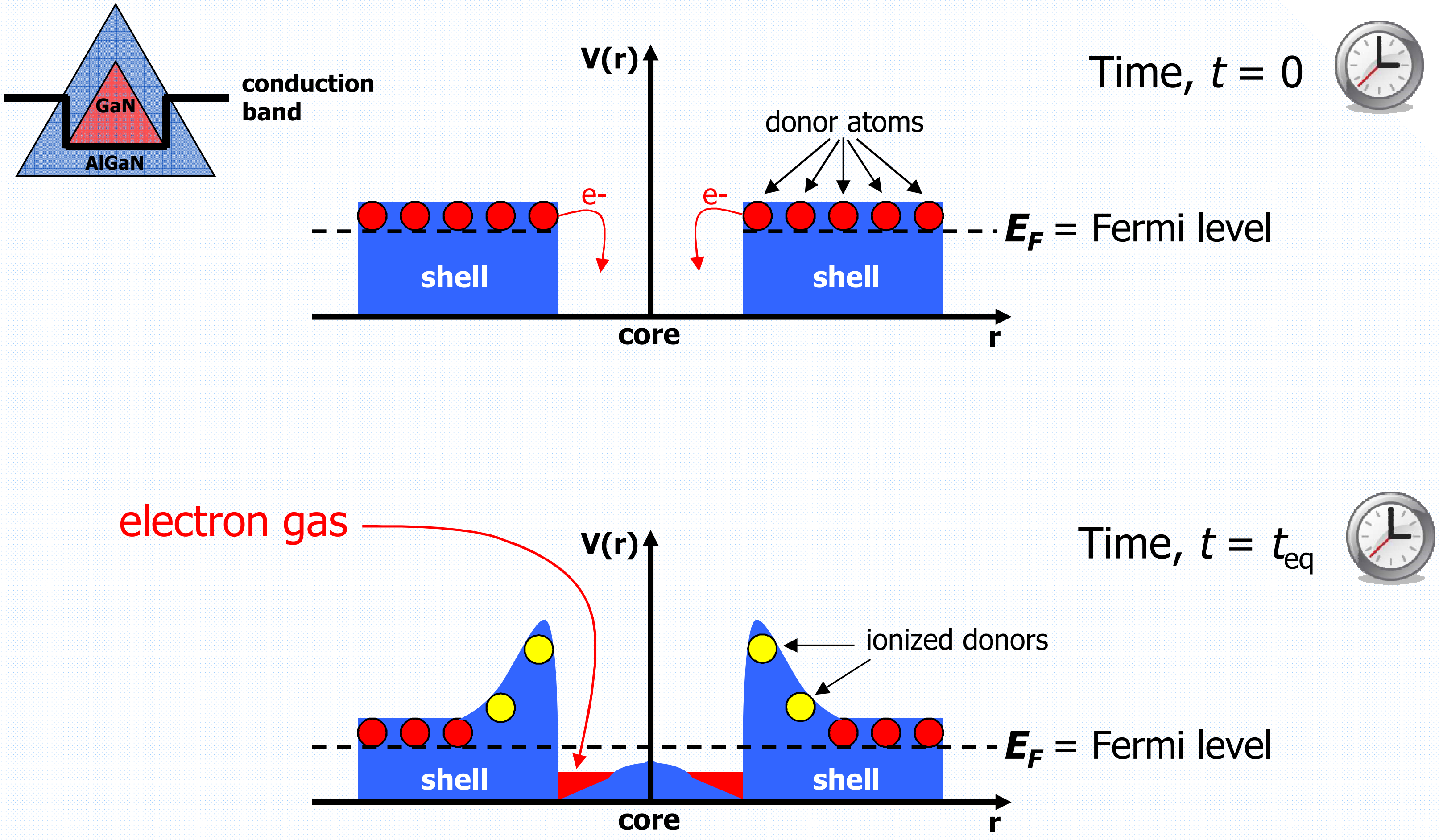
core geometry!

shell geometry!

- Theory plays important role in exploring large parameter space

Electron gas formation

- Forming an electron gas



Time, $t = 0$

E_F = Fermi level

Time, $t = t_{eq}$

E_F = Fermi level

Theoretical description

- Complex interplay between *quantum mechanics* and *electrostatics*

Theoretical description

- Complex interplay between *quantum mechanics* and *electrostatics*
- *Quantum mechanics* from Schrödinger equation

$$-\frac{\hbar^2}{2m^*}\nabla^2\Psi_i(\vec{r})+V(\vec{r})\Psi_i(\vec{r})=E_i\Psi_i(\vec{r})$$

Theoretical description

- Complex interplay between *quantum mechanics* and *electrostatics*
- *Quantum mechanics* from Schrödinger equation

$$-\frac{\hbar^2}{2m^*}\nabla^2\Psi_i(\vec{r})+V(\vec{r})\Psi_i(\vec{r})=E_i\Psi_i(\vec{r})$$

- *Electrostatics* from Poisson equation

$$\nabla\cdot\left[\varepsilon(\vec{r})\nabla V(\vec{r})+\mathbf{P}(\vec{r})\right]=-\rho(\vec{r})$$

$$\rho(\vec{r})=\rho_{\text{doping}}(\vec{r})+\sum_i\left|\Psi_i(\vec{r})\right|^2 f(E_i,E_F,T)$$

Theoretical description

- Complex interplay between *quantum mechanics* and *electrostatics*

- *Quantum mechanics* from Schrödinger equation

$$-\frac{\hbar^2}{2m^*}\nabla^2\Psi_i(\vec{r})+V(\vec{r})\Psi_i(\vec{r})=E_i\Psi_i(\vec{r})$$

- *Electrostatics* from Poisson equation

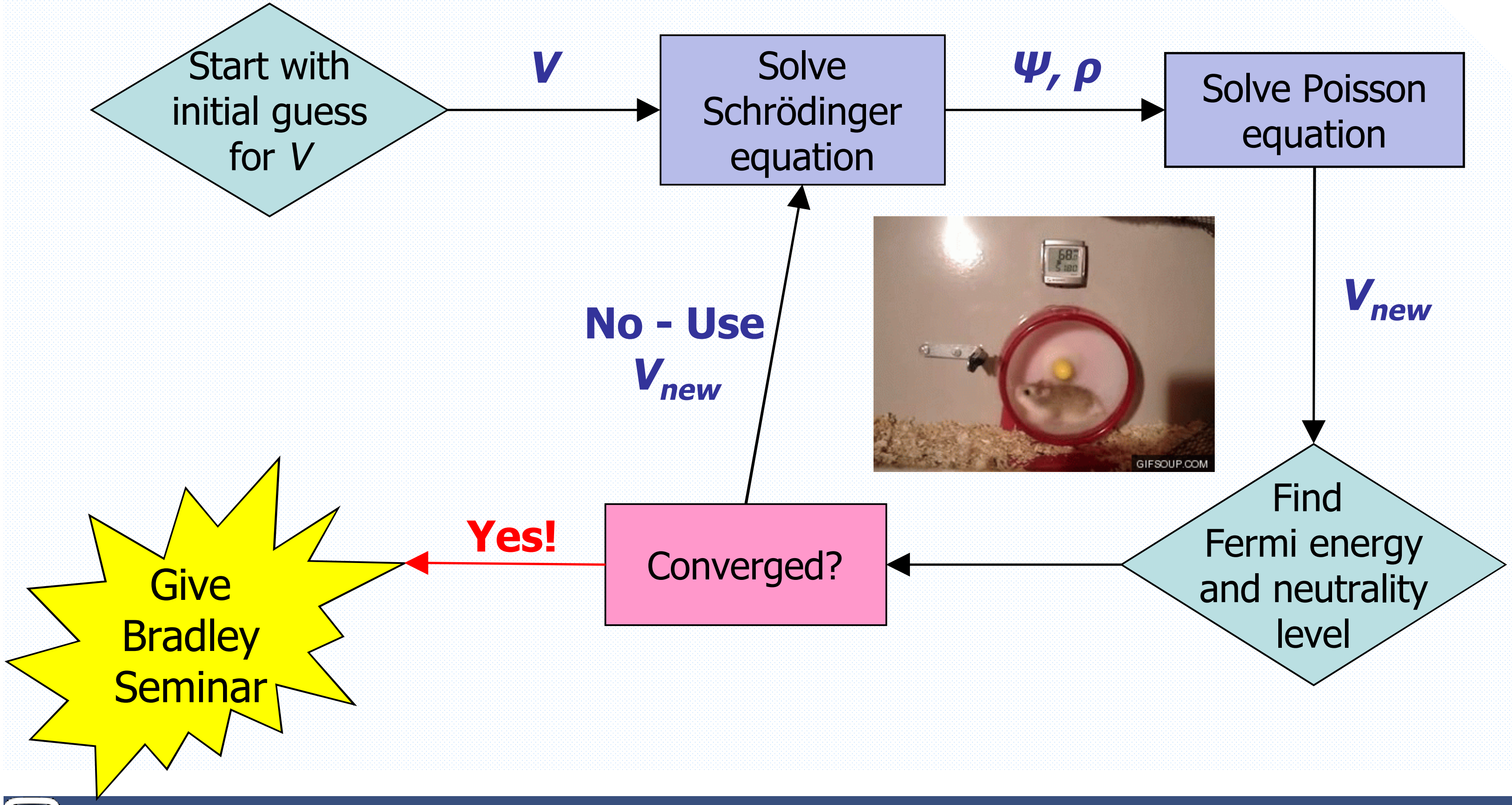
$$\nabla\cdot\left[\varepsilon(\vec{r})\nabla V(\vec{r})+\mathbf{P}(\vec{r})\right]=-\rho(\vec{r}) \qquad \rho(\vec{r})=\rho_{\text{doping}}(\vec{r})+\sum_i\left|\Psi_i(\vec{r})\right|^2 f(E_i,E_F,T)$$

- *Charge neutrality constraint*

$$\int\rho_{\text{positive dopants}}(\vec{r})\,d\vec{r}=\int\rho_{\text{negative dopants}}(\vec{r})\,d\vec{r}+\int\sum_i\left|\Psi_i(\vec{r})\right|^2 f(E_i,E_F,T)\,d\vec{r}$$

Self-consistent solution

- Must solve Poisson and Schrödinger equations *self-consistently*



Start with initial guess for *V*

V

Solve Schrödinger equation

ψ, ρ

Solve Poisson equation

V_{new}

Find Fermi energy and neutrality level

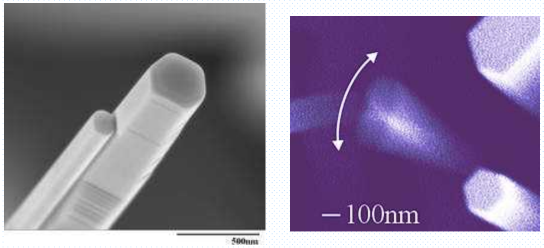
Converged?

No - Use V_{new}

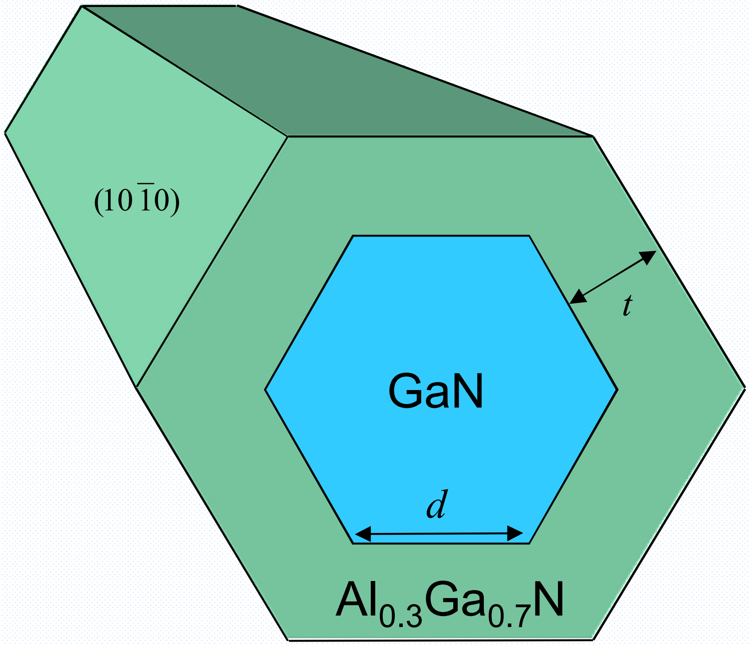
Yes!

Give Bradley Seminar

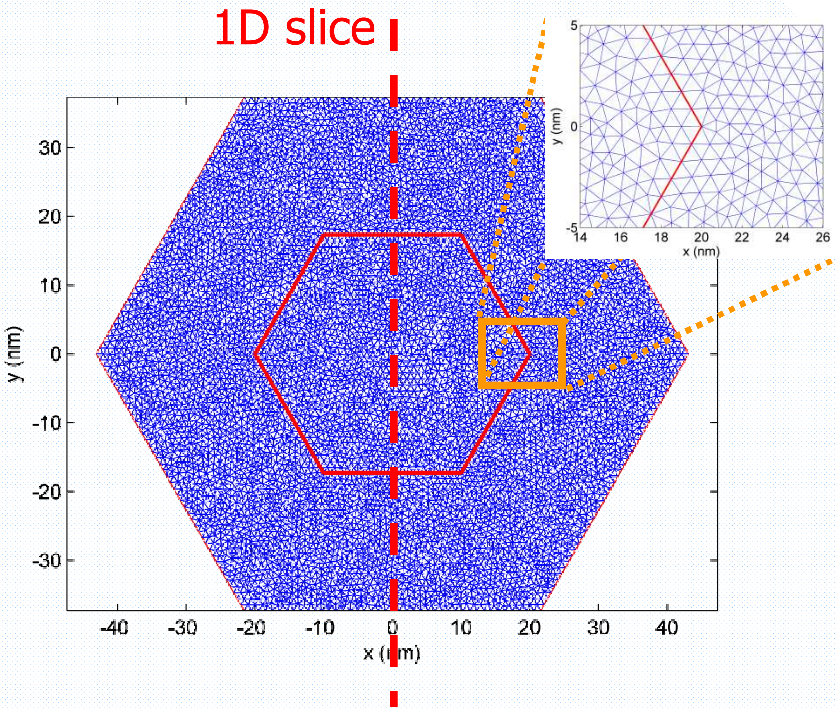
Hexagonal geometry



hexagonal
GaN nanowires

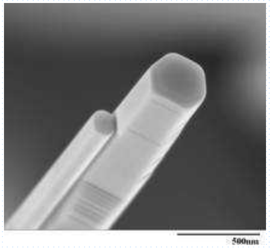


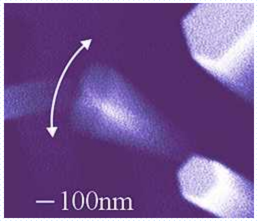
Axial direction: [0001]



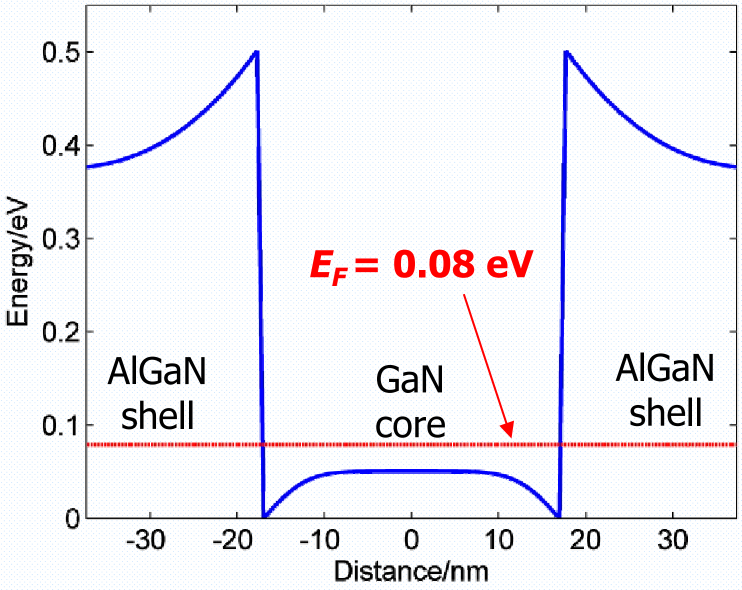
finite element mesh

Hexagonal geometry

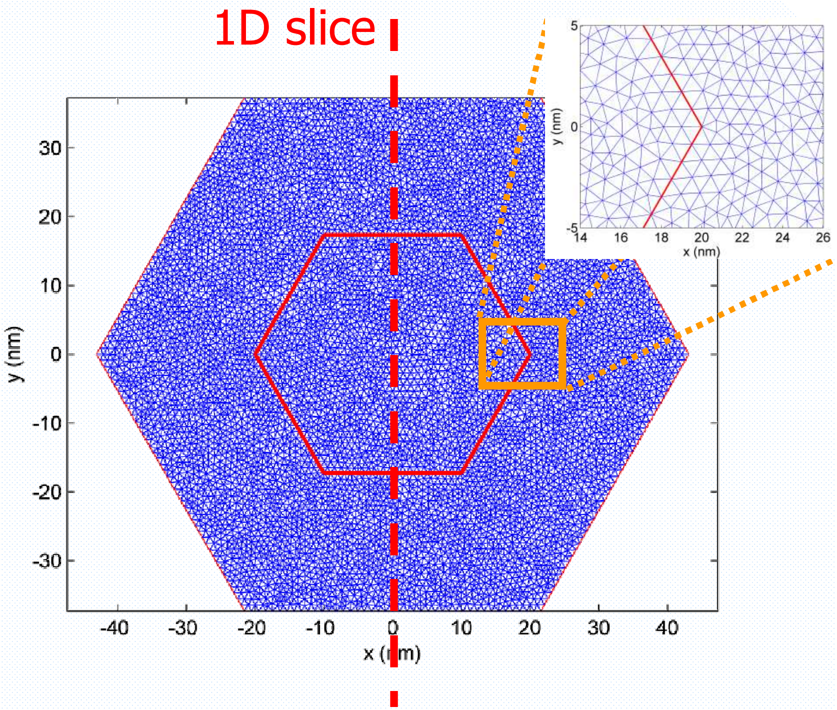




hexagonal
GaN nanowires

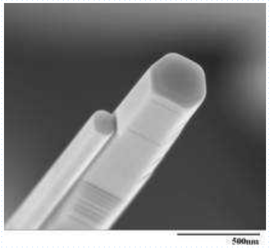


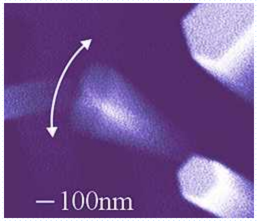
self-consistent
conduction band



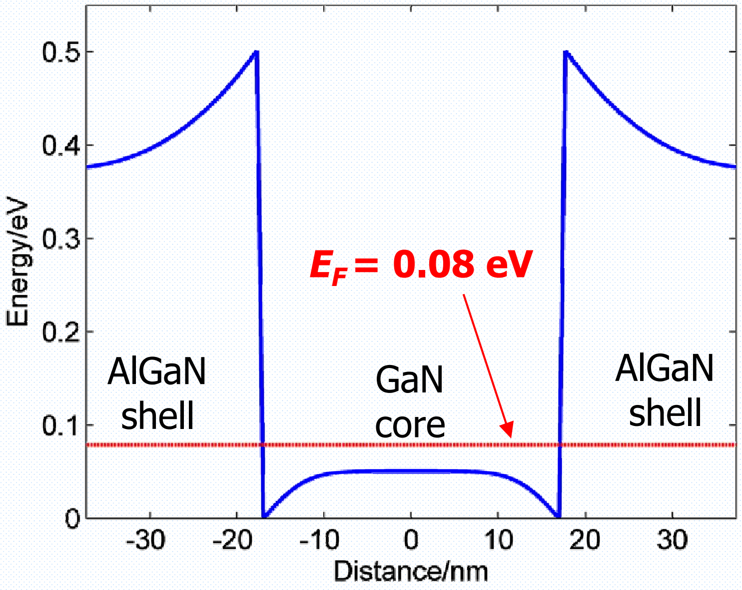
finite element mesh

Hexagonal band structure

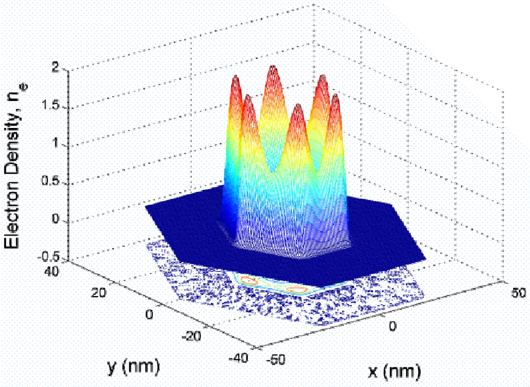




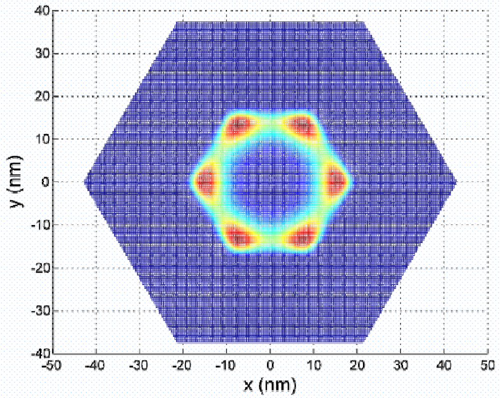
hexagonal
GaN nanowires



self-consistent
conduction band



electron density, 3D view



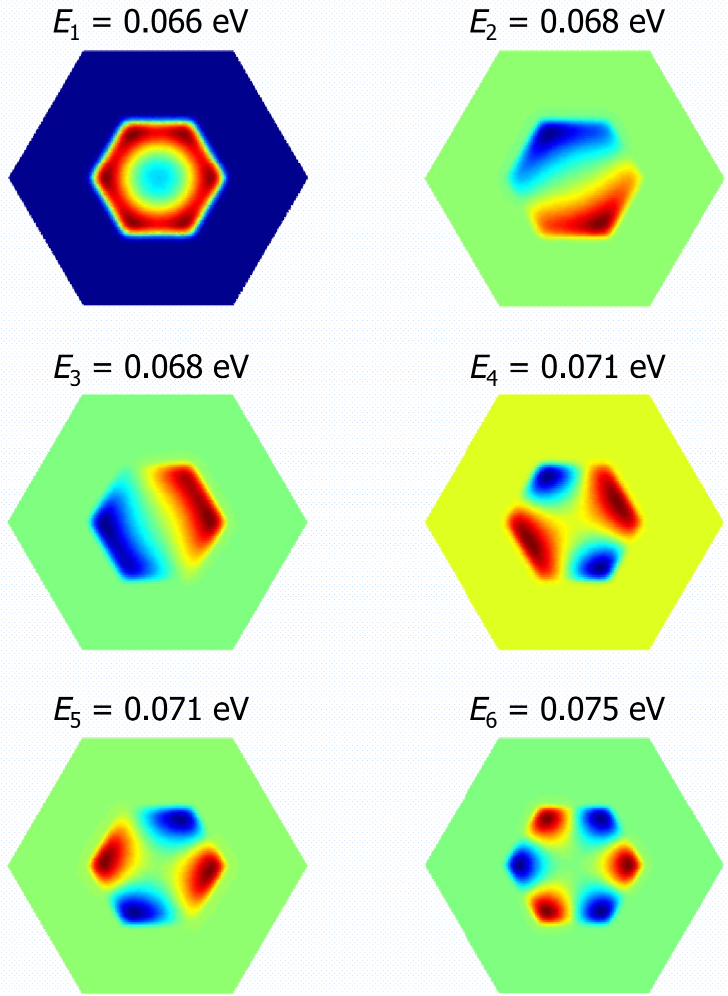
electron density, 2D view

high density at ***corners***
completely different than bulk/thin-film

B.M. Wong , F. Leonard, et al. *submitted* (2011)

Hexagonal electron density

electron wavefunctions



E_1 = 0.066 eV

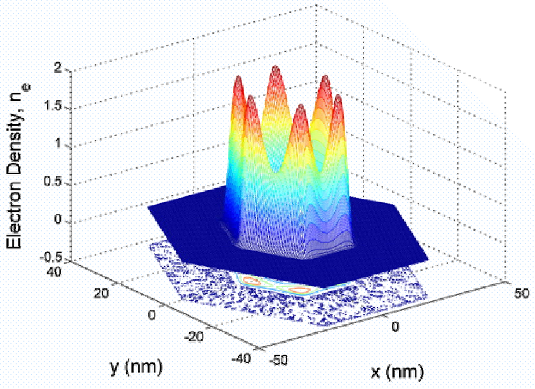
E_2 = 0.068 eV

E_3 = 0.068 eV

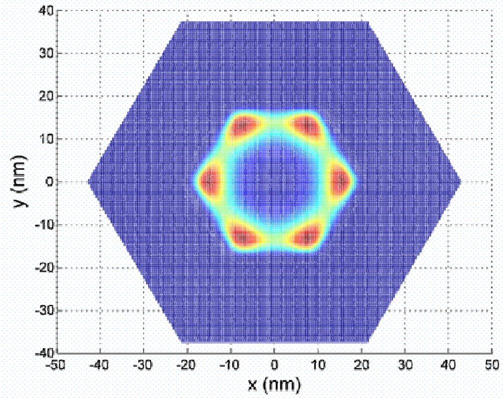
E_4 = 0.071 eV

E_5 = 0.071 eV

E_6 = 0.075 eV



electron density, 3D view

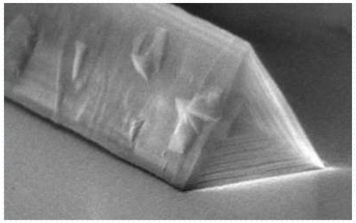


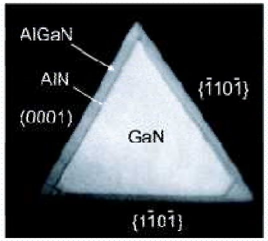
electron density, 2D view

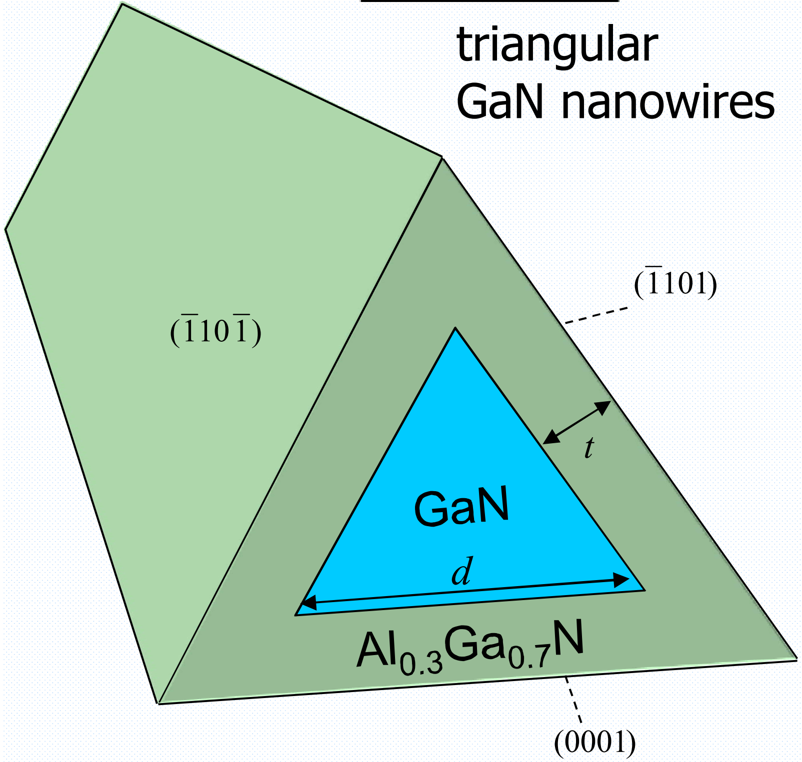
high density at ***corners***
completely different than bulk/thin-film

B.M. Wong , F. Leonard, et al. *submitted* (2011)

Triangular geometry



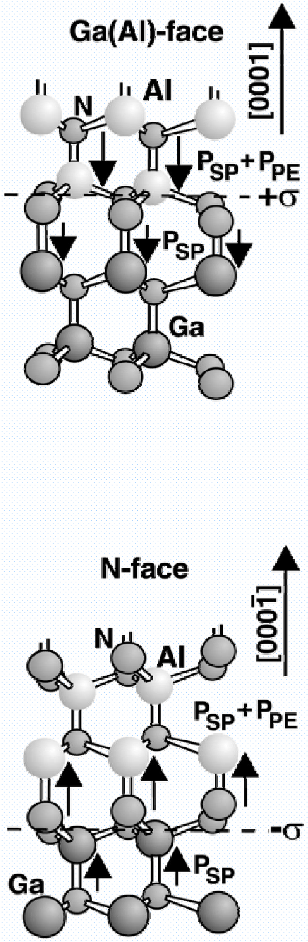


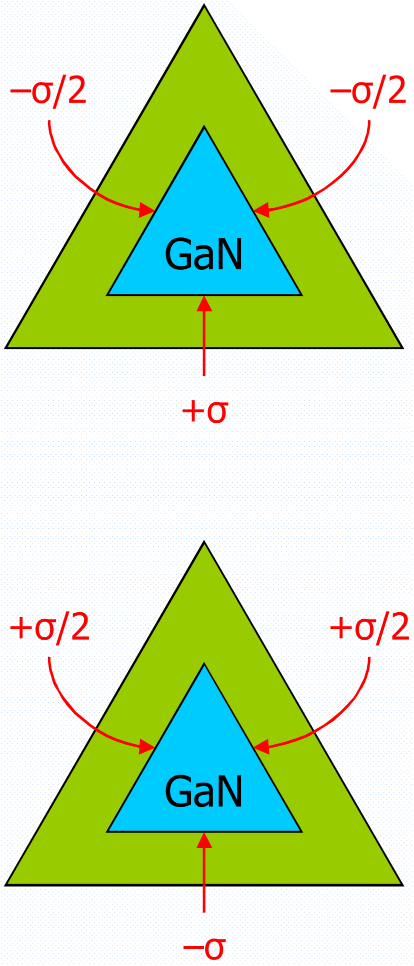


triangular
GaN nanowires

Axial direction: [1,1,-2,0]

The [0001] face is polar!

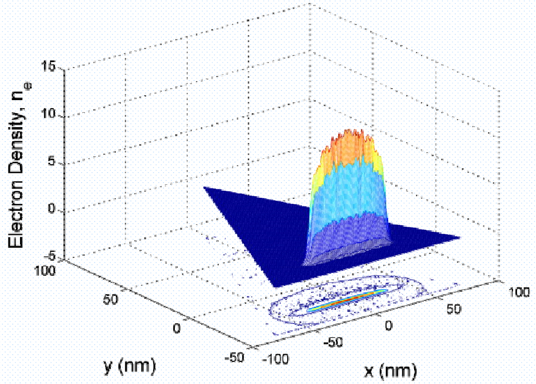




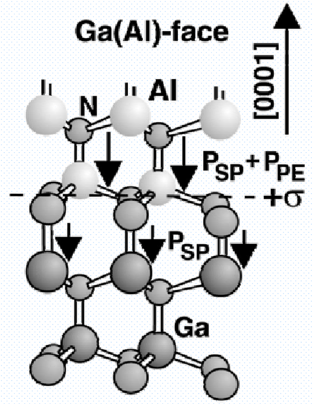
B.M. Wong , F. Leonard, et al. *submitted* (2011)

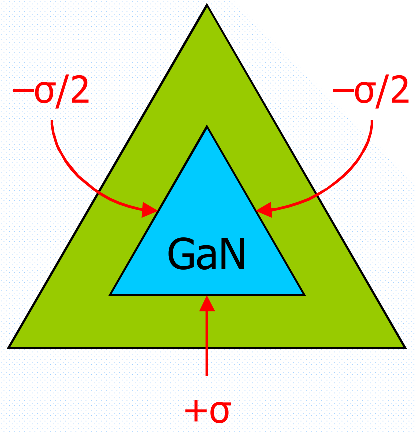
Polarization effects

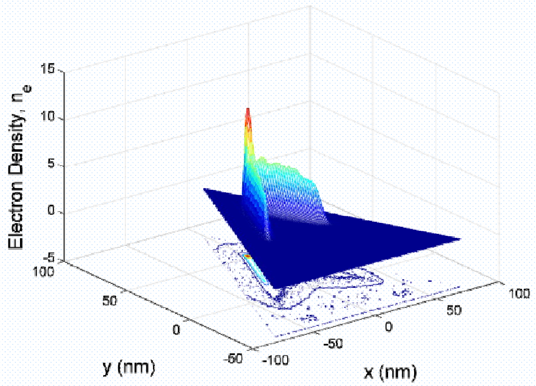
The [0001] face is polar!



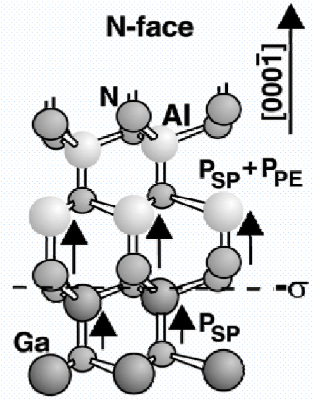
electron density, N-face

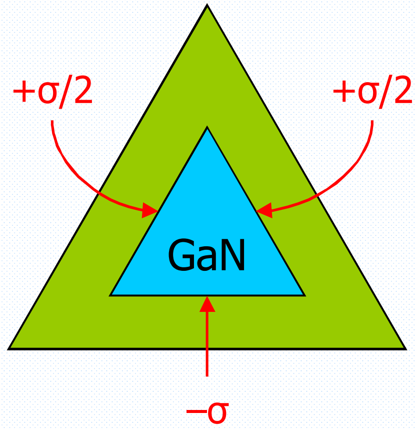






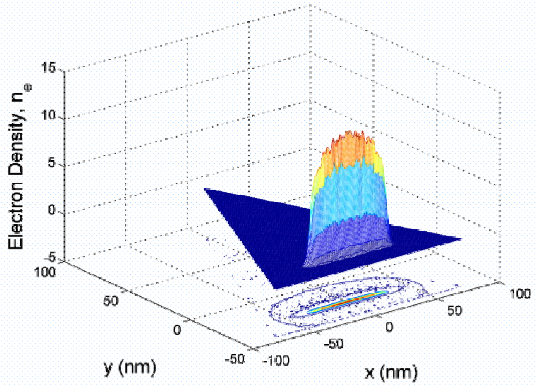
electron density, Ga-face



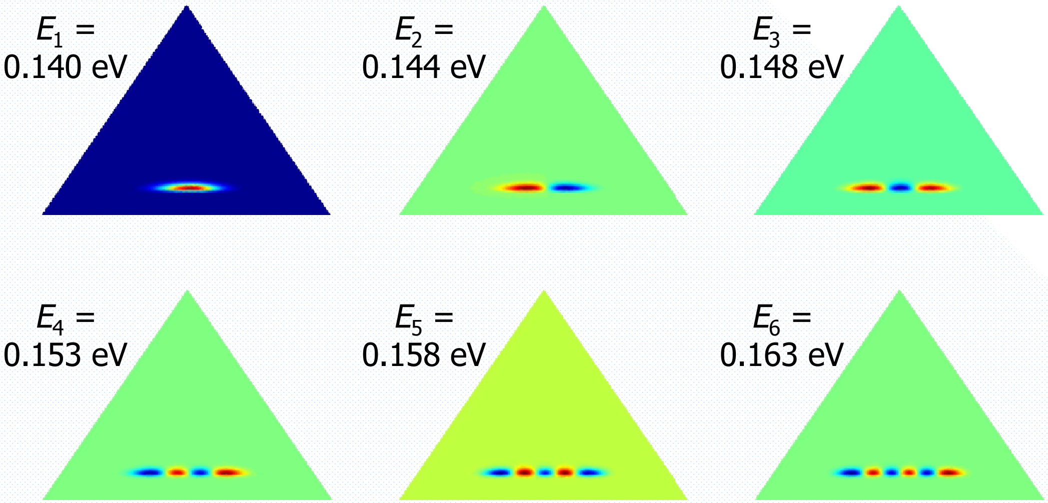


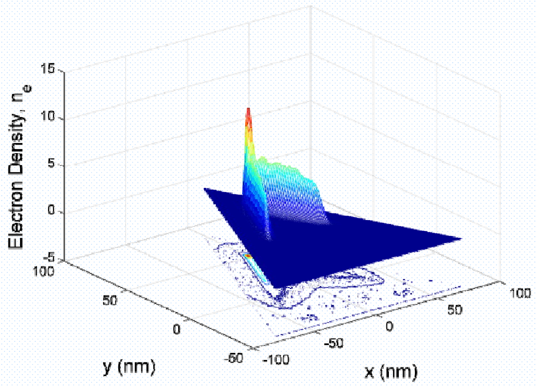
B.M. Wong , F. Leonard, et al. *submitted* (2011)

Electron density maps

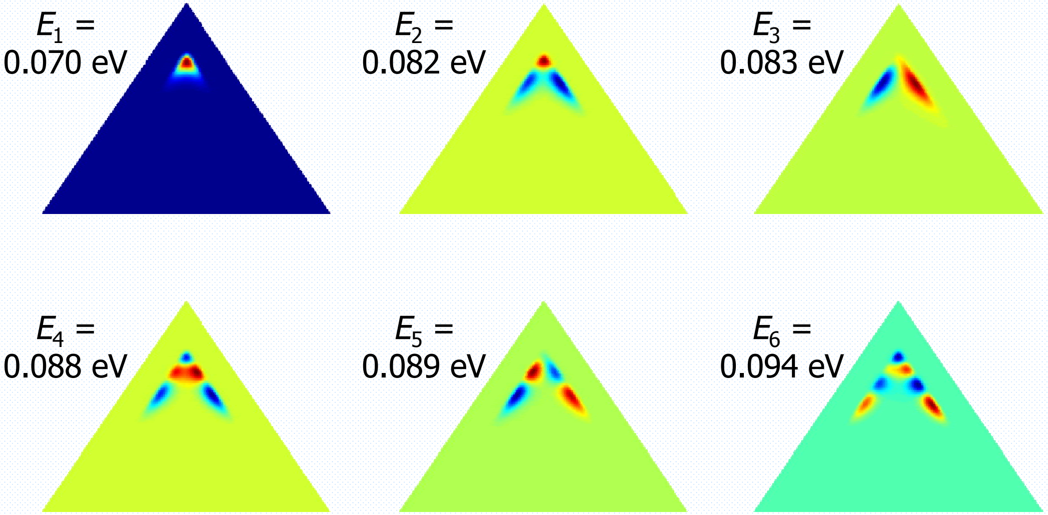


electron density, N-face





electron density, Ga-face

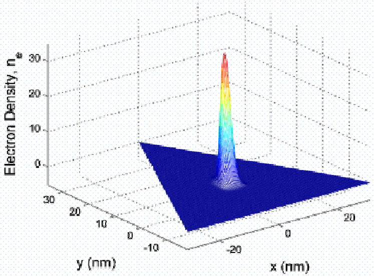


B.M. Wong , F. Leonard, et al. *submitted* (2011)

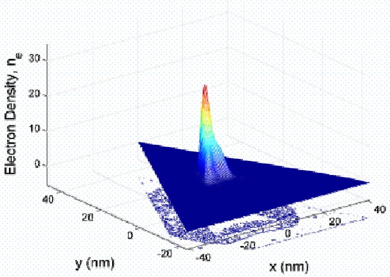
Variations in size

- How does electron gas *evolve with size?*

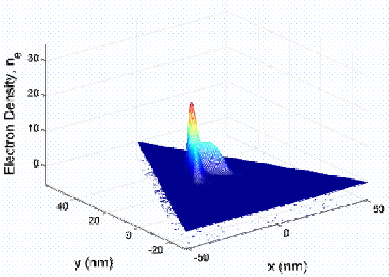
core size = 10 nm



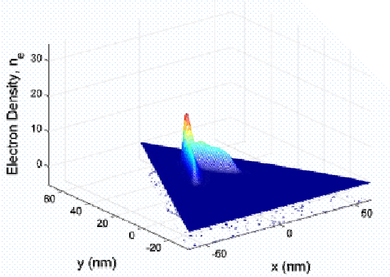
core size = 30 nm



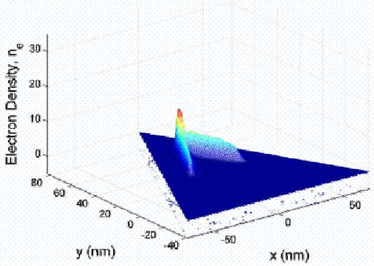
core size = 50 nm



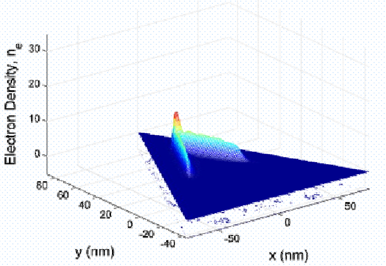
core size = 70 nm



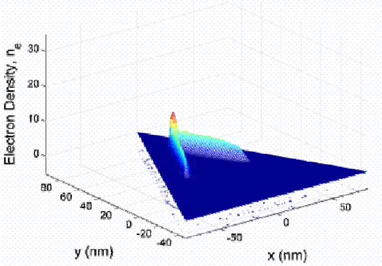
core size = 90 nm



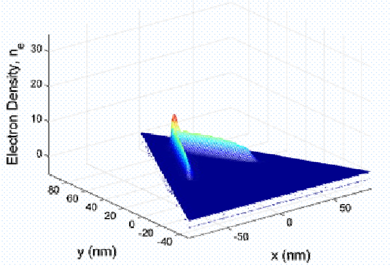
core size = 100 nm



core size = 110 nm



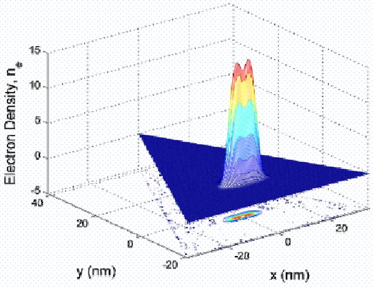
core size = 120 nm

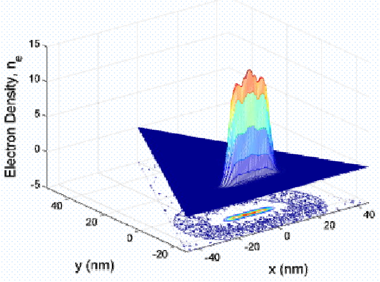


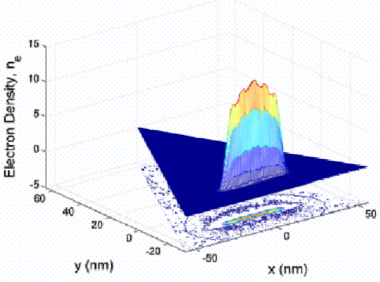
B.M. Wong , F. Leonard, et al. *submitted* (2011)

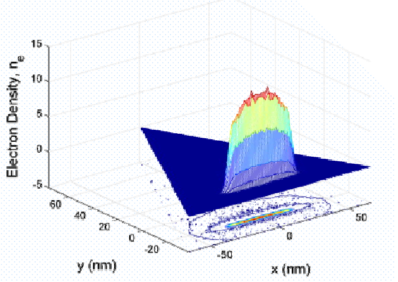
Variations in size

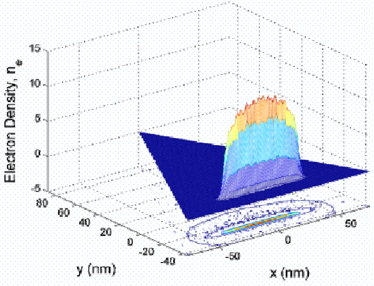
- N-face electron gas:

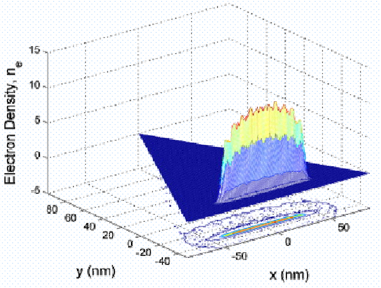

core size = 20 nm

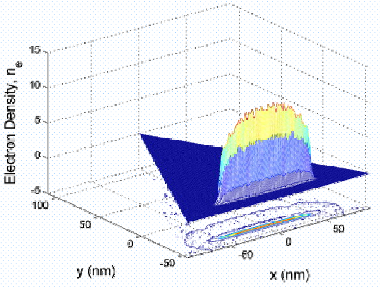

core size = 40 nm

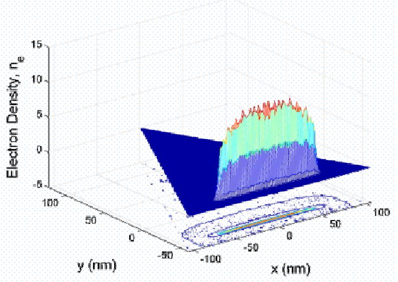

core size = 60 nm


core size = 80 nm


core size = 100 nm


core size = 120 nm


core size = 140 nm

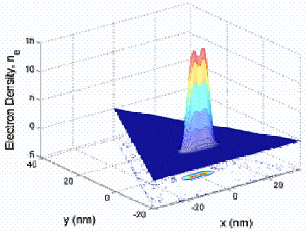

core size = 160 nm

- Core size large → recover bulk behavior

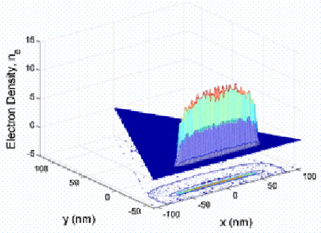
B.M. Wong , F. Leonard, et al. *submitted* (2011)

Critical doping level

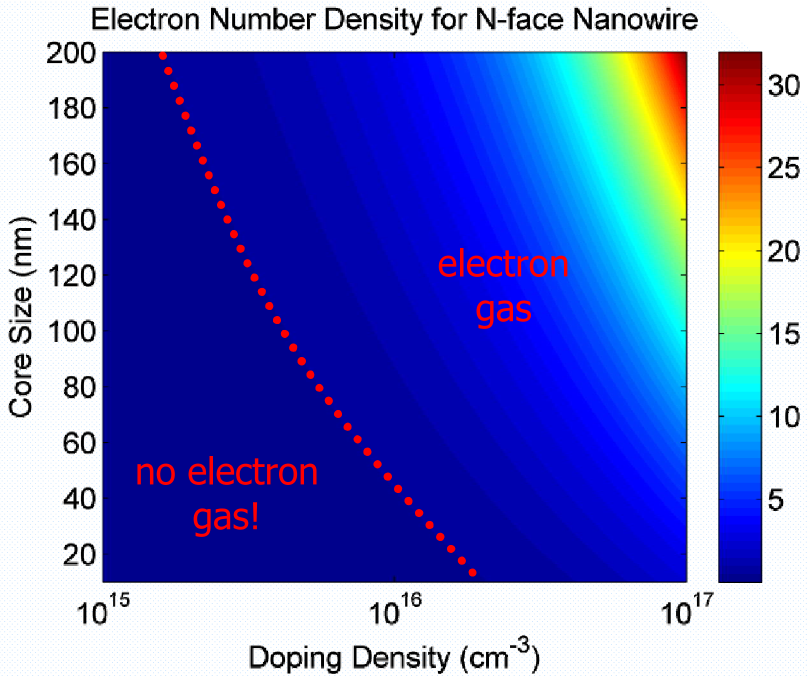
- Parametric study of electron gas formation



core size = 10 nm



core size = 200 nm

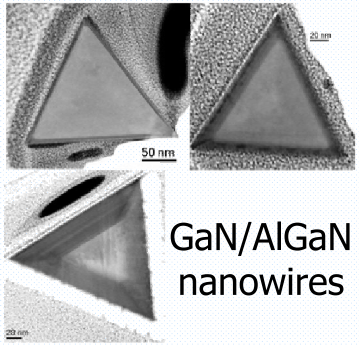


- Electron gas formation requires *higher doping* at *nanoscale dimensions*

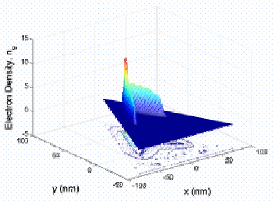
B.M. Wong , F. Leonard, et al. *submitted* (2011)

Conclusions

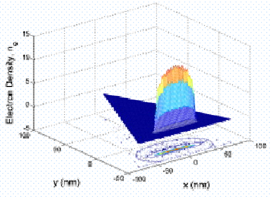
- Reduction in dimensionality leads to *quasi-1D electron gases at corners/interfaces*
- Methodology very *general* (can include other effects)
- Calculations allow *guided understanding of electron gas formation in heterostructure nanowires*
- Excellent *synergistic area* for theory and experiment



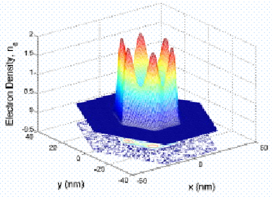
GaN/AlGaN nanowires



N-face



Ga-face

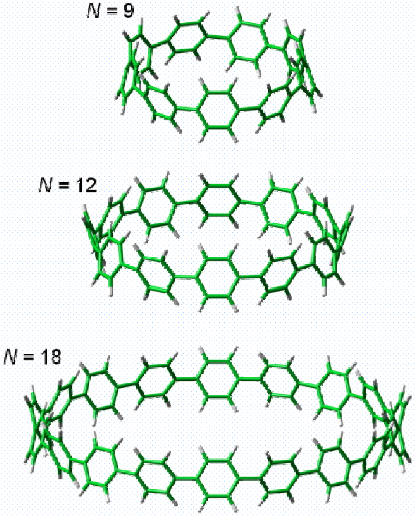


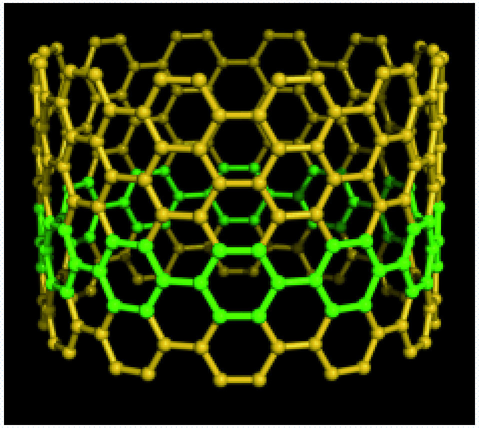
nonpolar hexagonal

B.M. Wong , F. Leonard, et al. *submitted* (2011)

Organic nanostructures

- Molecular carbon nanorings
- First synthesized in Sept. 2008 (Berkeley)
  - *J. Am. Chem. Soc.* **130**, 17646 (2008)





(12,12) carbon nanotube

  - Each nanoring is fundamental unit of armchair nanotube

Unexpected excitation spectra

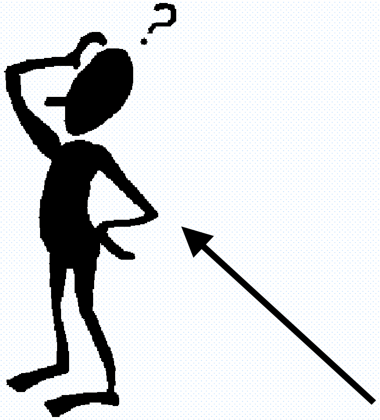
- Experiments showed absorption energy *increases* with nanoring size!
- Seems to contradict quantum confinement effects

Unexpected excitation spectra

- Experiments showed absorption energy *increases* with nanoring size!
- Seems to contradict quantum confinement effects

Particle in a box: $E_n = \dfrac{n^2 h^2}{8mL^2}$

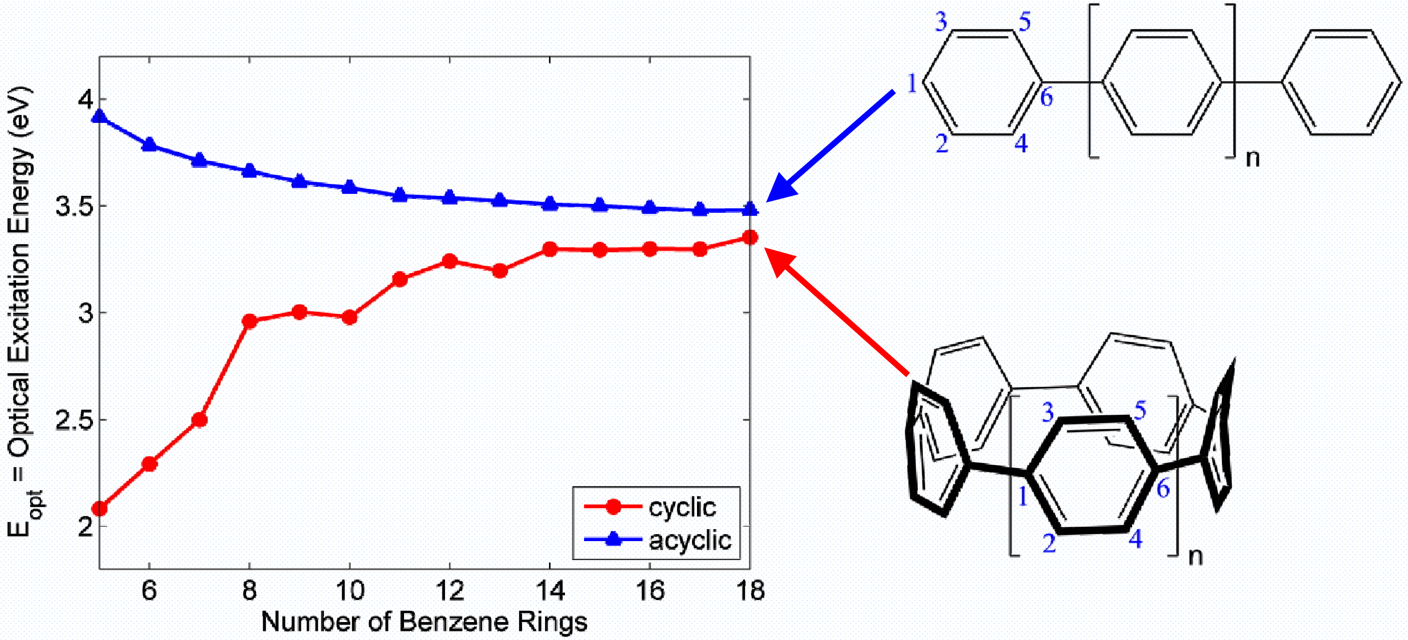
Particle on a ring: $E_n = \dfrac{n^2 \hbar^2}{2mr^2}$



Bryan M. Wong

Theoretical analysis

- Compared both linear and cyclic structures containing 5 – 18 phenyl units
- Excited-state quantum calculations (TD-DFT)



Excitonic effects

- *Transition density matrix*

$$\left(Q_v\right)_{mn} = \left\langle \psi_v \middle| c_m^\dagger c_n \middle| \psi_g \right\rangle + \left\langle \psi_g \middle| c_m^\dagger c_n \middle| \psi_v \right\rangle$$

Excitonic effects

- *Transition density matrix*

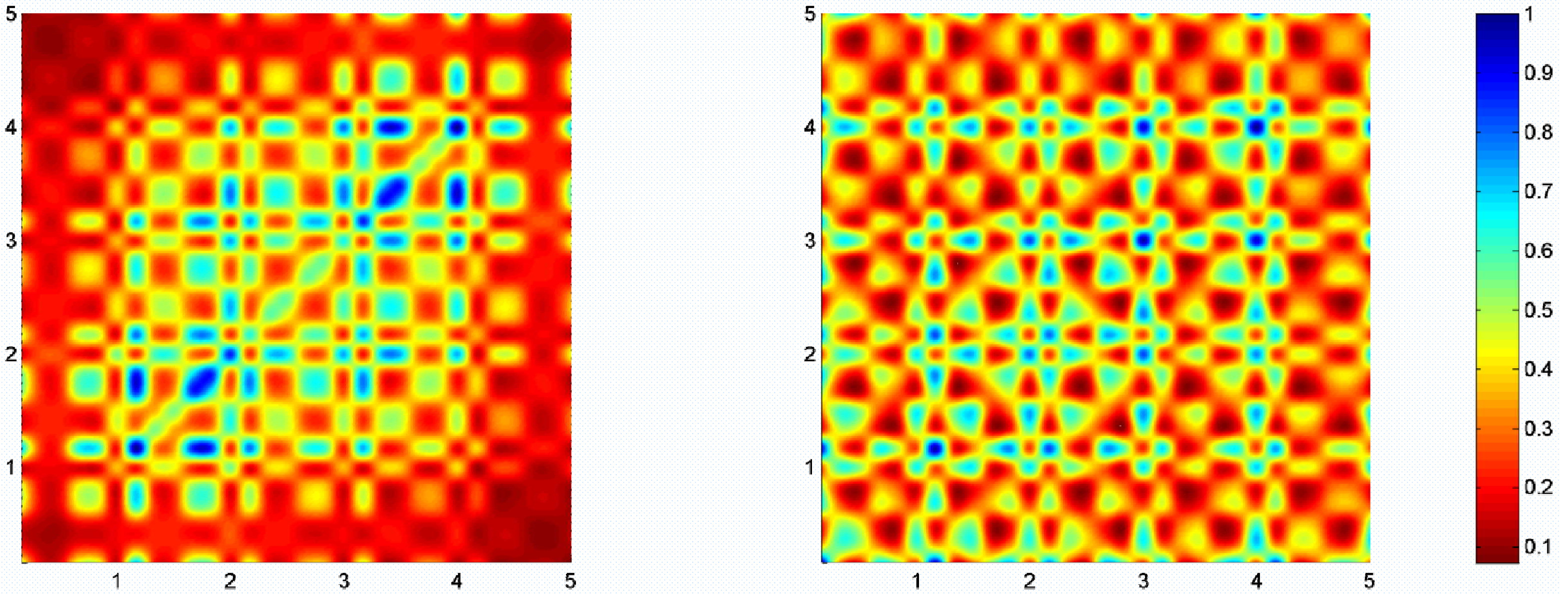
$$(Q_v)_{mn} = \langle \psi_v | c_m^\dagger c_n | \psi_g \rangle + \langle \psi_g | c_m^\dagger c_n | \psi_v \rangle$$

- ψ_g and ψ_v = ground and excited states
- $c_i^\dagger$ and c_i = creation and annihilation of electron in *i*th basis orbital in ψ
- $(Q)_{mn}$ gives *joint probability of electron-hole delocalization* between sites *m* and *n*

Transition density matrix

$$\left(Q_v\right)_{mn} = \left\langle \psi_v \middle| c_m^\dagger c_n \middle| \psi_g \right\rangle + \left\langle \psi_g \middle| c_m^\dagger c_n \middle| \psi_v \right\rangle$$

N = 5



linear

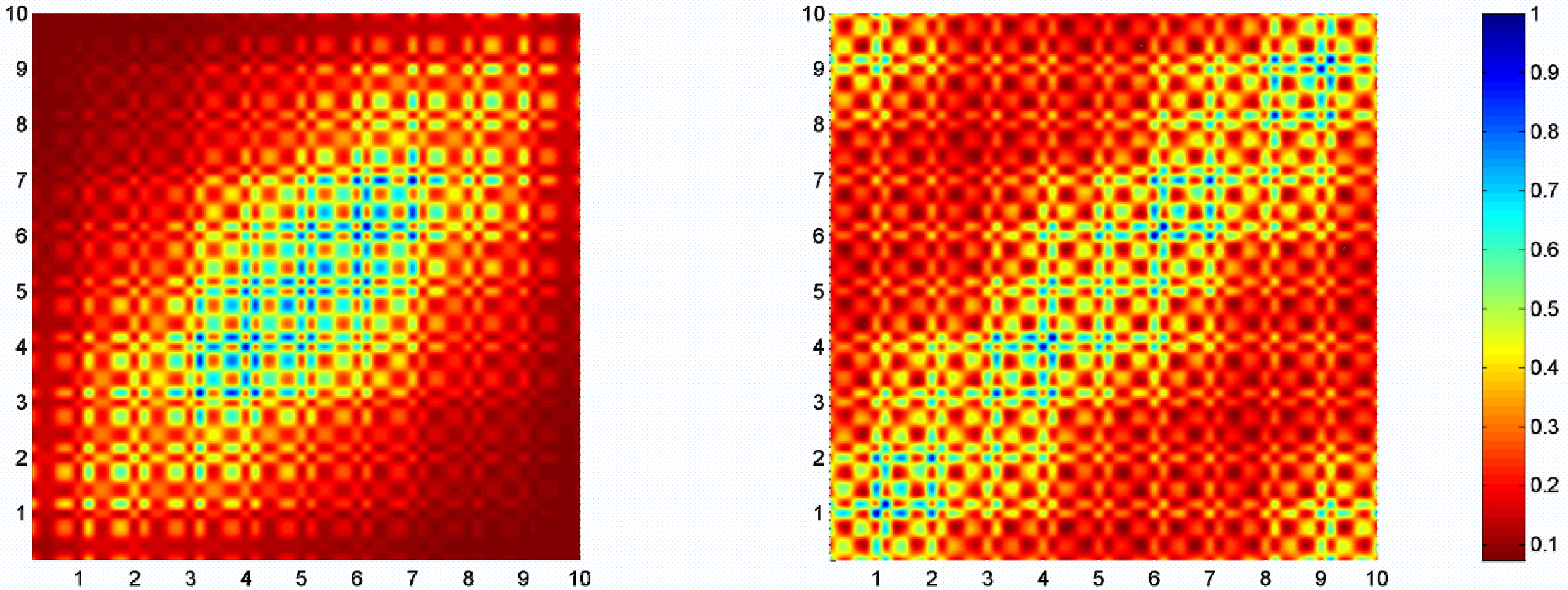
cyclic

B.M. Wong, *J. Phys. Chem. C* **113**, 21921 (2009)

Transition density matrix

$$(Q_v)_{mn} = \langle \psi_v | c_m^\dagger c_n | \psi_g \rangle + \langle \psi_g | c_m^\dagger c_n | \psi_v \rangle$$

N = 10



linear

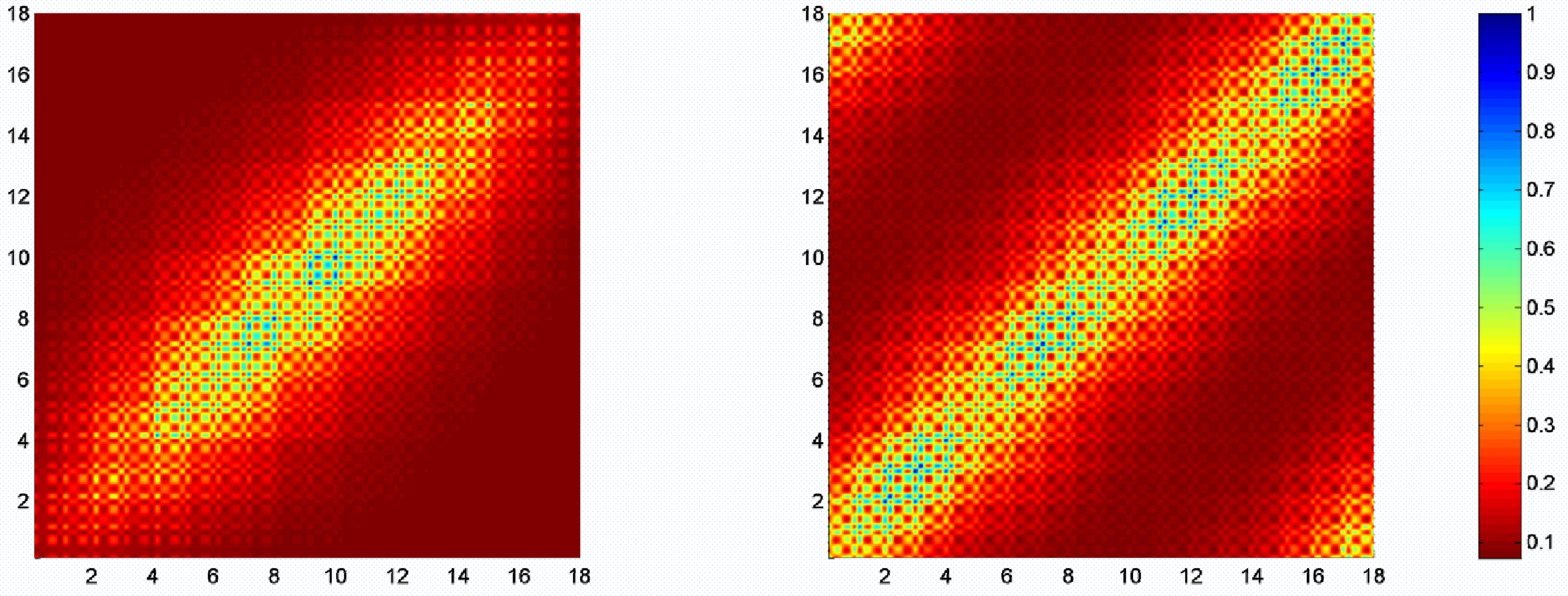
cyclic

B.M. Wong, *J. Phys. Chem. C* **113**, 21921 (2009)

Transition density matrix

$$(Q_v)_{mn} = \langle \psi_v | c_m^\dagger c_n | \psi_g \rangle + \langle \psi_g | c_m^\dagger c_n | \psi_v \rangle$$

N = 18

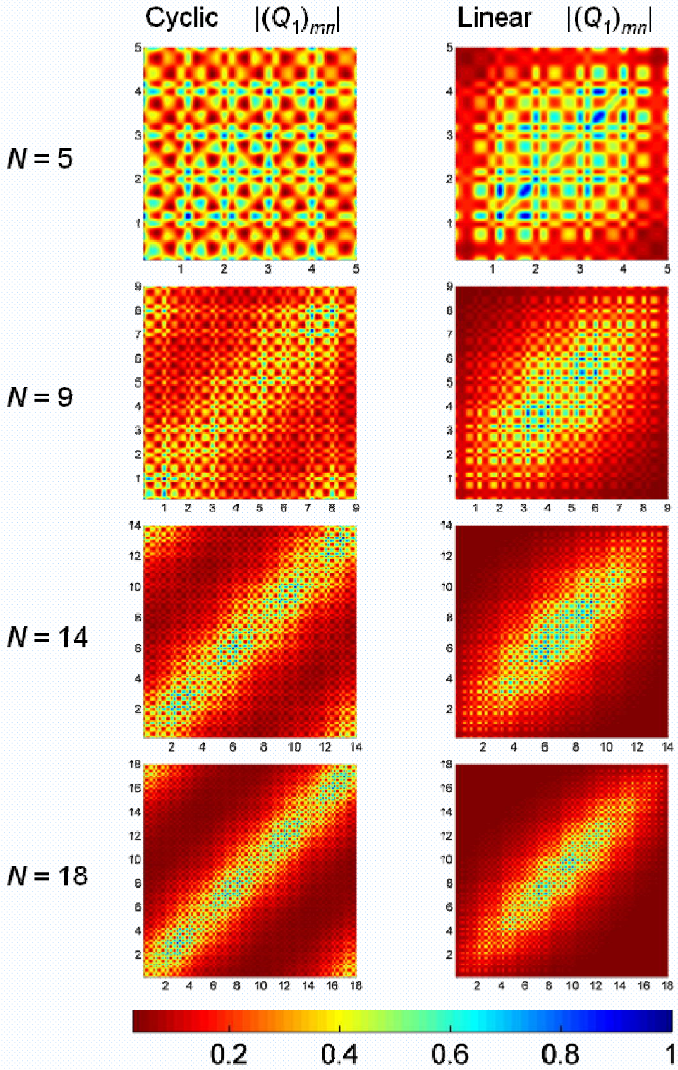


linear

cyclic

B.M. Wong, *J. Phys. Chem. C* **113**, 21921 (2009)

Exciton delocalization

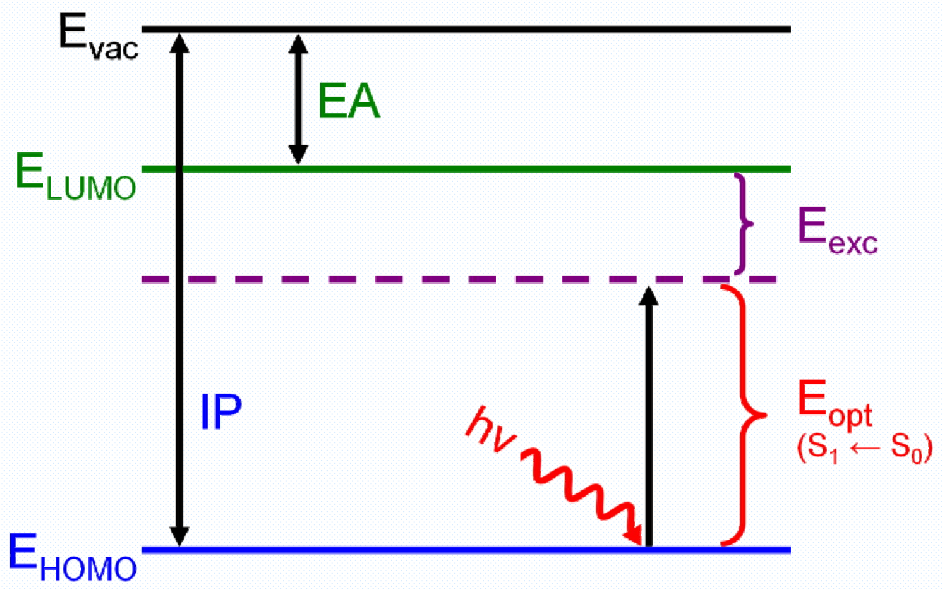


linear geometry: electron-hole pair localized in middle and *away from edges*

cyclic geometry: electron-hole pair delocalized over *entire circumference*

B.M. Wong, *J. Phys. Chem. C* **113**, 21921 (2009)

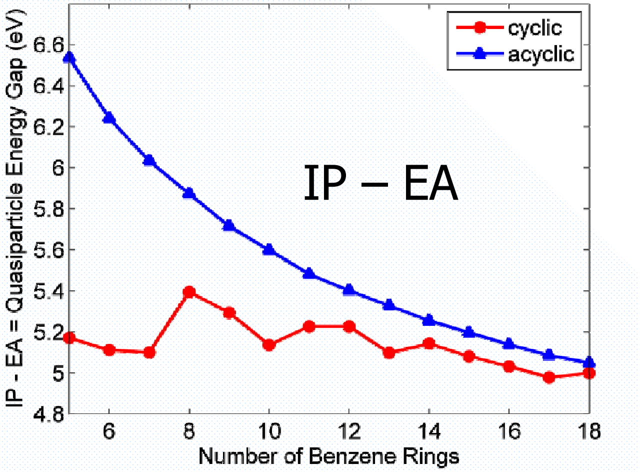
Exciton binding strength

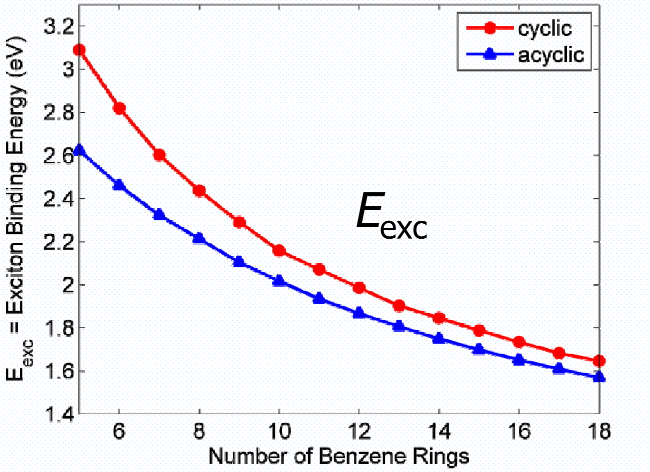


E_{exc} = IP – EA – E_{opt}

E_{opt} = IP – EA – E_{exc}

cyclic geometry: IP – EA decreases significantly slower than E_{exc}
→ ***E_{opt} increases with size***



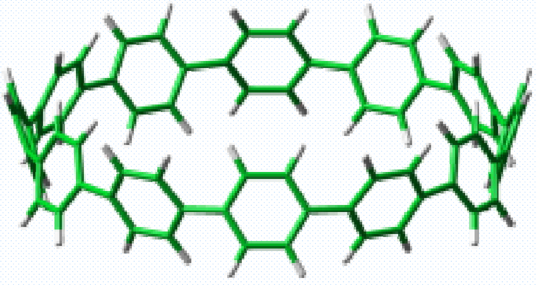


B.M. Wong, *J. Phys. Chem. C* **113**, 21921 (2009)

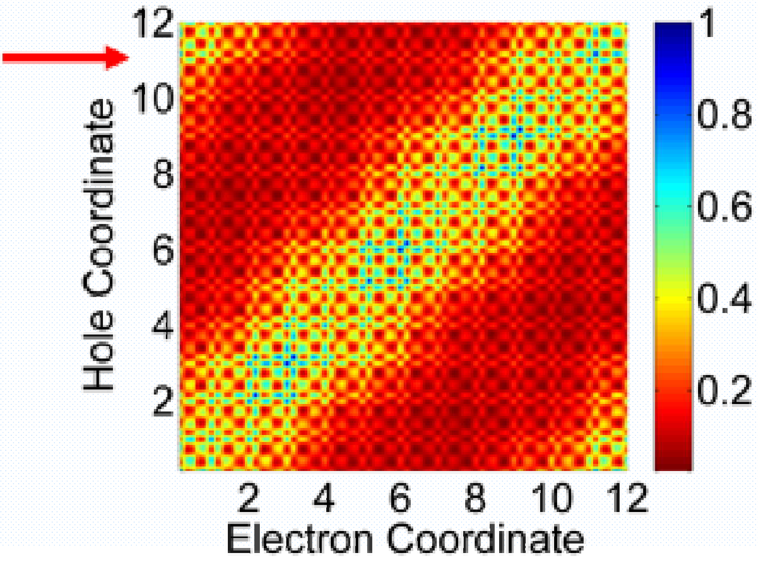
Conclusions

- *First-principles quantum calculations* reveal mechanism of unexpected excitation spectra
- *Excitonic effects* play important role in unusual optical properties of nanorings

delocalized electron-hole transition density matrix



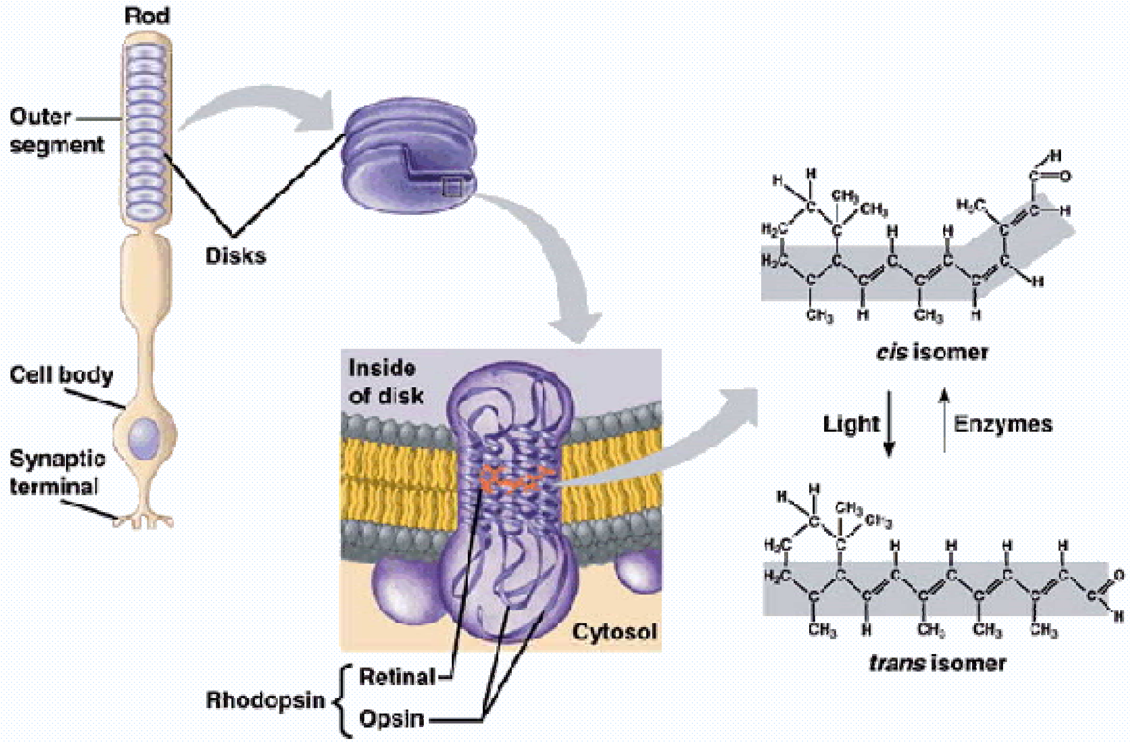
carbon nanoring



B.M. Wong, *J. Phys. Chem. C* **113**, 21921 (2009)

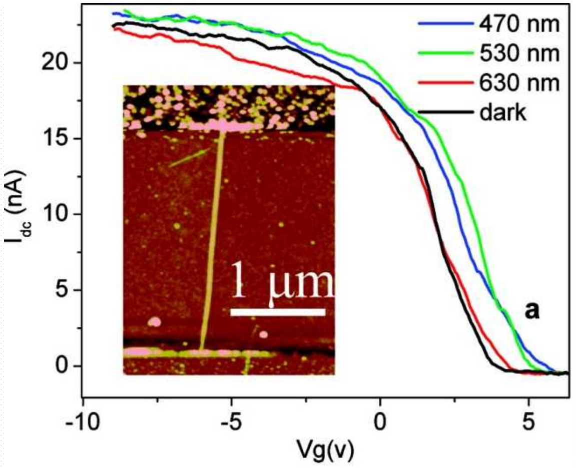
Optical detection in nanotubes

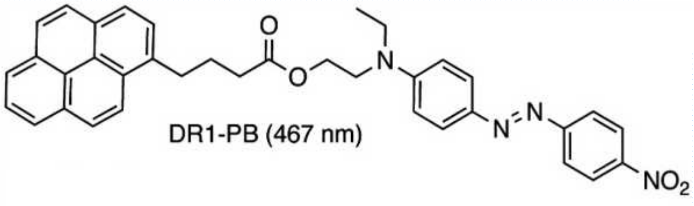
- Inspiration from Nature



  - Human vision relies on *conformational change* in rhodopsin

Optical detection in nanotubes



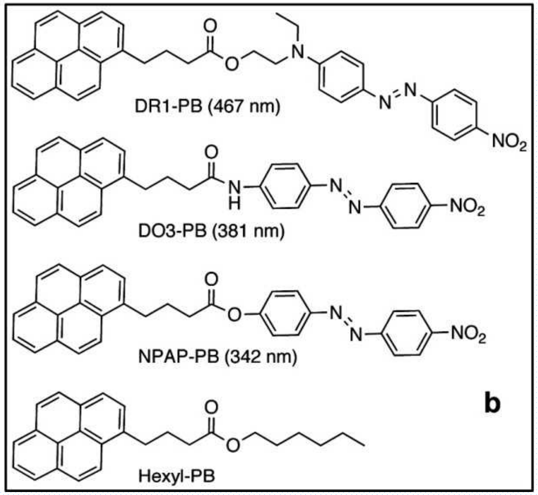


semi-conducting carbon nanotube
functionalized with DR1-PB

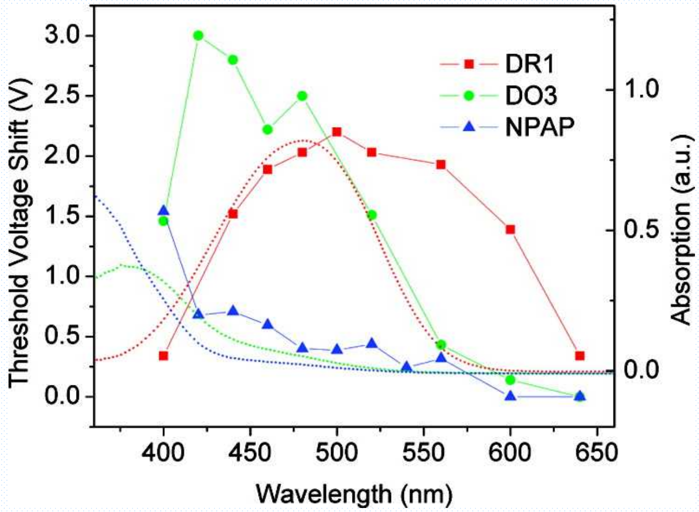
- Threshold voltage of nanotube shifts at 470 nm (blue) & 530 nm (green)
- Voltage unchanged for red light

Color Detection

- Can use different chromophores to make sensitive nanoscale color-detector



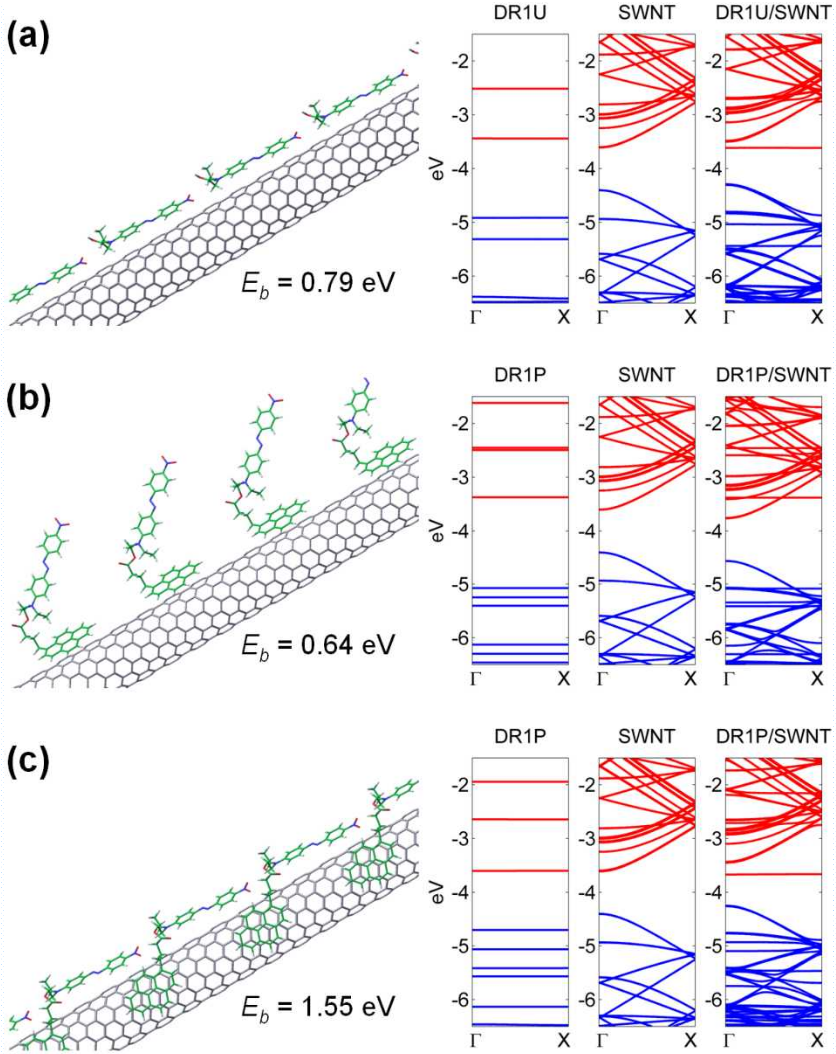
Structures and absorbance maxima of different chromophores



Threshold voltage of functionalized nanotube correlates with absorption spectra (dotted curves) of isolated molecule

X. Zhou, T. Zifer, B.M. Wong, et al. *Nano Letters.* **9**, 1028 (2009)

Quantum calculations



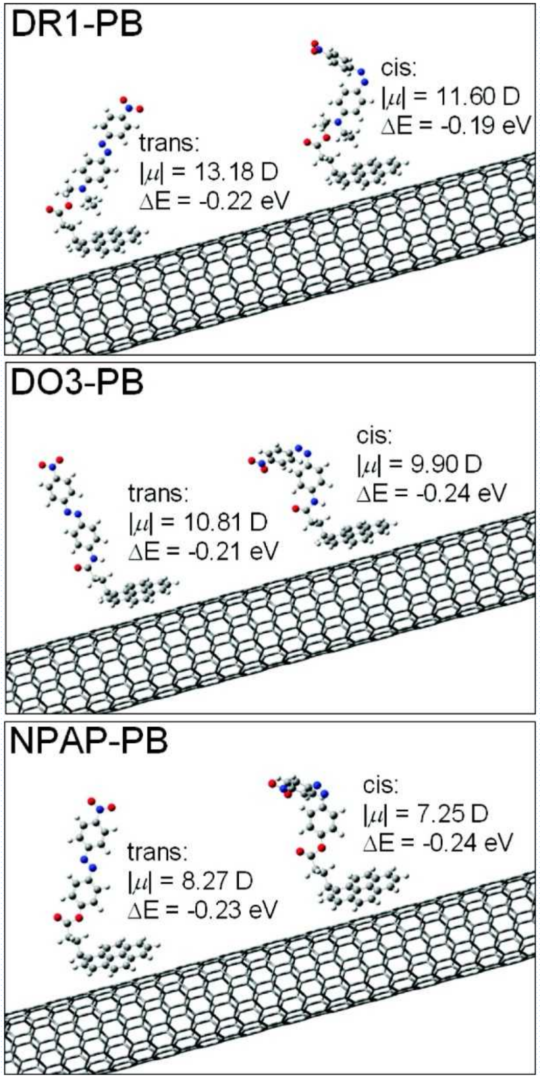
Calculations show DR1 binds *noncovalently* to nanotube surface

Binding relatively strong but *band gap of nanotube is unchanged*

Total bandstructure is superposition of molecule + nanotube

X. Zhou, T. Zifer, B.M. Wong, et al. *Nano Letters.* **9**, 1028 (2009)

Dipole-moment mechanism



Absorption of photon causes chromophore isomerization from *trans* → *cis* configurations

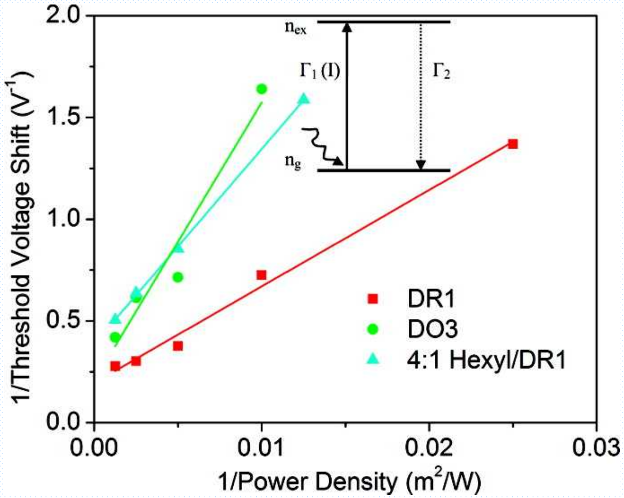
trans (stable) and *cis* (metastable) forms have very different dipole moments (> 1 Debye)

Large change in dipole moment modifies electrostatic environment of nanotube

X. Zhou, T. Zifer, B.M. Wong, et al. *Nano Letters.* **9**, 1028 (2009)

A simple model

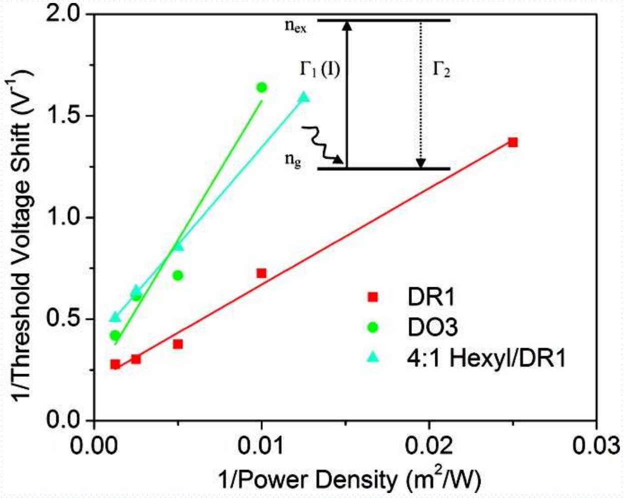
- *cis* → *trans* isomerization well described by two-level system



X. Zhou, T. Zifer, B.M. Wong, et al. *Nano Letters.* **9**, 1028 (2009)

A simple model

- *cis* → *trans* isomerization well described by two-level system



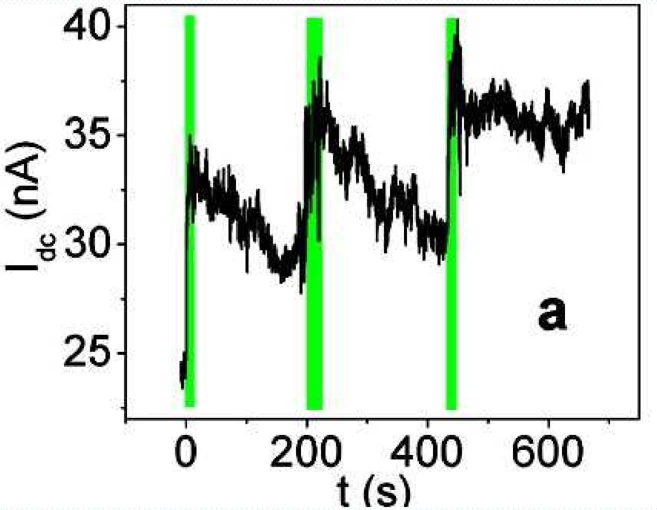
$$\Delta V_g^{-1} = \left(1+\frac{\Gamma_2}{\alpha} I^{-1}\right)\left[\frac{C_{\text{NT}}}{C_{\text{tot}}}\left(V_{\text{trans}}-V_{\text{cis}}\right)\right]^{-1}$$

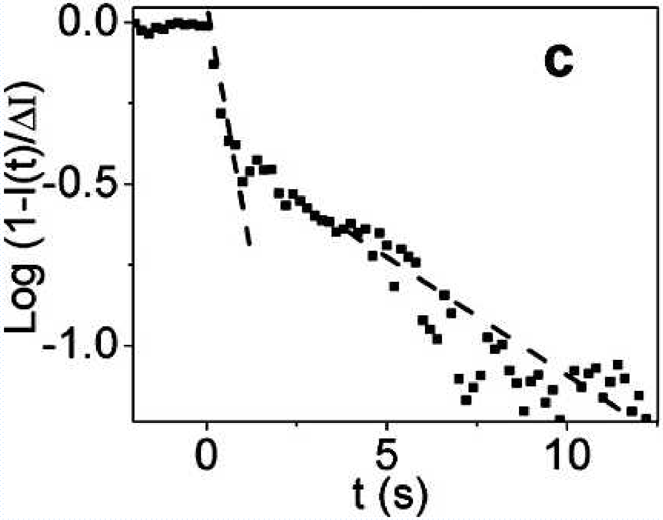
- Voltage^{-1} proportional to (illumination power)$^{-1}$

X. Zhou, T. Zifer, B.M. Wong, et al. *Nano Letters.* **9**, 1028 (2009)

Interesting kinetics

- Reversible photo-induced conductance





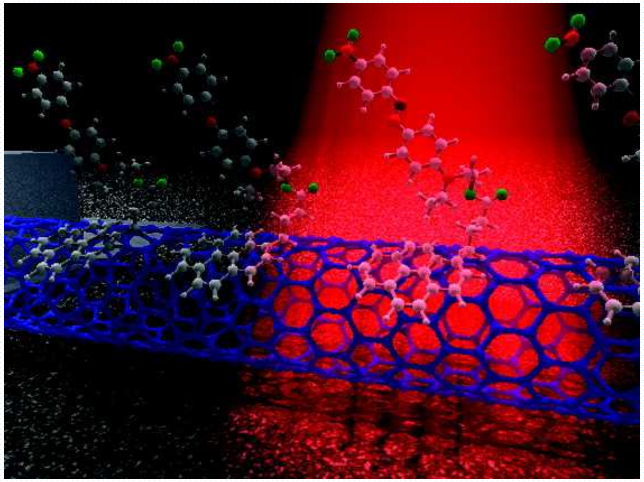
Conduction of nanotube device increases upon illumination & fully reversible

2 different time scales:
(1) fast illumination
(2) slow relaxation

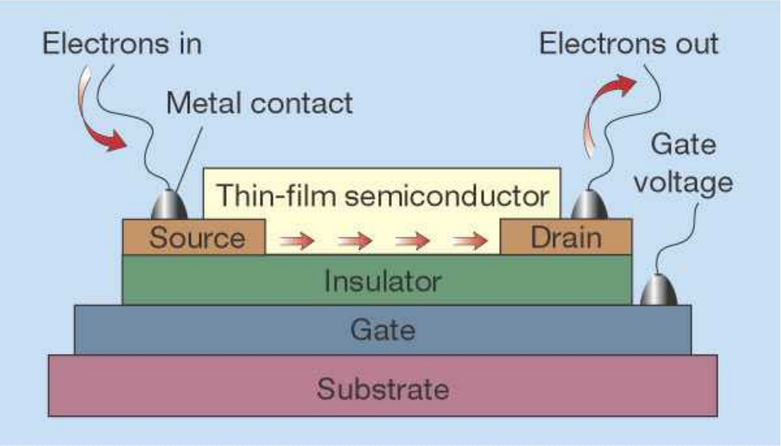
X. Zhou, T. Zifer, B.M. Wong, et al. *Nano Letters.* **9**, 1028 (2009)

Conclusions

- Sensitive nanoscale color detector
- Nanoscale field effect transistor (FET)!



carbon nanotube FET
with *tunable molecular gate*



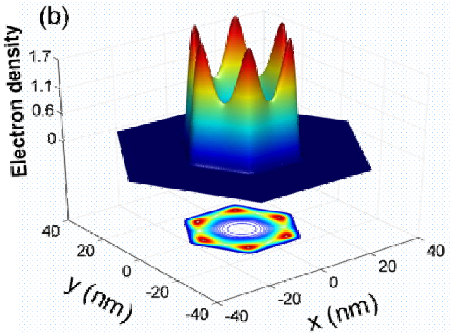
conventional solid-state FET

Featured in *Nature Photonics* **3**, 192 (2009)

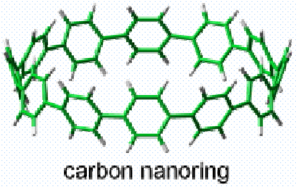
X. Zhou, T. Zifer, B.M. Wong, et al. *Nano Letters.* **9**, 1028 (2009)

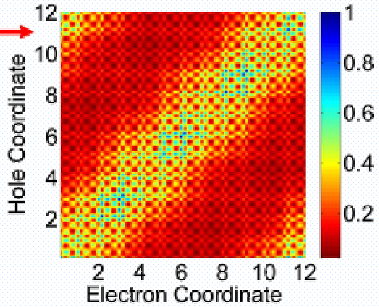
Wrap up

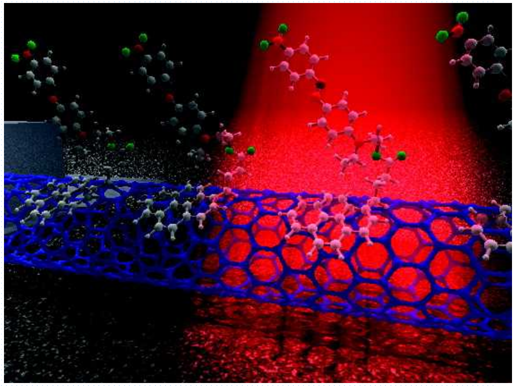
- Extremely interesting electronic effects at nanoscale dimensions
- *Synergistic area* for theory and experiment



delocalized electron-hole transition density matrix


carbon nanoring





(1) B.M. Wong
J. Phys. Chem. C **113**, 21921 (2009)

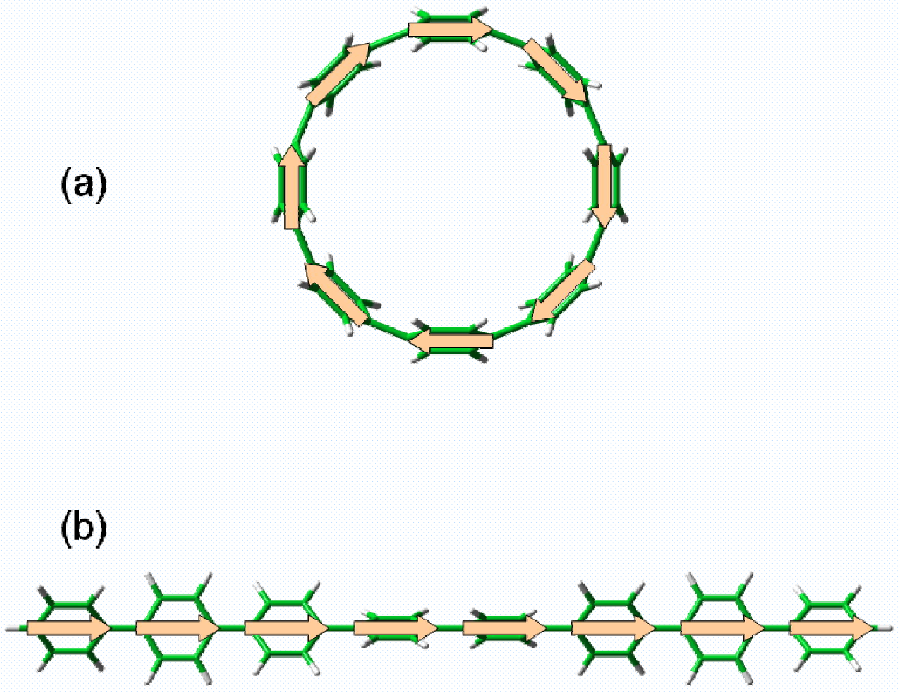
(2) B.M. Wong, T.H. Hsieh
J. Chem. Theor. Comput. **6**, 3704 (2010)

(3) X. Zhou, T. Zifer, B.M. Wong, K.L. Krafcik
F. Leonard, A.L. Vance
Nano Lett. **9**, 1028 (2009) & *Nature Photonics* **3**, 192 (2009)

Bryan M. Wong
bmwong@sandia.gov

Senior Member of Technical Staff
Sandia National Laboratories

Transition dipole moments

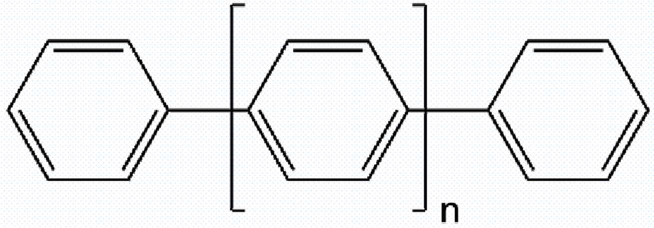


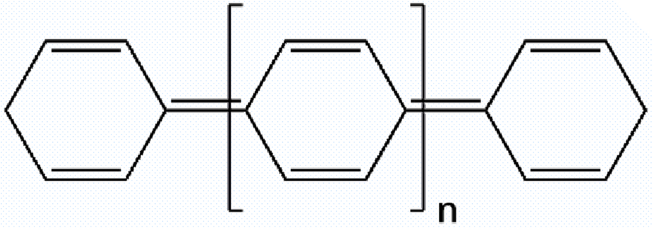
(a) Transition moments in cyclic geometry effectively cancel

(b) Total transition moment increases with length in linear system

B.M. Wong, *J. Phys. Chem. C* **113**, 21921 (2009)

Quasiparticle gap & aromaticity





aromatic

electrons *localized* within phenyl ring

energetically *stable*

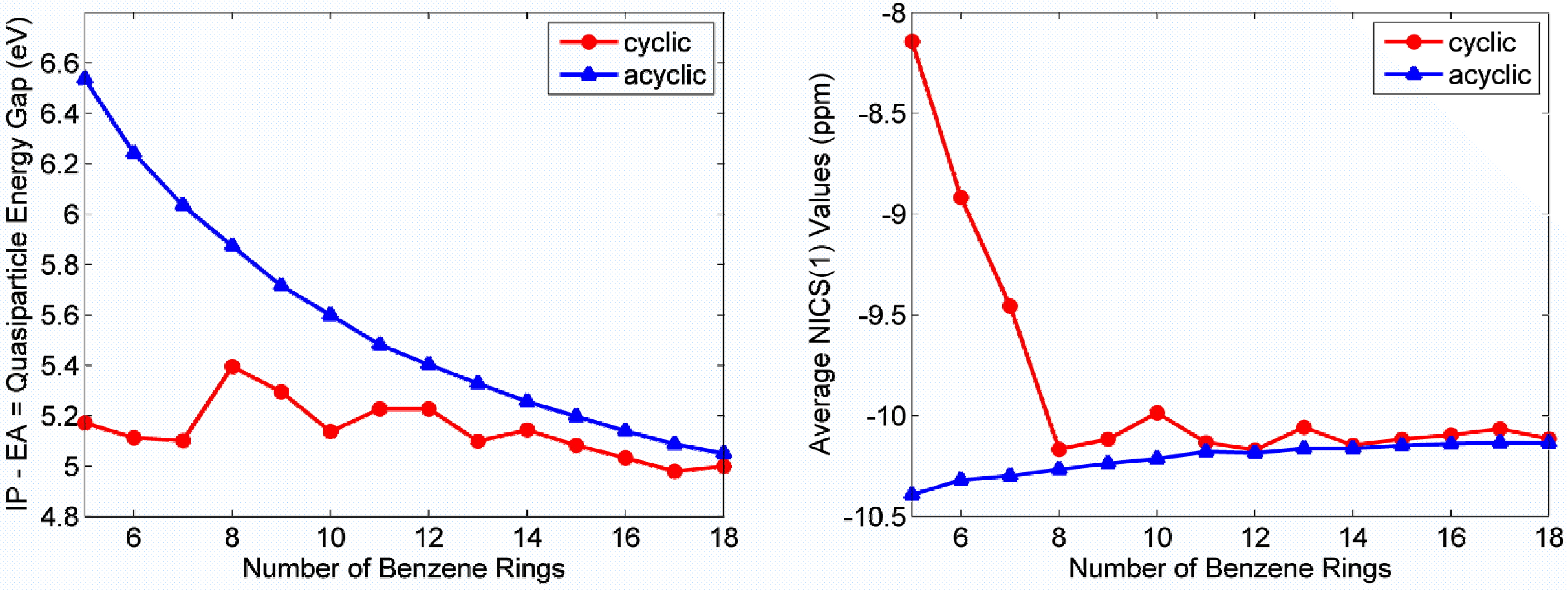
quinoid

electrons *delocalized* across entire structure

energetically *less stable*

B.M. Wong, *J. Phys. Chem. C* **113**, 21921 (2009)

Quasiparticle gap & aromaticity

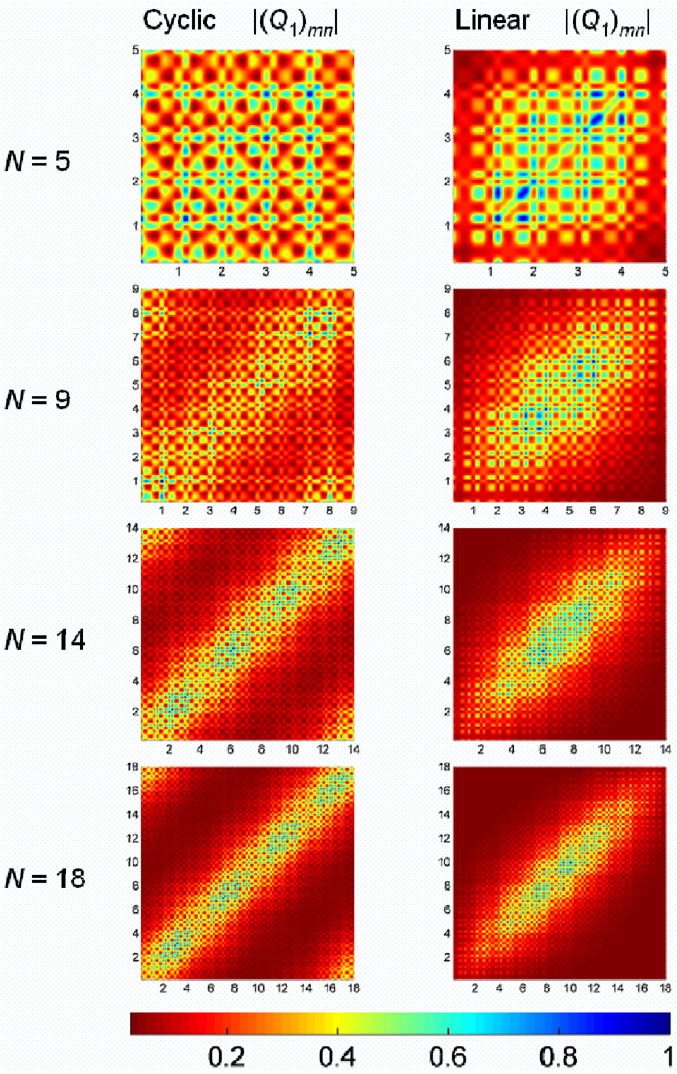


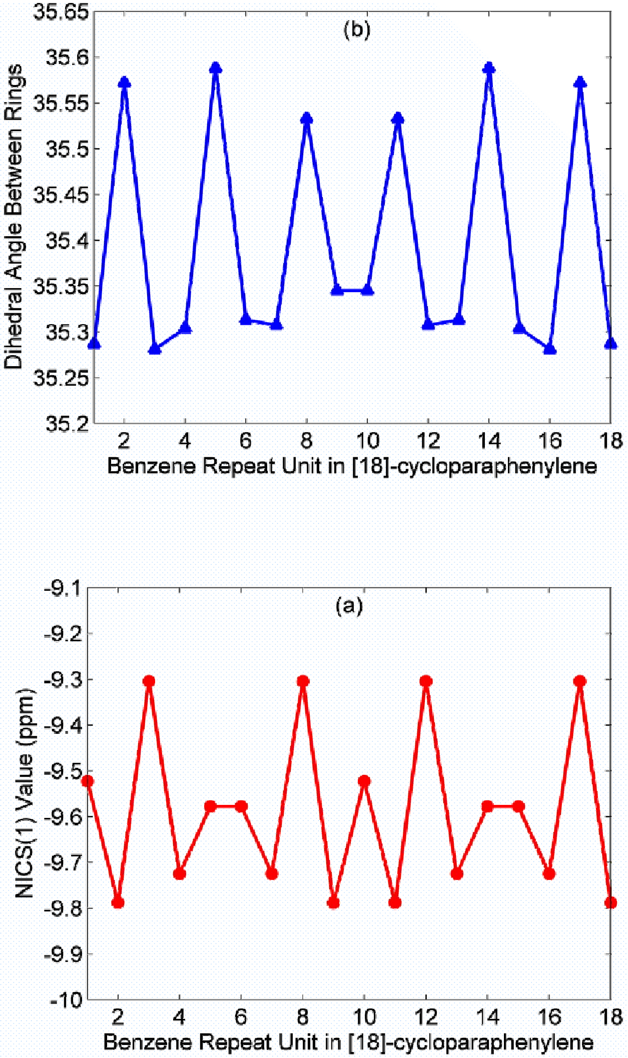
Less negative Nucleus-Independent Chemical Shift (NICS) values correspond to *quinoidal character (destabilization)*

Smaller nanorings are electronically destabilized (smaller quasiparticle gap)

B.M. Wong, *J. Phys. Chem. C* **113**, 21921 (2009)

Delocalization & aromaticity





B.M. Wong, *J. Phys. Chem. C* **113**, 21921 (2009)