Nano-Sensing, Nano-Electronics/Spintronics, and Nano-Optics

Kwang S. Kim

Center for Superfunctional Materials
Dept. of Chemistry
Pohang University of Science and Technology
Functional Molecules/Materials:
Design Strategy toward
* Creation of new paradigms for designing innovative quantum molecular/nanomaterial systems
* Extending the frontiers of current research in the creation of futuristic electronic/spintronics/optical devices
* Invention of revolutionary technologies for bio-nano-info interfaces

CAMD Examples: Quantum Theory, DFT, ab initio theory, MD, NEGF

Nano-recognition: Self-assembly, Self-synthesis

Organic Nanotubes, Metallic Nanostructures \((\text{Science})\)
Ionophores, Receptors, Enzymes; Fullerenes, CNT, Nanotori
Nanomechanical Devices, Photoswitches, DNA Sequencing

Transport Phenomena: DFT+NEGF

Molecular Electronics / Spintronics: Quantum Computing
Metals, CNT, Graphene: \((\text{Nature})\)
Electrodes: Graphene to replace ITO \((\text{Nature Nanotech.})\)
Super Magneto Resistance (SMR) in GNR: \((\text{Nature Nanotech.})\)

Nano-optics: nanolens: \((\text{Nature})\)
Near field focusing and magnification beyond diffraction limit thru nanolens
- Self-assembled materials & Self-engineered devices
- Extended supramolecular chemistry
  Host-guest interactions: Guests include electron/photon/proton
- Quantum phenomenon driven nano-materials/devices

Molecular architectures

Functional nano-materials

Material characterization
Correlation spectroscopy

Chemical/Bio-functional systems

Nano-devices

Superfunctional Materials/Devices

- Enzyme Mimetics
- Bioinformatics

- Single electron/photon molecular devices
- Electronics & Mechanics
- Molecular & quantum computing
- Biosensors, biochips, DNA sequencing
Motivation

Synthesis of Nanomaterials
Unusual electrochemical/photochemical properties
[Quantum properties <= CAMD]

Novel Nanostructures
Design of Nanodevices and Nanosensors
Self-engineered electronics
(Interaction forces: competition vs. cooperation)

Research Strategy

Computer-aided molecular design approach

Nanorecognition
Self-assembly, Self-synthesis

Synthesis of Building Blocks

Characterization
(structure, properties)

Nanomaterials Nanostructures

Nanodevices Nanosensors
Design Strategy:

Calculation Methods

Atomic and Molecular systems
  Semiempirical, Tight Binding
  Density Functional:
  Ab initio: MP2, CCSD(T)
Periodic crystal systems:
  PW-DFT
Simulations:
  MC
  MD
  CP-MD, ab initio MD
  Excited state ab initio MD
  Free energy Perturbation

Theor. Interpretation

Prediction & Design
  Quantum Devices – NT

Nonequilibrium
  Quantum Electrodynamics
Nanowires, \textit{PRL}, Nanotubes, \textit{JACS}, Fullerenes, \textit{PRL}

Nonlinear optical & Chiral Switches

(Achievements)

Functional Molecules, Materials, Sensors, Devices

Molecular Interactions: \textit{Chem. Rev.}

Moleculae electronics, \textit{PRL}


Electrochemical control of mechanical devices

\textit{Org. Lett.}


Angew Chem

PNAS

Nature Nanotech

Nano-electronic/spintronic Devices

Nanomechanical Devices

Medical Sensors
Electron tweezers

Electron Carriers

Dynamical motion of electron charge density in water for every 10 fs
Tuning Molecular Orbitals in Molecular Electronics/Spintronics
Spintronics: Spin + Electronics
utilizing electron spin for electronic devices

Key Features in Spintronics
Spin has long coherence or relaxation time (non-volatile)
Controlling spin requires much less energy than charges.
Spin has the information of phase (quantum coherence).

Spin Valve Devices

Applications
Hard Disk Drive
Giant Magnetoresistance
(Fert & Grünberg)
(Nobel Prize: 2007)

Magnetic Random Access Memory
Tunneling Magnetoresistance
Tunneling Magnetoresistance

\[ R_P = \frac{R_{\text{large}} R_{\text{small}}}{R_{\text{large}} + R_{\text{small}}} \approx R_{\text{small}} \]

\[ R_{\text{AP}} = \frac{R_{\text{large}}}{2} \]
Structure of Magnetic Junction

Non-magnetic metal
Insulator
Semiconductor
Superconductor

Non-magnetic metal (GMR): HDD Head

Parallel
small resistance

AParallel
large resistance

Insulator (TMR): MRAM
## Magnetoresistance

### MR in TMR

<table>
<thead>
<tr>
<th>Material</th>
<th>MR at RT</th>
<th>MR at 5K</th>
</tr>
</thead>
<tbody>
<tr>
<td>F/Al$_2$O$_3$/F</td>
<td>MR 30~70%</td>
<td></td>
</tr>
<tr>
<td>Fe/MgO/Fe</td>
<td>MR 220%</td>
<td>(CMR)</td>
</tr>
<tr>
<td>CoFeB/MgO/CoFeB</td>
<td>MR 472%</td>
<td>at RT</td>
</tr>
<tr>
<td></td>
<td>MR 804%</td>
<td>at 5K</td>
</tr>
</tbody>
</table>

### Difference in resistance between parallel (P) and anti-parallel (AP) magnetoresistance ratio:

\[
MR = \frac{R_{AP} - R_P}{R_P} = \frac{I_P - I_{AP}}{I_{AP}}
\]

To become an **ideal** spin valve, the MR ratio should be **infinite**.

**GMR**: MR 10~20%

The MR ratio for TMR is **larger** than that for GMR.
Density of States (DOS) for 3D, 2D, 1D, 0D Nano Materials

**Classical:**
$L > 100\text{nm}$

**Quantum:**
$L < 10\text{nm}$
<table>
<thead>
<tr>
<th>Metal</th>
<th>3D</th>
<th>2D</th>
<th>1D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td><img src="image1.png" alt="Graph" /></td>
<td><img src="image2.png" alt="Graph" /></td>
<td><img src="image3.png" alt="Graph" /></td>
</tr>
<tr>
<td>Co</td>
<td><img src="image4.png" alt="Graph" /></td>
<td><img src="image5.png" alt="Graph" /></td>
<td><img src="image6.png" alt="Graph" /></td>
</tr>
<tr>
<td>Ni</td>
<td><img src="image7.png" alt="Graph" /></td>
<td><img src="image8.png" alt="Graph" /></td>
<td><img src="image9.png" alt="Graph" /></td>
</tr>
<tr>
<td>Ru</td>
<td><img src="image10.png" alt="Graph" /></td>
<td><img src="image11.png" alt="Graph" /></td>
<td><img src="image12.png" alt="Graph" /></td>
</tr>
<tr>
<td>Rh</td>
<td><img src="image13.png" alt="Graph" /></td>
<td><img src="image14.png" alt="Graph" /></td>
<td><img src="image15.png" alt="Graph" /></td>
</tr>
<tr>
<td>Pd</td>
<td><img src="image16.png" alt="Graph" /></td>
<td><img src="image17.png" alt="Graph" /></td>
<td><img src="image18.png" alt="Graph" /></td>
</tr>
<tr>
<td>Os</td>
<td><img src="image19.png" alt="Graph" /></td>
<td><img src="image20.png" alt="Graph" /></td>
<td><img src="image21.png" alt="Graph" /></td>
</tr>
<tr>
<td>Ir</td>
<td><img src="image22.png" alt="Graph" /></td>
<td><img src="image23.png" alt="Graph" /></td>
<td><img src="image24.png" alt="Graph" /></td>
</tr>
<tr>
<td>Pt</td>
<td><img src="image25.png" alt="Graph" /></td>
<td><img src="image26.png" alt="Graph" /></td>
<td><img src="image27.png" alt="Graph" /></td>
</tr>
</tbody>
</table>

**Magnetism of 3D, 2D, 1D Metals**

**metallic nano-magnets**

**PW-DFT scalar-relativistic**

*Phys Rev B 69, 193404 (2004)*
Infinitely long nanowire: intriguing quantum effects: highly unstable

- Only one minimum for the linear structure of the CsAu chain.
- Relatively large ratio (~3) of break force of the CsAu chain to that of the bulk CsAu crystal.

Fractional Quantum Conductance in the Thinning Process

Conductance

4/3 : ~ 4.2 Go
4/1 : ~ 3.5 Go
2/2 : ~2.7 Go
2/1 : ~2.6 Go

Peaks in Exp: 2.4, 4 Go

Electrode effects: fractionally quantized G value
Length dependence for G values: not significant

Calculation: Electron and Spin transport: POSTRANS 0.6

K-points sampling,
Finite Bias,
Spin Polarized Calculation
Non-collinear Calculation
Parallel Calculation
GGA & LDA

DFT:
Basis Set: DZ
Functional: GGA-PBE
Mesh Cutoff: 400 Ry
Geometry Optimization: 0.04 eV/Å

Spin-polarized NEGF Calculations

\[ G_{\sigma}^{r}(E) = \left[ ES - H_{\sigma} - \Sigma_{L\sigma}^{r} - \Sigma_{R\sigma}^{r} \right]^{-1} \]

\[ A(E) = \frac{i}{2\pi} \left[ G(E) - G^{\dagger}(E) \right] \]

\[ T_{\sigma}(E,V_b) = Tr\left[ \text{Im}\left\{ \Sigma_{L\sigma}^{r}(E,V_b) \right\} G_{\sigma}^{r}(E,V_b) \text{Im}\left\{ \Sigma_{R\sigma}^{r}(E,V_b) \right\} G_{\sigma}^{r\dagger}(E,V_b) \right] \]

\[ I_{\sigma}(V_b) = \frac{e}{h} \int_{-\infty}^{\infty} \left[ T_{\sigma}(E,V_b) \{ f_{L}(E,V_b) - f_{R}(E,V_b) \} \right] dE \]
Electrical currents are determined by transmission probability

$$I = \frac{2e}{h} \int \left[ T(\varepsilon) \{ f_L(\varepsilon) - f_R(\varepsilon) \} \right] d\varepsilon$$

Landauer-Büttiker formalism

Keldysh Nonequilibrium Green’s function method: Non-interacting electron approximation

$$T(E) = Tr \left[ \Gamma_L(E) G^r(E) \Gamma_R(E) G^a(E) \right]$$
Self-Energy: Renormalization

Level shift

\( \Delta_{L/R} = \text{Re}(\Sigma_{L/R}) \)

Level broadening

\( \Gamma_{L/R} = \text{Im}(\Sigma_{L/R}) \)

\[
H_{\text{eff}} = H + \Sigma_L + \Sigma_R
\]
Set-up of Calculation: Quasi Stationary State

\[ H_{LL} \quad H_{LL} \quad H_{LL} \quad B \quad H_{MM} \quad B \quad H_{RR} \quad H_{RR} \quad H_{RR} \]

Left Lead \quad Scattering Region \quad Right Lead

\[
\begin{bmatrix}
    h_L & h_L & h_L & h_L \\
    v_L & h_L & V_{LC} & 0 \\
    0 & V_{CL} & H_{CC} & V_{CR} \\
    0 & 0 & V_{RC} & h_R \\
    \vdots & \vdots & \vdots & \vdots \\
\end{bmatrix}
\]

\[ h_L \quad h_L \quad h_L \quad h_L \quad H_{CC} \quad h_R \quad h_R \quad h_R \quad h_R \]

\[ v_L \quad v_L \quad v_L \quad v_L \quad v_R \quad v_R \quad v_R \quad v_R \]

Screening effect!!

\[
H^{\text{eff}} = \begin{bmatrix}
    h_L + \sum_L & V_{LC} & 0 \\
    V_{CL} & H_{CC} & V_{CR} \\
    0 & V_{RC} & h_R + \sum_R \\
\end{bmatrix}
\]

Self-energy

\[ M \times M \]
**Finite Bias Effect: Hartree Potential**

\[ V_{\text{eff}} (r) = \begin{cases} 
V_{M}^{\text{eff}} (r), & z \leq 0 \\
V_{L,\text{bulk}}^{\text{eff}} (r), & 0 \leq z \leq L \\
V_{R,\text{bulk}}^{\text{eff}} (r), & z \geq L 
\end{cases} \]

\[ \nabla^2 V^{\text{eff}} (r) = -4\pi\rho_{\text{scf}} (r) \]

\[ V^{\text{eff}} (r) = \varphi(r) + \bar{a} \cdot \bar{r} + b 
= \varphi(r) - V \left( \frac{z}{L} - \frac{1}{2} \right) \]

**Natural Boundary Condition**

\[ H_L + V_b/2 \]

\[ H_L \]

\[ \uparrow \]

\[ V_{\text{eff}} (r) \]

\[ \downarrow \]

\[ H_R - V_b/2 \]

\[ H_R \]
Contour Integration

\[
\int_{-\infty}^{\infty} G(E) f(E - \mu) dE = -\oint_C G(z) f(z - \mu) dz - 2\pi i k_B T \sum_{k=1}^{n} G(z_k)
\]

\[
\oint_C G(z) f(z - \mu) dz = \sum_{N\text{contour}} G(z_n) f(z_n - \mu) w_n
\]

Total ~40 contour points
Very efficient !!!
\[ \nabla^2 V_{\text{eff}}(r) = -4\pi \rho_{\text{scf}}(r) \]

\[ H = T[\rho_{\text{scf}}(r)] + V[\rho_{\text{scf}}(r)] \]

\[ H \phi_i(r) = \varepsilon_i \phi_i(r) \]

\[ \rho_{\text{scf}}(r) = \sum_{\mu, \nu} D_{\mu \nu} \phi_\mu(r) \phi_\nu(r) \]

\[ \rho_{\text{init}}(r) = \rho_{\text{scf}}(r) \]

\[ G = \left[ ES - H - \Sigma_L - \Sigma_R \right]^{-1} \]

\[ DM = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{\infty} \left[ G(E) f(E - \mu) \right] dE \]

Non-collinear Spin Calculations

\[ \rho_{\alpha\beta} = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{\infty} G_{\alpha\beta}^r(E) f(E - \mu) dE \]

\[ G^r(E) = \begin{bmatrix} G_{\alpha\alpha}^r(E) & G_{\alpha\beta}^r(E) \\ G_{\beta\alpha}^r(E) & G_{\beta\beta}^r(E) \end{bmatrix} = \frac{1}{ES^r - H^r - \Sigma^r} \]

\[ H = \begin{bmatrix} H_{\alpha\alpha} & H_{\alpha\beta} \\ H_{\beta\alpha} & H_{\beta\beta} \end{bmatrix} \quad S = \begin{bmatrix} S & 0 \\ 0 & S \end{bmatrix} \quad \Sigma^z(E) = \begin{bmatrix} \Sigma_{\alpha\alpha}^r(E) & \Sigma_{\alpha\beta}^r(E) \\ \Sigma_{\beta\alpha}^r(E) & \Sigma_{\beta\beta}^r(E) \end{bmatrix} \]
Parallel Calculation:

Most time-consuming steps

**Density matrix**

\[ G(E) = \left[ ES - H - \Sigma_L - \Sigma_R \right]^{-1} \]

\[ DM = -\frac{1}{\pi} \text{Im} \sum_{N\text{contour}} G(z_n) f(z_n - \mu) w_n \]

**Currents**

\[ T(E,V) = \text{Tr} \left[ \Gamma_L(E,V) G^R(E,V) \Gamma_R(E,V) G^A(E,V) \right] \]

\[ I = \frac{2e}{h} \sum_{N\text{trans}} T(E_n,V) \left\{ f_L(E_n - \mu_L) - f_R(E_n - \mu_R) \right\} w_n \]

**Parallelization:** Almost linear performance

Inversion of Green’s function: \( \sim O(N^3) \): 99% of the total cpu times

![Graph showing cpu times vs 1/ncpus]

**POSTECH TRANSPORT CODE**

<table>
<thead>
<tr>
<th>Spin</th>
<th>Kpoints-sampling</th>
<th>Bias</th>
<th>Parallel</th>
<th>Non-collinear</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
</tbody>
</table>

Carbon-based materials for Electronics/Spintronics

Advantages of Carbon-based materials in Spintronics

**Weak Spin-Orbit Interaction**

Spin-orbit (SO) interaction is proportional to $Z^4$. Organic atoms have weak SO interaction.

**Weak Hyperfine Interaction**

For carbon atoms, the most abundant isotopic form, $^{12}$C, has no nuclear spin. $I = 0$

Long spin relaxation length
Top-down vs. Bottom-up approaches

Top-down

Nanomaterials

limitations

Bottom-up
Interactions Forces for Atomic Molecular Assembly
(Ionic, Covalent, and Metallic Bondings)
* Noncovalent Bonding for Molelcular Assembly*

1. H-bonding

2. $\pi$-$\pi$ interaction

3. $\pi$- H$_2$O interaction

4. Cation-$\pi$ interaction

Chem. Rev. 100, 4145 (2000)
Self Assembly of Calix[4]hydroquinone

<table>
<thead>
<tr>
<th>Without water</th>
<th>With water</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dimer</strong></td>
<td><strong>Polymer</strong></td>
</tr>
<tr>
<td>10.2</td>
<td>44.2</td>
</tr>
<tr>
<td><strong>Trimer</strong></td>
<td><strong>39.7</strong></td>
</tr>
<tr>
<td>8.6</td>
<td></td>
</tr>
<tr>
<td><strong>Tetramer</strong></td>
<td><strong>37.4</strong></td>
</tr>
<tr>
<td>8.8</td>
<td></td>
</tr>
<tr>
<td><strong>Hexamer</strong></td>
<td><strong>21.6</strong></td>
</tr>
<tr>
<td>21.6</td>
<td></td>
</tr>
<tr>
<td><strong>Octamer</strong></td>
<td><strong>47.2</strong></td>
</tr>
<tr>
<td>11.0</td>
<td></td>
</tr>
</tbody>
</table>

Binding energy (kcal/mol)

electro/photo-chemical Nanorecognition

Competing vs. Cooperation effects

*Science* 294, 348 (2001)

Self-Assembled Nanolens

Near-Field Focusing and Magnification


Hyper-Refraction: Beyond Diffraction Limit
Nano-Micro Tech: advanced functionalization, minuaturization, high density packing

Top-down approach

Bottom-up approach (Fly’s eye)

Lens grinding/polishing

Fabrications of lenses

Thermal reflow
Self-assembled CHQ nanostructures

I. CHQ films & plates
II. CHQ nanotubes
III. CHQ nanospheres
IV. CHQ nanolenses

\( T \) temperature
\( \mu \) vaporization rate
\( t_d \) diffusion rate
Nanolens: CHQ plano-spherical convex lens

Thermodynamical Analysis: growth mechanism of CHQ nanospheres
Super-resolution of CHQ nanolens (below ½ wavelength) beyond diffraction limit

Far-field

Optical Microscope Images

SEM Images

Face-up

Face-down

30° tilted

250nm

220nm

1μm

2μm
Near–Field Focusing & Magnification
Beyond Diffraction Limit Through a Nanolens

Finite Difference Time Domain simulations using Maxwell equations for the optical path of a nanolens
FDTD simulations - Examples

- FDTD used to calculate intensity along the POI at different relative positions of the objective lens ($\Delta z$)
- Resolution is estimated from the FWHM of the POI intensity maximum

Numerical Scheme

- FDTD used to calculate intensity along the POI at different relative positions of the objective lens ($\Delta z$)
- Resolution is estimated from the FWHM of the POI intensity maximum
nSIL Resolution – Comparison with SIL

SIL (same objective)  
(NA = 1.44)

Max res. SIL  
(n = 1.6)

Regions where nSIL beats SIL

Improvements

Face Down ≈ 25%
Face Up ≈ 35%

Applications of Nanolens:

UV lithography using a nanoscale lens

Photochemical imaging through the CHQ lenses.

a, A FDTD simulation image ($|E_x|^2$) of the lens on resist polymer layers.
b, SEM images of developed patterns after irradiating 365nm UV light through the nanolenses, UV exposure time: 1s for $t=0$ -500nm, 4s for $t>2\mu$m.
c, FDTD simulation images corresponding to b.
d, $|E_x|^2$ corresponding to a, showing sharp peaks at $F=500$~600 nm.
Endo/Exo-hedral Fullerenes, Nanotubes, and Nano-tori Qubits

**Magnetic phase transition**

Change of spin state

Exohedral fullerenes $M^+\& C_{60}$

\[ X@C_{60}, \quad X=N, P, As, O, S \]


Magnetic phase transition

Trannulene

Cyclacene: side view

Cyclacene: perspective view

smallest carbon nanotube


Ultralong thinnest SWNT
d=0.4 nm

PNAS 102, 14155 (2005)

JACS 127, 15336 (2005)
Electron transfers

Endohedral spins of N@C_{60}; P@C_{60} for Quantum Computing
ultralong thinnest SWNT \( d = 0.4 \text{ nm} \)

**JACS** 127, 15336 (2005)

**PNAS** 102, 14155 (2005)
## Graphene Properties

### Mechanically
- Flexible
- Stable at high temperature (3000 °C) like diamond or CNT

### Electronically
- High carrier mobilities over 15,000 cm²V⁻¹S⁻¹
- Ballistic transport in submicrometer scale (0.3 mm) at 300K [Nature Mater. 6, 183 (2007)]

### Magnetically
- Long spin relaxation length: 1.5 ~ 2 mm at 300K
  due to weak SO and hyperfine interactions [Nature 448, 571 (2007)]

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Magnetoresistance

Magnetoresistance (MR) = 114 (%) over the whole $V_b$ range
Synthesis, etching and transferring processes of the large-scale and patterned graphene films. 
a, Synthesis of patterned graphene films on thin Ni layers. b, Etching by FeCl$_3$ (or acids) and transfer of floating graphene films. c, Etching by HF (or buffered oxide etchant) and transfer of graphene films by a PDMS stamp.

Flexible electronics — the kind that might be used in “smart” clothing, say, or in foldable displays that could make reading news online more like reading it in print — are still far from an everyday reality. But scientists in South Korea are reporting a significant advance toward the development of such devices.

Web Link

Large-scale Pattern Growth of Graphene Films for Stretchable Transparent Electrodes (Nature)


Large-scale pattern growth of graphene films for stretchable transparent electrodes,


Stretchable graphene electrode patterns transferred onto a silicon-based polymer.
Enhancement of micro-Raman intensity by a CHQ nanolens on graphene

Relocation of CHQ nanolenses for fabrication

FIB-SEM/SIM-images
Dual FIB technique
Molecular Electronics with CNT Electrodes

A: geometry relaxed region
B: scattering region
L: left electrode region
R: right electrode region

- PE: phenyl ethynyl
- PP: pyrrollo pyrrole

Non-equilibrium Green's function method (Implementation on SIESTA code based on LCAO DFT)

DFT functional: LDA-Perdue-Zunger

SZP basis sets

Landauer-Büttiker formula for I-V characteristics

Molecules

- PE: phenyl ethynyl
- PP: pyrrollo pyrrole
Molecular-wire / CNT-electrodes

Asymmetric Potential Drop at 2.4 V due to the change of molecular charge
Screening of the external bias voltage => change of the charge distribution

High bias voltage: no more screening
- change of molecular charge
- change of the local potential
- asymmetric potential drop

Effect of electrodes on electronic transport

Metals (Au : Ru)
-Hollow site on (111) surface

CNT
-covalent bond to C

Linker
-S or direct contact

Core molecule
-C6 or benzene

Calculation detail
-POSTRANS(SIESTA+NEGF)
-PBE
-150 Ry
-TM pseudopotential
Transmission

(a) with S  (b) without S  (c) C6 --> benzene

Extents of broadening and alignment of a peak are of an electrode origin.

Linker dependence
molecule dependence
I - V curve

Y. Cho. et al.
J. Phys. Chem. A
113, 4100 (2009).

Conductance
Higher for metals, smaller for CNT
(large coupling limit)

Non-linearity
CNT can offer I-V curve non-linearity that is of an electrode origin

Caveat
Electrodes are not a deterministic factor. but a useful factor contributing to molecular transport properties.
Creation of the Domain Wall

Energy required to create a magnetic domain wall

Spin direction: out of plane due to the dipole interaction

\[ E_{\text{dipole}} > 30 \times E_{\text{so}} \]

\[ W_{DW} = 10 \sim 15 \text{ nm} \]

If \( B \geq 30 \text{ mT} \), a DW is created.
The unique band symmetry of GNRs gives unrivalled MR and highly spin-polarized currents.

Mis-matching in orbital symmetry as well as spin symmetry leads to the striking enhancement in MR. *(super-MR: SMR)*


**Super-MagnetoResistance**

**300K:**
- Exponential dependence
- Width dependence
  - 8-ZGNR (1.79 nm): $\sim 10^6 \%$
  - 32-ZGNR (6.97 nm): $\sim 10^4 \%$

**5K:**
- Almost constant
- No width dependence
  - N-ZGNR: $\sim 10^6$-$10^7 \%$

\[ MR = \frac{R_{AP} - R_P}{R_P} \]

Only $\alpha$-spin contributes to currents $\rightarrow$ Spin-polarized currents
I-V Characteristics in Zigzag Graphene Nanoribbon

Current, Conductance, and Resistance

\[
I_\sigma (V_b) = \frac{e}{h} \int_{-\infty}^{\infty} \left[ T_\sigma (E, V_b) \left\{ f_L (E, V_b) - f_R (E, V_b) \right\} \right] dE
\]

\[
G = \frac{dI (V_b)}{dV_b} \quad R = \frac{1}{G}
\]

\( R_P \): The slope shows quantum conductance \((G_0 = 2e^2/h = 77.48 \text{ S})\) due to the perfect transmissions

\( R_{AP} \): Huge resistance due to the zero transmission gap

Spin-valve device based on GNR: Utilization of the edge spin states

A novel graphene analogue

**Modification:**
- Defects: Red circles
- N doping: Blue circles

**Physical properties**
- Aromaticity is retained
- Non-bonding Radicals
A novel graphene analogue

Ultra-Soft Pseudo potential
GGA (PW86) Functionals
7×7 k-point grid

Half-metallic band structure

Majority spin
Minority spin

Density of states

Transmission

Spin density
Design & Synthesis of ion receptors & ion sensors

Immense potentials in biological & environmental processes
Salts from Sea water; Poisonous materials from water & soils;
Radioactive materials from Nuclear wastes;
Drug delivery; Nanotech

Angew. Chem. 44, 2899 (2005)
JACS 126, 8892 (2004)
Molecular electronic sensor. The ON and OFF states would show different I-V characteristics.

DNA Sequencing

Nanomechanical Device: Conformation Change by Redox Process

Photo Switch

Sensor

Molecular Flipper/Robot

Cyclic Voltammogram

- <bio-nano-devices>
New Chemistry
New functional molecules, new chemical systems, molecular clusters, molecular wires, metal wires, 1D/2D molecular systems, hydrogen storage
Novel inophores/receptors (new class of organic molecular systems)
Enzyme mechanisms, Bio-macromolecules, Polymers, Condensed phase
Novel self assembly techniques: self-synthesis
Synthesis of organic nanotubes, nanowires, nanoparticles, nanostructures
Synthesis of ultralong ultrathinest single wall nanotubes
Synthesis of ultra-wide single-layer graphene
Synthesis of nanscale lens with ideal spherical shape through self-assembling

New Physics
Molecular electronics/spintronics: Super-magnetoresistance
Nanoscale lens comparable to wavelength: distinctive optical phenomena:
New nano-optical phenomena: Super-refraction near-field focusing and magnification (curvilinear beam trajectory)
super resolution beyond diffraction limit
Enhancing optical signal for analysis
Improving photolithographic techniques for nanodevices
Optical memory storage, optical nano-sensing, etc

Summary
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