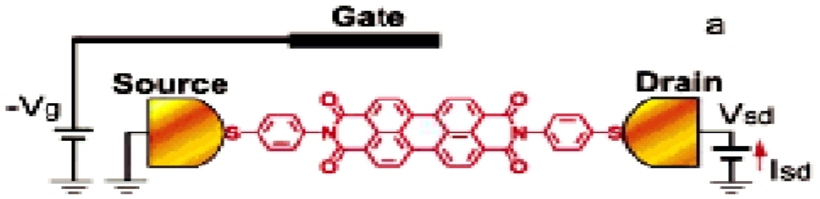
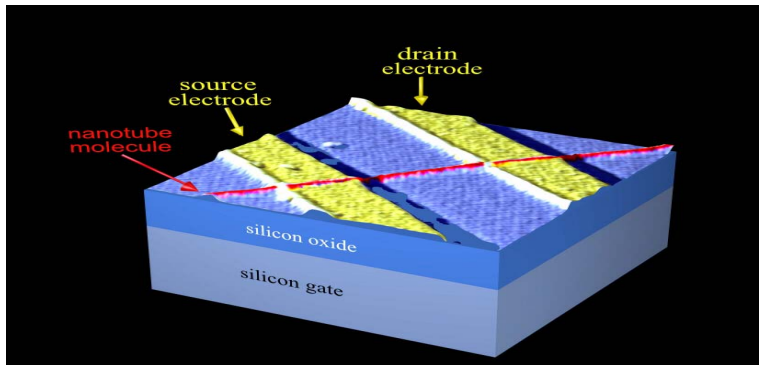
中国科学技术大学

Mark A. Reed and James M. Tour, Scientific American (June '00)





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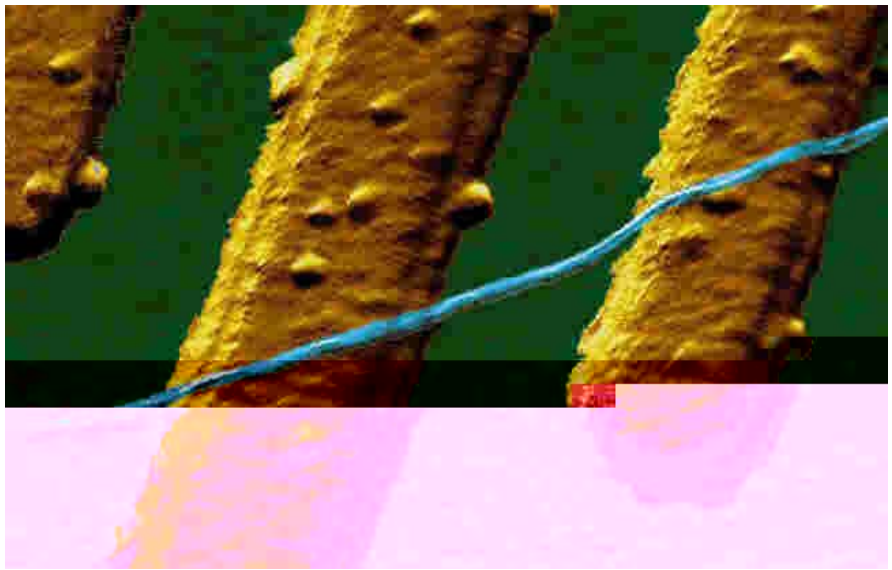

SWCNT across Pt Electrodes (C. Dekker, Delft)

Size: scale from 1 to 100 nm

Given the same amount of space, many times faster and more powerful than silicon based devices

Manufacturing:

fabricated identically and defect-free in enormous numbers

Self-assembly Manufactured

molecular synthesis tools highly developed

Quantized electron energy

Extended π systems

Provides thermodynamically favorable electron conduction

π Conjugation acts conduction switch

Elegance

Elegant solutions to non-volatile and inherently digital

The problems of chemistry and biology can be greatly helped if our ability to see what we are doing, and to do things on an atomic level, is ultimately developed — a development which I think cannot be avoided.

Richard Feynman

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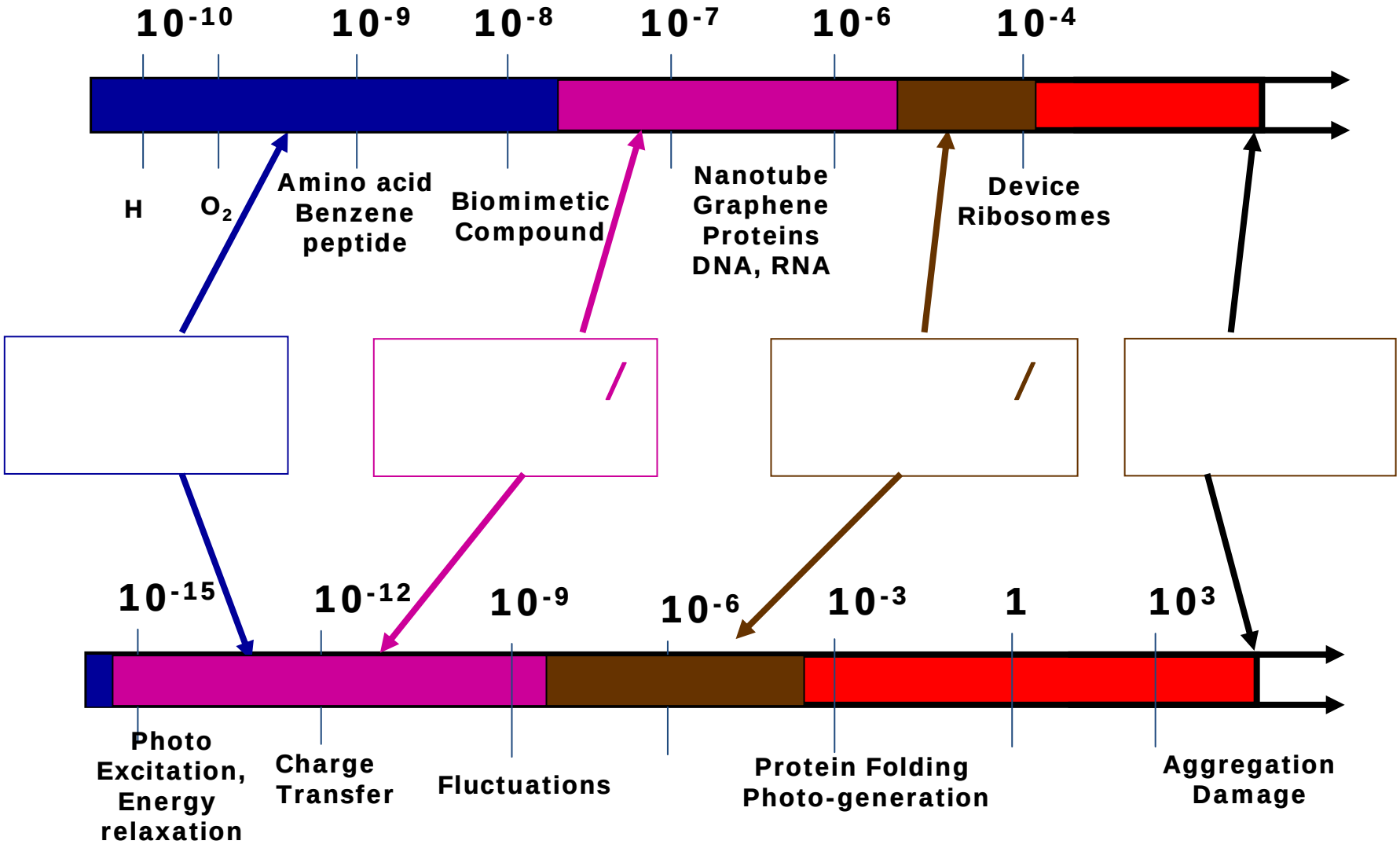
The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.

Paul. A. M. Dirac


10^{-10}
10^{-9}
10^{-8}
10^{-7}
10^{-6}
10^{-4}
H
O_2
Amino acid
Benzene
peptide
Biomimetic
Compound
Nanotube
Graphene
Proteins
DNA, RNA
Device
Ribosomes
10^{-15}
10^{-12}
10^{-9}
10^{-6}
10^{-3}
1
10^{3}
Photo
Excitation,
Energy
relaxation
Charge
Transfer
Fluctuations
Protein Folding
Photo-generation
Aggregation
Damage

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QCME ō Quantum chemistry for molecular electronics)

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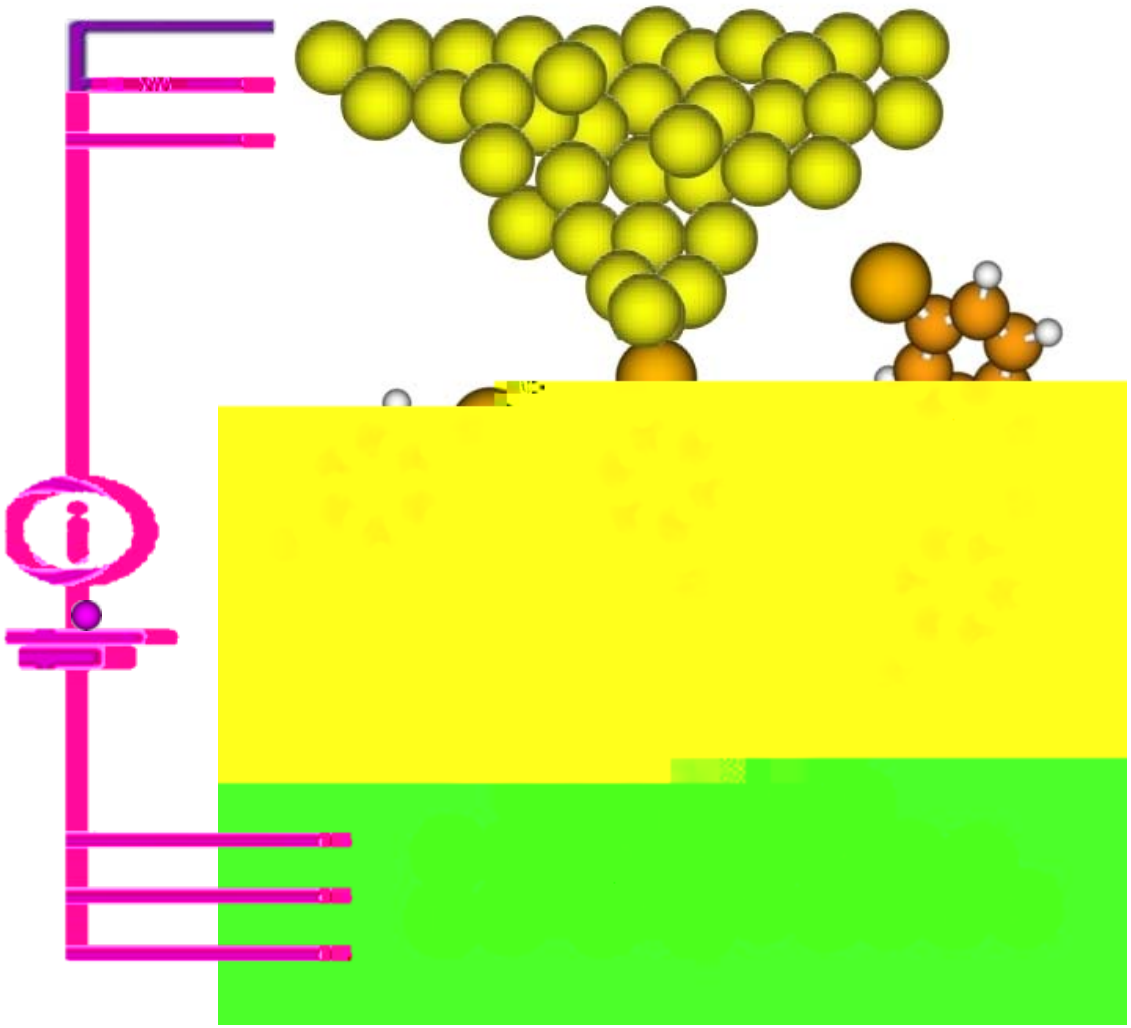
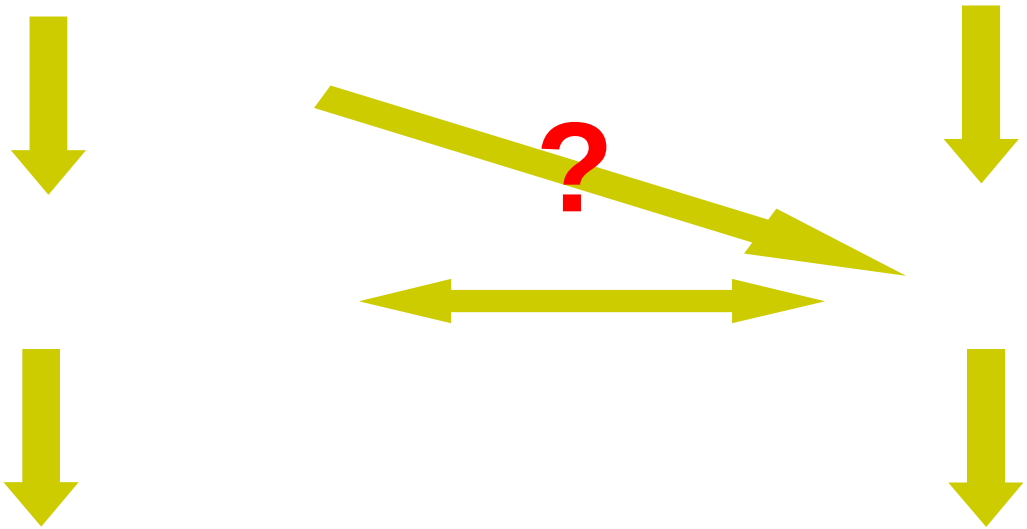
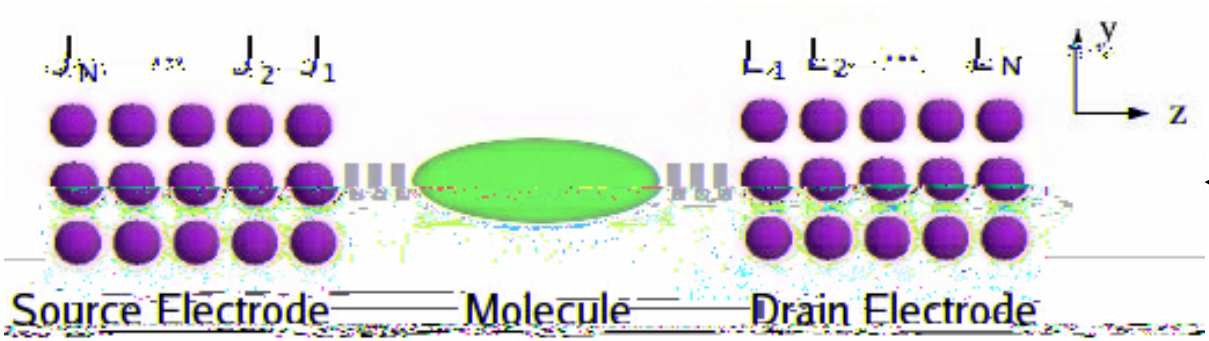
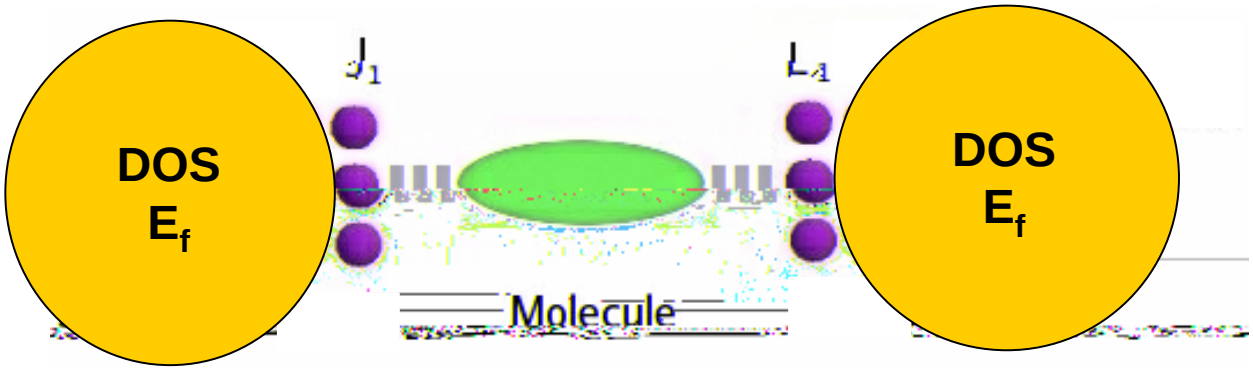






Surface adsorber
+
non-equilibrium
Green's function

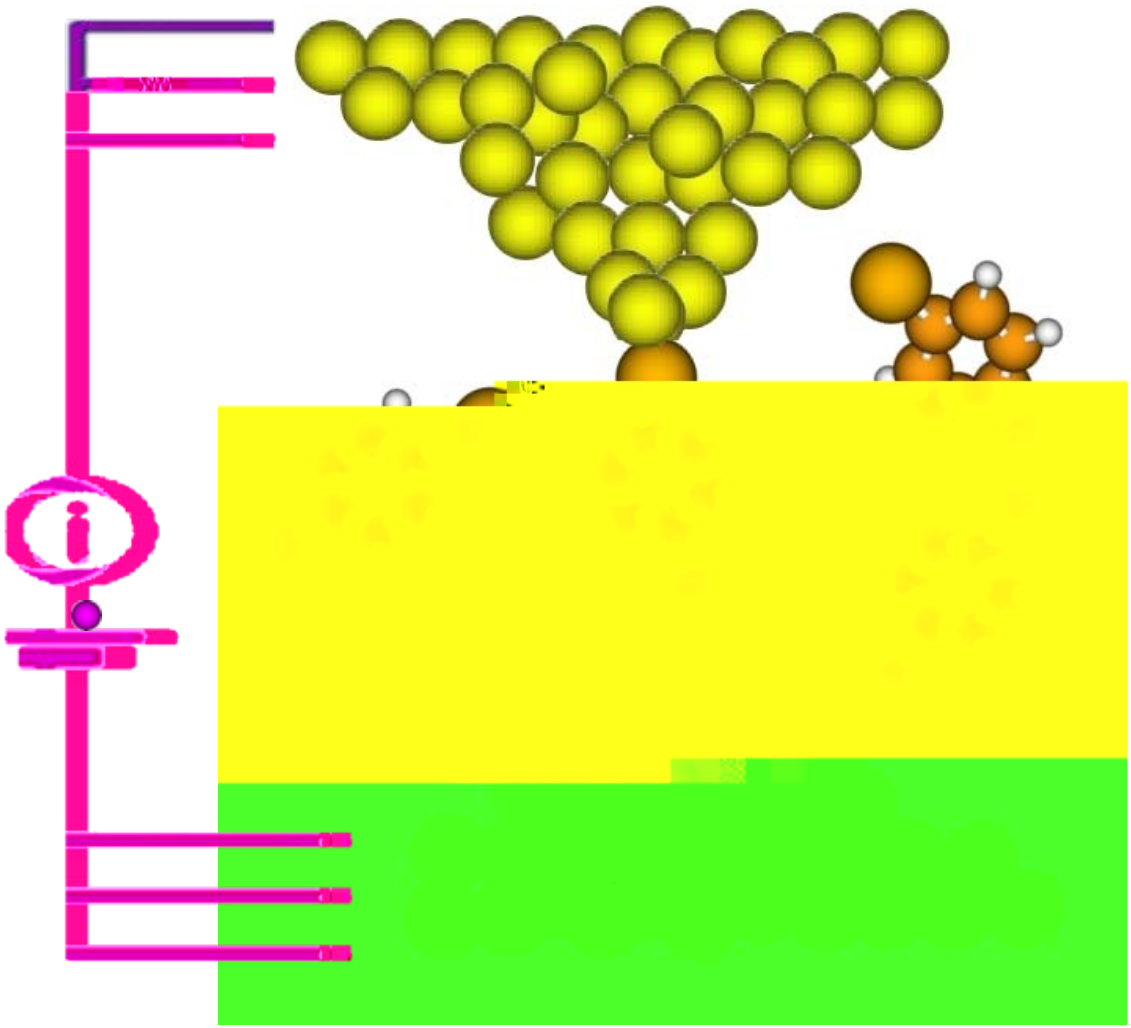
Landauer Formula

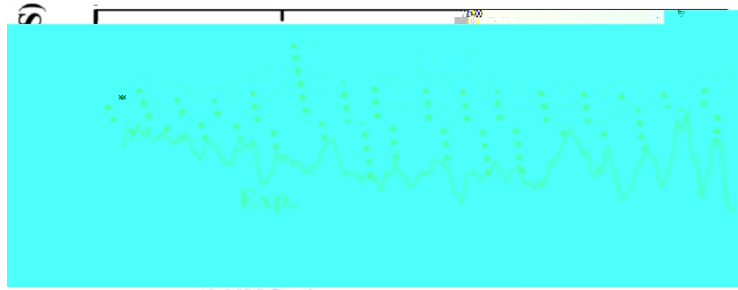


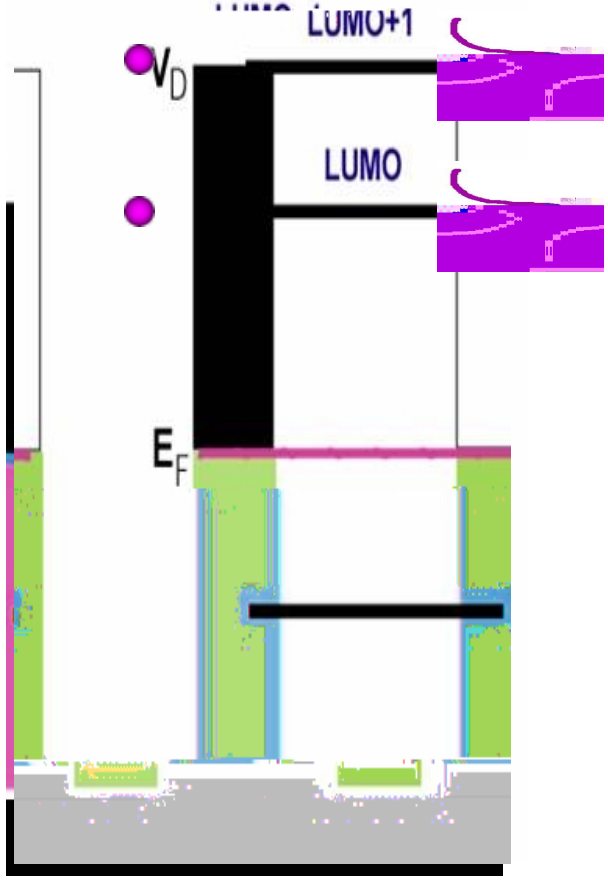
- Treat the “extended molecule” with Quantum Chemistry
- Describe the electrode with Density of States (DOS)
- The extended molecule is in equilibrium with the source and drain by lining up the effective Fermi level

Tunneling Current Density from Source to Drain:

$$\frac{2\pi}{\hbar}\sum_{k,q} T\times f(E_k)\times\left[1-f(E_q)\right]\times\delta(E_k-E_q)$$




Exp.


LUMO+1
V_D
LUMO
E_F

(CIS: Central Insertion Scheme)

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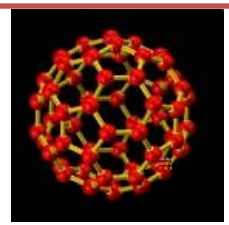
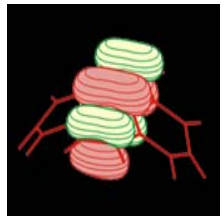
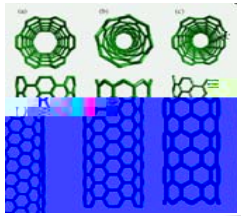
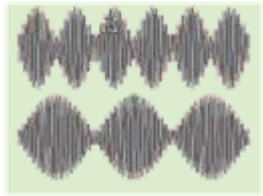
BioNano-Lego









Multi-scale Method ( )

A straightforward method can be interfaced with quantum chemistry approach

Allows to effectively treat very large nano-scale periodical systems without losing the accuracy

Electronic structure was obtained by solving the Schrondinger Equation $H \mid \Psi^{\eta} \rangle = \varepsilon_{\eta} \mid \Psi^{\eta} \rangle$

- Energy of electrons can be written as $\langle \Psi | \hat{H} | \Psi \rangle$
- By the *variational theorem*, this is an upper bound on the true electronic ground state energy
- We minimise the electronic energy as a function of weighting functions of molecular orbitals to obtain *self-consistent* solution (also called SCF approach)
- Use a linear combination of orbital basis functions, or sometimes Gaussian functions: $\Psi_i = \sum_{\mu=1}^{N} C_{\mu i} \phi_{\mu}$ LCAO
- Substituting these into a 1-electron T.I. Schrödinger eq.:

$$\mathrm{f}\Psi_i = \varepsilon_i \Psi_i \rightarrow \mathrm{f} \sum_{\mu=1}^{N} C_{\mu i} \phi_{\mu} = \varepsilon_i \sum_{\mu=1}^{N} C_{\mu i} \phi_{\mu}$$

Fock Matrix

- The hamitonian of the system can be described as:

$$H = \begin{pmatrix} H_{1,1} & \dots & H_{1,\frac{n}{2}} & H_{1,\frac{n}{2}+1} & \dots & H_{1,n} \\ \dots & \dots & \dots & \dots & \dots & \dots \\ H_{\frac{n}{2},1} & \dots & H_{\frac{n}{2},\frac{n}{2}} & H_{\frac{n}{2},\frac{n}{2}+1} & \dots & H_{\frac{n}{2},n} \\ H_{\frac{n}{2}+1,1} & \dots & H_{\frac{n}{2}+1,\frac{n}{2}} & H_{\frac{n}{2}+1,\frac{n}{2}+1} & \dots & H_{\frac{n}{2}+1,n} \\ \dots & \dots & \dots & \dots & \dots & \dots \\ H_{n,1} & \dots & H_{n,\frac{n}{2}} & H_{n,\frac{n}{2}+1} & \dots & H_{n,n} \end{pmatrix}$$

where F is the *Fock n* ; is the *overlap matrix*

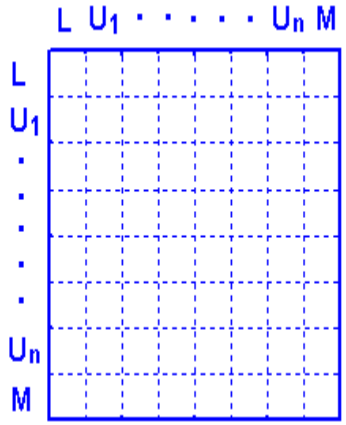
- The equation can be v pactly in matrix form :

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon}, \text{ or,}$$

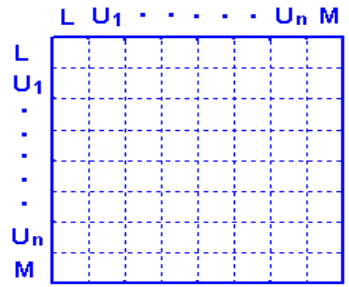
ll equations

$$(\mathbf{F} - \mathbf{S}\boldsymbol{\varepsilon})\mathbf{C} = 0$$

m)



The most resource consuming part in Quantum Chemistry calculation is to obtain Fock Matrix through SCF solution



- molecular orbital coefficients C_i that minimise the energy and give us the best single determinant
- In the secular equation, the Fock matrix itself depends on the coefficients C_i, and therefore it is necessary to use an iterative procedure when solving the equation
- We guess values for the C_i initially and the variational principal (which states that E_{guess} is always > E_{true}) allows us to optimise the C_i until we reach self-consistency
- However, the Fock matrix contains many two-electron integrals which are very time-consuming to calculate

(Central Insertion Scheme)

Deduce out the Fock matrix of large nano-scale systems from the smaller scale system

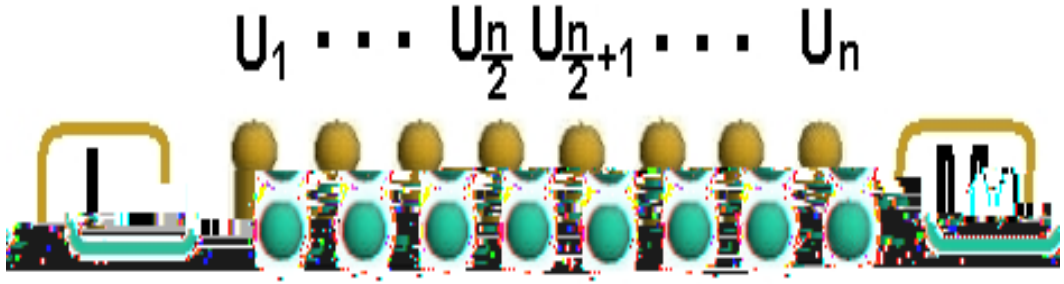
Greatly reduce computation time and resource by avoiding the SCF process

(Central Insertion Scheme)

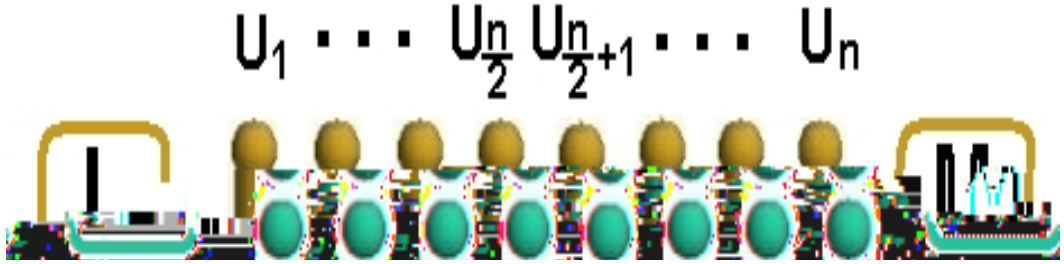
Approximations:

1) periodical short-nano-scale systems are long enough to have the electronic structures converged in the central parts

2) long distance interaction (> 20 Å) between subsystems dies out in the short-nano-scale systems



1) Electronic structures converged in the core parts



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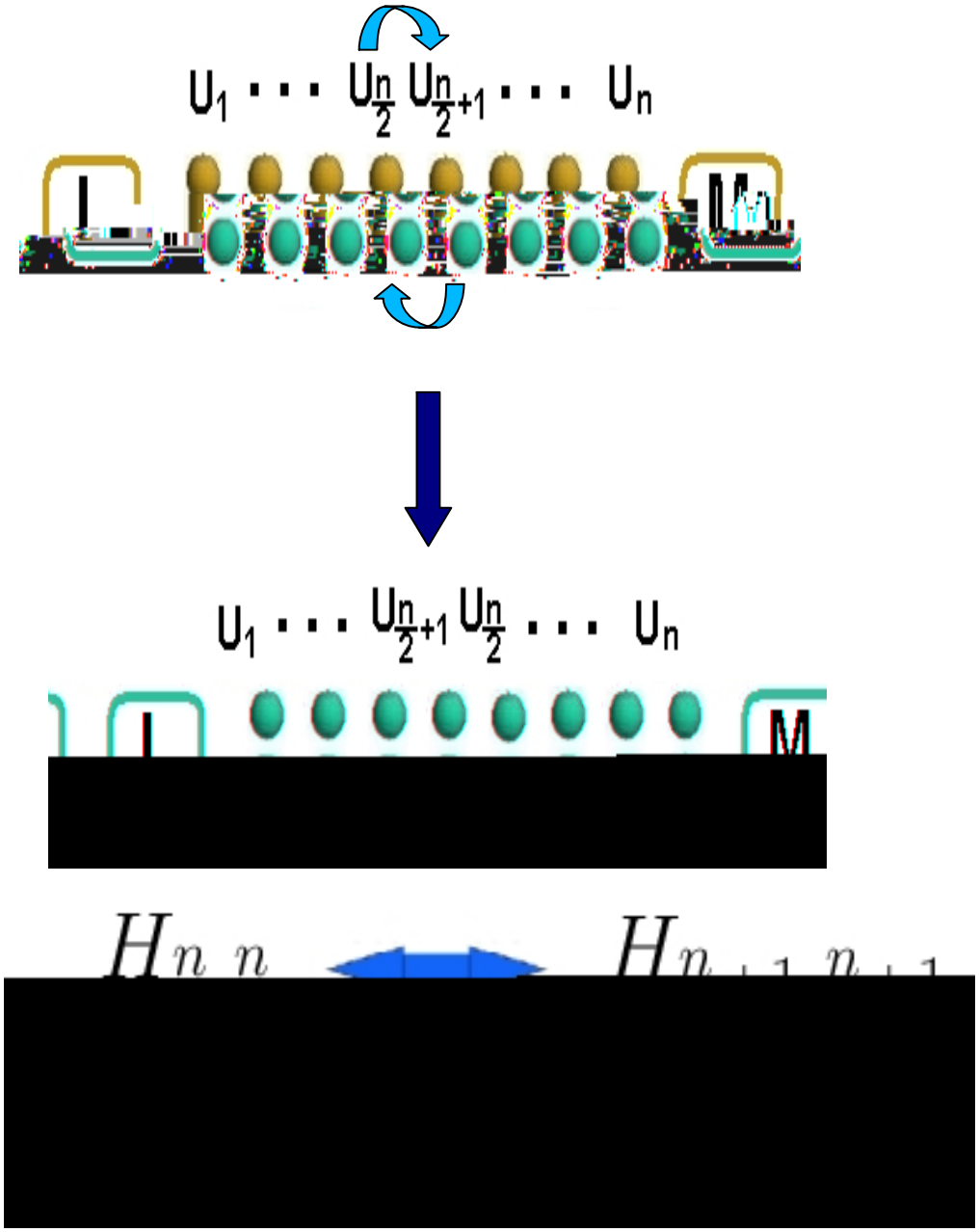
- The convergence of interaction

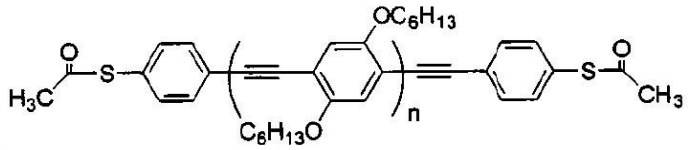
$$H_{\frac{n}{2},\frac{n}{2}} = H_{\frac{n}{2}+1,\frac{n}{2}+1}$$

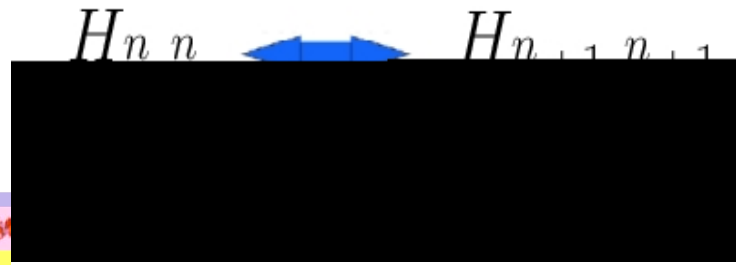
$$H_{\frac{n}{2},\frac{n}{2}+1} = H_{\frac{n}{2}+1,\frac{n}{2}+2}$$

1) Electronic structures converged in the core parts



Take polymer (n=10) as an example:





Gaussian03 computed HOMO(highest occupied orbital)-LUMO(lowest unoccupied orbital) gap: 2.784eV

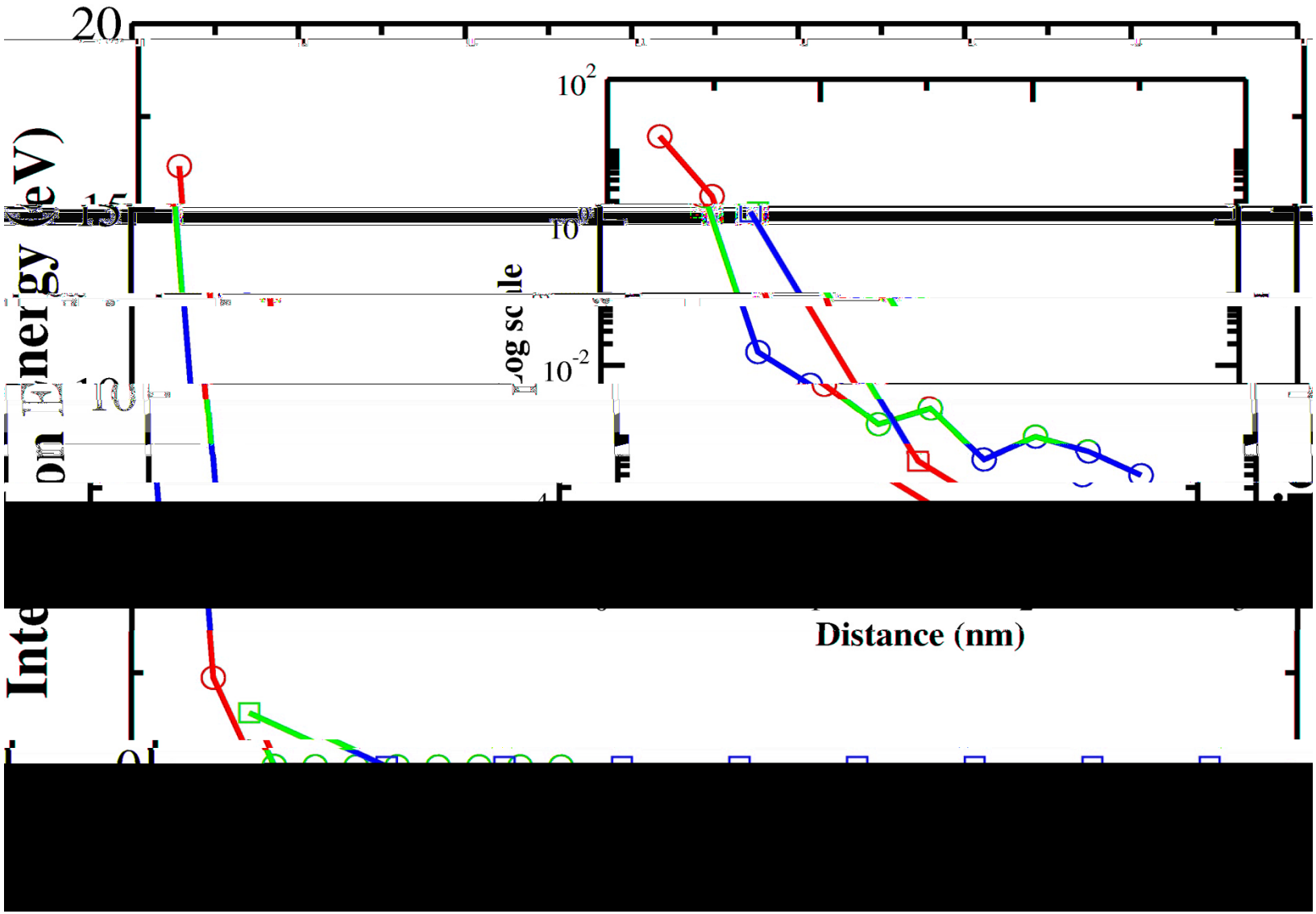
Reconstructing computed HOMO-LUMO gap: 2.786eV, error 2 meV

Orbital energy error in the range of (HOMO-20, LUMO+20):

Biggest error 8 meV smallest error 0.0005meV

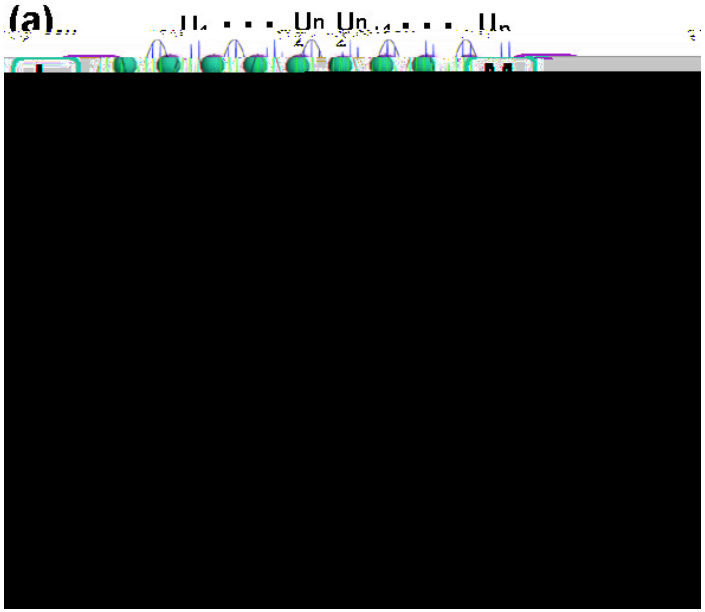
electron density	Reconstructing results	GAUSSIAN03 Results	error
U_1	0.0351	0.0357	0.0006
U_2	0.0766	0.0771	0.0006
U_3	0.1259	0.1251	0.0008
U_4	0.1684	0.1657	0.0027
U_5	0.1901	0.1847	0.0053
U_6	0.1835	0.1864	0.0028
U_7	0.1512	0.1550	0.0038
U_8	0.1041	0.1086	0.0045
U_9	0.0571	0.0603	0.0032
U_{10}	0.0227	0.0242	0.0015

2) long distance interaction dies out



Interaction energy between U1 and other units as a function of distance between them.

Blue Circle dots:CNT21; Red Square dots: POLY10



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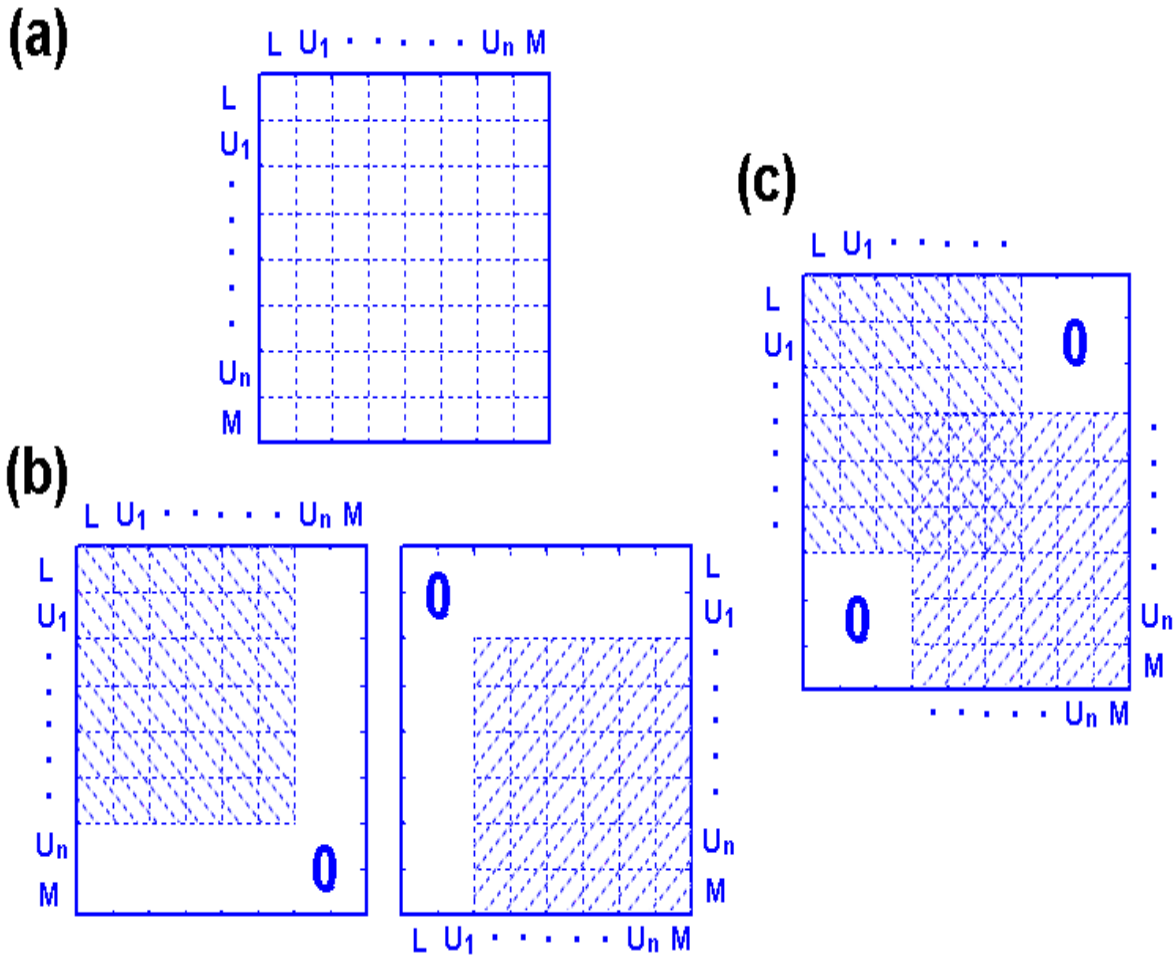
- The convergence of interaction

$$H_{\frac{n}{2},\frac{n}{2}} = H_{\frac{n}{2}+1,\frac{n}{2}+1}$$

$$H_{\frac{n}{2},\frac{n}{2}+1} = H_{\frac{n}{2}+1,\frac{n}{2}+2}$$

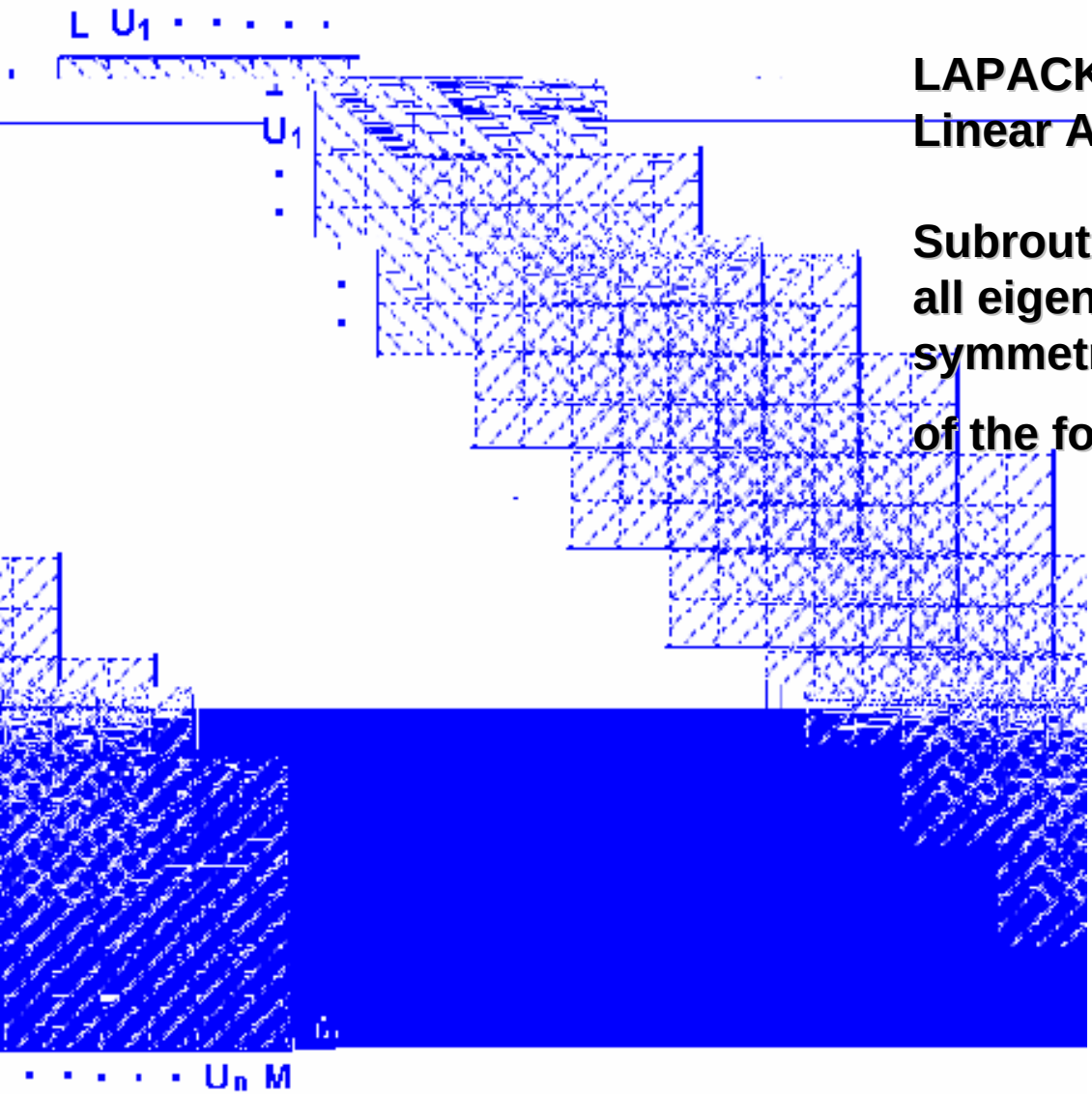


Bio-NanoLego

Jiang, Liu, Lu, and Luo, J. Chem. Phys. 124 (2006) 214711.

Eigen value solution

For very large scale



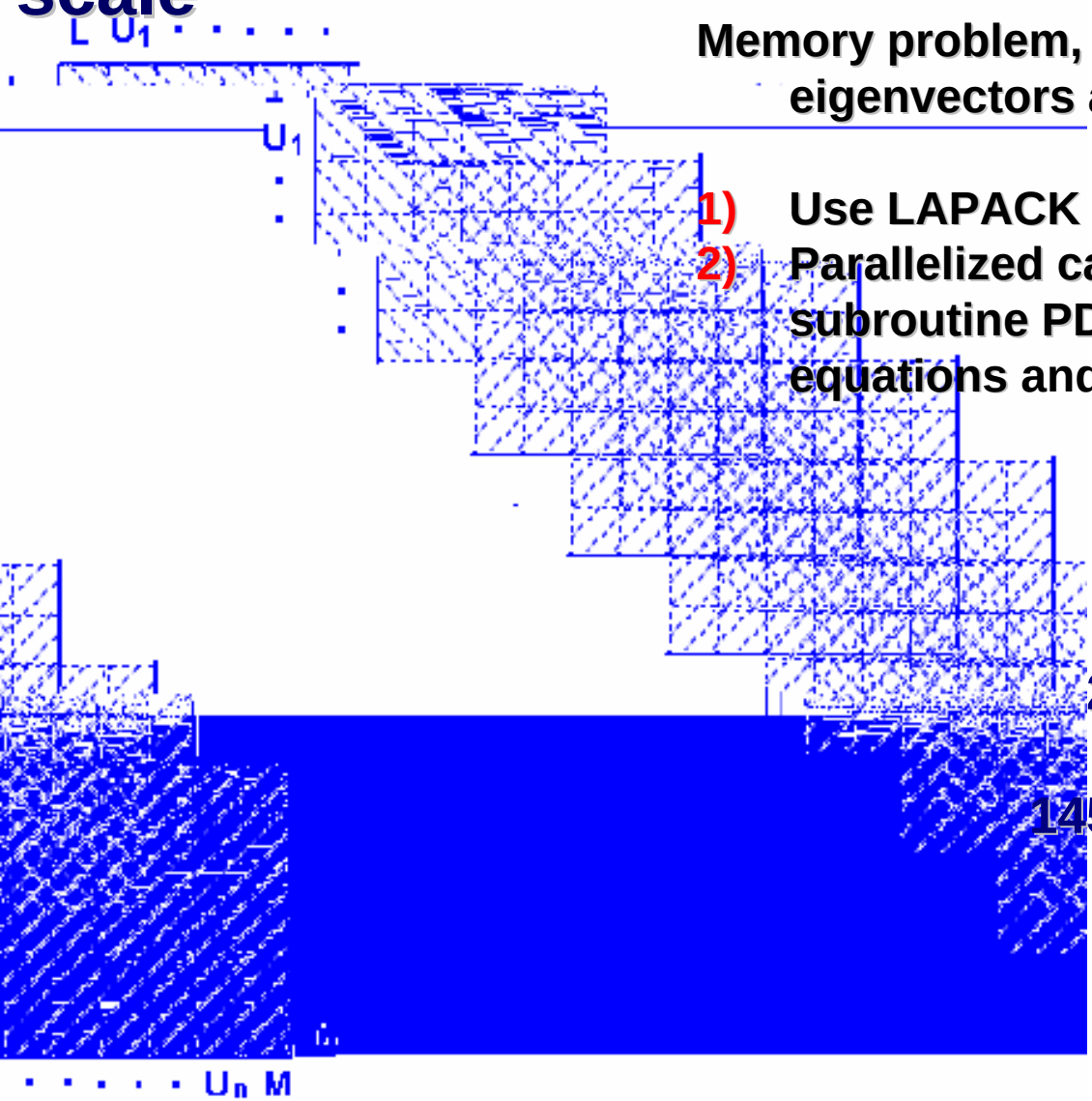
LAPACK –
Linear Algebra PACKage

Subroutine ssbgv() or dsbgv() Compute all eigenvalues, and eigenvectors of a symmetric-definite banded eigenproblem,

of the form A*x=(lambda)*B*x

Eigen value solution

For even larger scale



Memory problem, can not find eigenvalues and eigenvectors at the same time

1) **Use LAPACK Compute all eigenvalues,**
2) **Parallelized calculation with scalapack subroutine PDDBSV to solve the linear equations and find eigenvectors**

Biggest system:
200 nm (5 5) carbon nanotube
97, 020 electrons,
145, 570 gaussian basis functions
Maxtrix 145, 570*145,570

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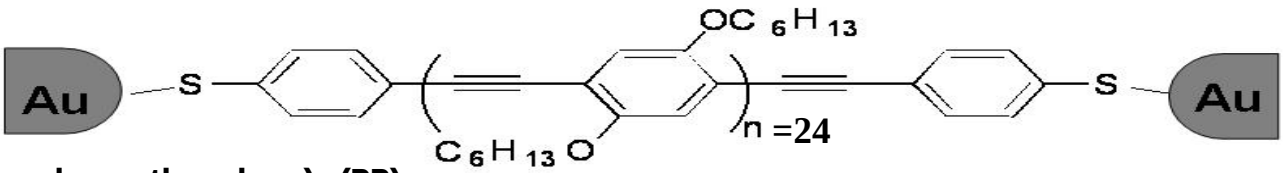
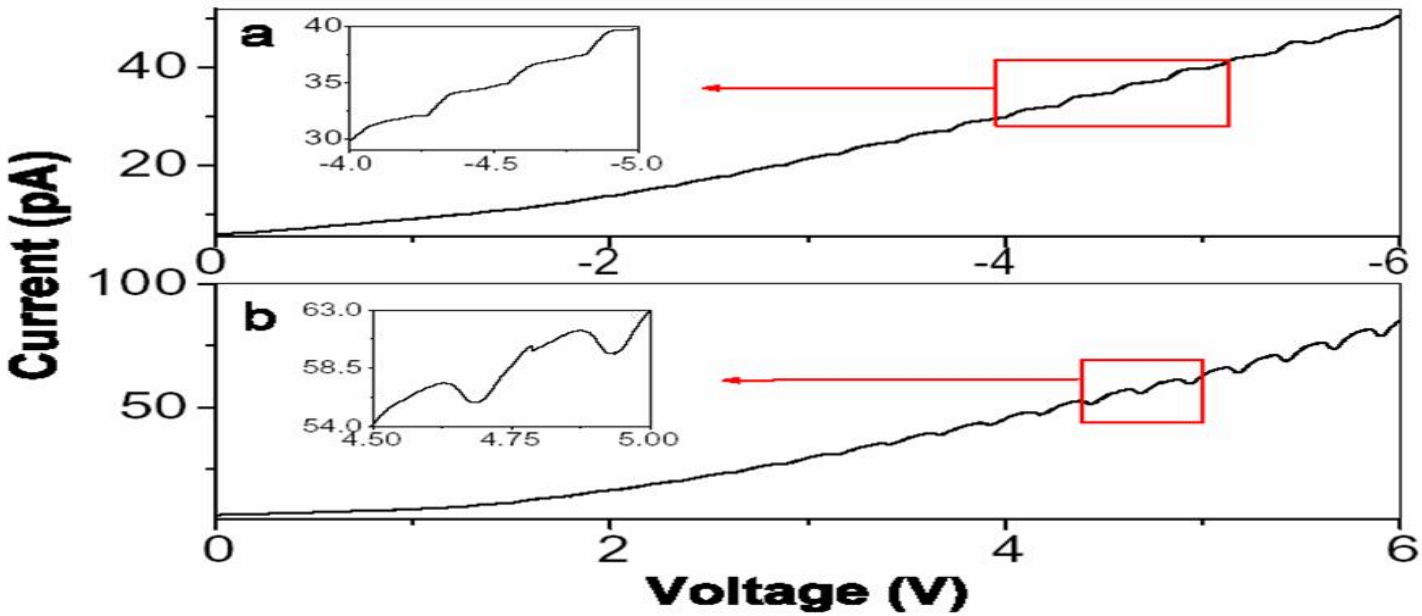
i 2005
18 (PPE)

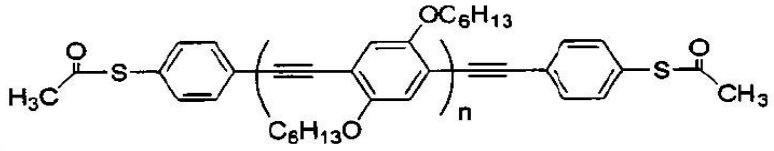


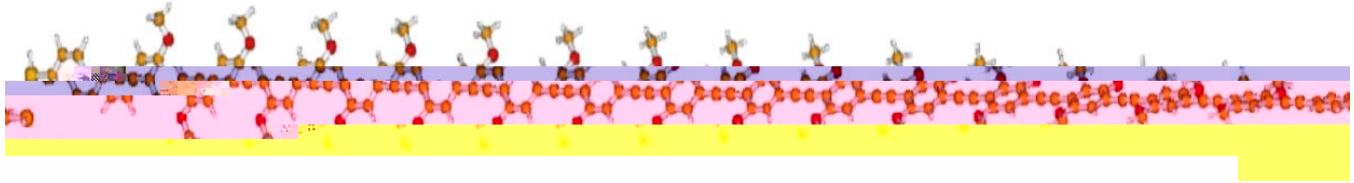
poly(*para*-phenylene ethynylene)s (PP)

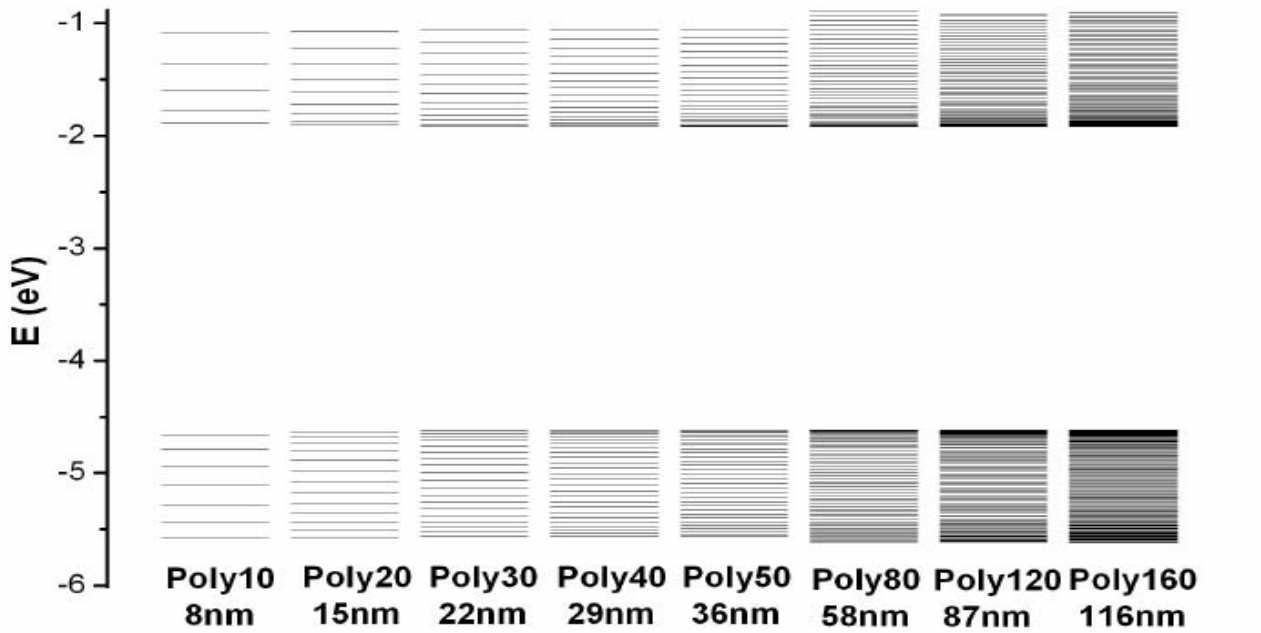
Au-Au : 18nm



Conjugated Polymer







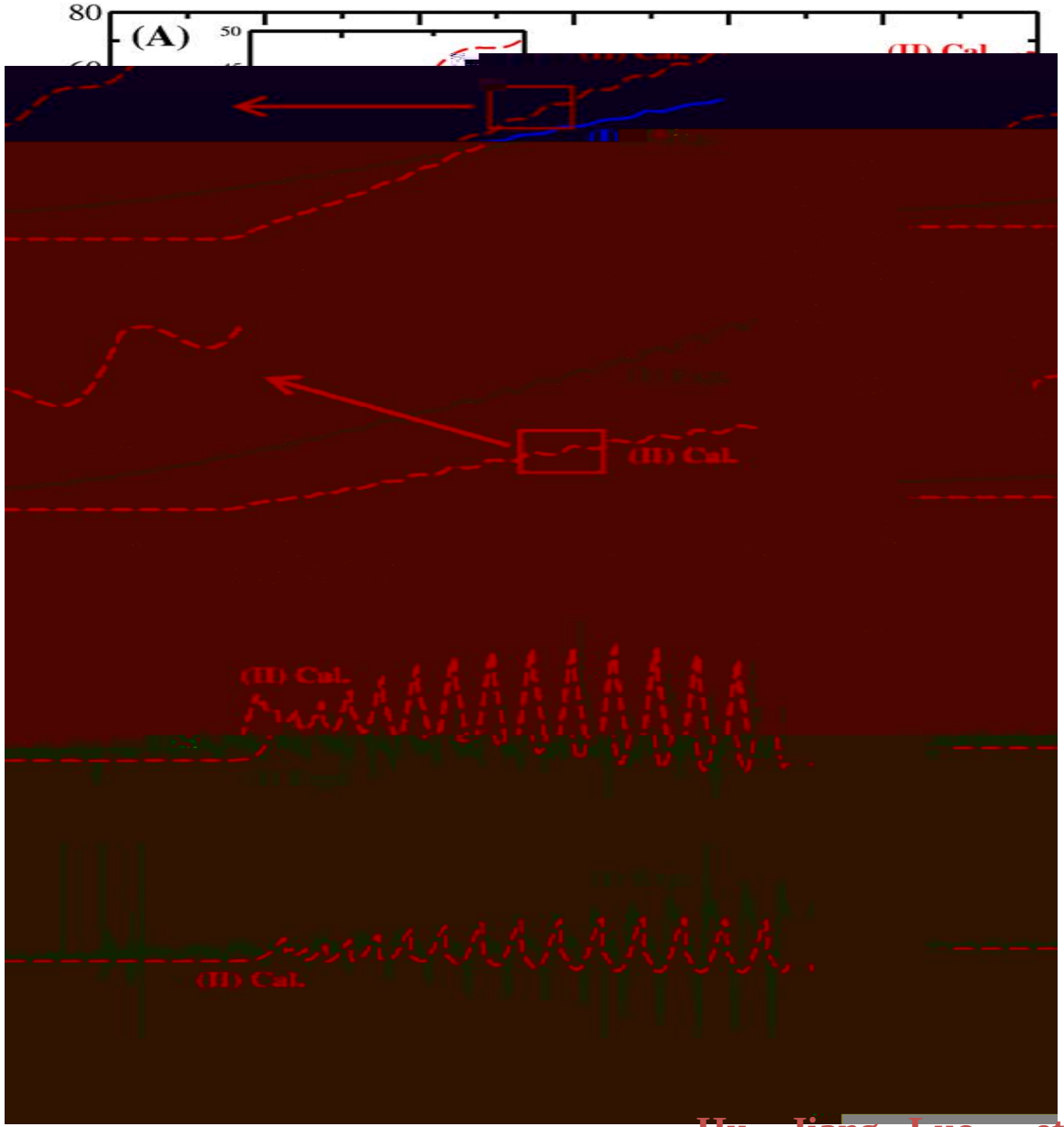
Increasing of size, Density of State(DOS) increases

Discrete molecular orbital to continuous band

HOMO-LUMO gap remains constant as 2.78eV

Energy structure analogous to inorganic Semiconductor

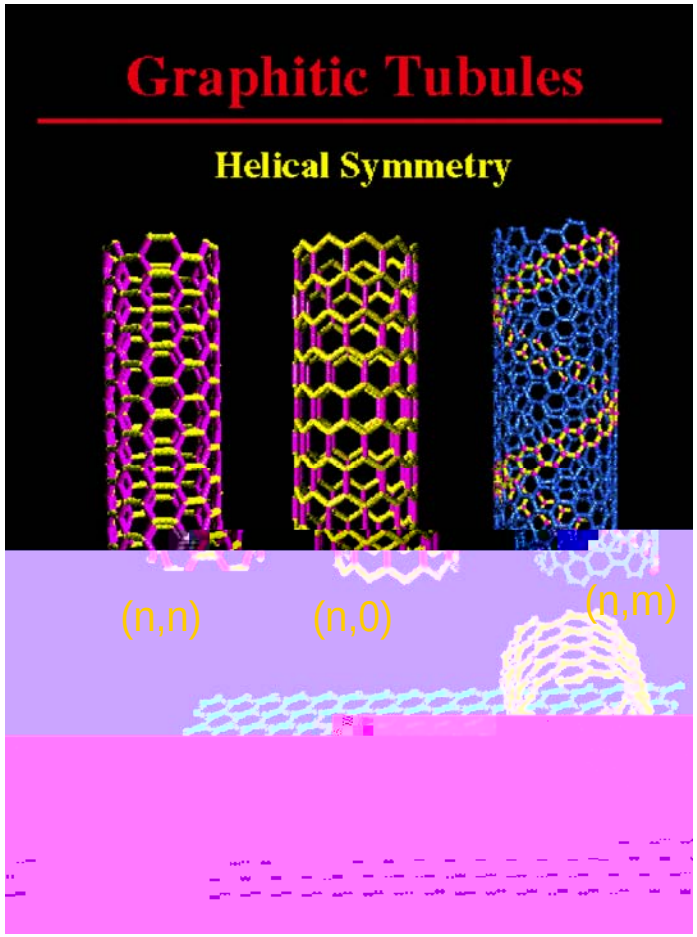
PPE ō n=24) 18.3



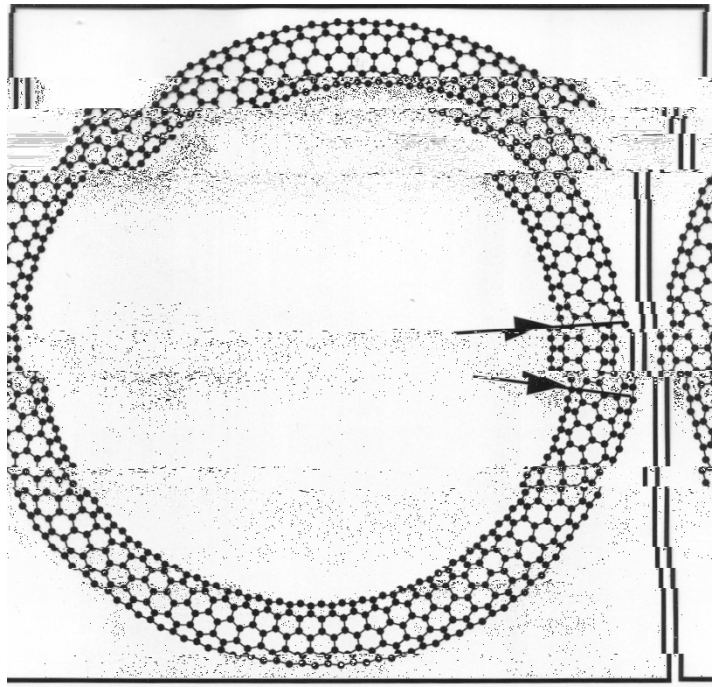
Hu, Jiang, Luo … et al. Phys. Rev. Lett., 96 (2006) 027801

- **CIS calculation provide accurate electronic structures for very long conjugated polymers**

Carbon Nanotube-based Structures



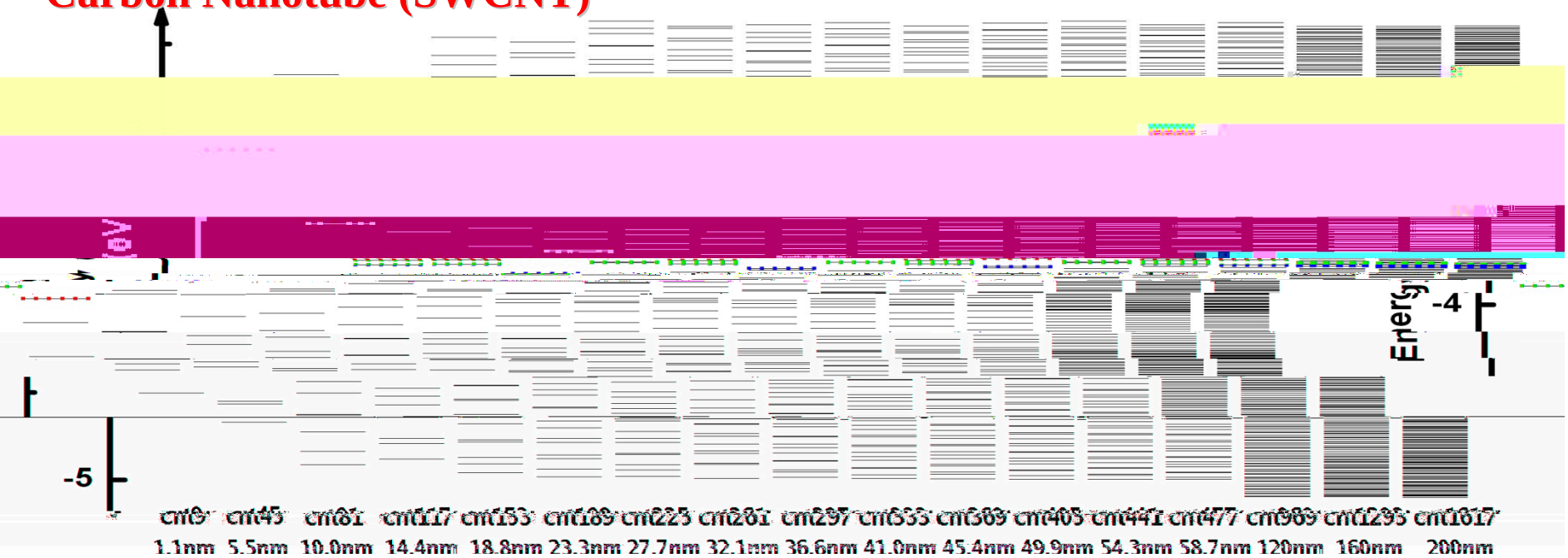
A Toroidal Carbon Nanotube



Carbon Nanotubes (CNTs) and toroidal carbon nanotubes (TCNs) are special class of low-dimensional systems which are expected to exhibit novel physical properties due to their special geometries (cylindrical/toroidal) as well as nanoscale sizes

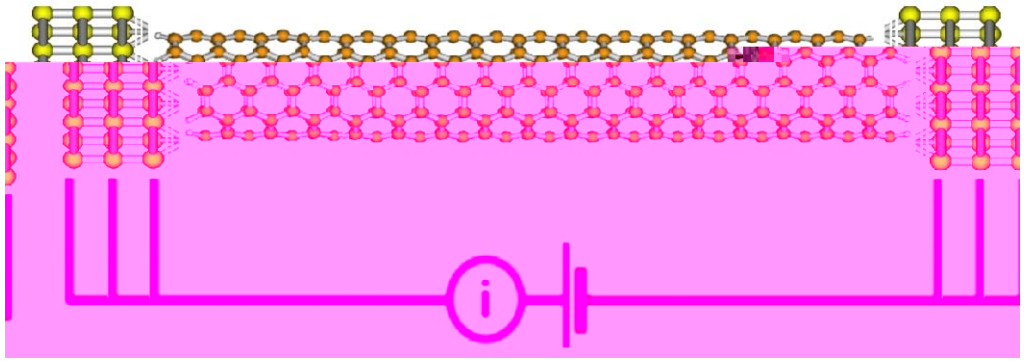
(5, 5) Metallic Single Walled Carbon Nanotube (SWCNT)

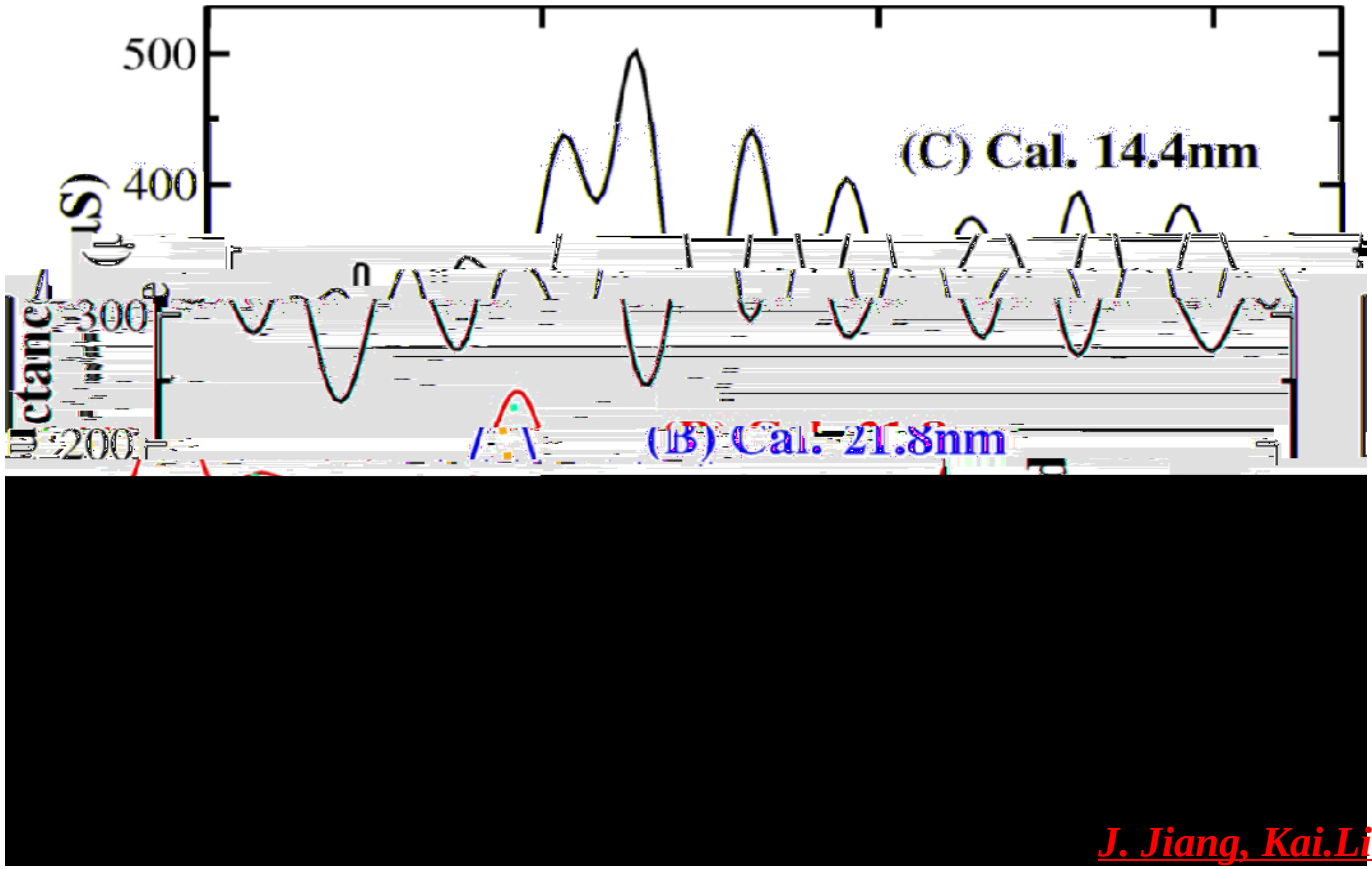
B3LYP/6-31G
Max: 16170 C atoms described by 150, 000 Gaussian Basis



G03 LUMO of 4.1 nm SWCNT | CIS LUMO of 4.1 nm SWCNT | CIS LUMO of 200 nm SWCNT

Electron transport in (5, 5) CNT

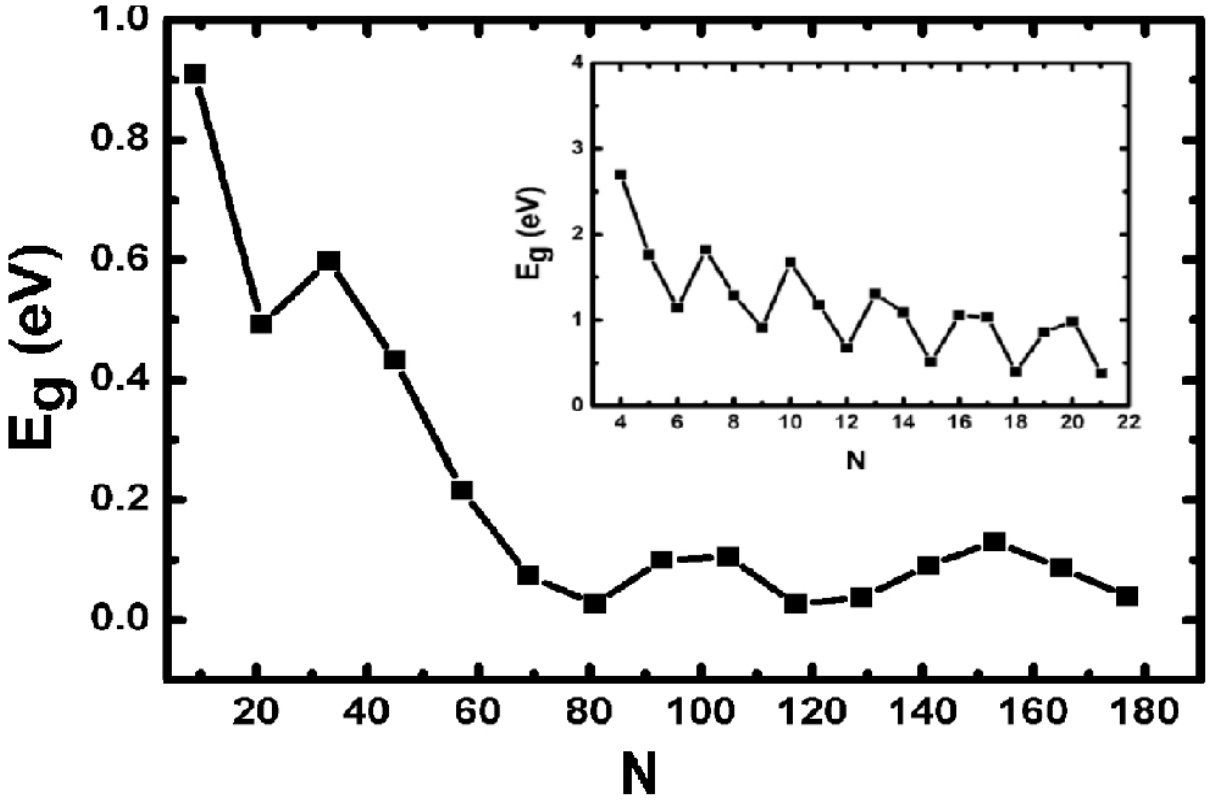




Exp: Javey et al. PANS, 101 (2004) 13408

J. Jiang, Kai.Liu, Y. Luo,
J. Chem. Phys. 124, 214711. 2006

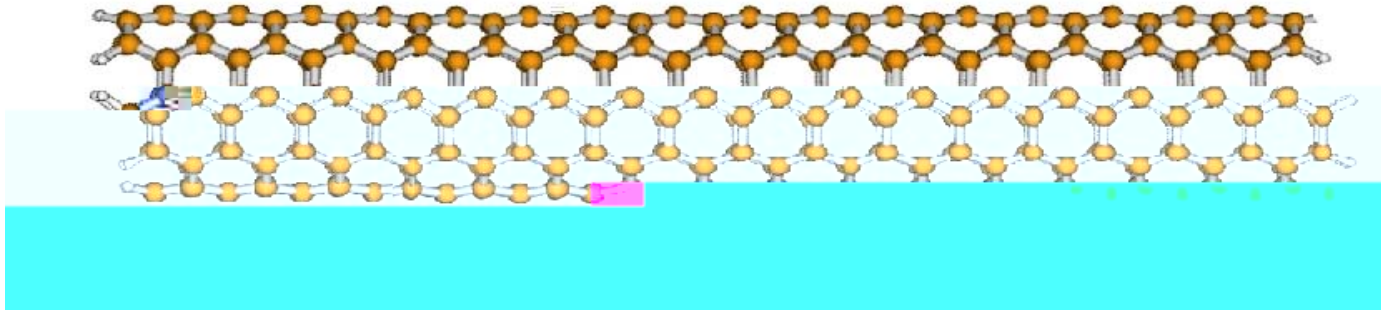
(5, 5) metallic CNT

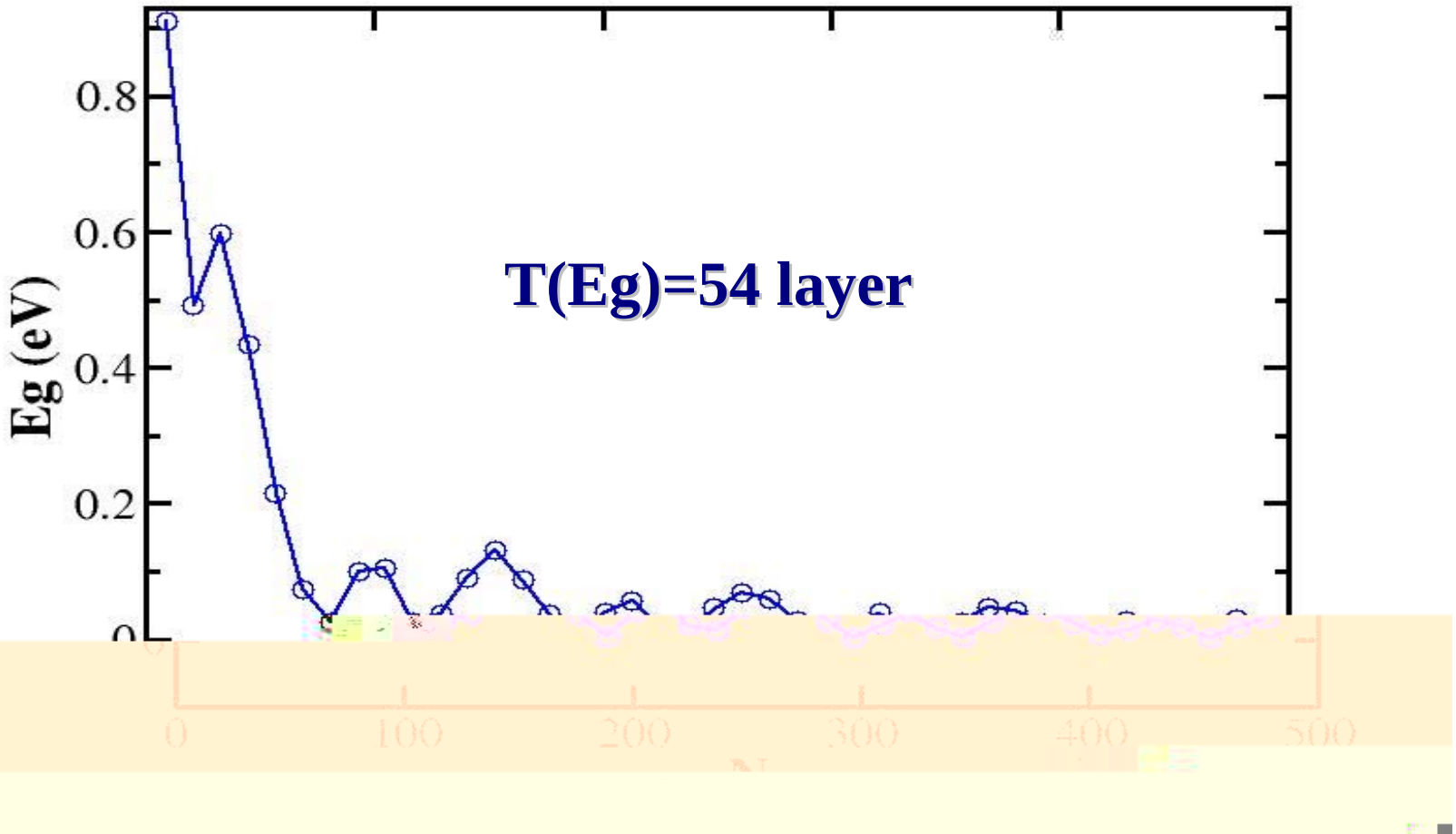


Bigger-period oscillation superimposed on the 3 units period oscillation:
Interference effect between the one dimensional quantum confinement along the tube direction and the two dimensional quantum confinement along the tube ring direction.

(5, 5) metallic CNT

DFT
B3LYP/6-31G

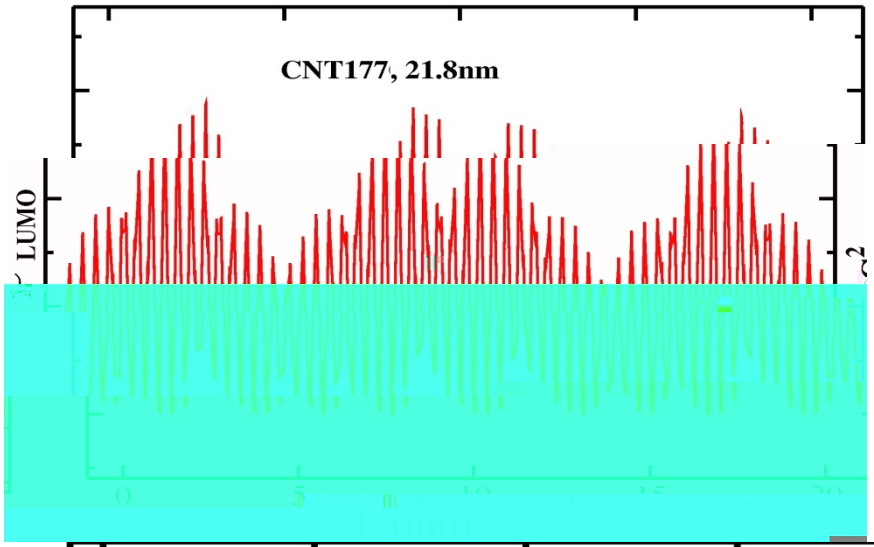




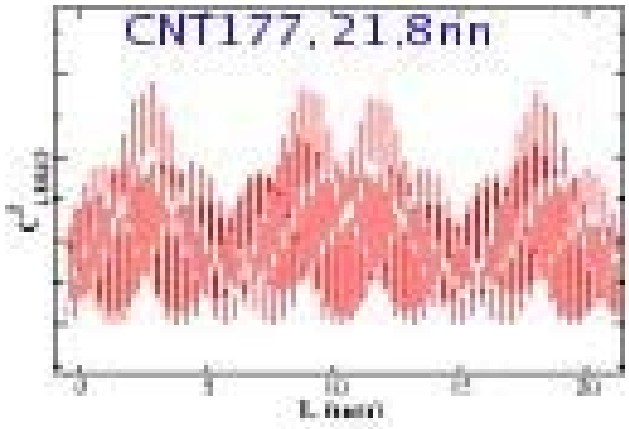
T(Eg)=54 layer

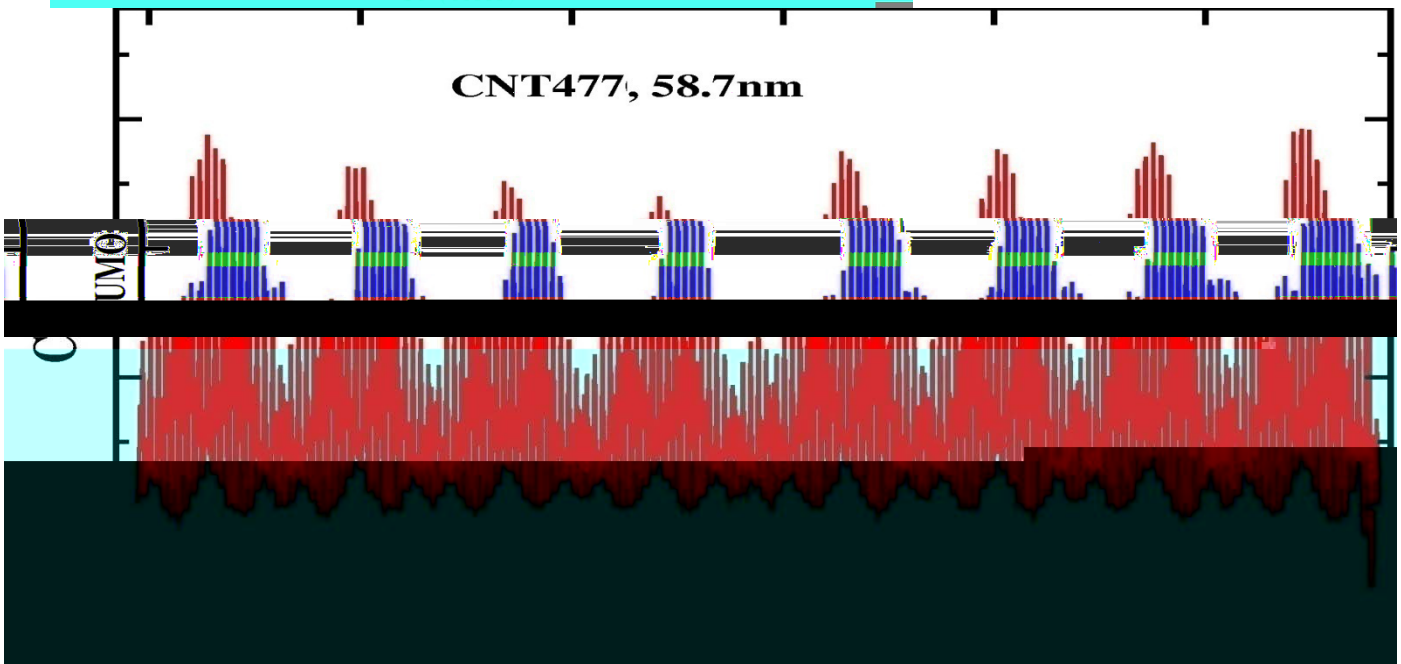
(5, 5) metallic CNT

1D Wavefunction along tube direction



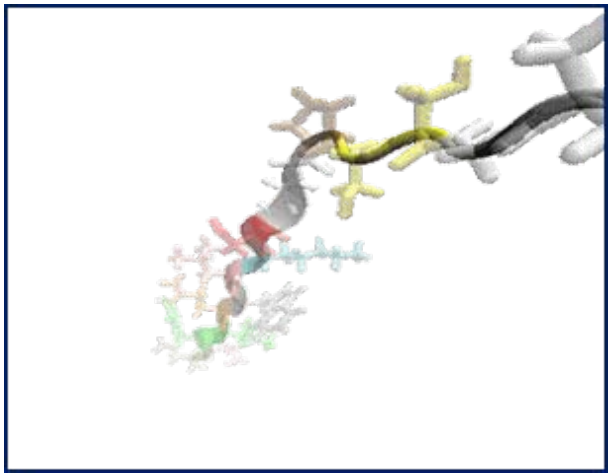
Blur effect

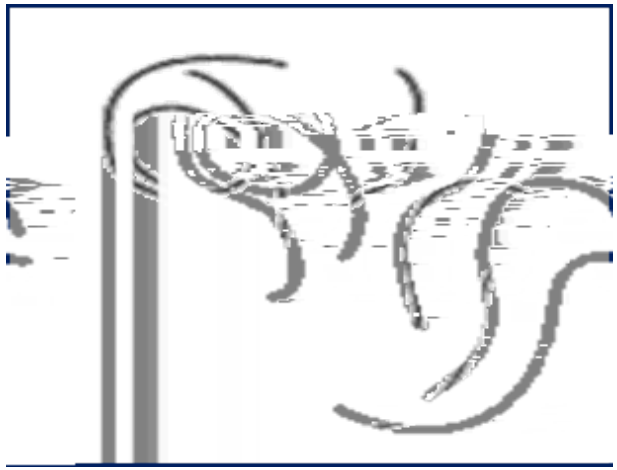


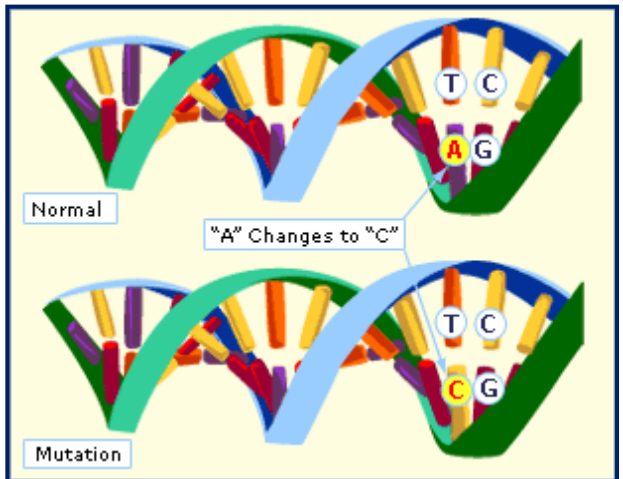


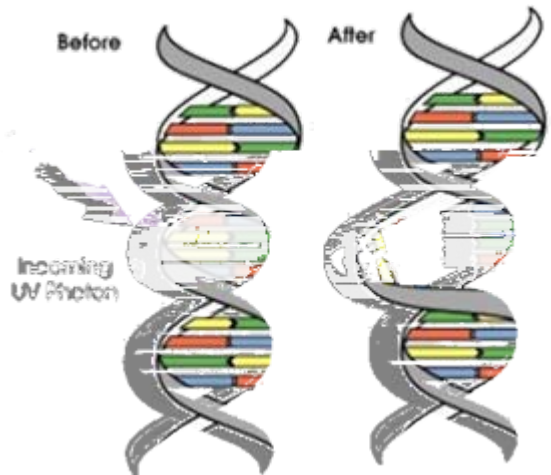
T(w)=36 layer

- **CIS calculation provide accurate electronic structures for very long CNT**
- **CIS found bloch-alike wavefunction in CNT without assuming any periodical boundary conditions.**

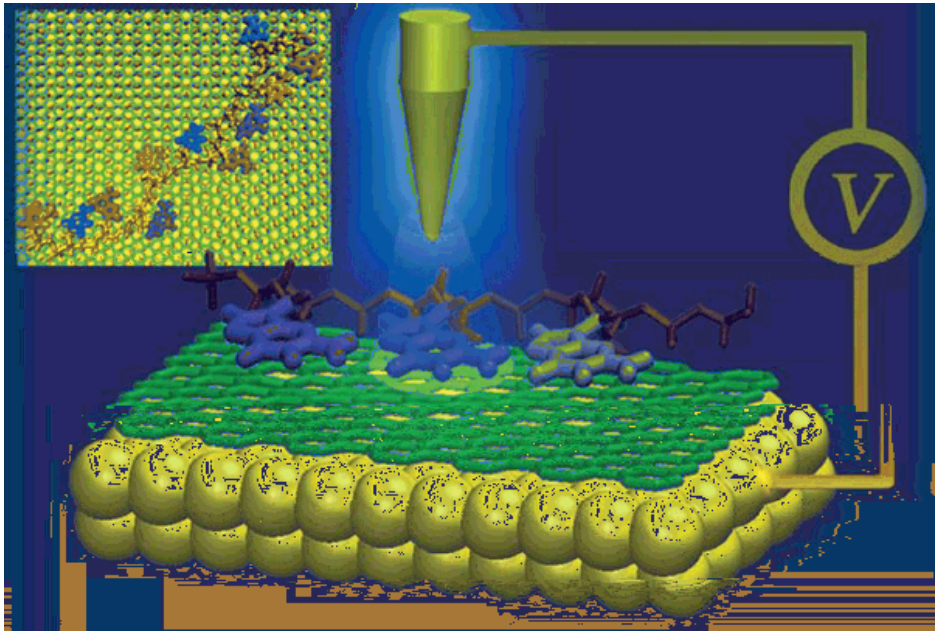


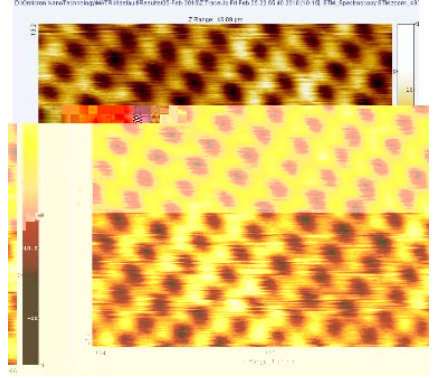


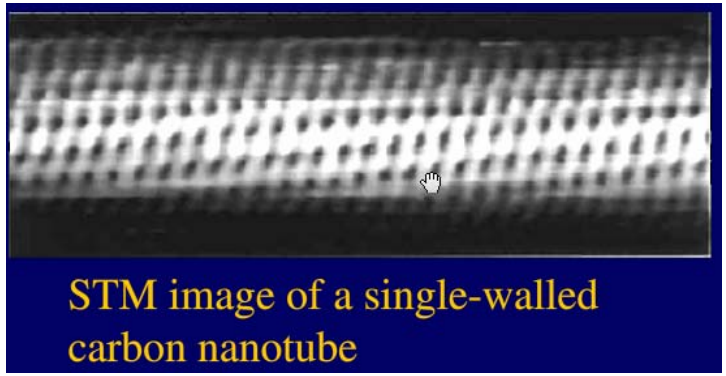

T
C
A
G
Normal
"A" Changes to "C"
T
C
C
G
Mutation

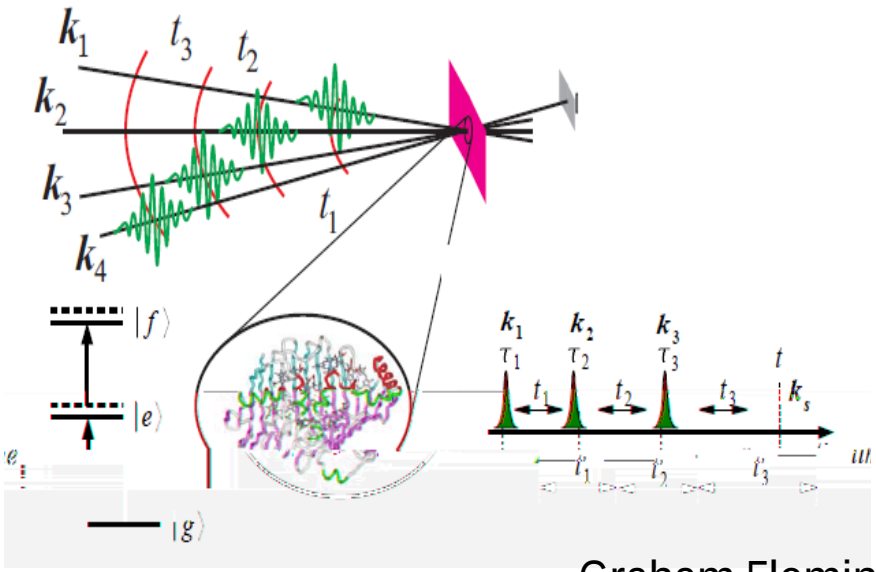

Before
After
Incoming
UV Photon

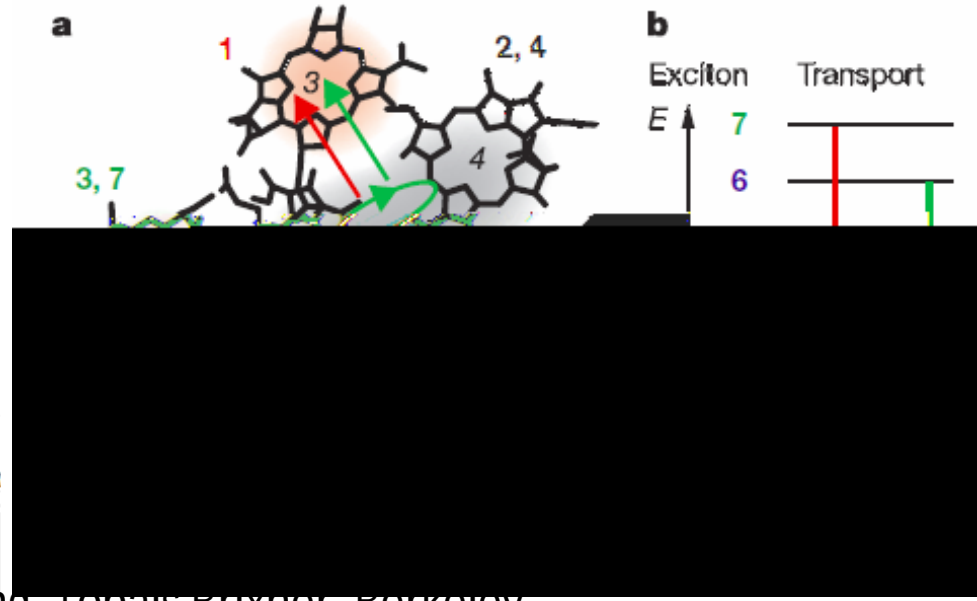
^ STM)









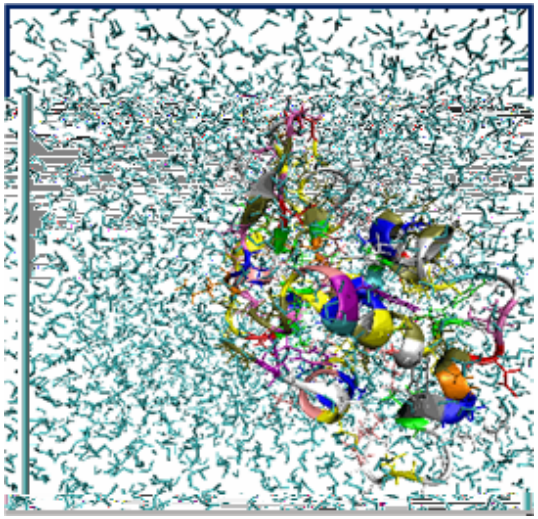


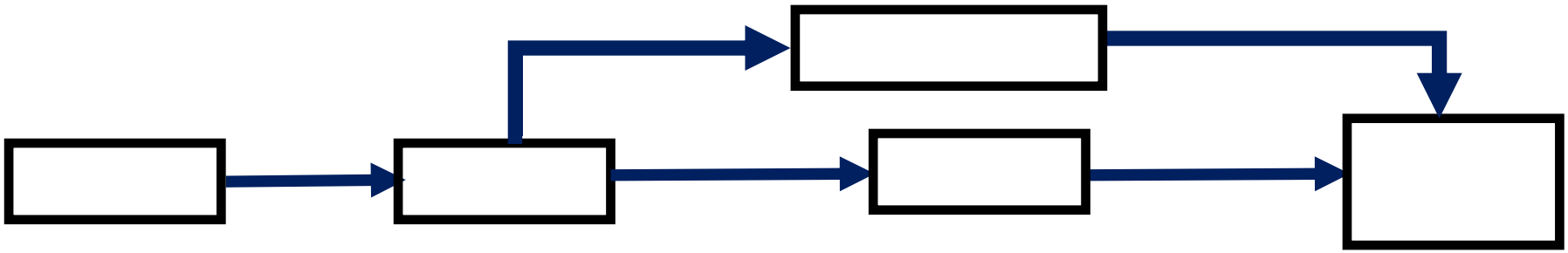
Graham Fleming, Tobais Brixner, Berkeley

EHEF(Exciton Hamiltonian with Electrostatic Fluctuations) ( )

( )

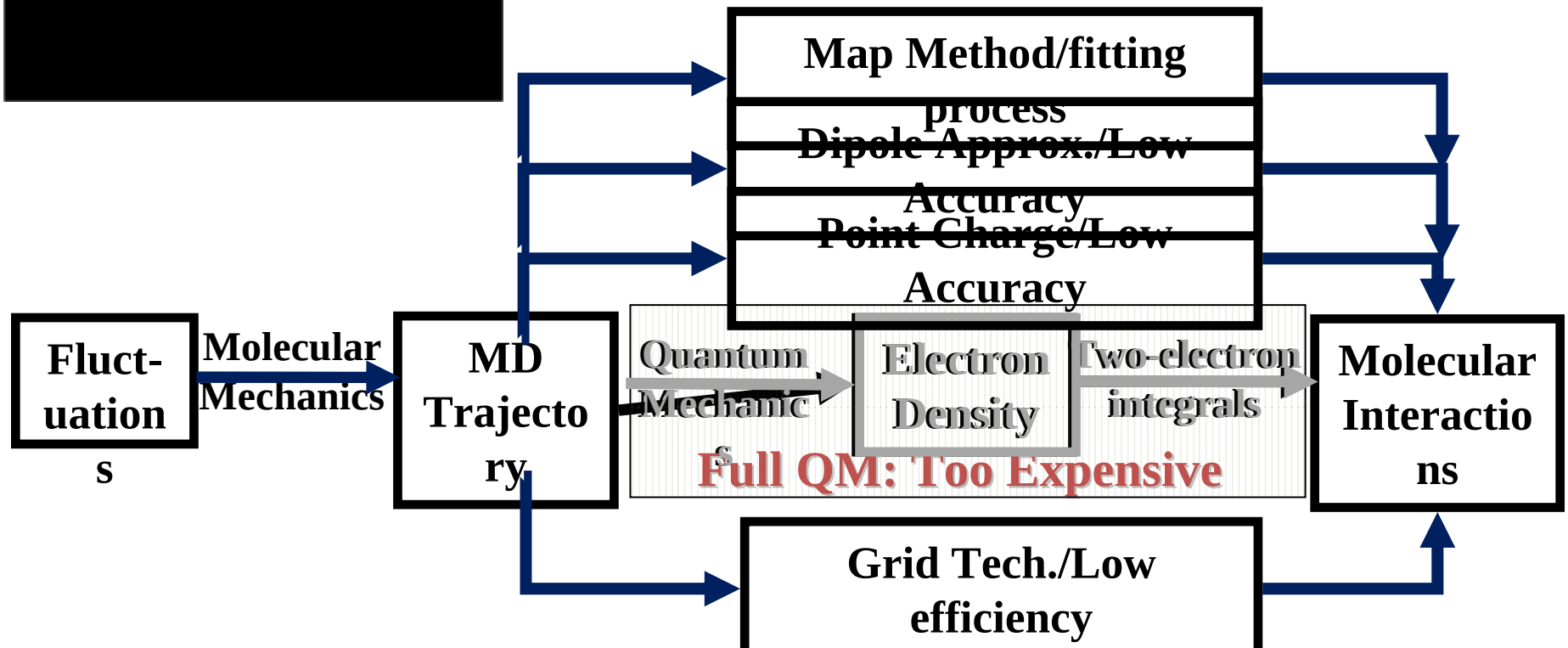
SPECTRON EHEF





Challenge for theoretical study

- Fluctuations of proteins and environment: Change spectral features



Map method for environmental fluctuations

Energy of a state can be expressed as

$$E = E_0 - \mu \cdot F$$

Map for excitation energy are constructed by

$$\varepsilon_m^F = \varepsilon_m + \sum_i \alpha_i \mathbf{F}_i + \sum_i \beta_i \frac{d\mathbf{F}_i}{dr} + \ldots$$

or

$$\varepsilon_m^F = \varepsilon_m + \sum_i \alpha'_i \mathbf{K}_i + \sum_i \beta'_i \mathbf{K}_i^2 + \ldots$$

Advantages: Cheap computation costs & Easy to test

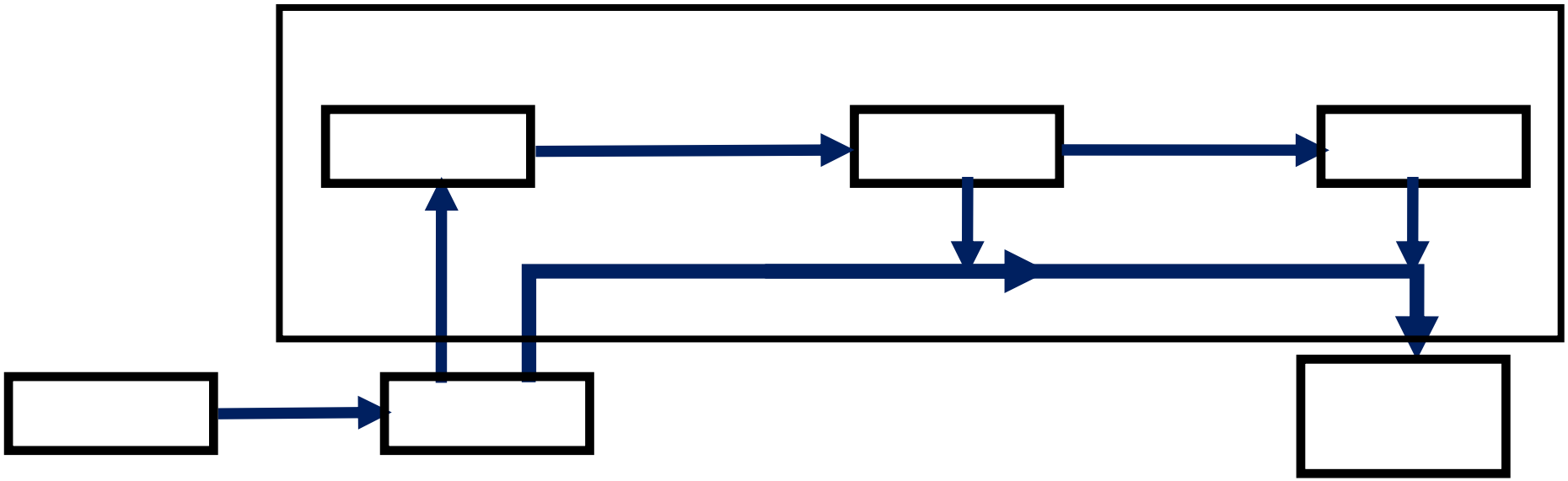
--successful utilizations in 2DIR studies

Disadvantages:

Rely on many QM calculations and heavy analysis

Fitted parameters are not transferable

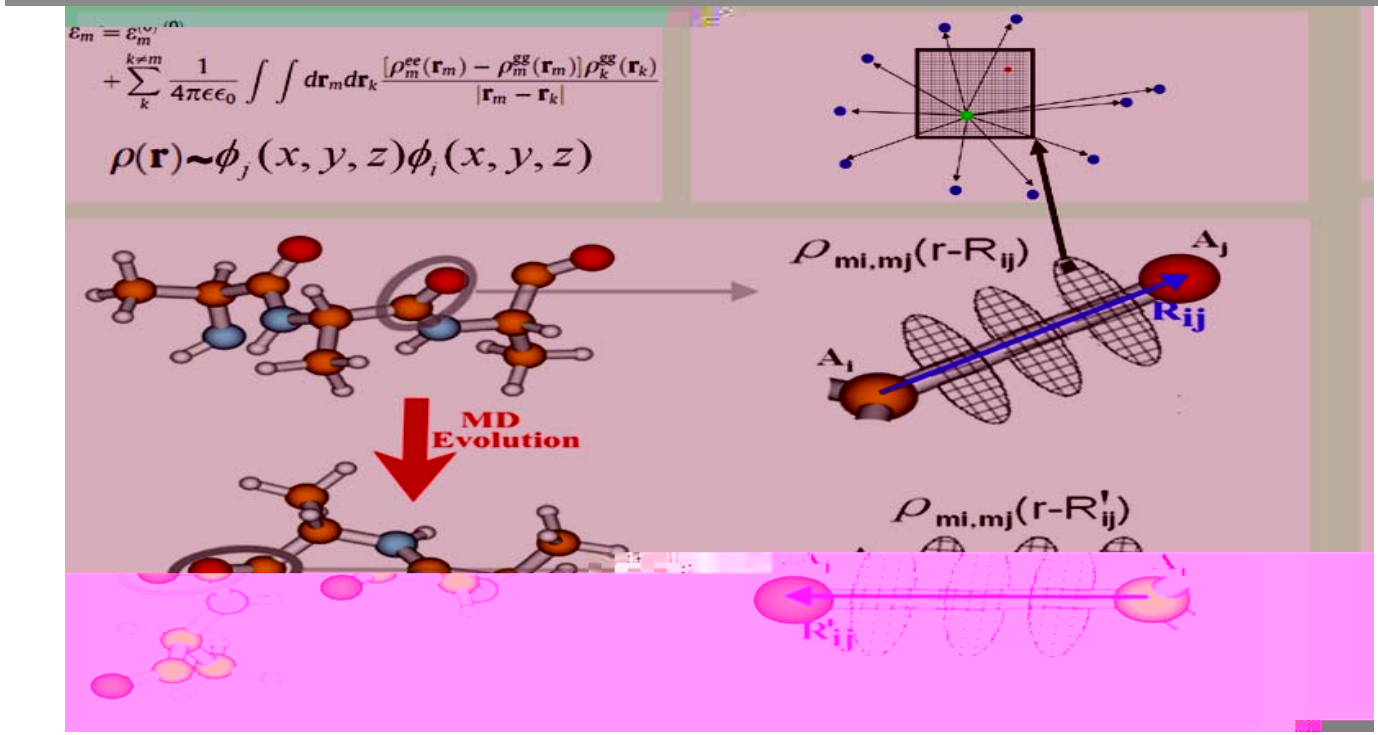
Lack of predict power



EHEF (Exciton Hamiltonian with Electrostatic Fluctuations) algorithm

EHEF, uses a limited number of charge grids to produce the same local electrostatic potential as that induced by charge density, and converts the integration of charge density to the product of two charge grids. It avoid repeated QM studies and calculate interactions with low cost, so that efficiently construct QM-based exciton Hamiltonian for thousands of MM snapshots

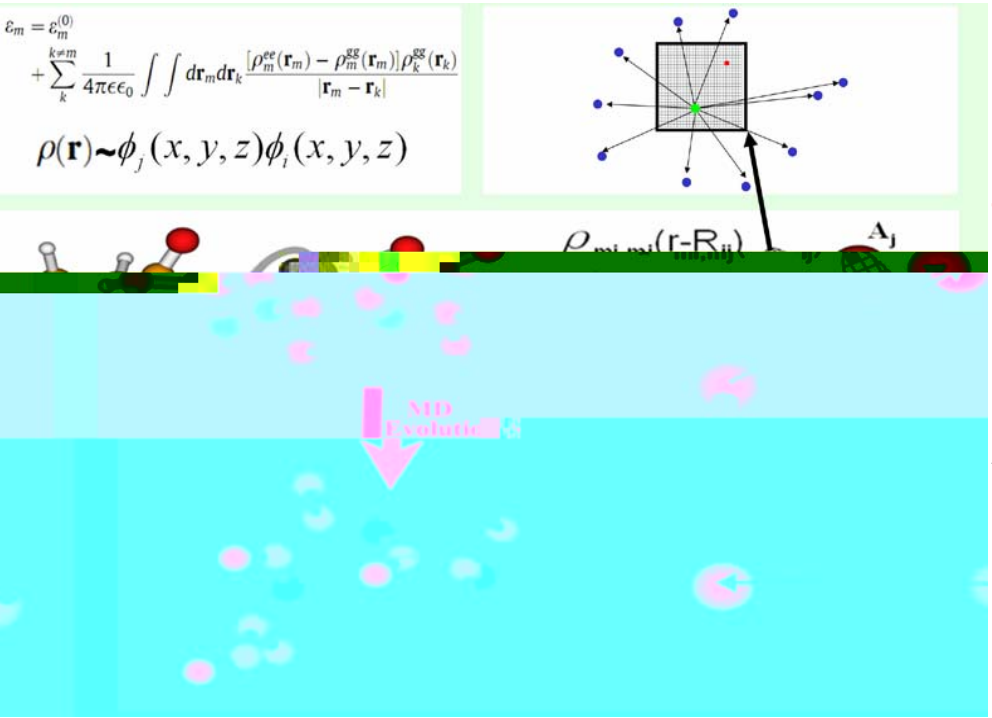
$$\frac{1}{4\pi\epsilon\epsilon_0}\int\int d\mathbf{r}_m d\mathbf{r}_k \frac{[\rho_m^{ee}(\mathbf{r}_m)-\rho_m^{gg}(\mathbf{r}_m)]\rho_k^{gg}(\mathbf{r}_k)}{|\mathbf{r}_m-\mathbf{r}_k|} \cong \sum_{i,j}\frac{M_m^{eg}(i)\,M_k^{ge}(j)}{4\pi\epsilon_0 r_{ij}}$$



J. Jiang, D. Abramavicius, S. Mukamel, J. Phys. Chem. B. 2010, *114*, 8270

J. Jiang, S. Mukamel, Phys. Chem. Chem. Phys. 2011, *13*, 2394

EHEF (Exciton Hamiltonian with Electrostatic Fluctuations) algorithm



1. Define atomic frame for each pair of atoms, (R, θ , γ)

2. Calculations involve charge densities (As expensive as calculating 2-e integrals)

3. To obtain low computation cost, use a limited number of large grids (10^3 for an amino acid).

4. Each Grid is divided into a large number of sub-grids (10^6 for an amino acid), to maintain the same precision as 2-e integrals.

5. Electrostatic potentials at random sample positions are calculated from charges in 10^3 sub-grids, and are used to fit one point charge for one grid.

6. Charge distributions are saved in the atomic frame.

7. Assume fixed charge distribution in the atomic frame

8. Update the new atomic frame during MD evolutions (R', θ ', γ ')

9. Update the charge density in the new atomic frame.

10. Calculate energy shift due to fluctuations.

J. Jiang, D. Abramavicius, S. Mukamel, J. Phys. Chem. B. 2010, *114*, 8270

J. Jiang, S. Mukamel, Phys. Chem. Chem. Phys. 2011, *13*, 2394

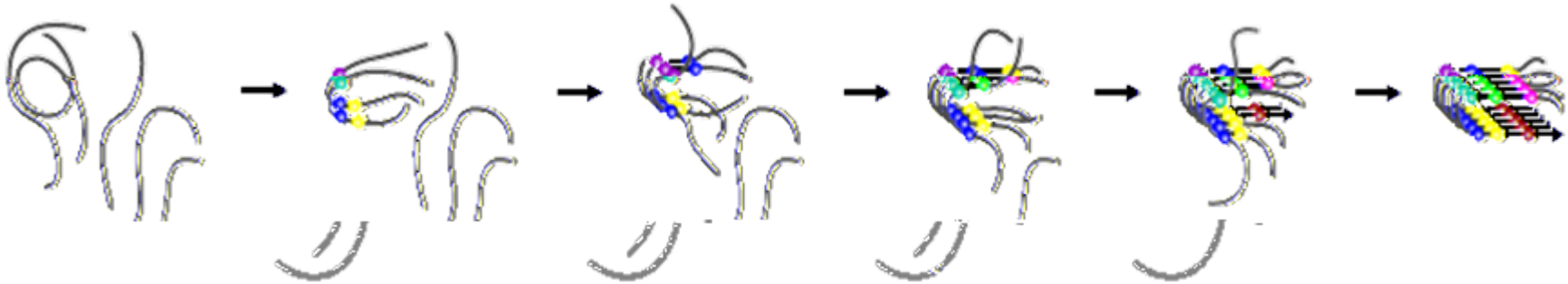
EHEF (Exciton Hamiltonian with Electrostatic Fluctuations) algorithm

Accurate -- calculations without fitting parameters

Efficient -- Atomic frame to avoid repeated QM studies, Grid charge fitted from electrostatic potential avoid integrations

Transferable for different systems and applications

Able to explain experiments and predict new information



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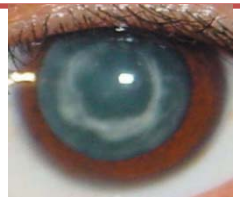

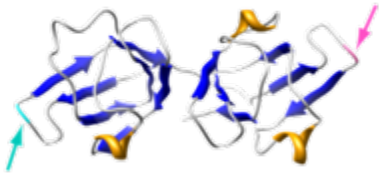

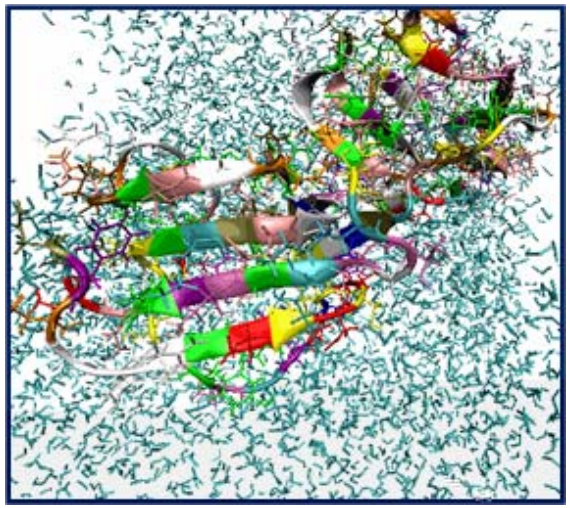

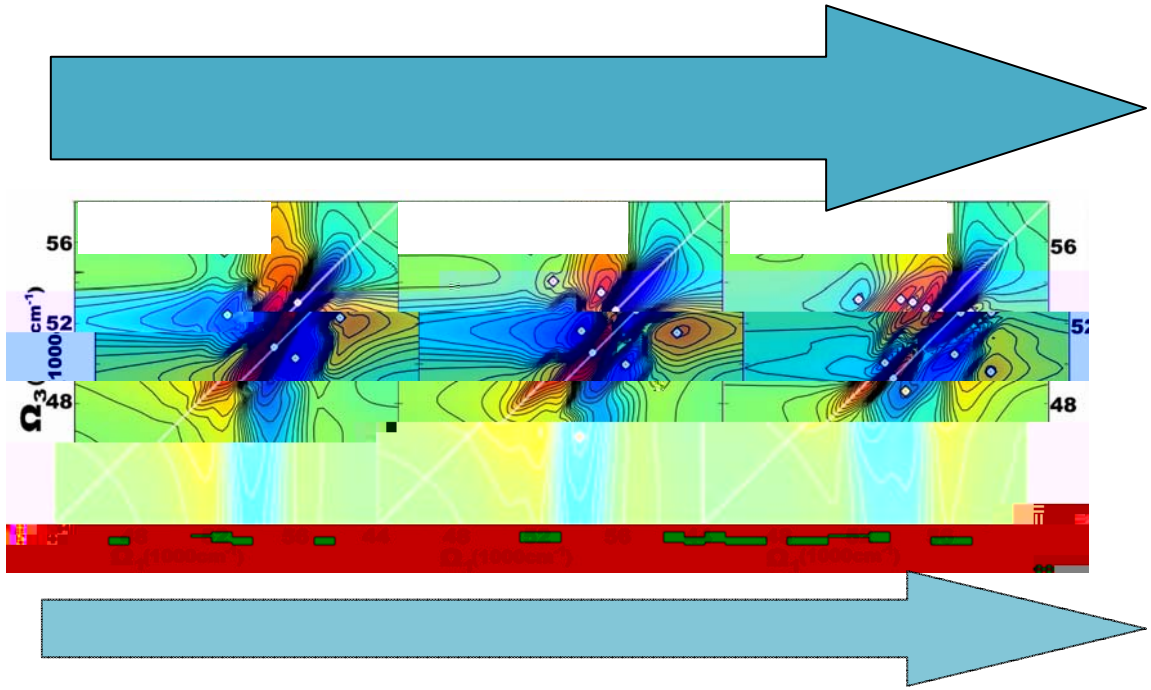
56
52
48
56
48
Ω_3 (1000 cm^{-1})

QM/MM

( )

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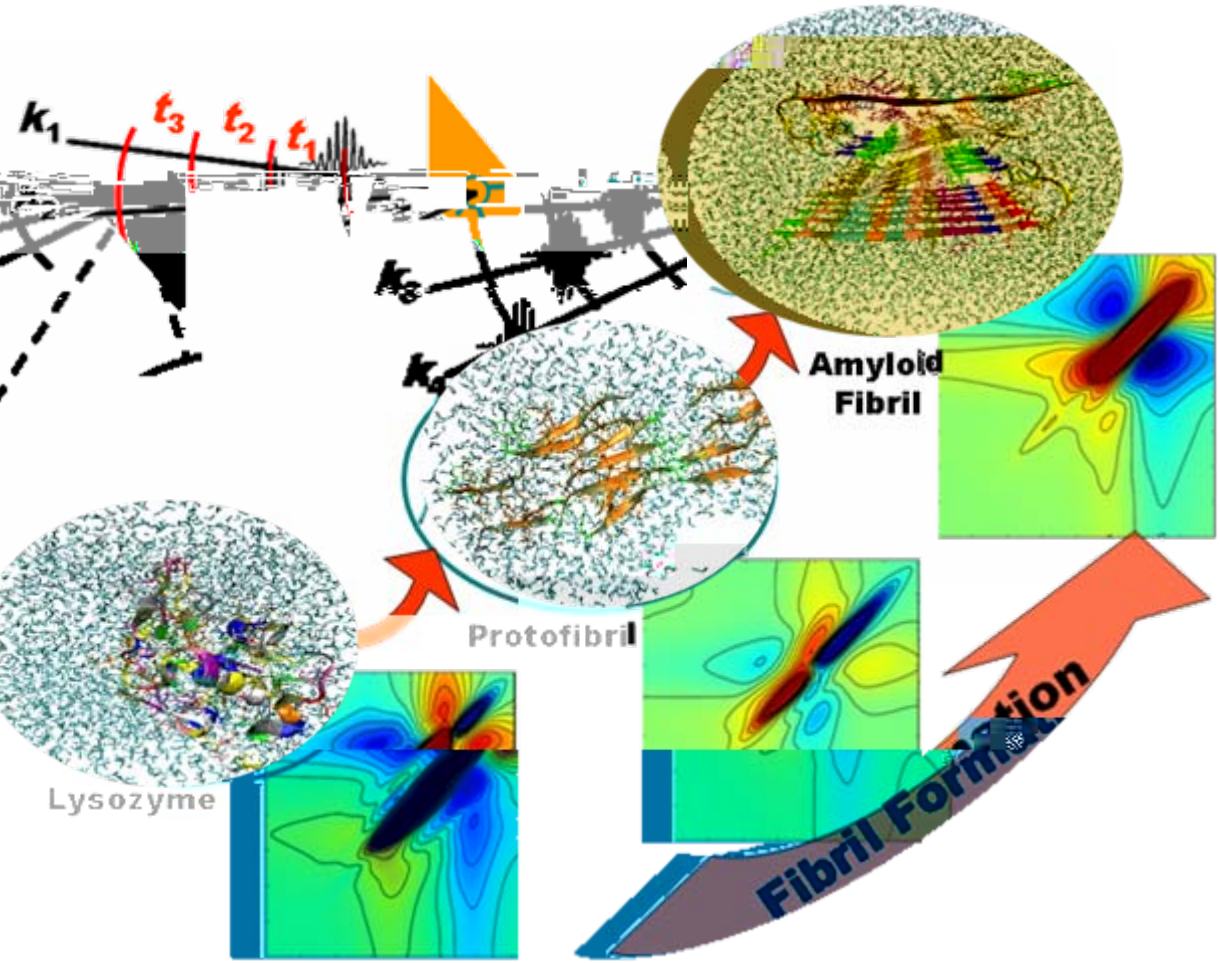
-

X-ray NMR CD



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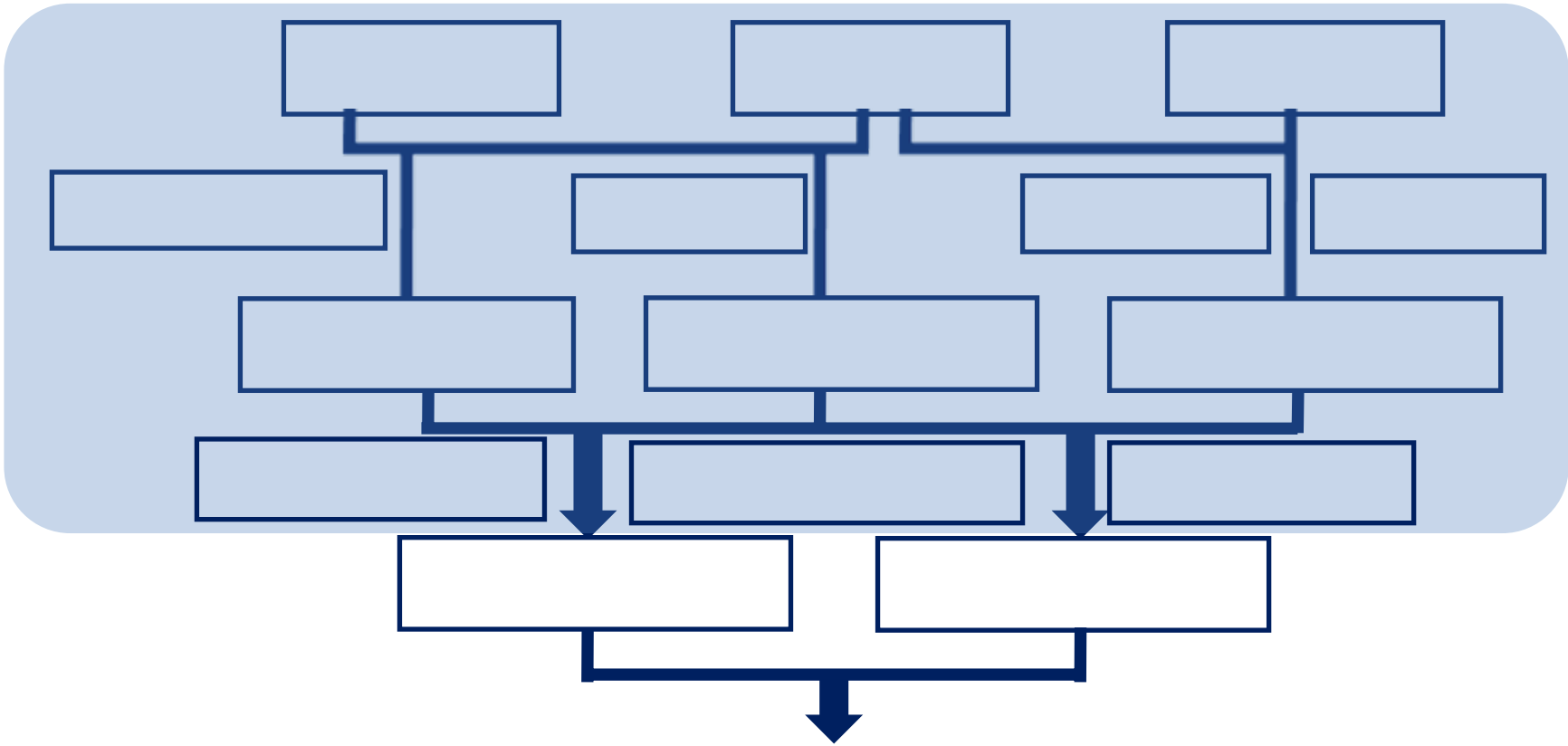
Jiang, Mukamel Angew. Chem. Int. E.d *49*, 9666(2010); J. Am. Chem. Soc., *132*, 7769(2010); J. Phys. Chem. B, *114*, 12150(2010);



- (Goddard:Caltech, Martinez:Stanford, Steinhauser:Fraunhofer)
- Gaussian70 ō 98 Ŏ
- Sidney Yip : “ ”¢
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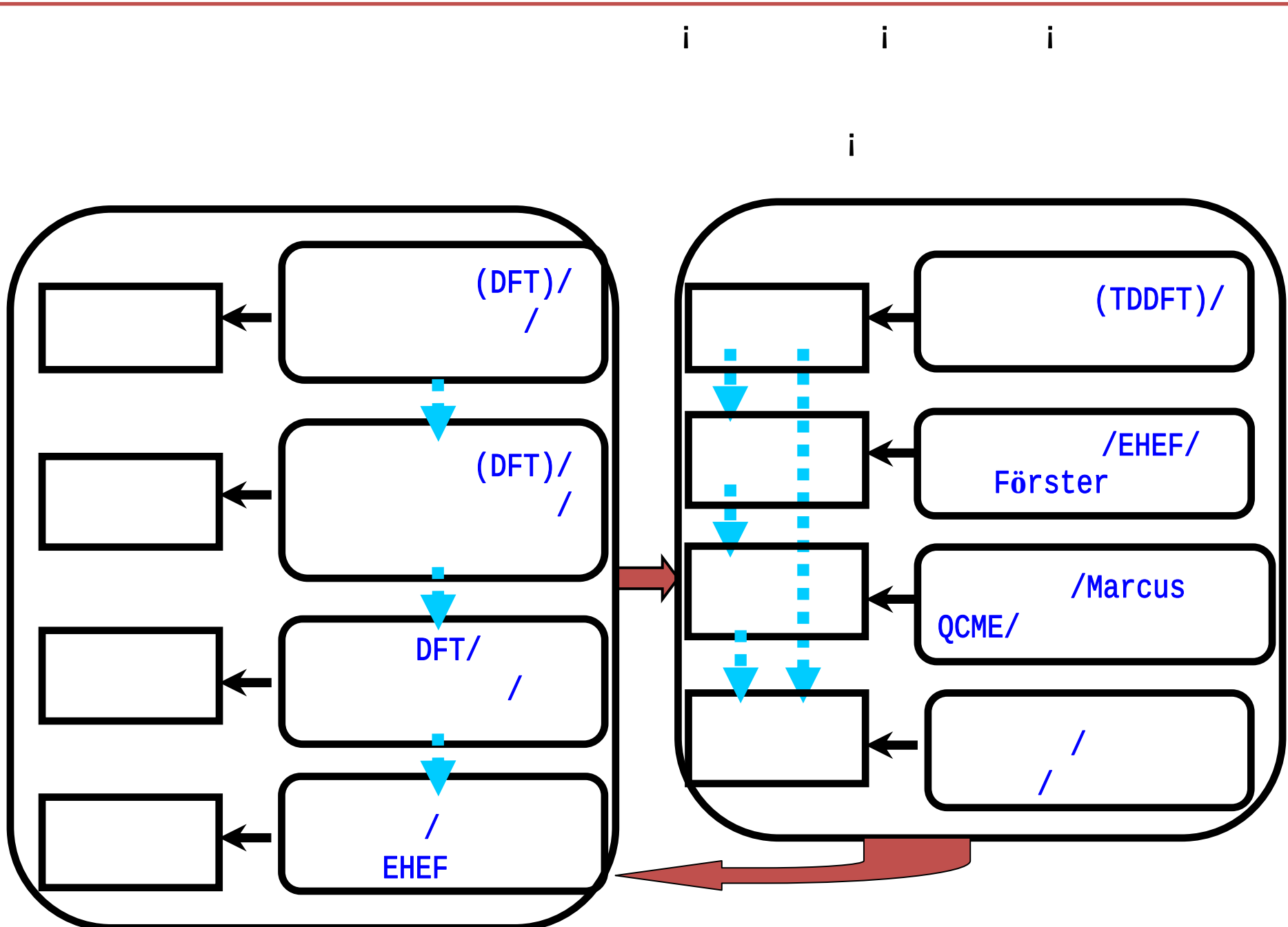
(DFT)/
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EHEF
(TDDFT)/
/EHEF/
Förster
/Marcus
QCME/
/
/

Royal Institute of Technology, Sweden

Hans Agren

(University of California, Irvine)

Prof. Shaul Mukamel

Dr. Darius Abramavicius

Dr. Daniel Healion

Dr. Lijun Yang