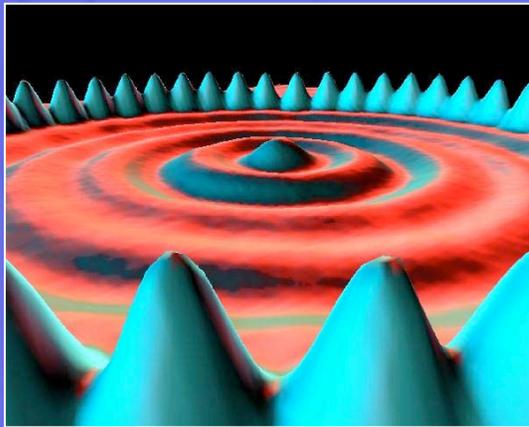


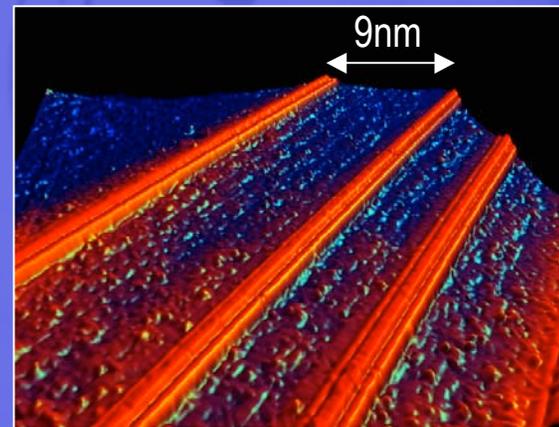
Computational Nano-Electronics

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Quantum Physics
Eigler (IBM)



Atomic Details
Williams (HP)

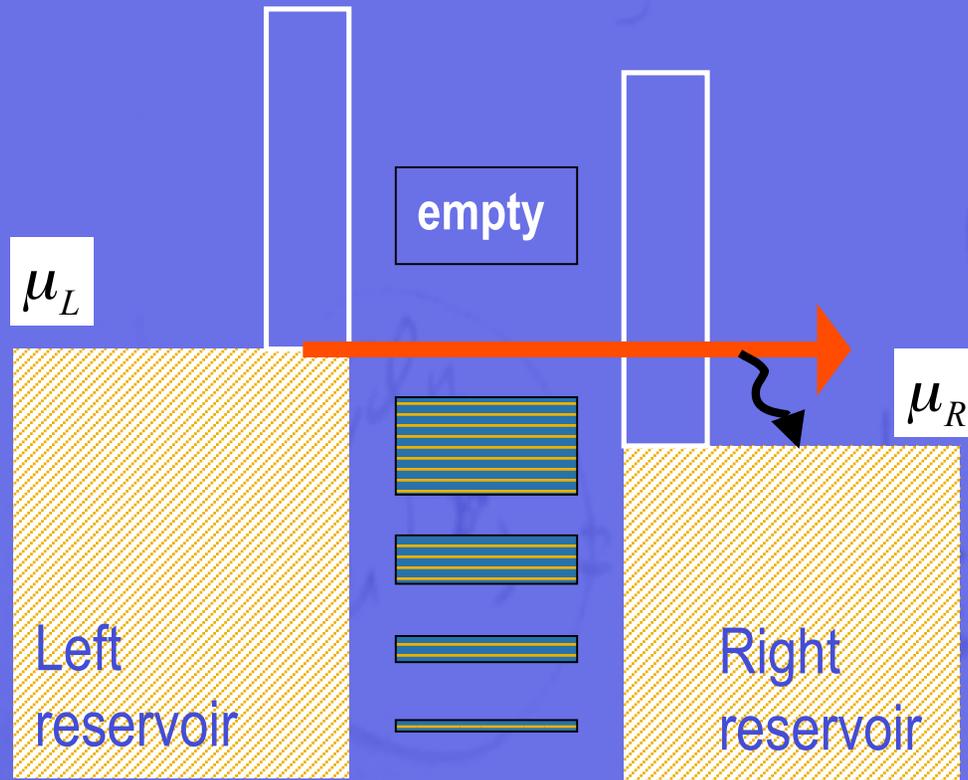
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Dr. Hatem Mehrez	General Electric	nanowires
Dr. Devrim Guclu	Cornell University	Quantum dots
Dr. C.C. Kaun	Academic Sinica, Taipei	Molecular wires
Dr. Eric Zhu	McGill	transient, statistical
Dr. Nikolai Sergueev	UT-Austin	electron-phonon at nonequilibrium
Dr. Dan Roubtsov	Chalk River National Lab	inelastic current
Prof. Q.R. Zheng	Grad. School, CAS, Beijing	Molecular electronics
Prof. Wengang Lu	Institute of Physics, CAS, Beijing	nanotubes and molecular wires
Dr. C. C. Wan, Dr. N.J. Zhu	Synopsis	Transport theory
Dr. Jose-Luis Mozos	Barcelona	DFT-Scattering Matrix
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Paul Haney, Prof. Allan MacDonald (UT-Austin), Prof. Xia Ke & H.J. Gao (IoP)		spintronics

Outline:

- 
- A review of state-of-the-art;
 - DFT atomistic methods;
 - The NEGF-DFT implementation details;
 - Some applications of NEGF-DFT;
 - Quantum mechanic forces during current flow;
 - Summary: outlook to the near future.

Quantum transport model (recall Prof. Datta's lectures):



Under a voltage bias, electrons ballistically traverse device from left to right. They are “hot” electrons on the right, and some dissipation occurs and electrons end up inside the right reservoir.

We compute the transmission process from left to the right.

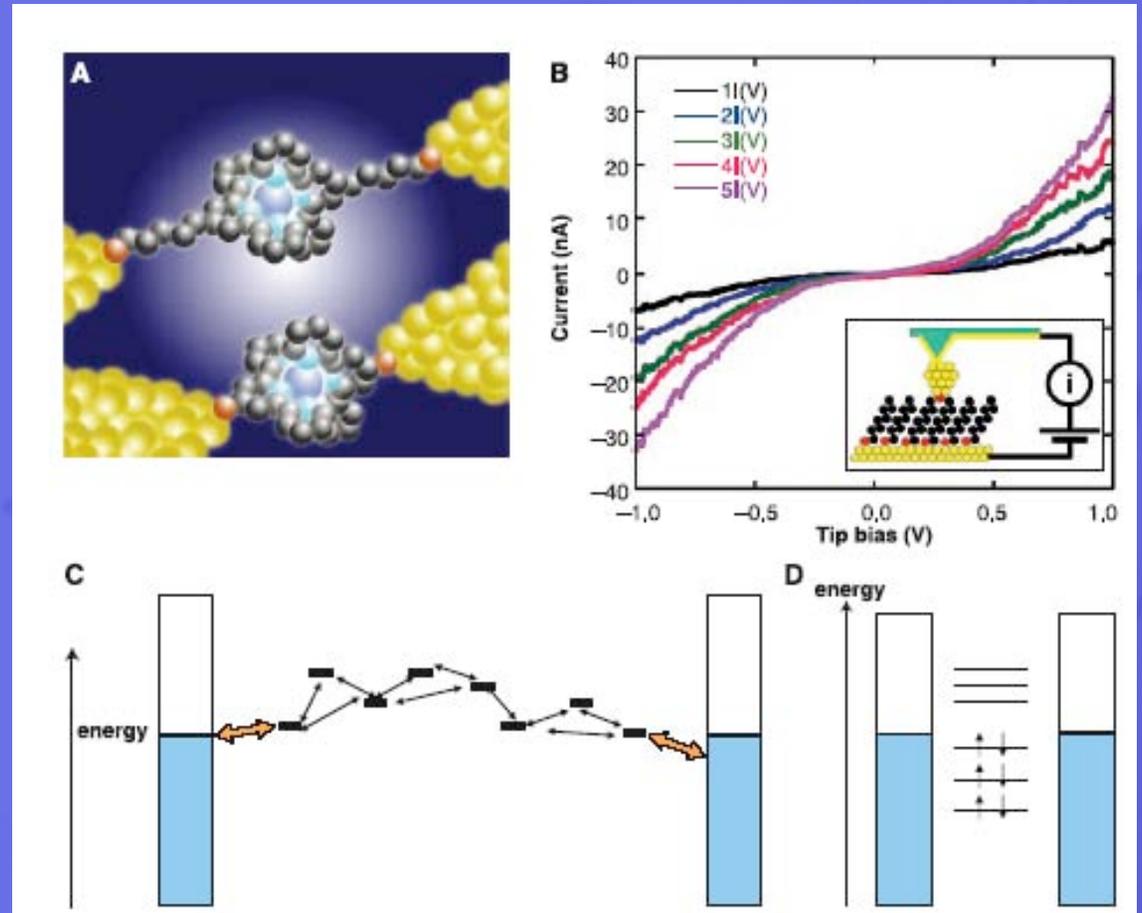
$$I(V) = -\frac{e}{h} \int_{-\infty}^{+\infty} \frac{dE}{2\pi} T(E, \Delta V) (f_l - f_r)$$

A few starting remarks:

- To do atomistic calculations of electric current (non-equilibrium), an important physics consideration is the non-equilibrium statistics of the scattering region.
- A important practical consideration is the device Hamiltonian H . H determines the energy levels of the device. How to fill these levels is given by the non-equilibrium statistics.
- Nonequilibrium statistics: NEGF, time-dependent evolution of density matrix from some initial condition, ...
- What H to use is a matter of numerical accuracy: effective mass, TB, HF, DFT, QMC, CI... In the end, one has to compare with real data.

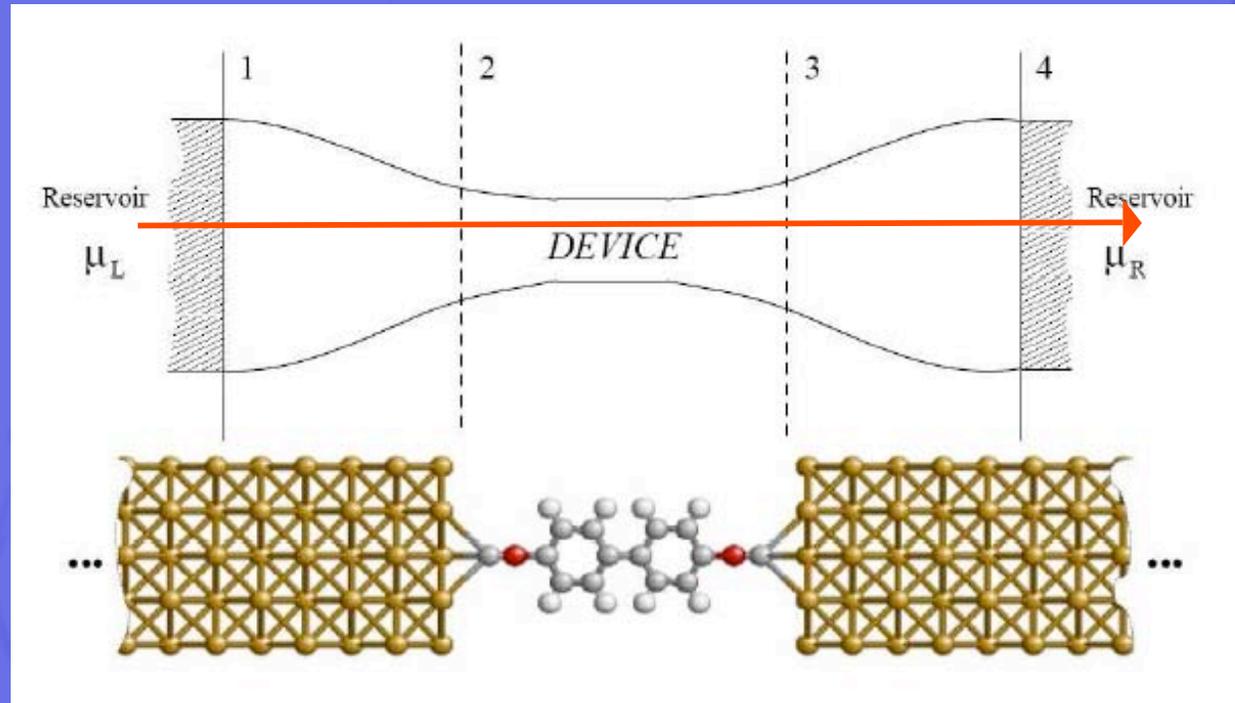
So, the basic ingredients to start a theory:

1. A transport model;
2. Atomic Hamiltonian;
3. Nonequilibrium Physics;
4. Transmission;
5. Fermi level alignment;
6. Calculable.



From: Nizan & Ratner, Science, 300, 1384 (2003).

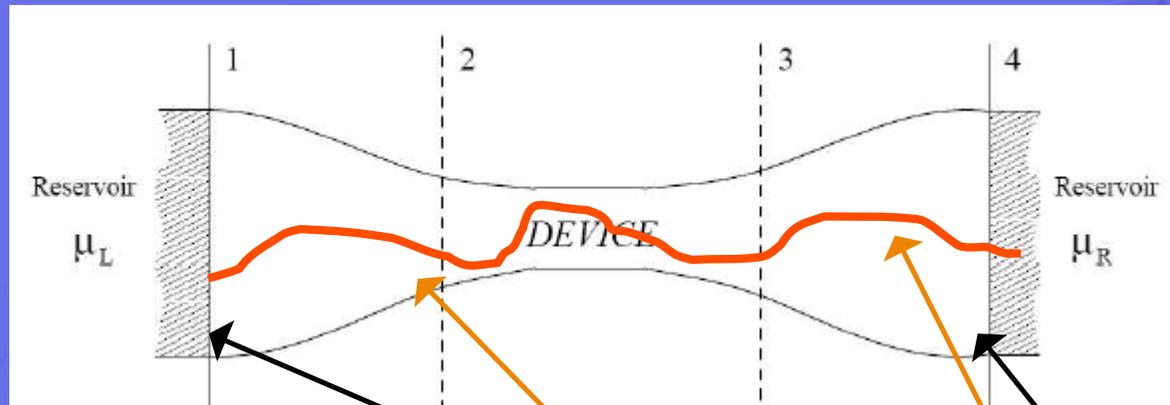
Again: Landauer-Buttiker transport model



It's a scattering problem:

$$I(V) = -\frac{e}{h} \int_{-\infty}^{+\infty} \frac{dE}{2\pi} T(E, \Delta V) (f_l - f_r)$$

Transmission coefficients:



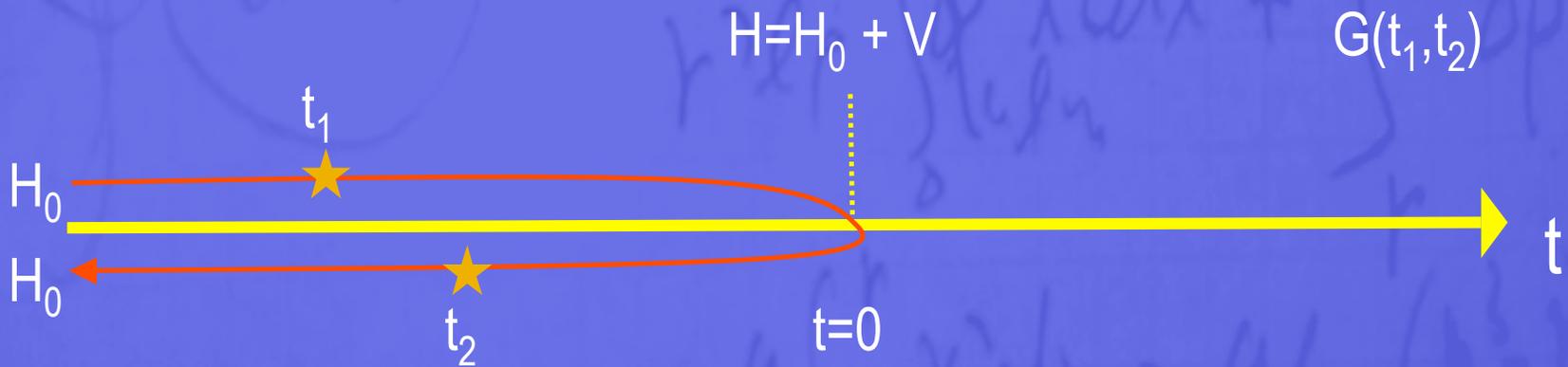
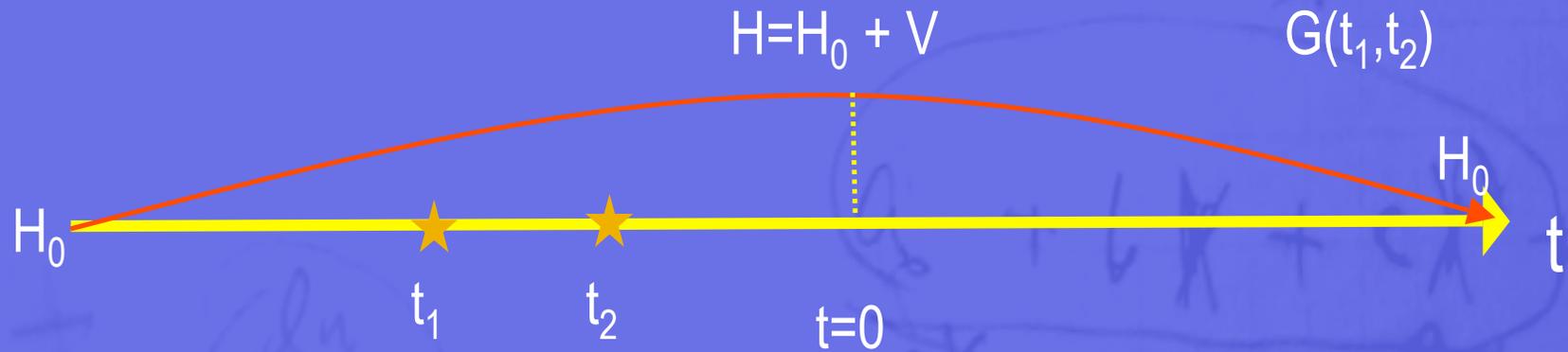
$$T(E, \Delta V) = \text{Tr}[G^r \Gamma_L G^a \Gamma_R]$$

(This is one of several ways of getting T)

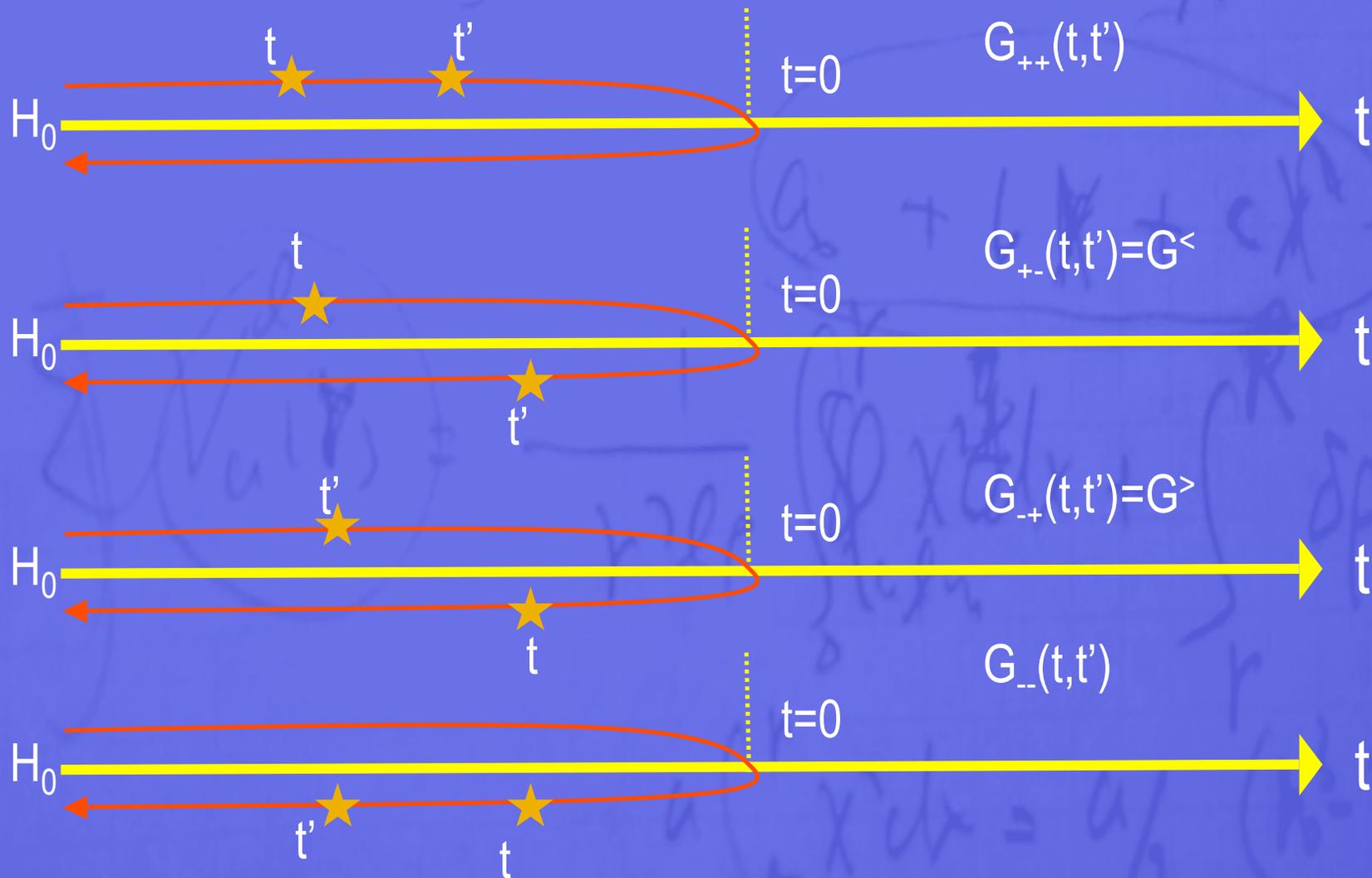
Non-equilibrium Physics

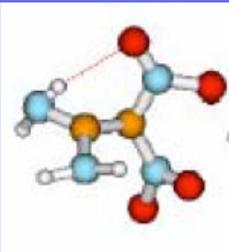
- Non-equilibrium means the statistical distribution of quasi-particles is NOT a Fermi-Dirac function.
- For a device described by $H=H_0 + V$, where V causes non-equilibrium, one may solve the equilibrium part H_0 first, then add V using a perturbation type approach. In many-body theory, such an approach leads to non-equilibrium Green's functions (NEGF). NEGF is most convenient to derive formula for transport problems.
- One may also evolve the density matrix of the entire H in time from the initial condition of equilibrium density matrix of H_0 .

Equilibrium vs Non-equilibrium: adiabatic turning on



Non-equilibrium: 4 basic Green's functions





Computing Hamiltonian for a device:

Electronic Hamiltonian in Born-Oppenheimer Approximation:

$$\left[-\frac{\hbar^2}{2m_e} \sum_i \nabla^2_{r_i} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 |r_i - r_j|} - \sum_{I,J} \frac{Z_I e^2}{4\pi\epsilon_0 |r_i - R_I|} \right] \psi(r; R) = E_{el}(R) \psi(r; R)$$

I, J label atoms with positions R_I, R_J , i, j label electrons with positions r_i, r_j

This is a many-body problem impossible to solve exactly. Approximations are needed: for example apply LSDA to density functional theory (DFT).

DFT treats e-e interaction in a mean field manner: each electron is moving inside a mean field created by all other electrons. Hence, instead of solving an N-particle problem, DFT solves N 1-particle problems self-consistently.

A typical DFT calculation with LSDA or GGA can solve a system of a few tens to a few hundred atoms reasonably accurately for many situations, using a modest computer facility.

The Kohn-Sham (KS) equation:

$$\frac{\delta E[\rho]}{\delta \psi^i(\mathbf{r}')} = 0.$$

Assuming:

$$\begin{aligned}\rho(\mathbf{r}) &= \sum_{i=1}^N (\psi^i(\mathbf{r}))^* \psi^i(\mathbf{r}) \\ \langle \psi^i | \psi^j \rangle &= \delta_{ij}.\end{aligned}$$

$$T_{\text{KS}} = \sum_{i=1}^N \left\langle \psi^i \left| \frac{-\nabla^2}{2} \right| \psi^i \right\rangle.$$

Can always write:

$$E_{\text{XC}}[\rho] \equiv T[\rho] - T_{\text{KS}}[\rho] + E_{\text{X}}[\rho] + E_{\text{C}}[\rho].$$

Obtain:

$$\left(\frac{-\nabla^2}{2} + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{\text{ext}}(\mathbf{r}) + V_{\text{XC}}(\rho(\mathbf{r})) \right) \psi^i(\mathbf{r}) = E^i \psi^i(\mathbf{r}).$$

Where:

$$V_{\text{XC}}[\rho] \equiv \frac{\delta E_{\text{XC}}[\rho]}{\delta \rho(\mathbf{r})}.$$

KS equation: solve an eigenvalue problem to build the Hamiltonian

Back to non-equilibrium transport situation:

- KS equation of DFT comes from a variation principle by minimizing some total energy (good for equilibrium).
- For non-equilibrium transport, it would be nice if some variational Lyapunov functional could be found. But so far no luck.

Ansatz:

$$\left(\frac{-\nabla^2}{2} + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{\text{ext}}(\mathbf{r}) + V_{\text{XC}}(\rho(\mathbf{r})) \right) \psi^i(\mathbf{r}) = E^i \psi^i(\mathbf{r}).$$

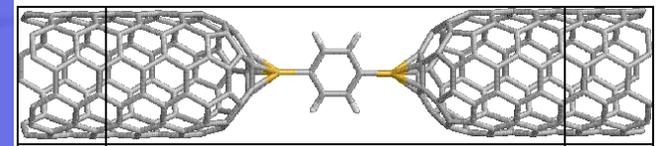
Assuming Hamiltonian of device still has a KS form, but plug in a non-equilibrium density ! This choice of H has obvious terms, it also has various right limits when going back to equilibrium. The resulting outcome is not a ground state anymore because the density used is not the equilibrium ground state density.

Practical implementations:

- Tight binding (TB) Hamiltonian combined with a transport code;
- Density functional theory (DFT) based Hamiltonian combined with Keldysh non-equilibrium Green's functions (NEGF);
- DFT Hamiltonian combined with scattering wavefunctions;
- Time-dependent DFT adapted with open transport boundary condition;
- Higher level electronic structure method with some transport code.

Modeling based on tight binding (TB) potential:

The interaction potential between atoms are parametrized and not calculated during device modeling.

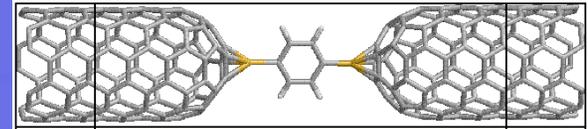


Very fast and can deal with large number of atoms, say $\sim 10,000$ atoms or more.

Problems: Not terribly accurate because Fermi level alignment has to be put in by hand. Parameters may not reflect quantum transport environment.

Research topic: can we find TB models with transport emphasis? Should the TB parameters change with bias?

Plane wave DFT + transport analysis



Computes Hamiltonian of the scattering region by DFT use planewave basis set. Afterward, use the computed Hamiltonian to analyze transport.

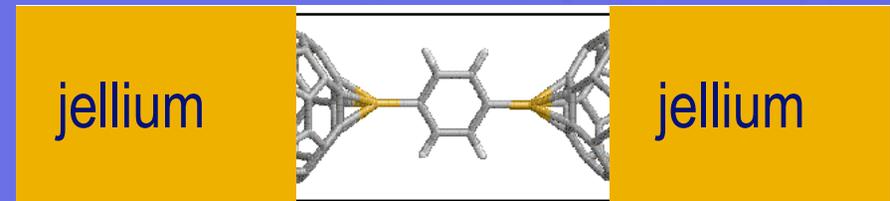
Planewaves form a complete basis set, thus can be more accurate than small basis set methods.

Problems: (i) needs periodic boundary condition thus difficult to naturally apply bias voltage. (ii) if using transfer matrix, computation is large and time consuming. (iii) if try to localize planewaves, atomic sphere approximation (ASA) is usually necessary, this is an “art”.

Wan et al. APL, 71, 419(1997); Choi and Ihm, PRB, 59, 2267(1999).

Planewave DFT within Lippmann-Schwinger Eqn.

Dealing with open and non-equilibrium device systems using LS equation, compute scattering states, construct charge density, and iterate DFT.



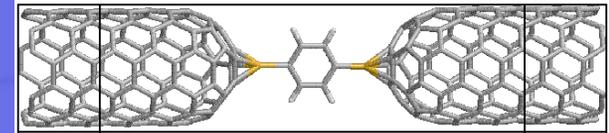
This is a nice method: planewaves, correct transport boundary condition, correct non-equilibrium physics, one-molecule in between two planar leads...

Problems: (i) it appears that the device leads must be jellium; (ii) it appears to need very large computation due to algorithm issues: seems no one has simulated more than 50 atoms so far.

Lang, PRB 52, 5335(1995); Tsukada, PRB 55, 4997(1997); Di Ventra & Lang, PRB 65, 045402 (2001).

Time dependent DFT with transport boundary condition

Solving density matrix by time dependent DFT:



Earlier attempts map open system into closed one to avoid leads, Di Ventura & Todrov, J. Phys. C. 16, 8025(2004); Burke et al PRL 94, 146803(2005).

More recent TDDFT attempts to include leads:

$$\frac{\partial \rho}{\partial t} \sim [H, \rho] + Q(\rho)$$

This functional Q accounts for all dissipative terms including effects of open boundaries, electrodes, etc...

This method can be useful, but it appears that actual implementation has been difficult to accomplish fully. Functional Q is set by some ansatz, and it appears to be very difficult to compute if atomic leads are included. It's potential computation power is yet to be seen.

Kurth et al PRB 72, 035308 (2005); **Zheng et al PRB 75, 195127 (2007)**; Li & Yan PRB 75, 075114(2007).

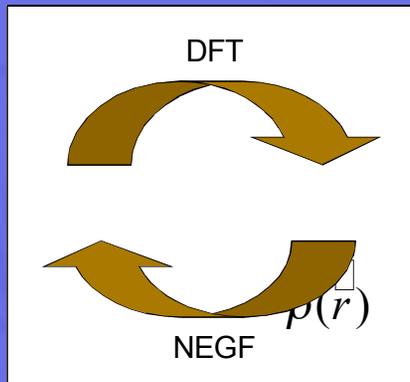
NEGF-DFT

NEGF:

$$\hat{\rho} = \frac{1}{2\pi i} \int dE G^<$$

$$G^< = G^R \Sigma^< G^A$$

$$G^R(E, U) = \frac{1}{E - H_0 - eU - V_{ps} - V_{xc} - \Sigma_R}$$



$$\Sigma^< = i f_l(E; \mu_l) \Sigma_{l,l}^R + i f_r(E; \mu_r) \Sigma_{r,r}^R$$

$$\nabla^2 U = -4\pi\rho$$

Correct non-equilibrium physics, correct transport boundary conditions, large systems (~500 atoms), easiness of adding new physics (e-p).

Problem: inversion of matrix dictates the use of small basis sets.

Book of Jauho; book of Datta; Wang et al. PRL 82, 398(1999)

Existing NEGF-DFT type implementations:

- Y. Xue, S. Datta and M.A. Ratner, JCP 115, 4292 (2001); Chem. Phys. 281, 151 (2002). (TB, Gaussian)
- J. Taylor, H. Guo and J. Wang, Phys. Rev. B. 63, 245407 (2001); *ibid*, 63, 121104 (2001). (LCAO)
- M. Brandbyge, J.-L. Mozos, P. Ordejon, J. Taylor, and K. Stokbro, Phys. Rev. B 65, 165401 (2002).
- J.J. Palacios *et.al.*, Phys. Rev. B 66, 035332 (2002). (Gaussian)
- S.-H. Ke, H.U. Baranger and W. Yang, Phys. Rev. B 70, 085410 (2004). (LCAO)
- S. Faleev *et.al.*, Phys. Rev. B 71, 195422 (2005). (LMTO)
- Lu *et al*, PRL (2005). (LCAO)
- A.R. Rocha, *et.al.*, Nature Materials 4, 335 (2005). (LCAO)
- Darancet *et al* cond-mat/0611404 (GW correction)
- ...

What's different between these NEGF-DFT codes ?

- Basis: Gaussian, LCAO-Siesta or the like;
- XC potentials: various GGA, LSDA, LDA, one GW;
- The way of handling electro-static boundary conditions: solution of Poisson equation;
- Pseudopotential: more or less the same;
- Other numerical details (k-sampling, grids, etc).

They make differences in final numbers, but give similar qualitative results.

Several codes are checked against each other to some extent: e.g. McDcal vs transiesta; Duke code vs McDcal; Palacios code vs McDcal; etc.. But these checks were done on simple systems such as C60, Al wire or Au wires.

More careful checks are still desired.

NEGF-DFT comparison to real data on alkanethiol wires: works

$$R_n = R_o \exp(\beta n)$$

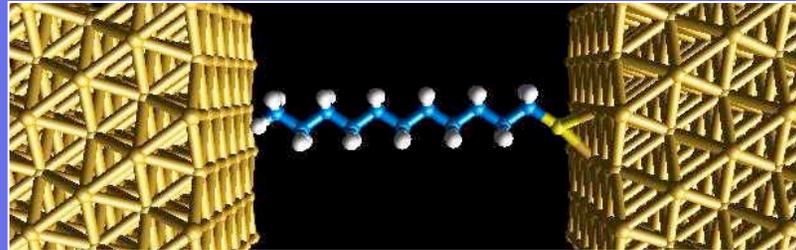


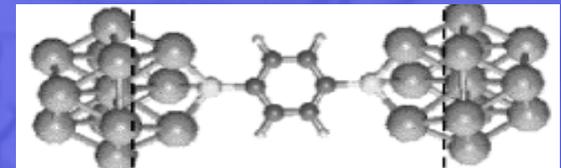
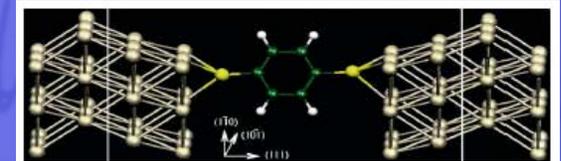
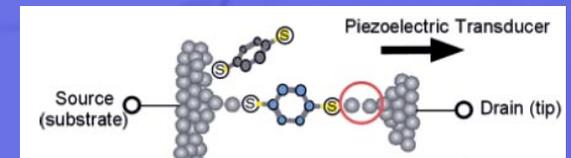
TABLE 1: Summary of Alkanethiol Tunneling Characteristic Parameters^a

junction	β (\AA^{-1})	J (A/cm^2) at 1 V	Φ_B (eV)	technique	ref
(bilayer) monothiol	0.87 ± 0.1	$25-200^b$	2.1^f	Hg-junction	11
(bilayer) monothiol	0.71 ± 0.08	$0.7-3.5^b$		Hg-junction	13
monothiol	0.79 ± 0.01	1500 ± 200^c	1.4^f	solid M-I-M	22
monothiol	1.2			STM	5
dithiol	0.8 ± 0.08	$3.7-5 \times 10^5^d$	5 ± 2^g	STM	6
monothiol	0.73-0.95	1100-1900 ^e	2.2^f	CAFM	7
monothiol	0.64-0.8	10-50 ^e	2.3^f	CAFM	9
dithiol	0.46 ± 0.02	$3-6 \times 10^5^d$	$1.3-1.5^f$	CAFM	10
monothiol	1.37 ± 0.03		1.8^g	tuning fork AFM	23
monothiol	0.97 ± 0.04			electrochemical	16
monothiol	0.85			electrochemical	17
monothiol	0.91 ± 0.08			electrochemical	18
monothiol	0.76	2×10^4 (at 0.1 V) ^d	$1.3-3.4^h$	theory	24
monothiol	0.76			theory	25
monothiol	0.79			theory	26

From: Lee et al J. Phys. Chem. 108, 8742 (2004).

NEGF-DFT comparison to real data on gold-BDT junctions: problems

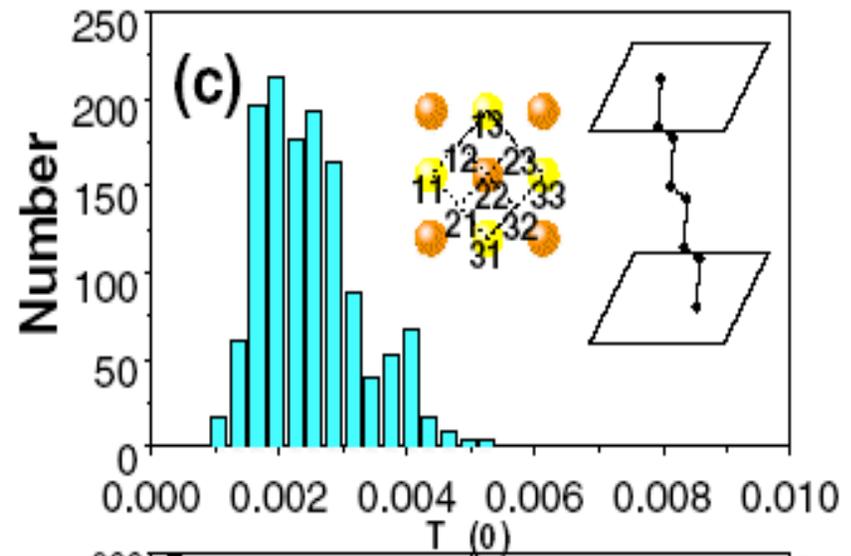
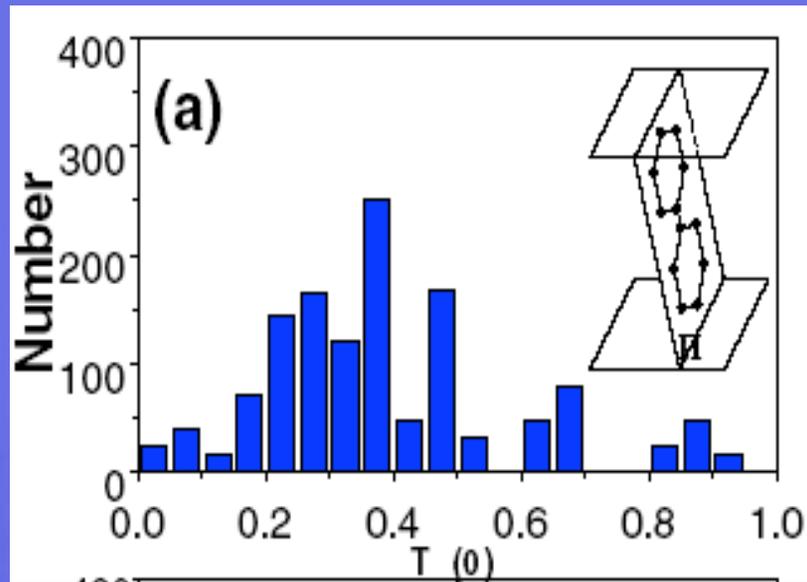
Tao et al. Nano Lett 4, 267(2003). Experiment: measures large number of systems and average.	0.85us
Stokbro et al. Comput. Matter. Sci 27,151(2003) . NEGF + LDA	~20us
Delaney et al, PRL93,36805(2004) Cluster CI + Wigner function on boundary	~0.05us
Bauschlicher Jr. et al. Chem. Phys. Lett 388,427(2004). NEGF+B3PW91 or B3LYP	3-5us
Ning et al., PRB72, 155403(2005) NEGF+B3LYP + correction from UPS reference data	0.6 – 0.9 us
Varga et al. PRL 98,76804(2007). Closed system with complex boundary potential	1.55us



It appears to suggest that Fermi level alignment is critical for this problem.

NEGF-DFT statistical analysis of many wires: issue of contacts

Statistical analysis of hundreds wires each having slight different contact geometry.



Theory:

$G = 0.0023g$

Experiment:

$G = 0.0012 g$

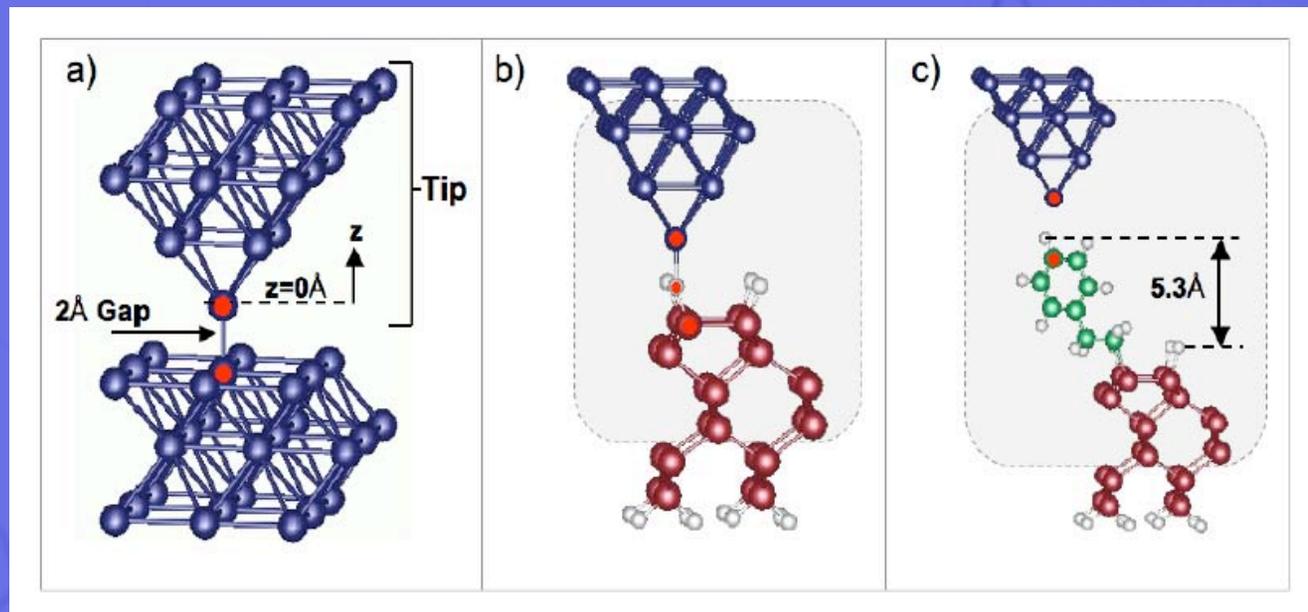
NEGF-DFT (LDA)

Hu et al PRL 95, 156803 (2005)

Contact structure critical !

NEGF-DFT STM simulation: height reversal

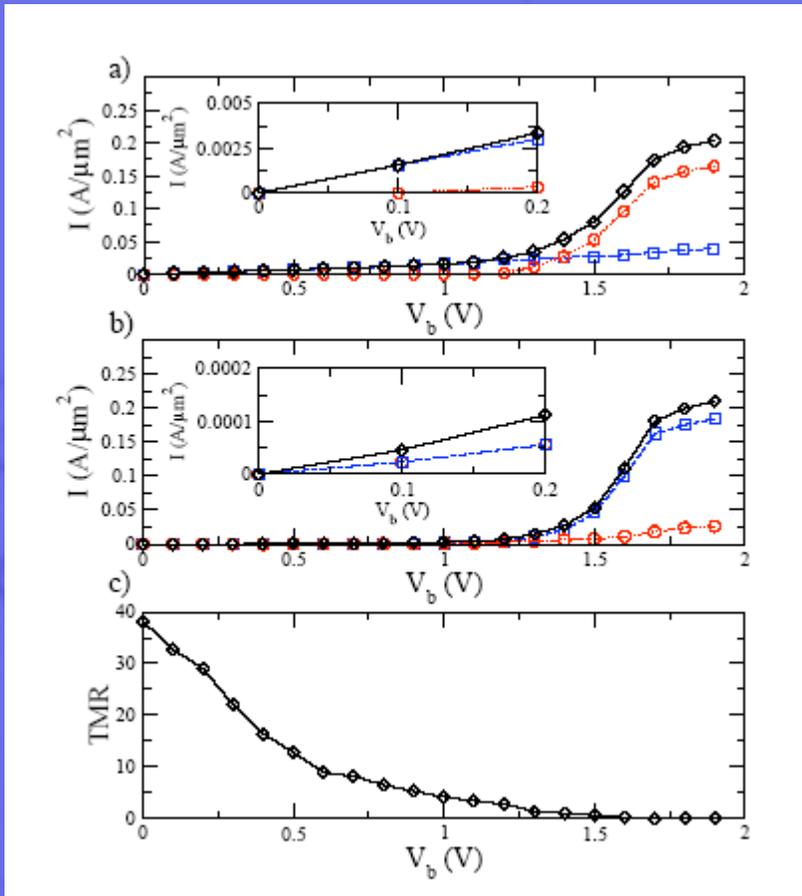
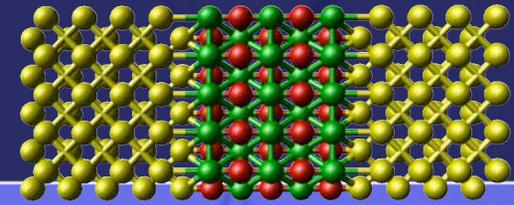
Theory from S. Datta group: K. Bevan et al. PRB (2007).



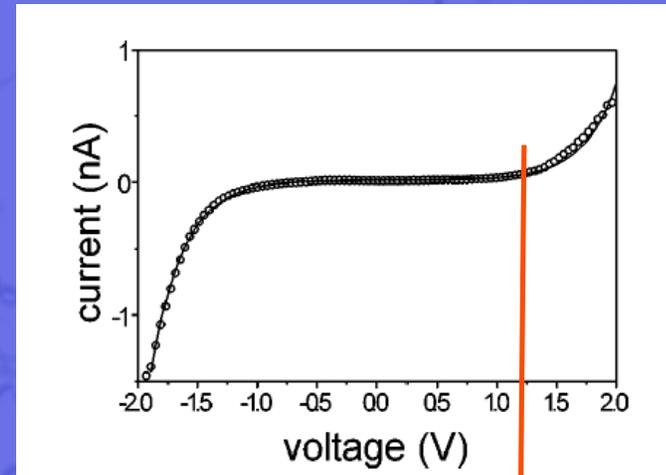
Experiment: Wolkow et al. Chem. Phys. Lett. 365, 129(2002).

Bias & set current	Experimental height	Theory height
-3V, 50pA	3.3 Å	3.4 Å
-2V, 50pA	2.6 Å	2.5 Å
-1.2V, 50pA	-0.25 Å	0.1 Å

Fe-MgO-Fe Tunnel Junction



NEGF+LSDA, Waldron et al PRL 97, 226802 (2006).

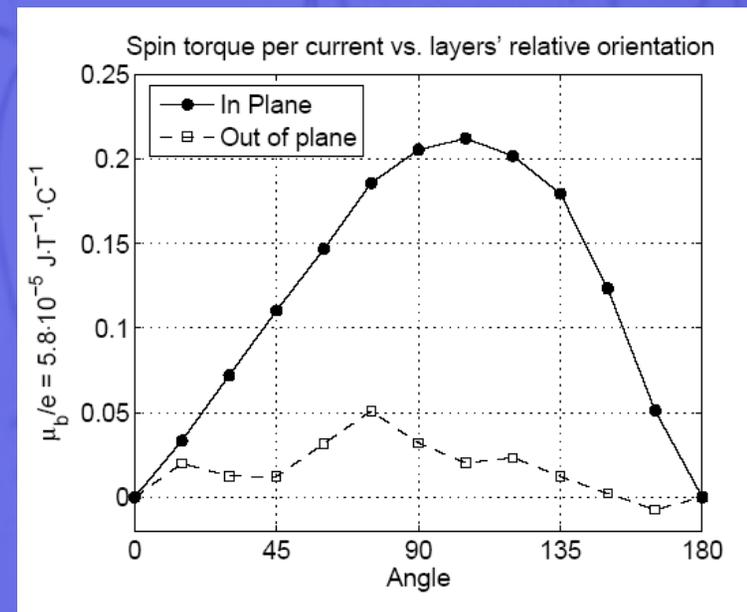
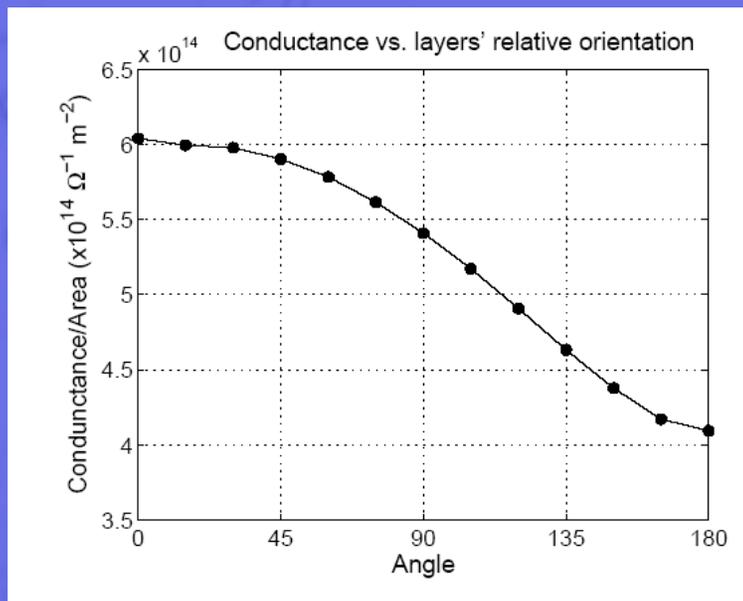


5-layer MgO, measured by Wulfhekel et al APL 78, p509 (2001).

TMR for perfect interface: 4000%,
oxidized interface: ~1000%.

Experiment: ~200 to 800% percent
achieved in the last 2 years.

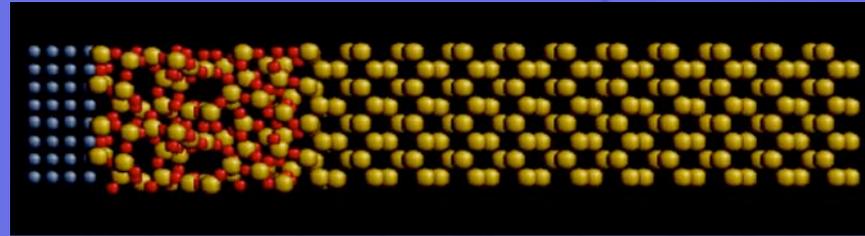
NEGF-DFT for Spin Transfer Torque: atomic simulation



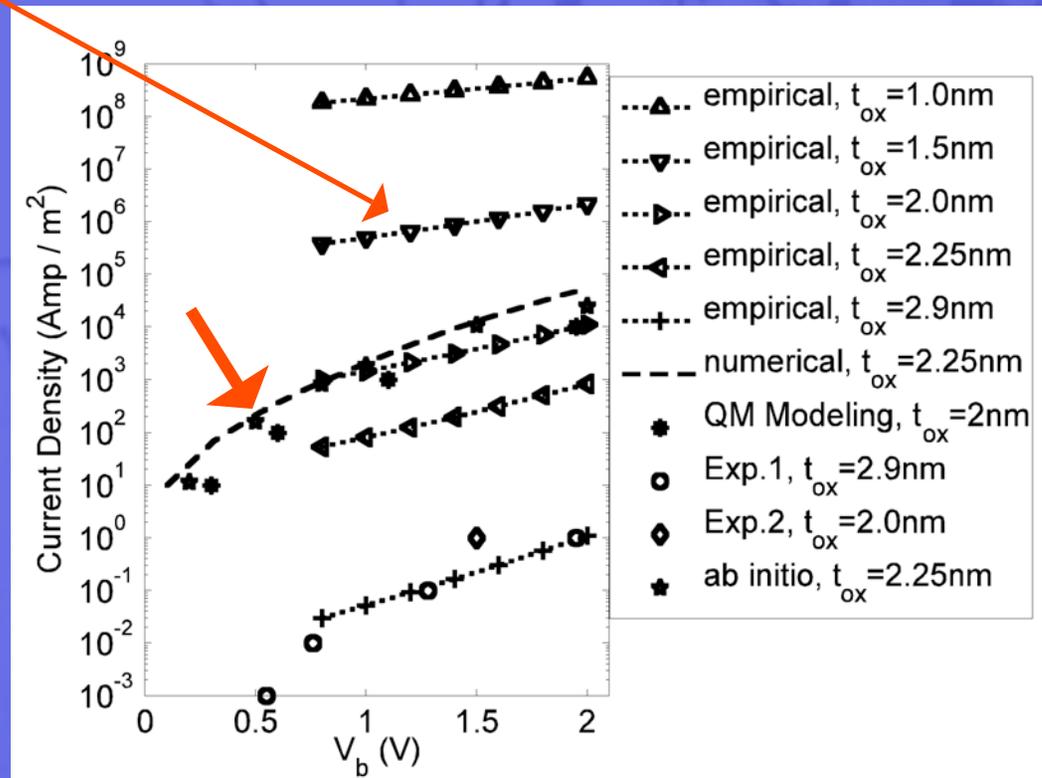
Haney et al. PRB (2007).

Gate leakage current in Si MOS structure:

Typically one uses empirical Fowler-Nordheim (FN) formula to model tunnelling in MOS.

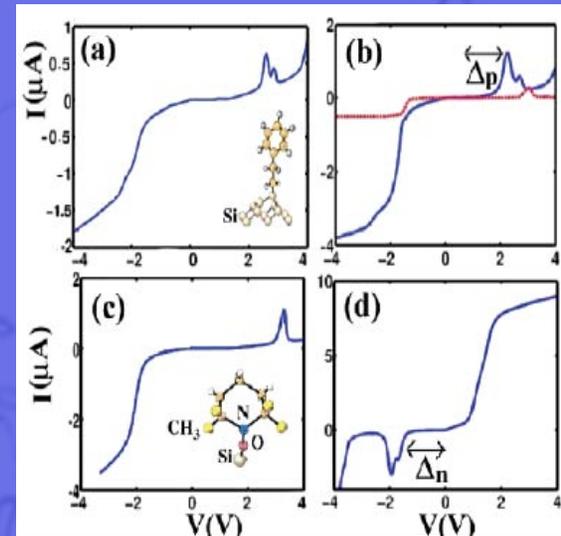
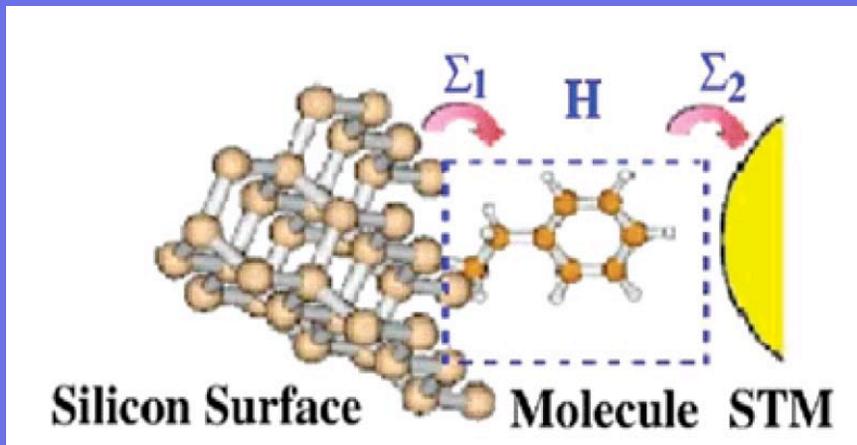


By extracting parameters from NEGF-DFT analysis and use proper FN formula, one can predict leakage current from atomic point of view. FN result obtained this way agrees with direct result from NEGF-DFT.



L. Liu et al, IEEE Proceeding (2006).

NEGF analysis for silicon based device



- T. Rakshit.etc Nano Lett. 4,1803(2004)
- Negative differential resistance(NDR) effect was found in this type of system.The polarity reverses due to reversed doping, which agrees with the experiment
- Silicon Related paper: PRL95,206805(2005)

NEGF-DFT: capacitance of nano devices

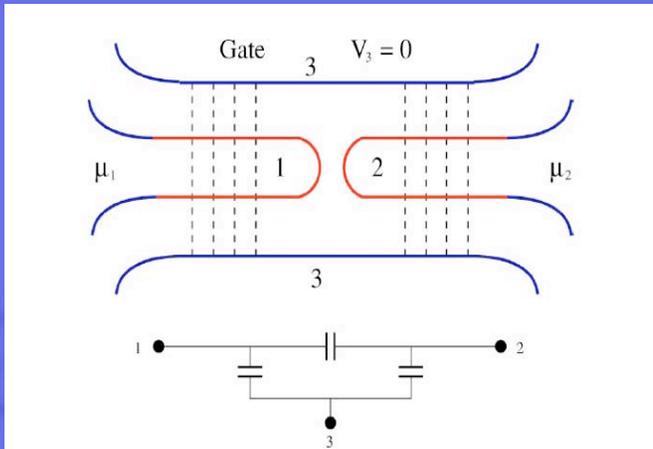


FIG. 2. (Color online) Schematic of the device used to calculate capacitance for a generic two-probe system. Note that the system is

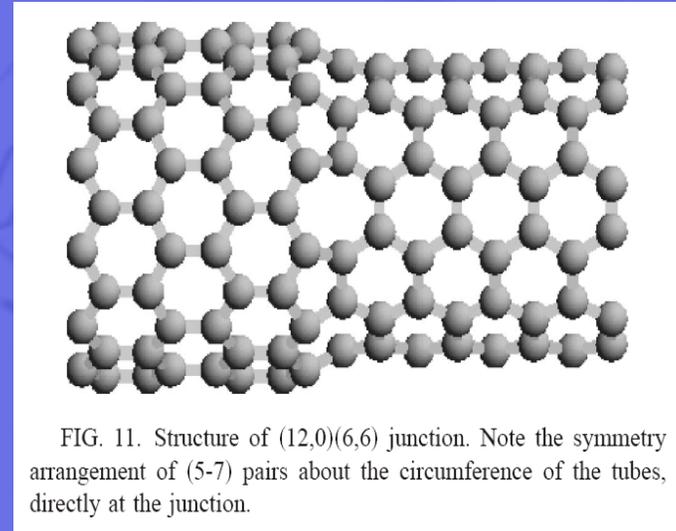
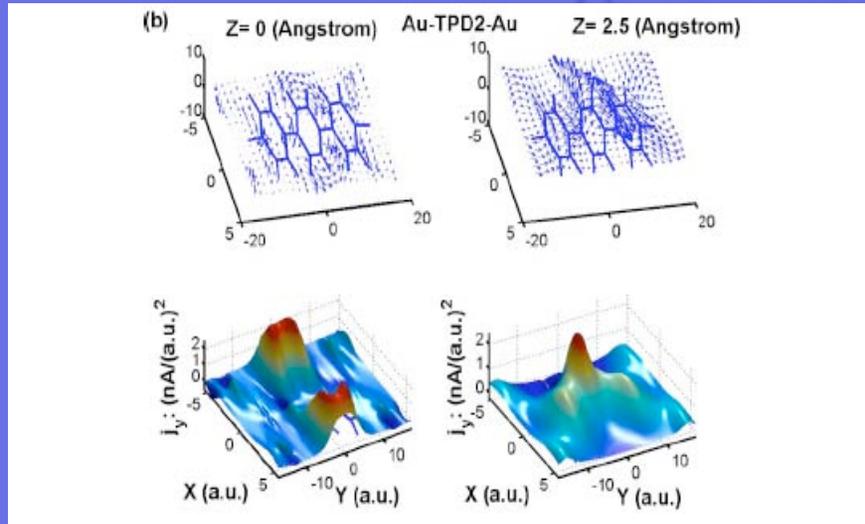


FIG. 11. Structure of (12,0)(6,6) junction. Note the symmetry arrangement of (5-7) pairs about the circumference of the tubes, directly at the junction.

- P. Pomorsky, et al PRB69, 115418(2004)
- A general implementation of NEGF to calculate the capacitance of nano devices. A CNT-junction was introduced as an example.
- Capacitance related paper: PRB74,113310(2006)

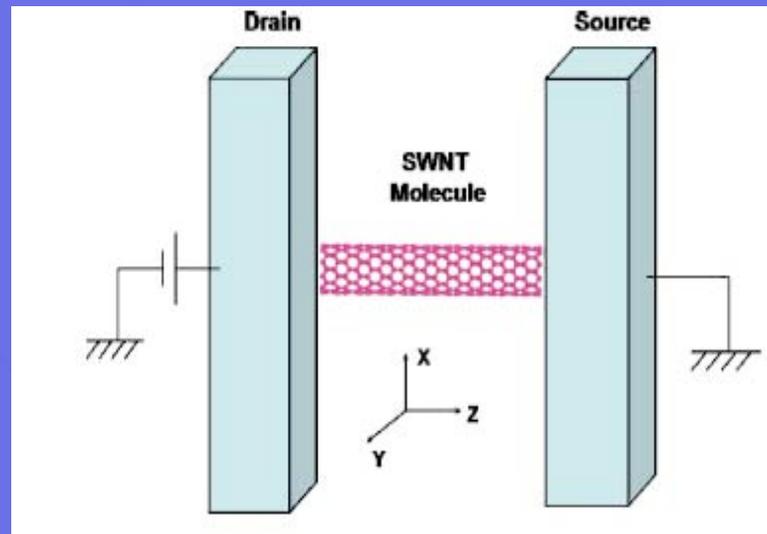
NEGF calculation of current density profile in nano devices

$$\begin{aligned} \mathbf{j}(\mathbf{r}) &= 1/2 \lim_{\mathbf{r}' \rightarrow \mathbf{r}} (\nabla' - \nabla) \int dE G^<(\mathbf{r}, \mathbf{r}'; E) \\ &= 1/2 \sum_{ij} \left[\int dE G_{ij}^<(E) \right] dS_{ij}(\mathbf{r}), \end{aligned}$$



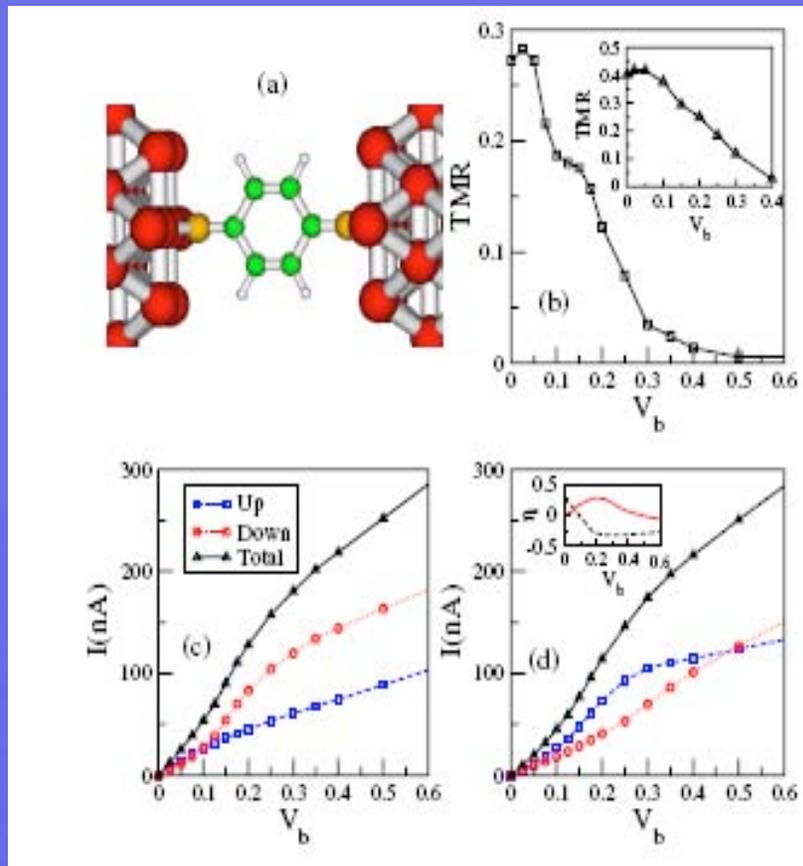
- Y. Xue and M. Ratner PRB 70, 81404(2004); Y, Liu & H.Guo, PRB 69, 115401(2004).
- Several molecular junctions were calculated to show how and where current actually flows through a device. Recent experiment appears to show that this is measurable.

NEGF analysis of CNT-metal junctions



- Y.Xue,etc PRB70,205416(2004)
- CNT-metal junctions were studied by NEGF, Several issues are discussed: Schottky barrier formation, band lineup and conductance versus length and coupling strength.
- CNT related paper: PRB69,115401(2004), PRB73, 233402(2006), PRL98,76804(2007)

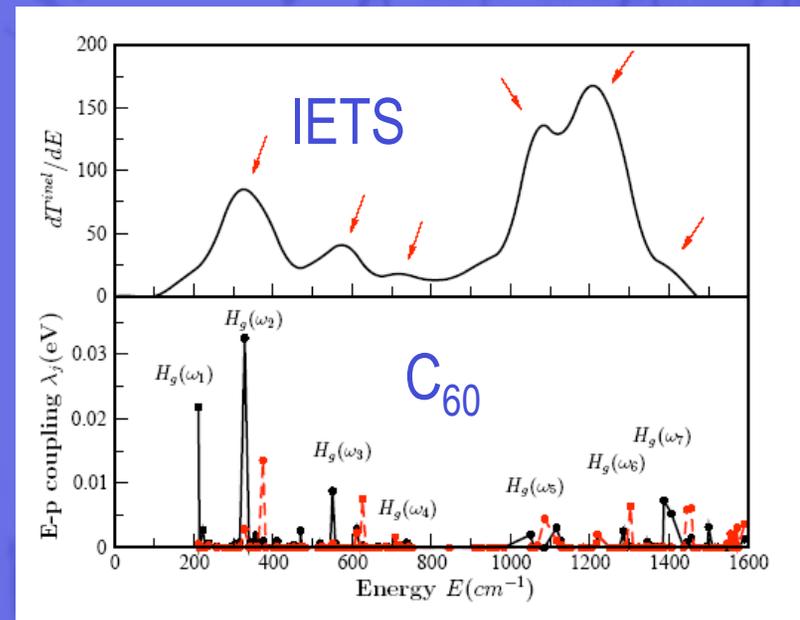
NEGF-DFT for spin transport in molecules



- D. Waldron, et al PRL96,166804(2006).
- Tunneling magnetic resistance (TMR) of spin polarized junctions can be calculated and compared to real data.
- Related paper: PRL97,226802(2006), PRB73, 094439 (2006)
- Several molecular magnetic tunnel junctions were fabricated and measured.
- Interesting science here: how chemistry affect spin transport.

NEGF-DFT with electron-vibron interaction, IETS

- M. Galperin, M. Ratner, A. Nitzan. Nano Lett. 9,1605(2004), electron-phonon coupling is introduced by a self-energy term into NEGF that can be computed self-consistently.
- Related papers: PRB73,205404(2006), PRB74,75326(2006), PRB75, 155312(2007), PRL95,146803(2005), PRL96,255503(2006)...

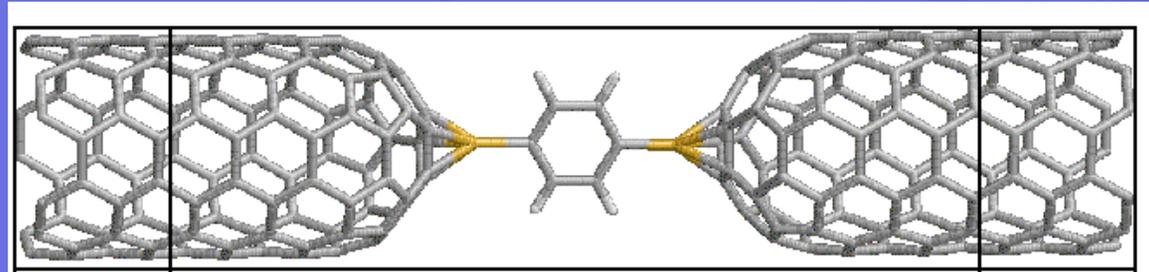
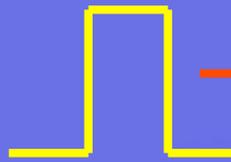


Sergueev, Roubtsov, Guo, PRL 95, 146803(2005).

Sergueev, Demkov, Guo PRB (2007)

Transient currents: very big challenge

How fast can a molecule turn on/off a current? Capacitance?



Voltage
pulse

The time dependent current can actually be written in terms of NEGF using steady-state Hamiltonian as H_0 . As such the transient current becomes computable within the NEGF-DFT formalism.

Recent TDDFT (by Chen of HKU) calculations show totally consistent results.

E. Zhu et al PRB 71, 075317 (2005). Majecko et al PRB 74, 085324 (2006). G.H. Chen, private communication (2007).

Some major lessons learned so far from state-of-the-art

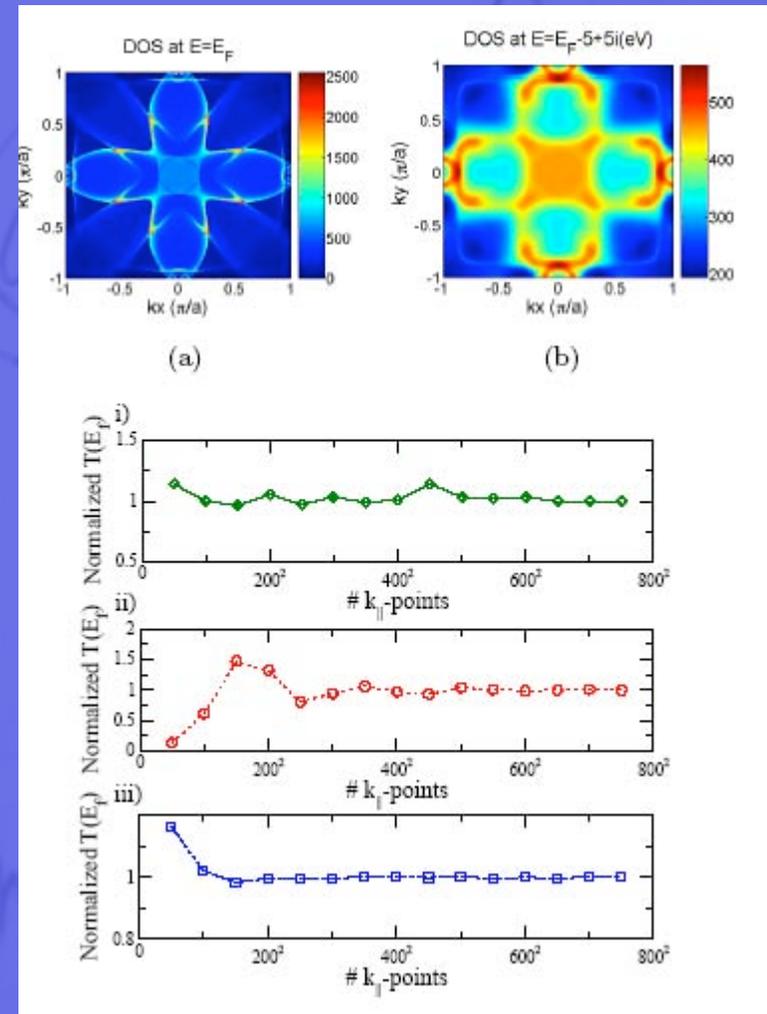
- Fermi level alignment can be critical for some devices. This is a very hard problem : a small error in charge transfer can make a big difference in alignment. **Must pin down charge transfer.**
- Contact structure is critical for many situations. **How can we ever know this detail with certainty ?**
- Coulomb blockade need to be considered for some situations.
- Structures can change during current flow: some studies exist.
- Details of DFT (SIC, XC, pseudopotential, basis, k-sampling, etc) can make quantitative difference--easier improvements.
- **Lack of checking and benchmarking between different codes.**
- Not enough solid comparison with experimental data.
- **Lack of a self-consistent method that can compute large systems.**
- ...

Hot spots in transmission: Fe/MgO/Fe

For systems having periodic x-y extent, one must compute transmission for each (k_x, k_y) .

Huge number of k-sampling must be made for numerical convergence.

Waldron & Guo, preprint (2007).



Some summary remarks:

- It appears that NEGF-DFT type formalism has emerged as the main theoretical tool for practical atomistic calculations of molecular electronics. The results are qualitative but can also be quantitative for some situations in comparison with measured data.
- NEGF-DFT type formalism has direct connection to quantum transport theory which is usually done using NEGF (e.g. molecular superconducting tunnel junction).
- It appears that people in NEGF-DFT are moving toward various practical applications of it, and **are not working hard enough for its basic theoretical foundation.**
- Technical improvements are more often seen (SIC, GW, CI, etc...).
- A potentially fruitful direction is the TDDFT type approach. There are several recent reports for extending TDDFT to open boundary problems so that transport becomes possible. Only a few real calculations exist so far, and even fewer (if at all) compare to measured data. But this is just the beginning and the real outcome is yet to be seen.
- Size limit so far: a few hundred atoms.

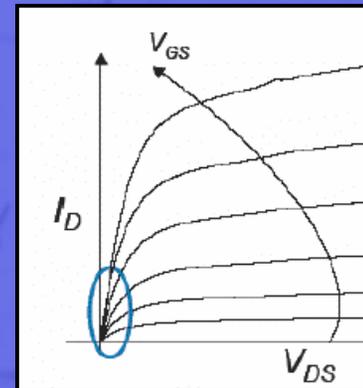
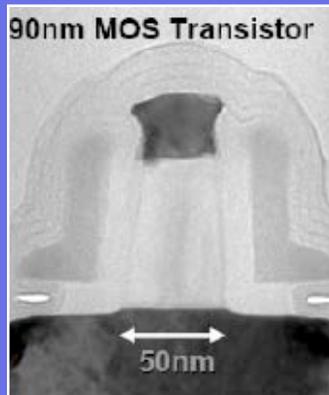
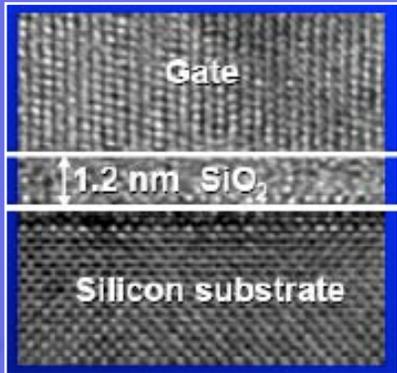
Challenging theoretical problems:

1. At single device level, thoroughly understand what works, what does not work, what's the limit, how to improve, on formalisms which are practically calculable. I think NEGF-DFT-type and TDDFT-type are good starting point.
2. How to add more correlations? GW or something drastic like CI ? Computation becomes too complicated will discourage people.
3. Truly far from equilibrium: transients, quantum dissipation etc.
4. Large numbers: how can we go beyond devices with 500 atoms?
5. Solve the Fermi level alignment problem: more experimental data exist now.
6. Solve the contact problem: find better linkers? Switch to semiconductor leads? Also a job for experimentalists.
7. How to efficiently gate a molecular transport junction?
8. Finite temperature effects.

Challenging theory problems (cont.)

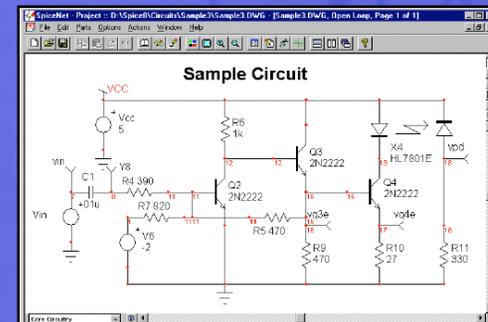
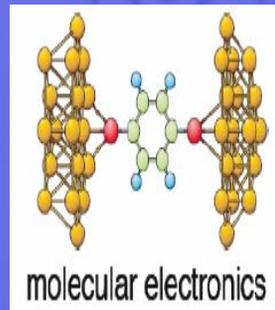
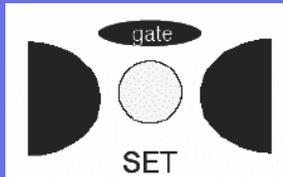
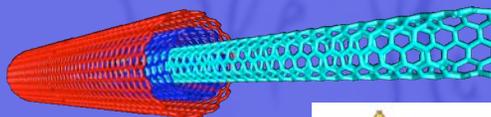
- **Multiple devices:** how to connect them into some thing more interesting? Partially coherent addition of devices?
- **Impurities:** cannot always do “super-cell” type averages. Need to develop efficient approaches like CPA, vertex correction, and implement them atomistically and at non-equilibrium level.
- **Biomolecules:** long history of theory work but seems to be a mess (my lack of knowledge). How to efficiently deal with solvent effects while current is flowing?
- **Hybrid systems:** transport problems where molecules are interacting with other materials such as superconductors, magnets, etc.

The impact of molecular electronics goes way beyond itself



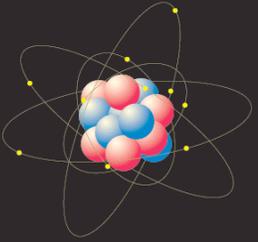
materials,
chemicals,
molecules,

atomic quantum modeling
software with accuracy



Outline:

- A short review of state-of-the-art;
- • DFT atomistic methods;
- The NEGF-DFT implementation;
- Applications of NEGF-DFT;
- Quantum mechanic forces during current flow;
- Summary: outlook to the near future.

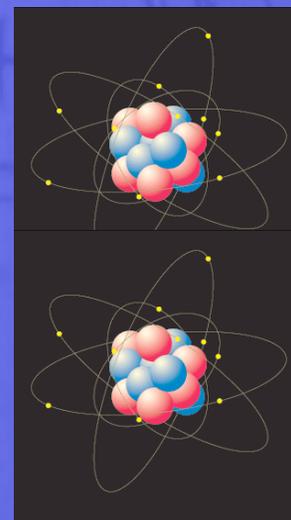


Atomistic modeling of materials:

- There are many electrons in a device: they interact via Coulomb interaction. Exact solution is impossible to obtain.
- The de facto standard technique for atomistic calculation is DFT: DFT has been widely applied to solve problems of solid state physics, materials science, chemistry, molecular modeling, biological systems, drug design, ...
- DFT treats e-e interaction in a mean field manner: each electron is moving inside a mean field created by all other electrons. Hence, instead of solving an N-particle problem, DFT solves N 1-particle problem.
- A typical DFT calculation can solve a system of a few tens to a few hundred atoms very accurately.

Basics for DFT and total energy methods:

- The Schrödinger equation for an isolated system:
say a molecule
- Born-Oppenheimer approximation
- The Variational Principle and Kohn-Sham equation
- The Hellman-Feynman theorem
- Molecular Mechanics and Molecular Dynamics



The Hamilton operator for a general system with n nuclei and N electrons

- The Schrödinger equation is:

$$\hat{H}\Psi(r, R) = E\Psi(r, R)$$

– with the Hamiltonian

Nucleus-nucleus
interaction

$$\left[-\frac{\hbar^2}{2m_e} \sum_i \nabla^2_{r_i} - \frac{\hbar^2}{2M_I} \sum_I \nabla^2_{R_I} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 |r_i - r_j|} - \sum_{i,I} \frac{Z_I e^2}{4\pi\epsilon_0 |r_i - R_I|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{4\pi\epsilon_0 |R_I - R_J|} \right]$$

Electron K.E.

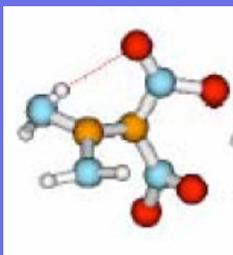
Nuclear K.E.

Electron-electron interaction

Electron-nucleus interaction

I, J label atoms with positions R_I, R_J

i, j label electrons with positions r_i, r_j



The Born-Oppenheimer Approximation

- The large difference in mass between electron and nuclei allows us to separate the electronic and the nuclear problem (*adiabatic approximation*)
- The interatomic forces and potential energy are determined by the electrons, which itself depends parametrically on the atomic structure
- Within the Born-Oppenheimer approximation:

Full
wavefunction

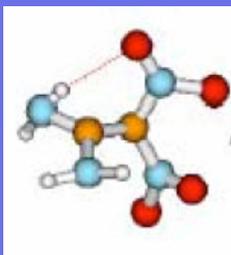
$$\Psi(r, R) = \psi(r; R) \chi(R)$$

Electron
coordinates

Atomic (nuclear)
positions

Electron
wavefunction for
given nuclear
positions R

Nuclear
wavefunction



The Born-Oppenheimer Approximation (cont.)

- The effective potential for the nuclei is determined by solving the electronic Schrödinger equation and then adding in the nuclear-nuclear repulsion:

$$\left[-\frac{\hbar^2}{2m_e} \sum_i \nabla^2_{r_i} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 |r_i - r_j|} - \sum_{i,I} \frac{Z_I e^2}{4\pi\epsilon_0 |r_i - R_I|} \right] \psi(r; R) = E_{\text{el}}(R) \psi(r; R)$$

$$V_{\text{eff}}(R) = E_{\text{el}}(R) + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{4\pi\epsilon_0 |R_I - R_J|}$$

I, J label atoms with positions R_I, R_J

i, j label electrons with positions r_i, r_j

This is a many-body problem impossible to solve exactly. Further approximations are needed: we will use density functional theory (DFT).

The theorem of Hohenberg-Kohn:

The non-degenerate ground state energy of an N electron system, E_N , is a unique, universal functional of the single-particle density $\rho(\mathbf{r})$:

$$E_N = E_N[\rho(\mathbf{r})].$$

However, no one knows what this total energy functional is. But we can always write it as:

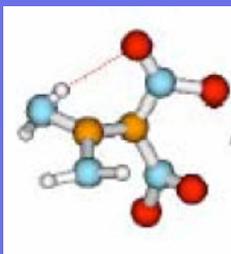
$$E[\rho] = T[\rho] + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d\mathbf{r} \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) + E_{\text{XC}}[\rho],$$

Kinetic

Hartree

External

exchange-
correlation



Variational principle:

- In the vast majority of cases the system moves on the *ground-state* potential surface, for which the electronic energy is the minimum possible:

$$E_{e_1}(R) = \min \langle \psi | \hat{H}_{e_1}(R) | \psi \rangle;$$

- The **variational principle** states that an approximate wave function has an energy which is above the exact energy.

$$\langle \psi | \psi \rangle = 1$$

The Kohn-Sham (KS) equation:

$$\frac{\delta E[\rho]}{\delta \psi^i(\mathbf{r}')} = 0.$$

Assuming:

$$\begin{aligned}\rho(\mathbf{r}) &= \sum_{i=1}^N (\psi^i(\mathbf{r}))^* \psi^i(\mathbf{r}) \\ \langle \psi^i | \psi^j \rangle &= \delta_{ij}.\end{aligned}$$

$$T_{\text{KS}} = \sum_{i=1}^N \left\langle \psi^i \left| \frac{-\nabla^2}{2} \right| \psi^i \right\rangle.$$

Can always write:

$$E_{\text{XC}}[\rho] \equiv T[\rho] - T_{\text{KS}}[\rho] + E_{\text{X}}[\rho] + E_{\text{C}}[\rho].$$

Obtain:

$$\left(\frac{-\nabla^2}{2} + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{\text{ext}}(\mathbf{r}) + V_{\text{XC}}(\rho(\mathbf{r})) \right) \psi^i(\mathbf{r}) = E^i \psi^i(\mathbf{r}).$$

Where:

$$V_{\text{XC}}[\rho] \equiv \frac{\delta E_{\text{XC}}[\rho]}{\delta \rho(\mathbf{r})}.$$

KS equation: an eigenvalue problem

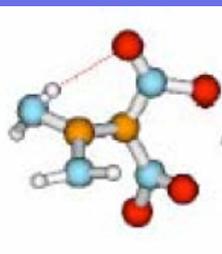
The Hartree potential:

$$\left(\frac{-\nabla^2}{2} + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{\text{ext}}(\mathbf{r}) + V_{\text{XC}}(\rho(\mathbf{r})) \right) \psi^i(\mathbf{r}) = E^i \psi^i(\mathbf{r}).$$

Hartree potential satisfies the Poisson equation:

$$\nabla^2 V = -4\pi\rho$$

One has to solve this equation numerically. Usually one uses Fourier transform. But for device simulation (later), this equation must be solved subject to device electrostatic boundary conditions.



The Hellman-Feynman theorem:

The Hellman-Feynman Theorem states that for any perturbation λ we have

$$\begin{aligned}\frac{\partial \langle E \rangle}{\partial \lambda} &= \left\langle \frac{\partial \Psi}{\partial \lambda} \left| H \right| \Psi \right\rangle + \left\langle \Psi \left| \frac{\partial H}{\partial \lambda} \right| \Psi \right\rangle + \left\langle \Psi \left| H \right| \frac{\partial \Psi}{\partial \lambda} \right\rangle \\ &= E \left\{ \left\langle \frac{\partial \Psi}{\partial \lambda} \left| \Psi \right\rangle + \left\langle \Psi \left| \frac{\partial \Psi}{\partial \lambda} \right\rangle \right\} + \left\langle \Psi \left| \frac{\partial H}{\partial \lambda} \right| \Psi \right\rangle \\ &= E \frac{\partial}{\partial \lambda} \langle \Psi | \Psi \rangle + \left\langle \Psi \left| \frac{\partial H}{\partial \lambda} \right| \Psi \right\rangle = \left\langle \Psi \left| \frac{\partial H}{\partial \lambda} \right| \Psi \right\rangle\end{aligned}$$

For computing forces we set : $\lambda \Rightarrow R$

The total energy functional:

$$E_{\text{tot}} = T_{\text{KS}} + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{XC}}[\rho(\mathbf{r})] \\ \int d\mathbf{r} \rho(\mathbf{r}) V_{\text{ion-el}}(\mathbf{r}) + \int d\mathbf{r} \rho(\mathbf{r}) V_{\text{ext}} + E_{\text{ion-ion}}[\{\mathbf{R}_I\}],$$

$$E_{\text{tot}} = E_{\text{BS}} + \delta E_{\text{H}} + \delta U_{\text{XC}} + E_{\text{ion-ion}}[\{\mathbf{R}_I\}],$$

$$E_{\text{BS}} = \sum_{i=1}^N E^i \\ \delta E_{\text{H}} = -\frac{1}{2} \int d\mathbf{r} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ \delta U_{\text{XC}} = \int d\mathbf{r} \rho(\mathbf{r}) \left(\frac{E_{\text{XC}}(\rho(\mathbf{r}))}{\rho(\mathbf{r})} - V_{\text{XC}}(\rho(\mathbf{r})) \right) \\ E_{\text{ion-ion}} = \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}.$$

$$E^i = \int d\mathbf{r} (\psi^i(\mathbf{r}))^* \left\{ \frac{-\nabla^2}{2} + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{\text{XC}}(\rho(\mathbf{r})) V_{\text{ion-el}}(\mathbf{r}) + V_{\text{ext}}(\mathbf{r}) \right\} \psi^i(\mathbf{r}).$$

↑
The KS eigen-values

Summary of DFT computation procedure:

- Step 1: Starting from some trial initial electron density, compute the KS potential which is a functional of density.
- Step 2: Solve the KS equation to find KS single particle wavefunctions.
- Step 3: Construct new electron density from the KS wavefunctions.
- Step 4: Go back to Step 2 until numerical convergence is reached.
- Step 5: From the obtained KS Hamiltonian, compute physical quantities of interest.

Detail 1: Local Density Approximation (LDA):

So far all terms in the total energy and KS equation can be computed, the only unknown is the exchange-correlation (XC) potential and XC-energy functional. This functional is not known exactly, and approximations must be used.

For uniform electron gas, XC term can be analytically derived at high electron density limit, and it is a function of charge density. For system with very low electron density, this term can also be derived. Thus one extrapolates between the high and low density limits---LDA.

There are many forms of LDA.

Other functionals such as Generalized Gradient Approximation (GGA) are also widely used.

Book of Parr and Yang.

Example of LDA:

$$E_{\text{XC}}(\rho_0) = -\rho_0 \frac{a_0 + a_1 r_s + a_2 r_s^2 + a_3 r_s^3}{b_1 r_s + b_2 r_s^2 + b_3 r_s^3 + b_4 r_s^4}$$

$$r_s = \left(\frac{3}{4\pi\rho} \right)^{1/3}$$

$$E_{\text{XC}}[\rho(\mathbf{r})] = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{\text{XC}}^{\rho_0}(\rho(\mathbf{r}))$$
$$\epsilon_{\text{XC}}^{\rho_0} \equiv \frac{E_{\text{XC}}(\rho_0)}{\rho_0}.$$

$$a_0 = 0.458165293$$

$$a_1 = 2.217058676$$

$$a_2 = 0.74055173$$

$$a_3 = 0.019682278$$

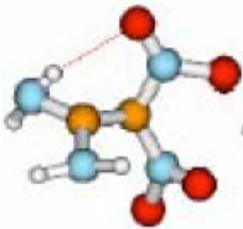
$$b_1 = 1.0$$

$$b_2 = 4.504130959$$

$$b_3 = 1.110667363$$

$$b_4 = 0.023592917$$

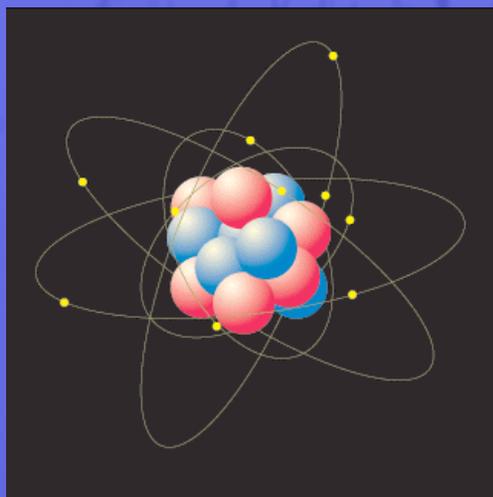
Goedecker et al. PRB 54 1703(1996).



Detail 2: pseudopotential approximation

There is another unknown potential in the KS equation named: $V_{\text{ext}}(\mathbf{r})$.
A most important piece of this external potential is due to the atomic core. The core is the nuclei plus the close shell core electrons.

Properties of materials are largely determined by valence electrons. For example,



Therefore, to reduce calculation, we only focus on valence electrons and put the nuclei potential and core electron potential into a “pseudopotential”

$$V_{ps}(r)$$

Ex: Au has 79 electrons, but only 11 valence electrons.

Periodic table:

The periodic table of the elements

	1A	2A	3A	4A	5A	6A	7A	8	1B	2B	3B	4B	5B	6B	7B	0		
1	H															He		
2	Li	Be									B	C	N	O	F	Ne		
3	Na	Mg									Al	Si	P	S	Cl	Ar		
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	L	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	A															
	L	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
	A	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Metals
 Metalloids
 Non-metals
 Transition Metals
 Gases

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Pseudopotentials:

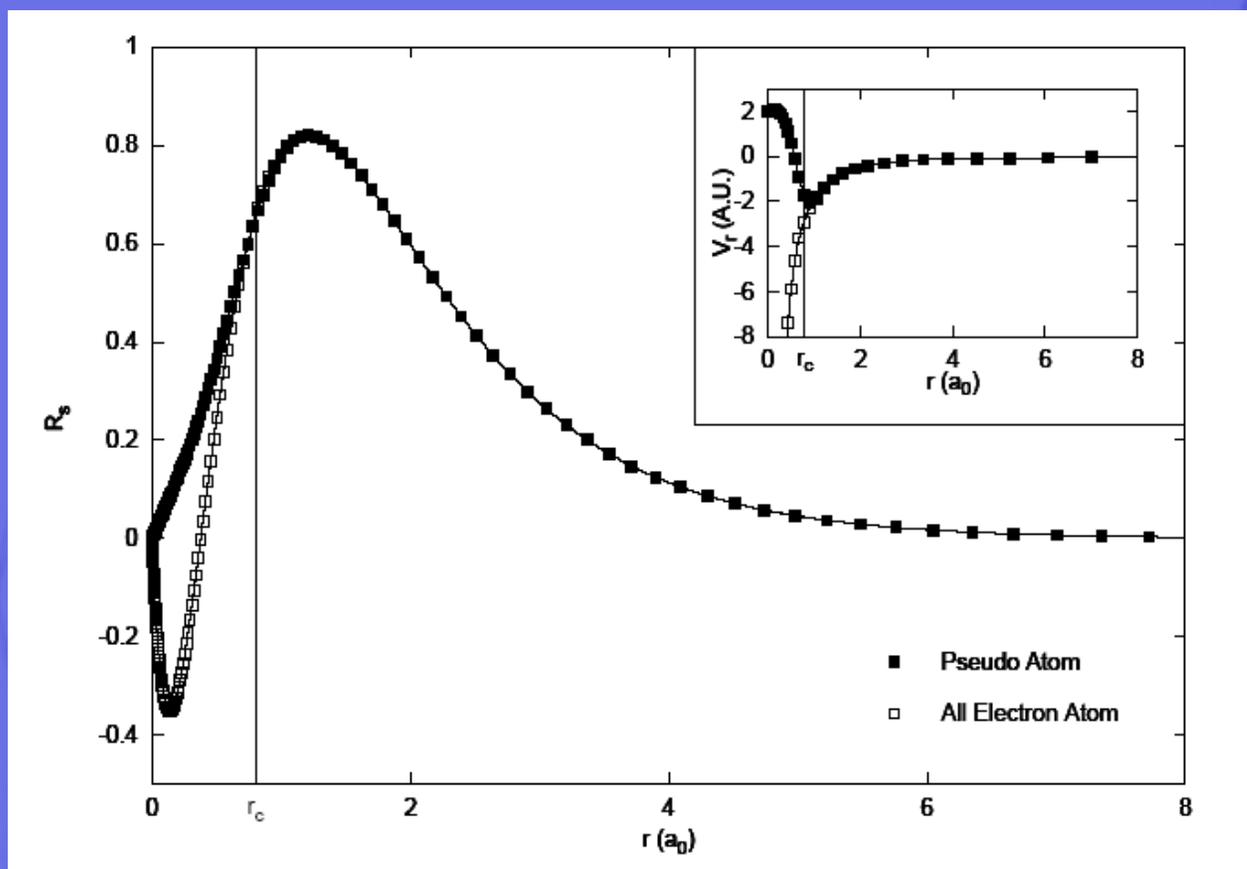


Figure 2.1: **Pseudorbitals and pseudopotential of a carbon atom.** The pseudopotential, $V_r(r)$, (inset) is constructed so that it matches the all-electron potential of the reference carbon atom outside the core $r > r_c$. The resulting nodeless pseudorbital, $R_s(r)$, matches the all-electron orbital outside the core $r > r_c$.

Detail 3: Basis sets

To solve the KS equation, we expand the KS wavefunction in terms of some basis sets. There are many choices of basis function: plane waves; LCAO; real-space grids, etc...

Plane wave basis: this is very natural for periodic solid state systems where Bloch theorem holds,

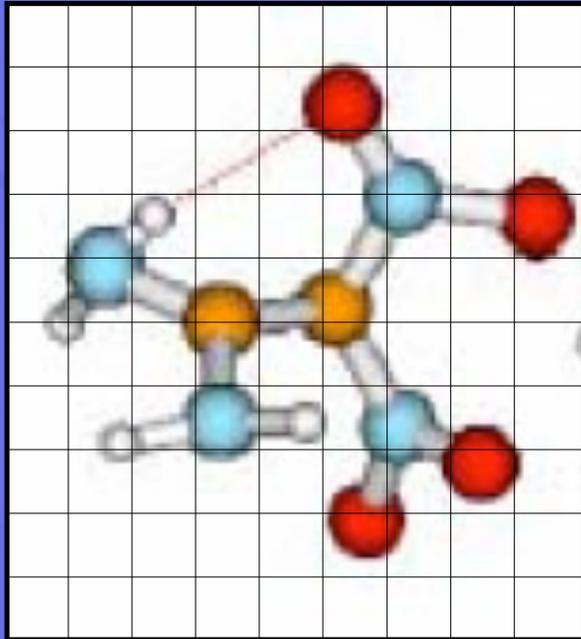
$$\psi_{i\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_i(\mathbf{r}),$$

$$u_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$$

$$\psi_{i\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

Real space grids:

Discretize the simulation box by real space grids:



Very fine grids must be used. This basis makes program very simple and easy to code. The calculation is very large, but is gaining popularity in recent years.

Linear combination of atomic orbitals (LCAO):

Solve the atomic orbitals of one atom, and use the atomic orbitals as basis. Thus the basis functions are centered at each atom. The atomic orbitals are written as:

$$\phi_{lm}(\mathbf{r}) = R_l(r)Y_{lm}(\Omega_{\mathbf{r}})$$

$$\phi_s(\mathbf{r}) = \phi_{00} = C_s R_s(r)$$

$$\phi_{p_x}(\mathbf{r}) = \frac{1}{\sqrt{2}}(\phi_{1,-1} - \phi_{11}) = C_p R_p(r) \frac{x}{r}$$

$$\phi_{p_y}(\mathbf{r}) = \frac{i}{\sqrt{2}}(\phi_{1,-1} + \phi_{11}) = C_p R_p(r) \frac{y}{r}$$

$$\phi_{p_z}(\mathbf{r}) = \phi_{10} = C_p R_p(r) \frac{z}{r},$$

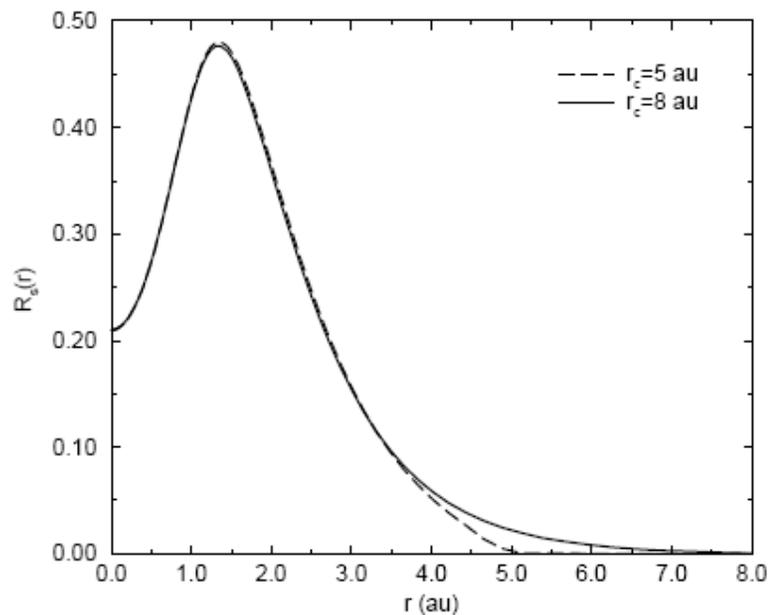
Therefore:

$$\psi_i(\mathbf{r}) = \sum_{I,\mu} a_i(I\mu)\phi_{\mu}(\mathbf{r} - \mathbf{R}_I),$$

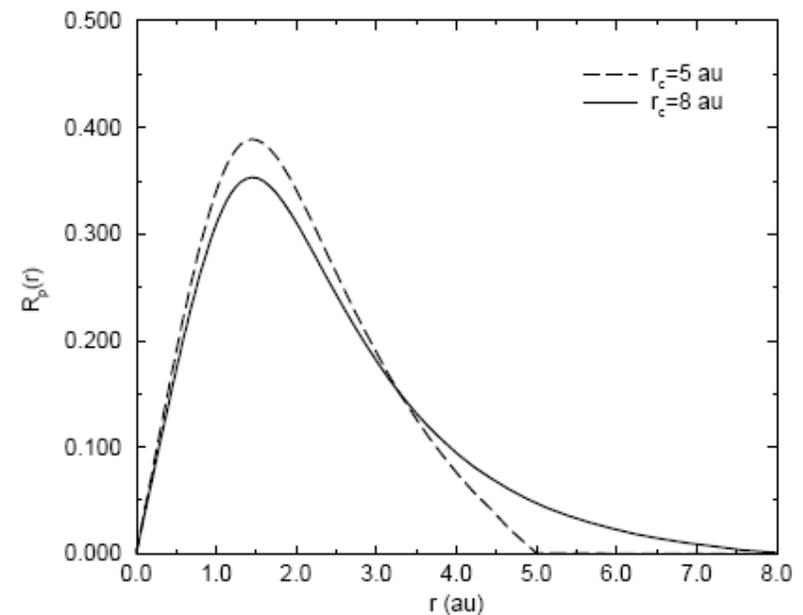
$$\mu = s, p_x, p_y, p_z, d_{1-5}$$

Atomic orbitals (cont.):

To reduce calculation, we can cut off the radial atomic orbital:



(a)



(b)

Figure 3.1: Plots of Si pseudo-atomic orbitals with confinement radii of $r_c = 5$ and $8au$: (a) s orbital (b) p orbital.

LCAO (continue):

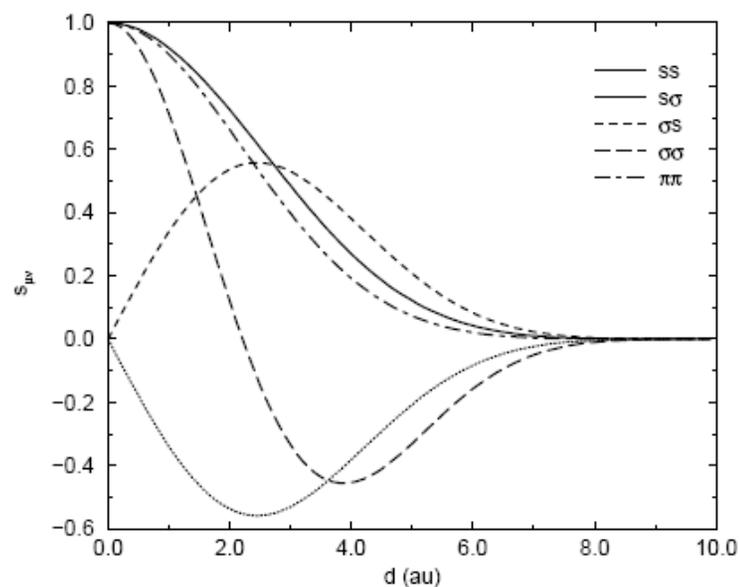
$$h_{\mu I, \nu I'} = \langle \phi_{\mu}(\mathbf{r} - \mathbf{R}_I) | \hat{h} | \phi_{\nu}(\mathbf{r} - \mathbf{R}_{I'}) \rangle = \int \phi_{\mu}^*(\mathbf{r} - \mathbf{R}_I) \hat{h} \phi_{\nu}(\mathbf{r} - \mathbf{R}_{I'}) d\mathbf{r}$$

$$\hat{h} = -\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(\mathbf{r}) = \frac{\hat{p}^2}{2m} + V_{eff}(\mathbf{r})$$

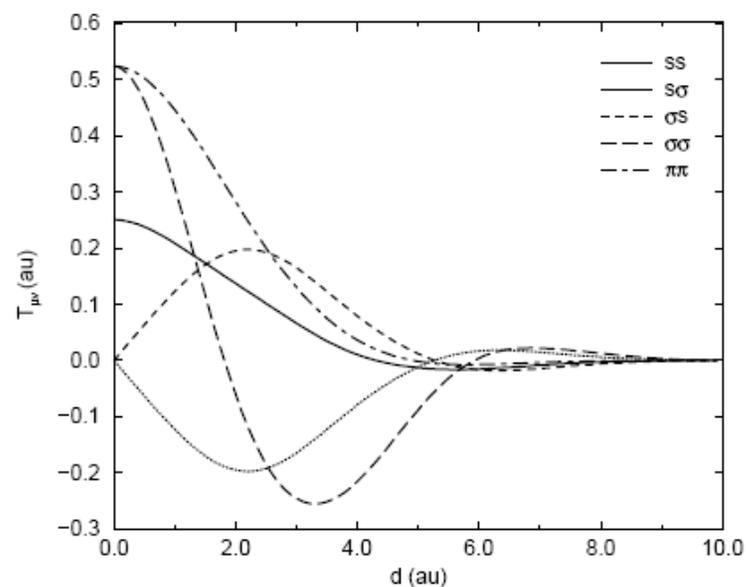
$$s_{\mu I, \nu I'} = \langle \phi_{\mu}(\mathbf{r} - \mathbf{R}_I) | \phi_{\nu}(\mathbf{r} - \mathbf{R}_{I'}) \rangle = \int \phi_{\mu}^*(\mathbf{r} - \mathbf{R}_I) \phi_{\nu}(\mathbf{r} - \mathbf{R}_{I'}) d\mathbf{r}$$

The LCAO code is about the computation of these matrix elements.

Matrix elements in LCAO basis:



(a)



(b)

Figure 3.3: Plots of (a) overlap and (b) kinetic energy matrix elements with respect to molecular frame orbitals, as a function of the atom spacing d .

Matrix elements in s,p basis:

$$R_s(q) = \sqrt{\frac{2}{\pi}} \int_0^\infty R_s(r) j_0(qr) r^2 dr$$

$$R_p(q) = \sqrt{\frac{2}{\pi}} \int_0^\infty R_p(r) j_1(qr) r^2 dr.$$

$$s_{ss}^{MF}(d) = \int_0^\infty R_s(q) R_s(q) j_0(qd) q^2 dq$$

$$T_{s\sigma}^{MF}(d) = -\sqrt{3} \int_0^\infty R_s(q) \frac{\hbar^2 q^2}{2m} R_p(q) j_1(qd) q^2 dq$$

$$s_{s\sigma}^{MF}(d) = -\sqrt{3} \int_0^\infty R_s(q) R_p(q) j_1(qd) q^2 dq$$

$$T_{\sigma s}^{MF}(d) = \sqrt{3} \int_0^\infty R_p(q) \frac{\hbar^2 q^2}{2m} R_s(q) j_1(qd) q^2 dq$$

$$s_{\sigma s}^{MF}(d) = \sqrt{3} \int_0^\infty R_p(q) R_s(q) j_1(qd) q^2 dq$$

$$T_{\sigma\sigma}^{MF}(d) = \int_0^\infty R_p(q) \frac{\hbar^2 q^2}{2m} R_p(q) [j_0(qd) - 2j_2(qd)] q^2 dq$$

$$s_{\sigma\sigma}^{MF}(d) = \int_0^\infty R_p(q) R_p(q) [j_0(qd) - 2j_2(qd)] q^2 dq$$

$$T_{\pi\pi}^{MF}(d) = \int_0^\infty R_p(q) \frac{\hbar^2 q^2}{2m} R_p(q) [j_0(qd) + j_2(qd)] q^2 dq$$

$$s_{\pi\pi}^{MF}(d) = \int_0^\infty R_p(q) R_p(q) [j_0(qd) + j_2(qd)] q^2 dq,$$

Comparison of basis sets;

	Plane Waves	Real Space Grids	Atomic Orbitals
Memory	Huge	Large	Small
Runtime	Huge	Large	Small
Completeness	Good	Good	Acceptable
Analytic Work	Easy	Easy	Hard
Programming	Easy	Average	Hard
Periodicity	Required	Optional	Optional

Detail 4: solutions of the KS equation:

$$\hat{h}\psi_i = -\frac{\hbar^2}{2m}\nabla^2\psi_i + V_{eff}(\mathbf{r})\psi_i = \varepsilon_i\psi_i$$

or

$$\hat{h}|\psi_i\rangle = \varepsilon_i|\psi_i\rangle.$$

$$\langle b_\alpha|\hat{h}|\psi_i\rangle = \varepsilon_i \langle b_\alpha|\psi_i\rangle$$

Because:

$$|\psi_i\rangle = \sum_{\beta} a_{i\beta}|b_\beta\rangle$$



$$\sum_{\beta} h_{\alpha\beta} a_{i\beta} = \varepsilon_i \sum_{\beta} s_{\alpha\beta} a_{i\beta},$$

$$h_{\alpha\beta} = \langle b_\alpha|\hat{h}|b_\beta\rangle$$

$$s_{\alpha\beta} = \langle b_\alpha|b_\beta\rangle$$

$$\mathbf{h}\vec{a}_i = \varepsilon_i \mathbf{s}\vec{a}_i$$

Becomes a matrix eigenvalue problem.

Solution of KS equation (cont.):

$$\mathbf{h}\vec{a}_i = \varepsilon_i \mathbf{s}\vec{a}_i$$

The most direct solution is by matrix diagonalization. If the basis set N_b has functions, the matrix is $N_b \times N_b$

Matrix diagonalization scales as N_b^3 , thus if one uses large basis sets, the computation is huge.

For plane wave basis, typically we need 100 plane waves per electron. Thus for 1000 electrons, we have 100,000 plane waves. The matrix is very large indeed. But if we use LCAO, for s,p,d basis we have 9 orbitals per atom. Thus matrix size is rather small: for 100 atoms we have 900 basis functions.

Direct minimization of KS total energy:

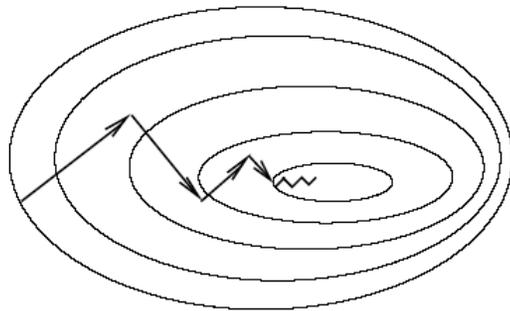
Since KS equation comes from minimization of the KS total energy, why not directly minimize the total energy?

KS total energy:

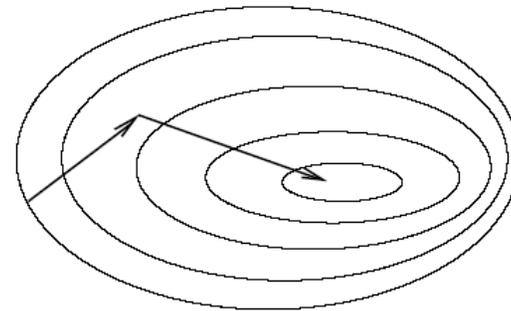
$$E_{\text{tot}} = E_{\text{BS}} + \delta E_{\text{H}} + \delta U_{\text{XC}} + E_{\text{ion-ion}}[\{\mathbf{R}_I\}],$$

$$\frac{\delta E[\rho]}{\delta \psi^i(\mathbf{r}')} = 0.$$

→ KS equation



steepest decent



conjugate gradient

Review Literature on DFT details:

M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos. Iterative minimization techniques for *ab initio* total-energy calculations: molecular dynamics and conjugate gradients. *Rev. Mod. Phys.*, 64:1045, 1992.

G. B. Bachelet, D. R. Hamann, and M. Schlüter. Pseudopotentials that work: From h to pu. *Phys. Rev. B*, 26:4199, 1982.

P. Ordejón, E. Artacho, and J. M. Soler. Self-consistent order-n density-functional calculations for very large systems. *Phys. Rev. B*, 53:10441, 1996.

R. G. Parr and W. Yang. *Density-Functional Theory of Atoms and Molecules*. Oxford University Press, New York, 1989.

Summary of typical DFT implementation:

- Basic theorem of Hohenberg-Kohn leads to KS-total energy functional, and variational principle leads to KS-equation.
- With LDA (or GGA), all potential terms in KS-functional are determined by charge density.
- Charge density matrix is obtained by KS-eigenstates which are computed by solving the KS-equation which is a self-consistent problem.
- Several methods are available for solving KS-equation.
- Further details of pseudopotentials, basis sets, boundary conditions, etc, are used to simplify numerics.
- We obtain: Hamiltonian of the system and its electronic states. For solids, we obtain band-structures.

Outline:

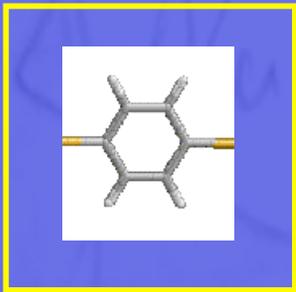
- A short review of state-of-the-art;
- DFT atomistic methods;
- • The NEGF-DFT for transport: implementation details;
- Some applications of NEGF-DFT;
- Quantum mechanic forces during current flow;
- Summary: outlook to the near future.

NEGF-DFT:

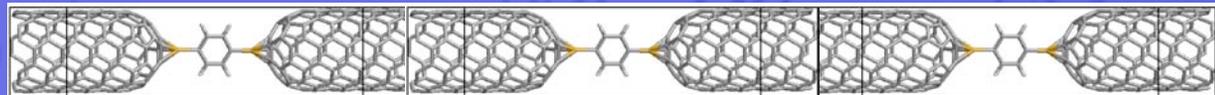
Taylor, Guo, Wang, PRB 63, 245407(2001)

- Using density functional theory (DFT) to compute the electronic structure of the Ni-BDT-Ni device;
- Using Keldysh non-equilibrium Green's function (NEGF) to populate this electronic structure (quantum statistics);
- Using real space numerical techniques to deal with the device boundary conditions.

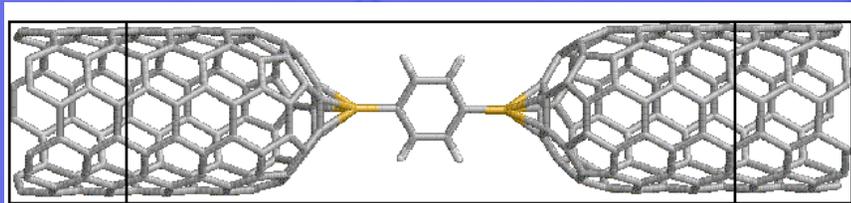
Note: conventional DFT solves two kinds of problems: isolated or periodic



Isolated (Gaussian)

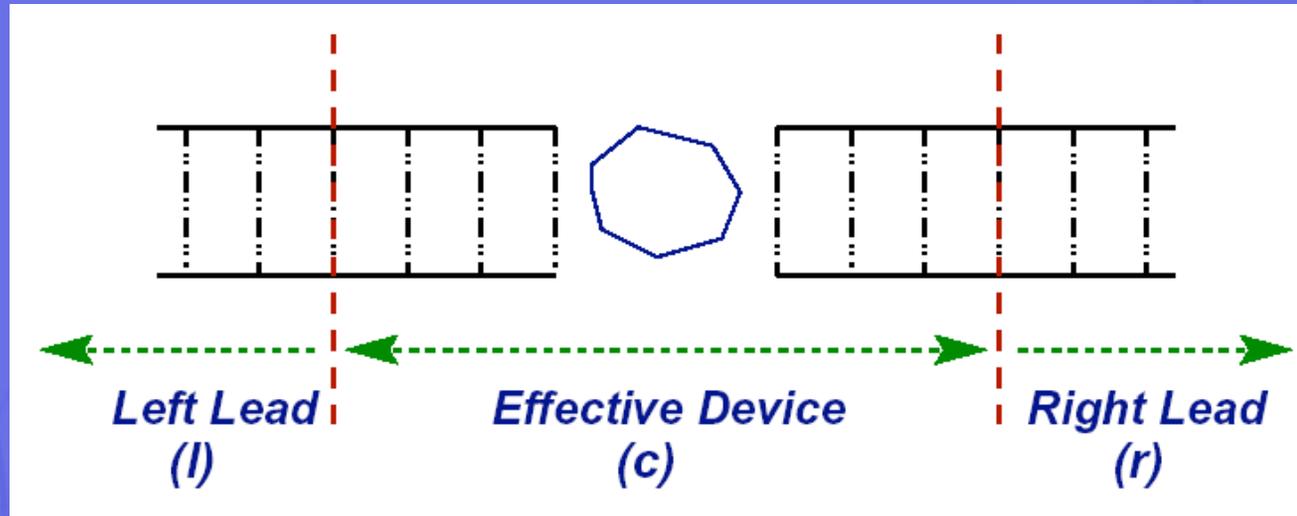


Periodic (VASP)



A device is neither isolated nor periodic

A device is an OPEN system:

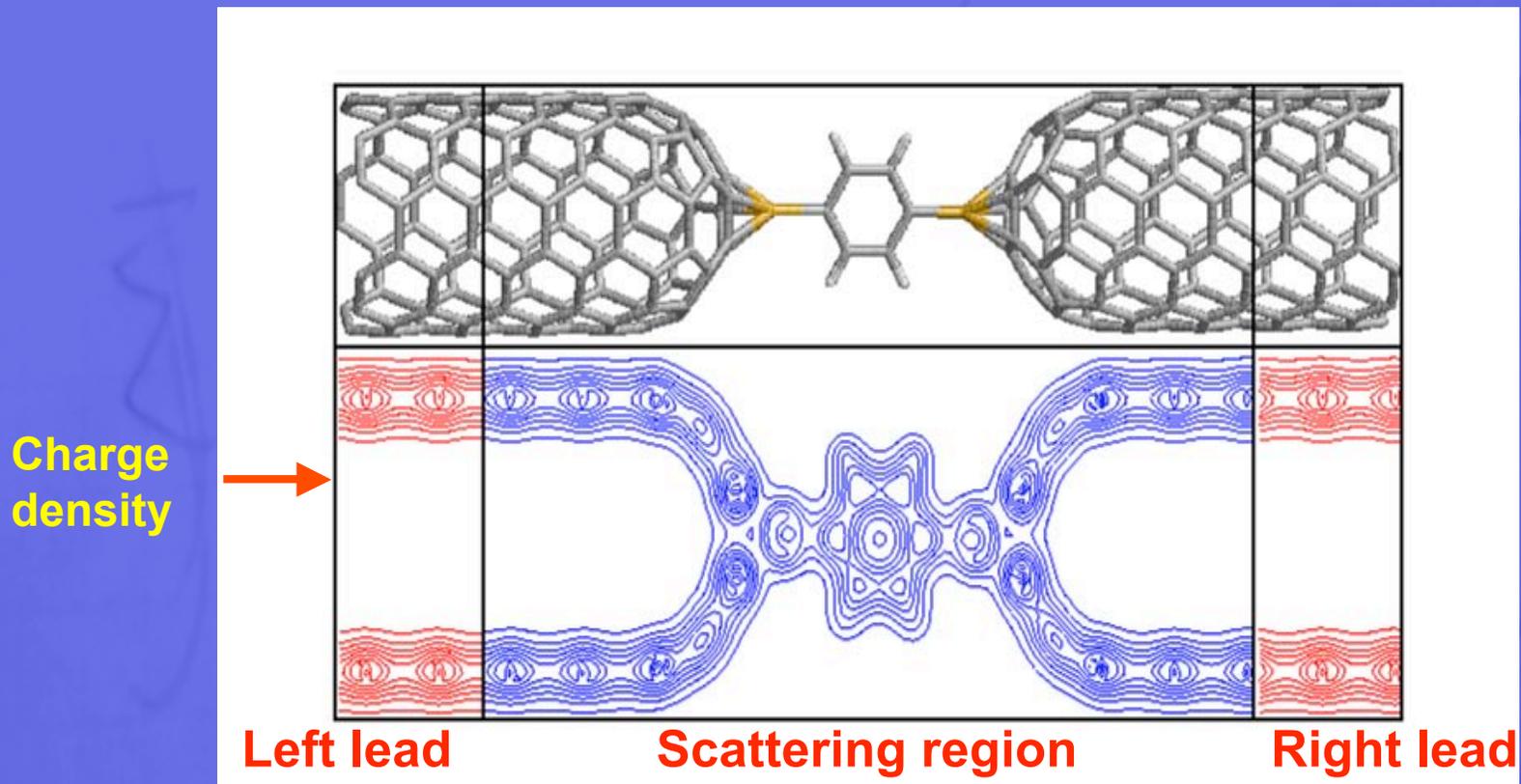


Two new problems must be solved:

1. How to reduce the infinitely large system to something calculable on a computer?
2. How to compute charge density when there is an external bias potential (non-equilibrium)?

Screen approximation---reducing the infinitely large problem:

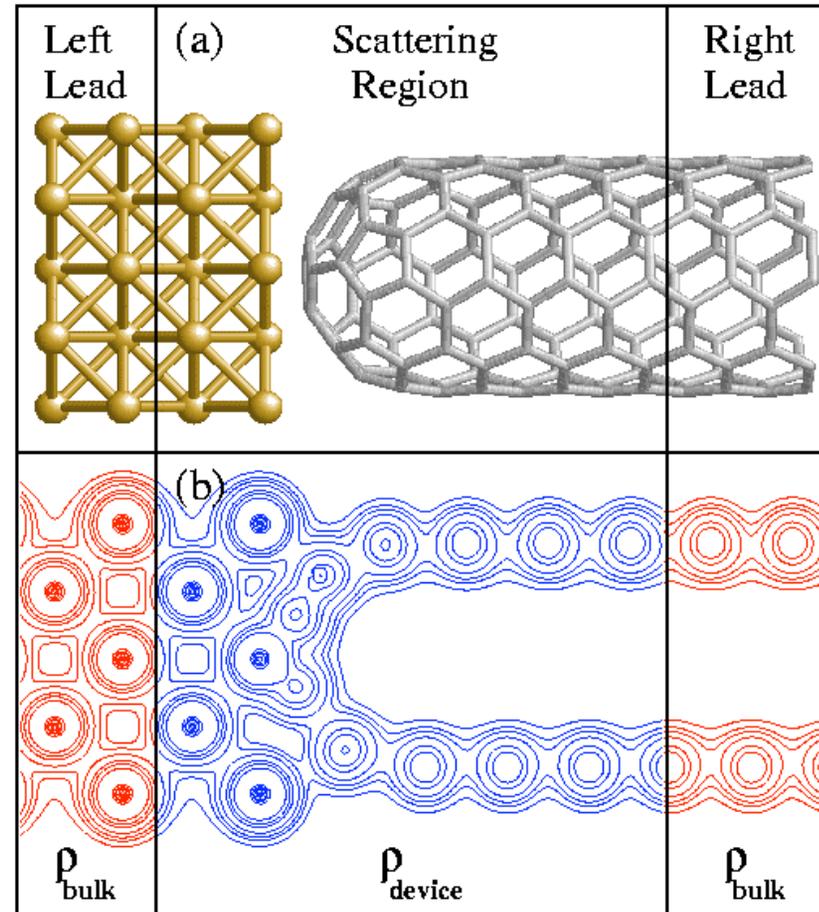
A device is “infinitely” large due to the large leads. So typically all theories divide the system into 3 parts: left/right leads and central region.



Within screen approx., we only have to worry about a finite scattering region .

Another example

Using the screening approximation and solving Poisson Eq. in real space, we can deal with systems with different leads.



The Matdcal NEGF-DFT implementation

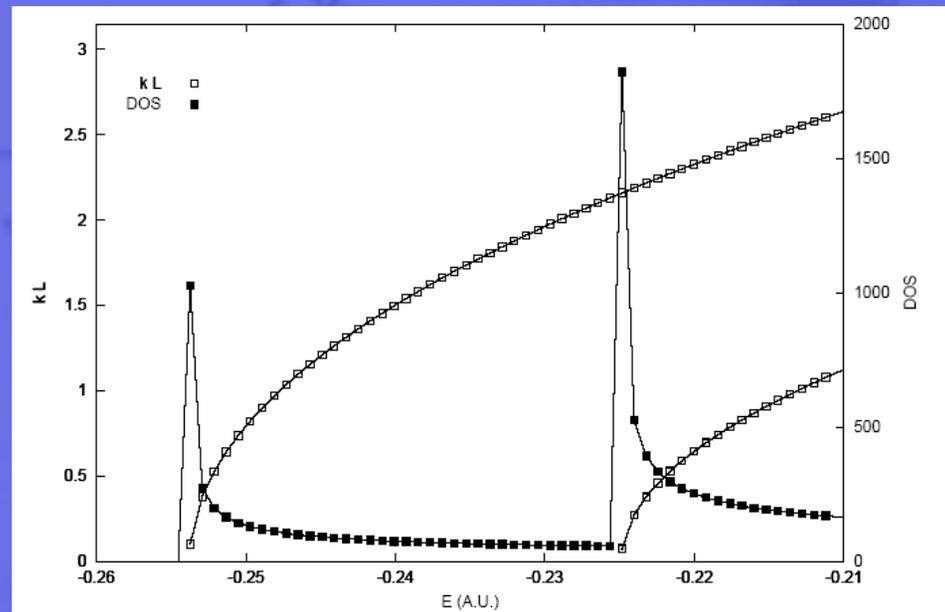
- Matdcal---matlab based Device Calculator. It evolved from our earlier versions which were written in Fortran and C.
- About 90% of Matdcal codes are written in matlab. The 10% numerical intensive parts is written in Java (will be migrated to C++).
- A parallel toolbox is developed by wrapping MPI into C and called by matlab. The code is well parallelized to run on PC clusters efficiently. For typical calculations involving <200 atoms in the scattering region, 16 or 32 nodes are used with near linear scaling.

Details: (1) Density matrix integration

$$\hat{\rho} = \frac{1}{2\pi i} \int dE G^$\hat{\rho} = \frac{1}{2\pi i} \int dE G^$$$

The NEGF has poles in both upper and lower half energy plane, as well as on the real axis. These poles represent electronic states of the device scattering region. Thus the energy integral in density matrix is impossible to do for most situations: the integrand has huge peaks at these poles.

Example: density of states (the integrand) of an 1d atomic wire: the sharp peaks give numerical trouble.



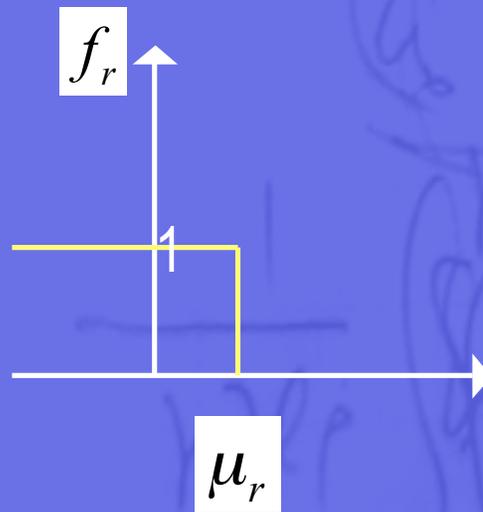
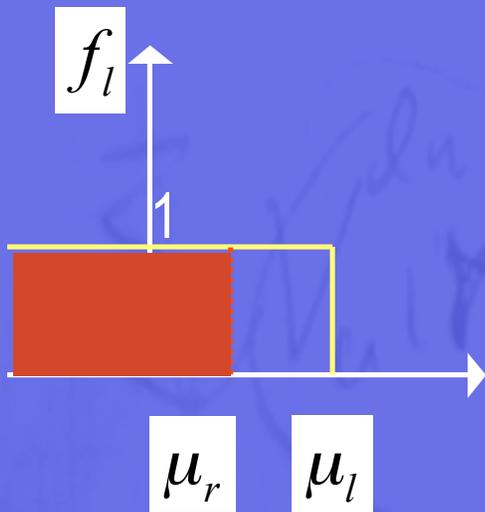
Density matrix integration (cont.):

$$\hat{\rho} = \frac{1}{2\pi i} \int dE G^<$$

$$G^< = G^R \Sigma^< G^A$$

$$\Sigma^< = i f_l(E; \mu_l) \Sigma_{l,l}^R + i f_r(E; \mu_r) \Sigma_{r,r}^R$$

$$G^R(E, U) = \frac{1}{E - H_0 - eU - V_{ps} - V_{xc} - \Sigma_R}$$



when $f_l(E) = f_r(E) = 1$,

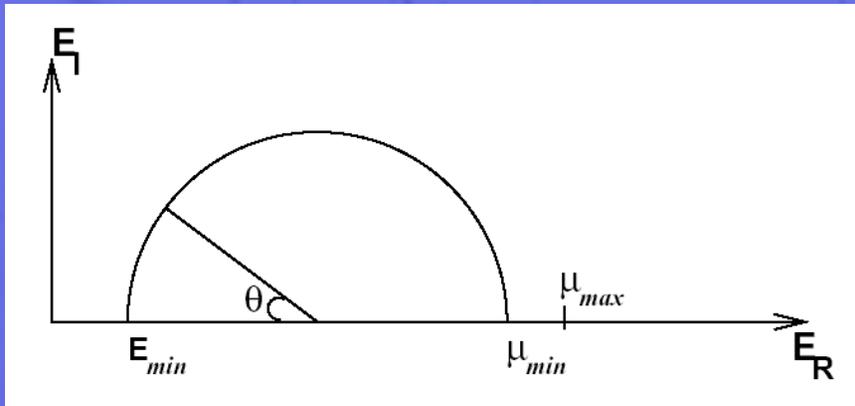
$$\text{Re}[G^<(E)] = 2 \text{Im}[G^R(E)].$$

$$\rho = \frac{2}{\pi} \text{Im} \left[\int_{-\infty}^{\min(\mu_l + V_l, \mu_r + V_r)} dE G^R(E) \right] + \frac{1}{\pi} \text{Re} \left[\int_{\min(\mu_l + V_l, \mu_r + V_r)}^{\max(\mu_l + V_l, \mu_r + V_r)} dE G^<(E) \right].$$

Contour integration for most part:

$$\rho = \frac{2}{\pi} \operatorname{Im} \left[\int_{-\infty}^{\min(\mu_l + V_l, \mu_r + V_r)} dE G^R(E) \right] + \frac{1}{\pi} \operatorname{Re} \left[\int_{\min(\mu_l + V_l, \mu_r + V_r)}^{\max(\mu_l + V_l, \mu_r + V_r)} dE G^<(E) \right].$$

$G^R(E)$ has poles only on or below real axis



The second part still has to be done on real axis. But since the voltage is usually not large, this can be done for most of situations without difficulty.

Example: a 4-Carbon atomic chain (16 charges total)

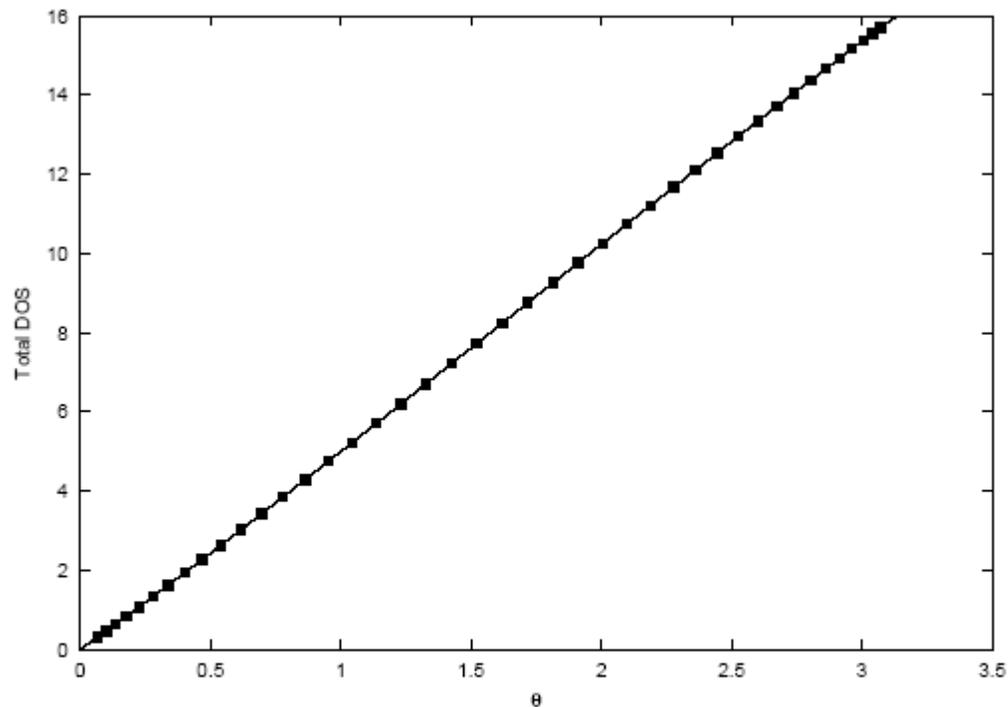
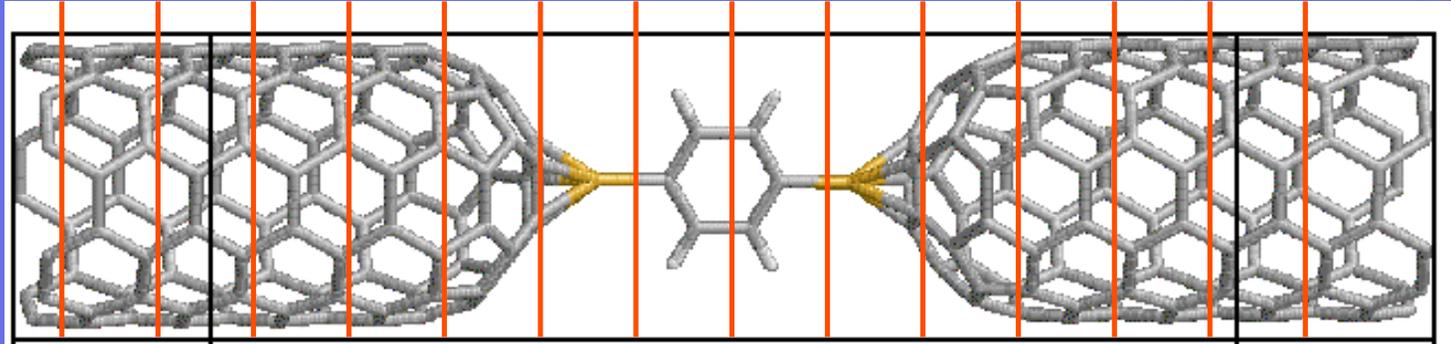


Figure 5.4: **Integrated density of states along a complex contour.** The total density of states is plotted as a function of the parameter θ for a 4-atom carbon chain. The density of states is very smooth and the integral converges with a small number of Gaussian quadrature points.

The lead's Hamiltonian are the same for each cell



“C”

Relevant matrices:

$$\begin{aligned}
 H &= \begin{bmatrix} h_{l,c} & h_{c,c} & h_{c,r} \end{bmatrix} \\
 S &= \begin{bmatrix} s_{l,c} & s_{c,c} & s_{c,r} \end{bmatrix}.
 \end{aligned}$$

$$\rho = \begin{bmatrix} \rho_{l,l} & \rho_{l,c} & 0 \\ \rho_{c,l} & \rho_{c,c} & \rho_{c,r} \\ 0 & \rho_{r,c} & \rho_{r,r} \end{bmatrix}.$$

The leads will enter as “self-energies”

Retarded Green's function of two-probe structure

$$[H-ES]G = I$$

$$\begin{bmatrix} H_{LL} & H_{LC} & 0 \\ H_{CL} & H_{CC} & H_{CR} \\ 0 & H_{RC} & H_{RR} \end{bmatrix} \begin{bmatrix} G_{LL} & G_{LC} & G_{LR} \\ G_{CL} & G_{CC} & G_{CR} \\ G_{RL} & G_{RC} & G_{RR} \end{bmatrix} = \begin{bmatrix} I_{LL} & 0 & 0 \\ 0 & I_{CC} & 0 \\ 0 & 0 & I_{RR} \end{bmatrix},$$

$$H_{L,L} \equiv \begin{bmatrix} \dots & \dots & \dots \\ & h_{i,l-1}^E & h_{i,l}^E & h_{i,l+1}^E \\ & 0 & h_{i,l-1}^E & h_{i,l}^E \\ h_{r,r}^E & h_{r,r+1}^E & 0 \\ h_{r,r-1}^E & h_{r,r}^E & h_{r,r+1}^E \\ & \dots & \dots & \dots \end{bmatrix}$$

$$H_{CC} = \begin{bmatrix} h_{i,l}^E & h_{i,c}^E & 0 \\ h_{c,l}^E & h_{c,c}^E & h_{c,r}^E \\ 0 & h_{r,c}^E & h_{r,r}^E \end{bmatrix}.$$

$$\begin{aligned} H_{LC} &\equiv h_{i,l+1}^E \\ H_{CL} &\equiv h_{i,l-1}^E \\ H_{RC} &\equiv h_{r,r-1}^E \\ H_{CR} &\equiv h_{r,r+1}^E \end{aligned}$$

We can expand the above matrix equation, and solve for the central region Green's function G_{CC}

Green's functions:

$$G_{CC} = \left[H_{CC} - \Sigma_{CC}^L - \Sigma_{CC}^R \right]^{-1}$$
$$= \begin{bmatrix} h_{l,l}^E - \Sigma_{l,l}^L & h_{l,c}^E & 0 \\ h_{c,l}^E & h_{c,c}^E & h_{c,r}^E \\ 0 & h_{r,c}^E & h_{r,r}^E - \Sigma_{r,r}^R \end{bmatrix}^{-1},$$

$$\Sigma_{CC}^L \equiv H_{CL} H_{LL}^{-1} H_{LC}$$
$$\Sigma_{CC}^R \equiv H_{CR} H_{RR}^{-1} H_{RC}.$$

The Green's function of the device central scattering region is obtained by inverting this matrix. The quantities $\Sigma_{CC}^L, \Sigma_{CC}^R$ are the self-energies due to the leads.

These self-energies can be computed exactly for periodic structures, which is exactly what we have for the leads.

Details: (4) Computation of self-energies

$$\Sigma_{CC}^L \equiv H_{CL}H_{LL}^{-1}H_{LC}$$

$$\Sigma_{CC}^R \equiv H_{CR}H_{RR}^{-1}H_{RC}.$$

To compute these quantities, we need the “surface Green’s functions” which are

$$H_{LL}^{-1}, H_{RR}^{-1}$$

There are two (may be more) methods for evaluating the surface Green’s functions:

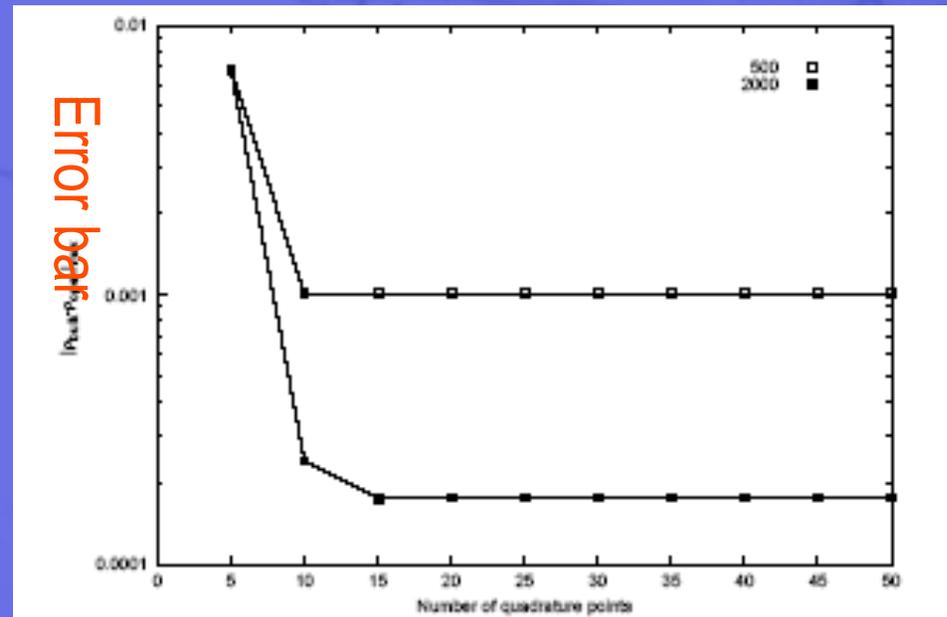
- (1) Iterative method, Sancho et al. J. Phys. F 14, 1205 (1984);
- (2) Direct method, Sanvito et al. Phys. Rev. B 59, 11936 (1999).

Some checks: check density matrix at equilibrium

$$\rho = \sum_b f_b |\Psi_b|^2$$

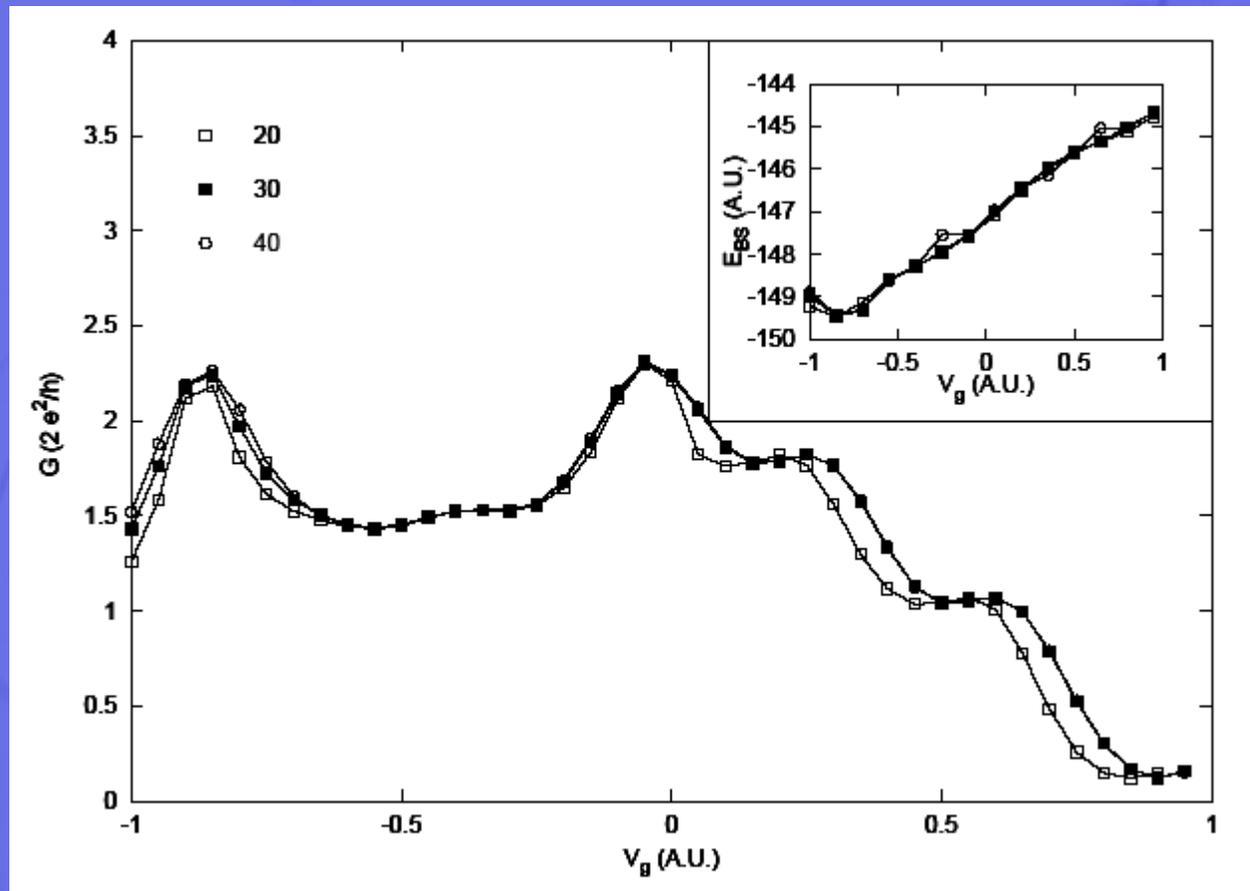
$$\hat{\rho} = \frac{1}{2\pi i} \int dE G^\gamma$$

4-carbon chain: with 20 or more contour integration points, the Green's function converges to the same results as using wave functions.



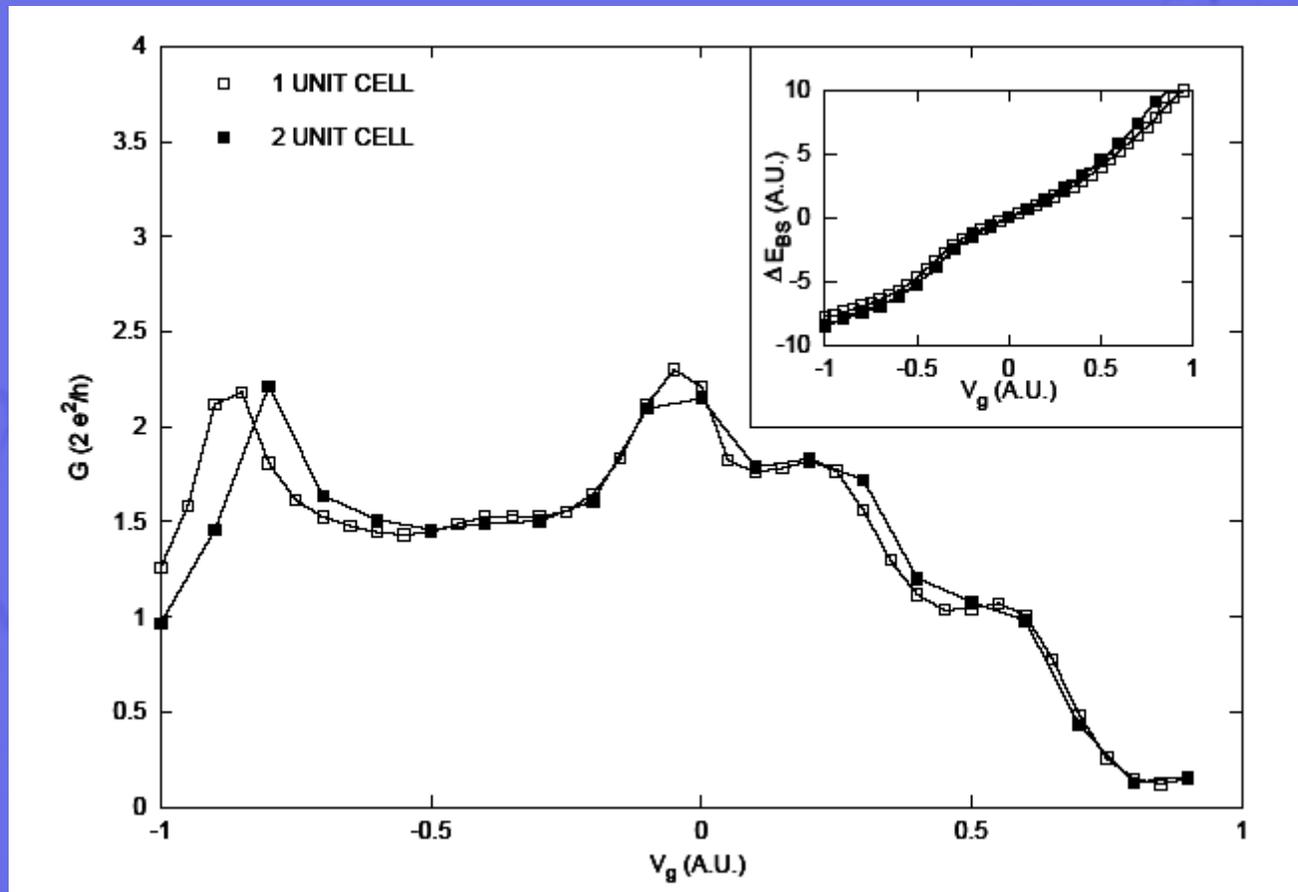
of contour integration points

Check: # of contour integration points



Conductance of Al-C60-Al device versus a gate voltage

Check: effects of more lead atoms in center cell



Adding more lead layers into central cell

Calculating physical quantities:

Any physical quantity A is obtained by trace over density matrix:

$$\text{Tr}_c[\rho A] \equiv \rho_{c,l} A_{l,c} + \rho_{c,c} A_{c,c} + \rho_{c,r} A_{r,c}.$$

$$\langle A \rangle_{\mathbf{r}} \equiv \int_c d\mathbf{r} A(\mathbf{r}).$$

Examples:

Band structure energy:

$$E_{BS} = \text{Tr}_c[\rho H] = \rho_{c,l} h_{l,c} + \rho_{c,c} h_{c,c} + \rho_{c,r} h_{r,c}$$

Total charge in central cell:

$$N_{\text{tot}} = \text{Tr}_c[\rho S] = \rho_{c,l} s_{l,c} + \rho_{c,c} s_{c,c} + \rho_{c,r} s_{r,c}.$$

Total charge on n-th atom:

$$N_n = \text{Tr}_{c_n}[\rho S] = \rho_{c_n,l} s_{l,c} + \rho_{c_n,c} s_{c,c} + \rho_{c_n,r} s_{r,c}.$$

Calculating physical quantities:

Equilibrium conductance:

$$G = \frac{2e^2}{h} \text{Tr}[\Gamma_{l,l}(\mu_l) G_{l,r}^R(\mu_l) \Gamma_{r,r}(\mu_l) G_{r,l}^A(\mu_l)].$$

Current-voltage curves:

$$I = \frac{2e}{h} \int_{\min(\mu_l, \mu_r)}^{\max(\mu_l, \mu_r)} dE (f_l - f_r) \text{Tr}[\Gamma_{l,l}(E) G_{l,r}^R(E) \Gamma_{r,r}(E) G_{r,l}^A(E)].$$

Merits of NEGF-DFT formalism:

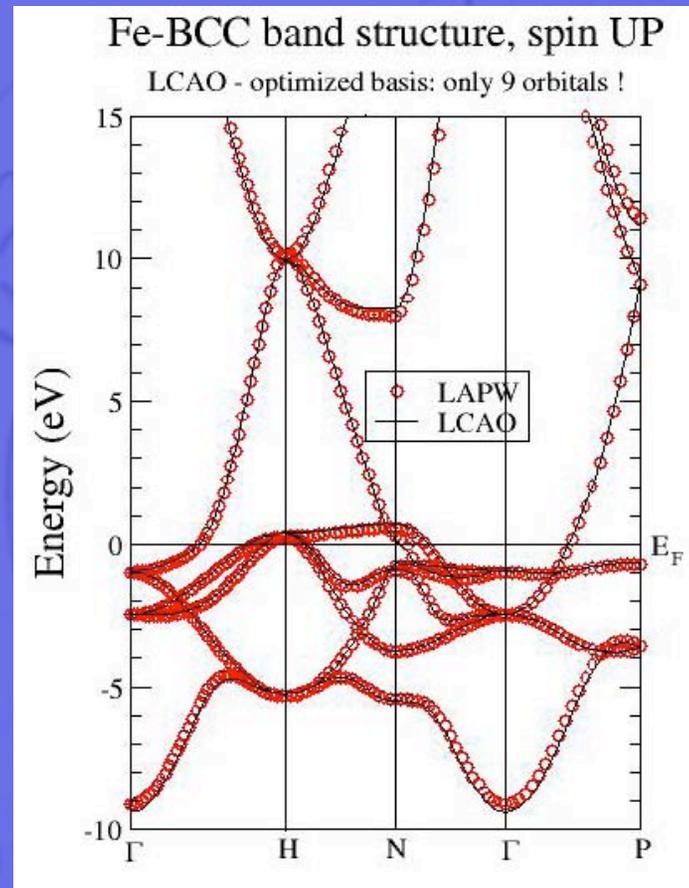
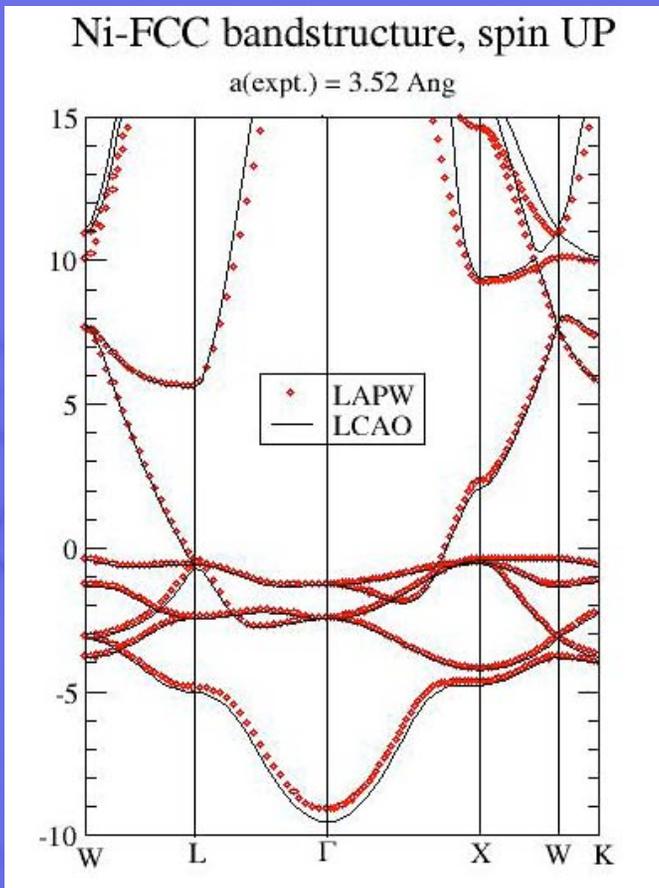
- The NEGF-DFT formalism is state-of-the-art method for analyzing open systems with current flow.
- It correctly treats the transport boundary conditions. It treats atoms in the leads and in the scattering region on equal footing with same accuracy and same atomic scheme.
- It correctly deal with non-equilibrium physics using NEGF. It treats bound states and scattering states on equal footing with equal accuracy.
- It can deal device structures with many more atoms than any other known self-consistent methods.
- It is a quantitative method: no phenomenological parameters are used.

Three approximations in DFT part of NEGF-DFT:

1. In DFT, we use local density approximation (LDA), or local spin density approximation (LSDA), or generalized gradient approximation (GGA). These reflect all DFT based methods at present time. This lead to problems if correlations are strong.
2. In practical implementations, one uses LCAO (or Gaussian) basis set. This is a finite basis set and careful tests must be done.
3. In Matdcal, we use conventional norm conserving nonlocal pseudopotentials.

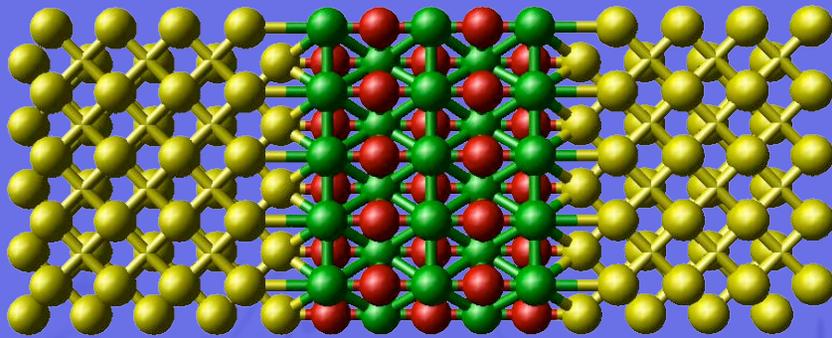
Approximations 2,3 are controlled by comparing equilibrium results to FP-LAPW code (full potential linearized augmented plane wave).

Ni and Fe: test basis sets



It is crucial to have accurate LCAO basis sets.

Fe/MgO periodic lattice:



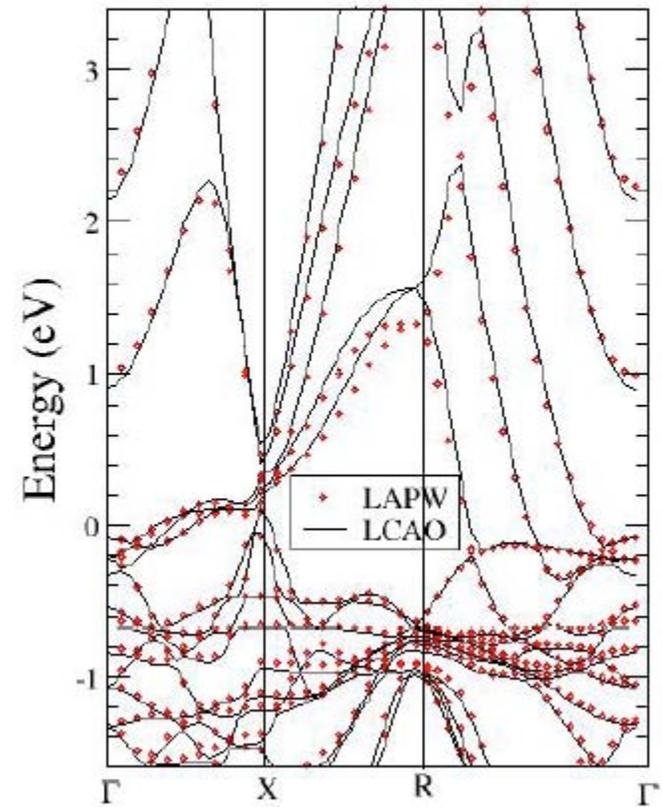
.....Fe

MgO

Fe

FeMgO band structure, spin UP

Fe pseudopotential is "softer" than in the bulk !



“Standard” Methodology

Generation of System

Geometry Optimization with All-Electron Plane Wave Code

Calculation of band structure of center cell using All-Electron Plane-Wave Code

Optimization of LCAO pseudopotentials and orbitals to match band structure

Import pseudopotentials and orbital into MatDCAL

Transport Calculation

Applications domain of present NEGF-DFT

- Molecular electronics;
- Nanoscale semiconductor devices;
- Nanowires;
- STM;
- Spin injection into magnetic tunnel junctions;
- Electronic structure of bulk, surface, interfaces;
- Any transport problems whose electronic structure can be described by DFT or any mean field theory;
- Can be used to compute conductance, I-V curves, frequency dependent conductance, capacitance, admittance, charge, scattering states, current density, current induced forces, etc...
- ...