AIST

First Principles Nonequilibrium Transport Theory of Real Molecular Electronics

－Orbital Engineering, Contact Chemistry, and Electron-phonon Interactions－

Hisao Nakamura

"Research Initiative of Computational Science (RICS)"
**Nanosystem Research Institute (NRI)**
National Institute of Advanced Industrial Science and Technology (AIST)

－Introduction－
Electronic device at molecular scale
# (single molecule / molecular film / nano-contact)

Post Si device

Device molecular scale
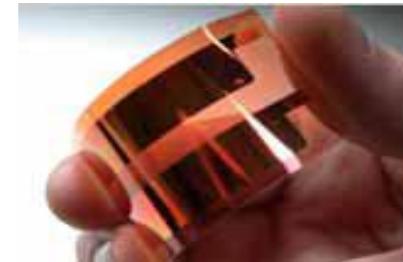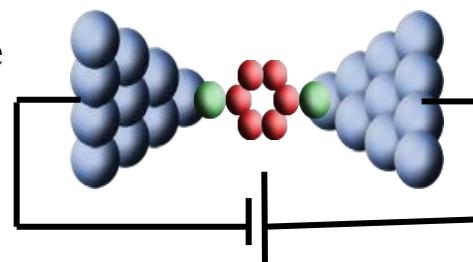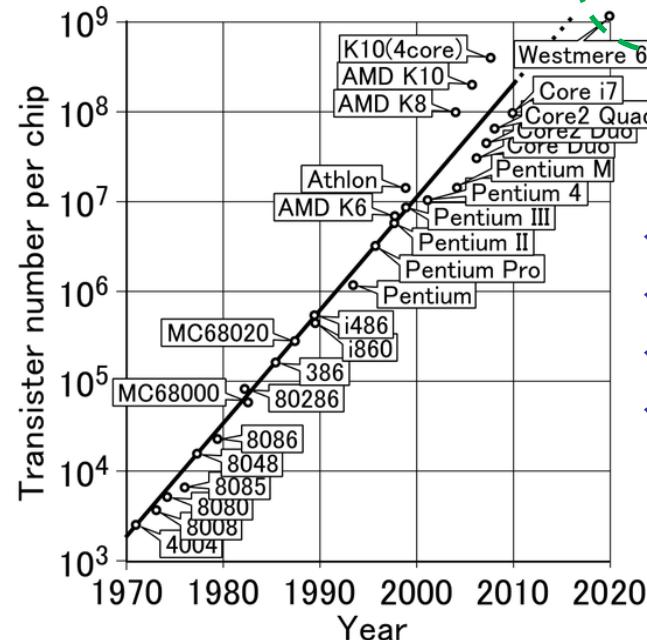
✓ **Flexible conformation/integration.**
✓ **Molecular Diode（pn photoelectromotive force）**
✓ **Thermopower（Giant seebeck, phonon-mismatch ）**
✓ **Bio-electronics**
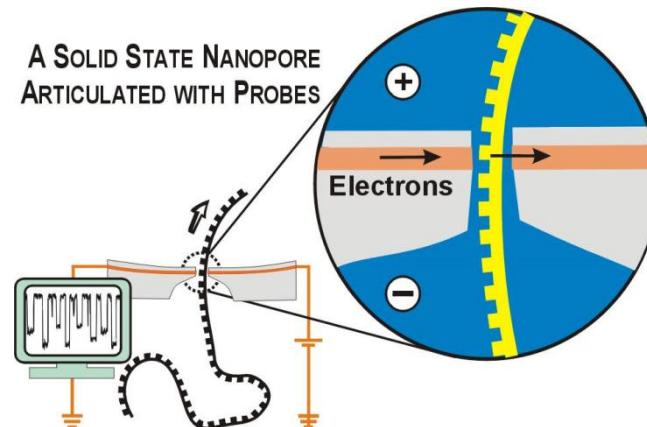
－From coherent transport to sequential tunneling－

sequential tunneling (TIH)

Coherent (ballistic)
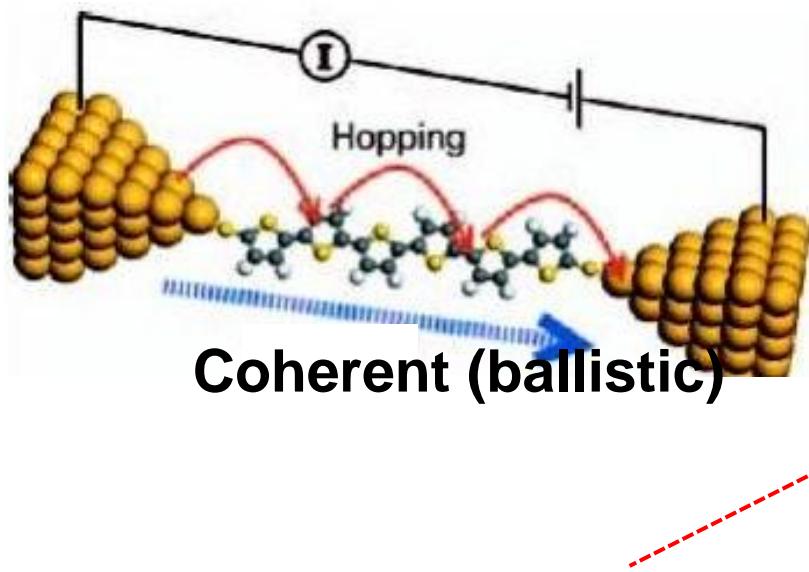
coherent (tunneling) transport

$$g = 1/R \propto \exp(-\beta L)$$

Independent of temperature
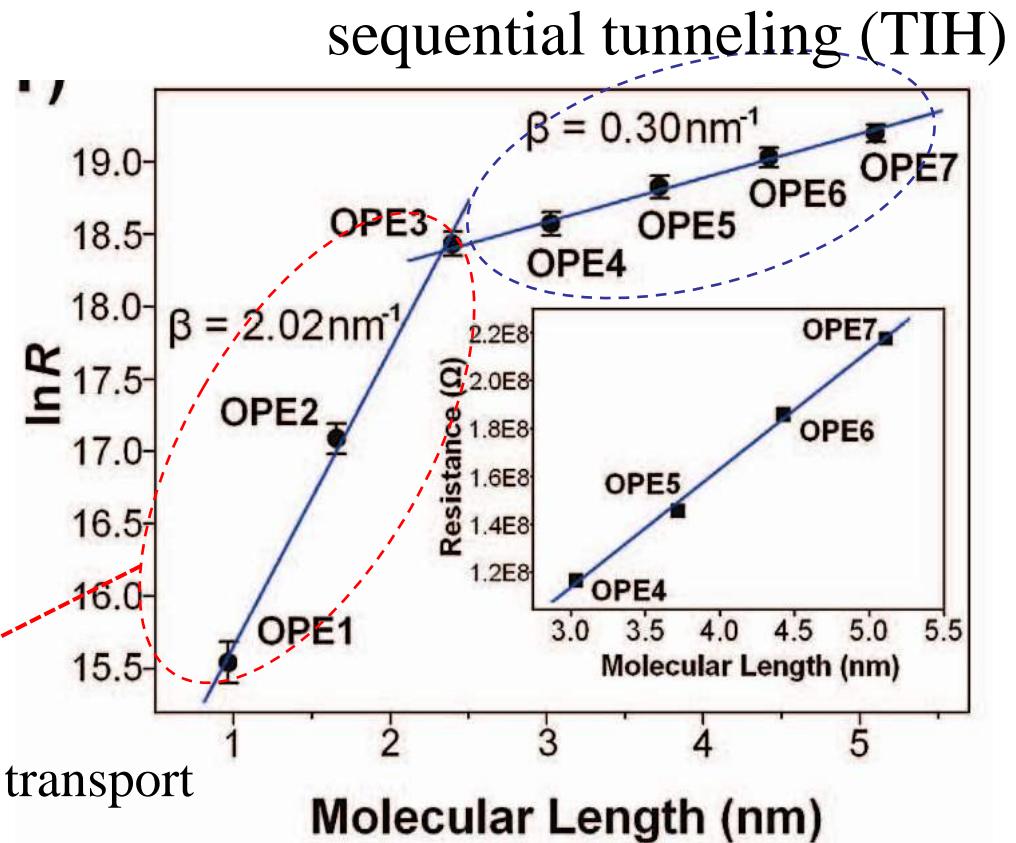
Lu *et al.* *ACS Nano* **12** 2861 (2009)

Analytical theory of length dependence of conductance (coherent)
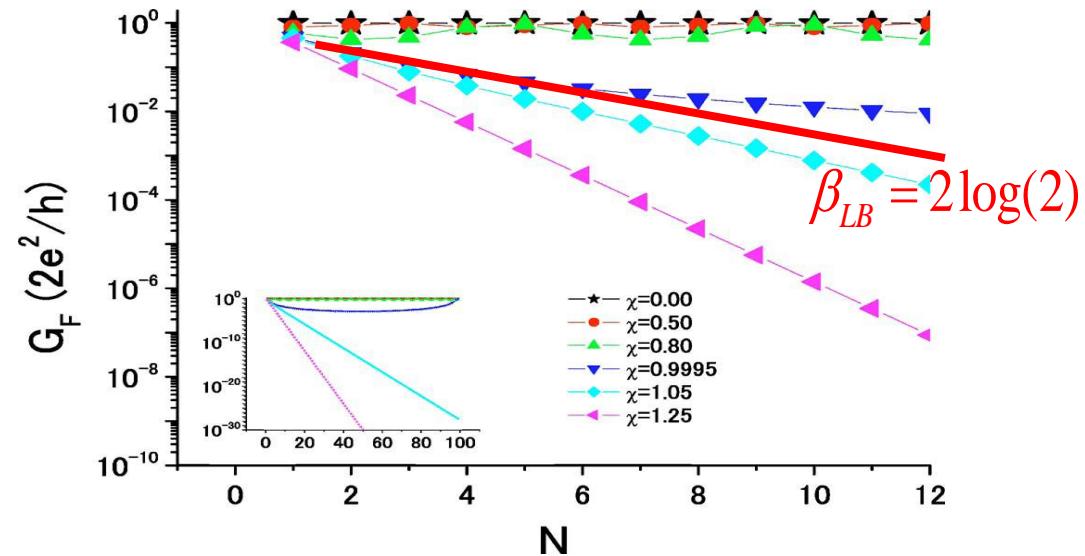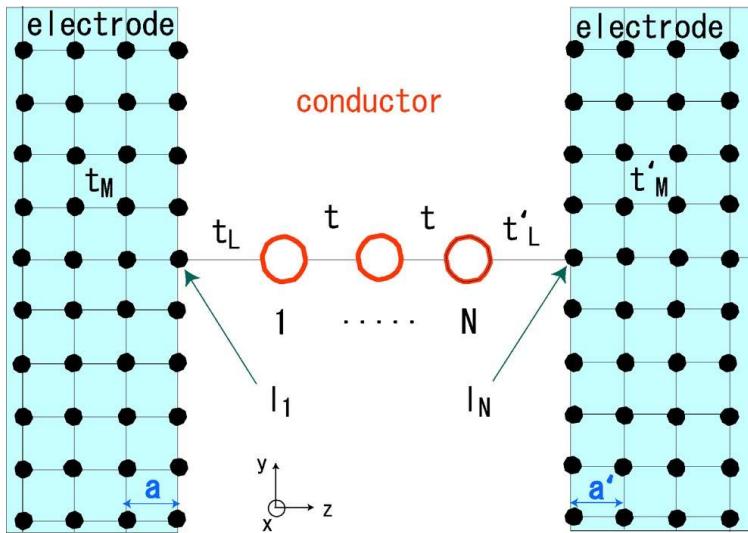
Y. Asai and H. Fukuyama *Phys.Rev.B* **72** 085431 (2005)

$$g \simeq \frac{4\pi^2 t_L^4 \rho_{\text{electrode}} \, |\lambda_1 - \lambda_2|^2}{|\lambda_1 + \Sigma^r|^2} \exp(-2\,||\Delta_F/2t| + \sqrt{(\Delta_F/2t)^2 - 1}|\,(N-1))$$

$$\rightarrow \exp(-\beta N)$$

$$\beta = 2\ln(|\Delta_F/t|)$$

Resonant (coherent) tunneling

$$\chi = \Delta_F/2t \leq 1$$

Off-resonant (coherent) tunneling

$$\chi = \Delta_F/2t > 1$$

Decoherence : <u>electron-phonon</u>, Coulomb blockade , *etc*

Rate equation (FGR) approach *between* hopping sites

$$H = \varepsilon_0 c^\dagger c + \sum_\mu \varepsilon_k c_k^\dagger c_k + \sum_k (V_k c^\dagger c_k + H.C) + M\Omega_0 (b + b^\dagger) c_k^\dagger c_k + b^\dagger b$$

$$\varepsilon_{k=i} \quad \varepsilon_0 \quad \varepsilon_{k=f}$$
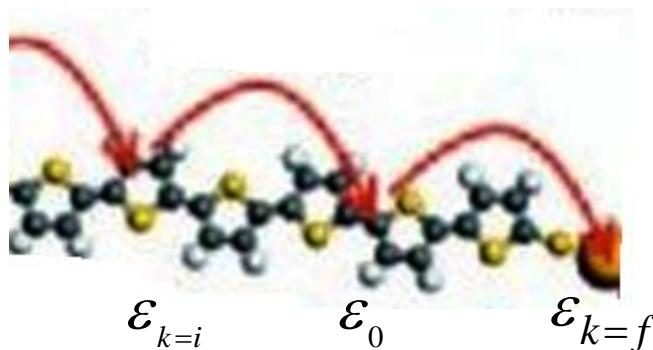
Lang-Firsov transformation

$$\rightarrow \overline{H} = \exp(\frac{M}{\Omega_0} c^\dagger c(b^\dagger - b)) H \exp(-\frac{M}{\Omega_0} c^\dagger c(b^\dagger - b))$$

$$= (\varepsilon_0 - \frac{M^2}{\Omega_0})\overline{c}^\dagger \overline{c} + \sum_\mu \varepsilon_k c_k^\dagger c_k + \sum_k (\overline{V}_k c^\dagger c_k + H.C)$$

electronic coupling   coupling

Γ_i Γ_f
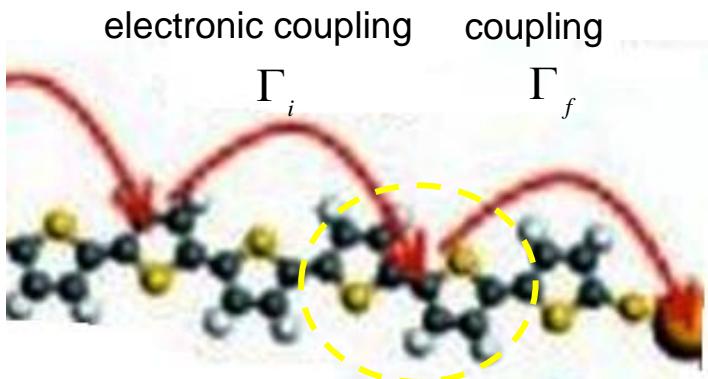
Transition from "i" to "f"

$$\Gamma \simeq \frac{\Gamma_i \Gamma_f}{\Gamma_i + \Gamma_f} \to 2\pi \,|\, H_{fi} \,|^2\, \delta(\varepsilon - \varepsilon_i)$$

Decoherence $\to$ FGR $k_{ET} = -2\,|\,H_{fi}\,|^2\, \mathrm{Im}\, G^r(\varepsilon_i)$

$$G^r(\varepsilon) = \sum_{l=0}^{\infty} \exp\{-S(2N_{BE}+1)\} I_l\left[2S\sqrt{N_{BE}(N_{BE}+1)}\right] \exp(\beta l \Omega_0/2)\{\varepsilon - \bar{\varepsilon}_0 - l\Omega_0 + i\delta\}^{-1}$$

$$S = \left(\frac{M}{\Omega_0}\right)^2$$

In high temperature limit: $I_n(x) \to \dfrac{\exp(x - n^2/2x)}{\sqrt{2\pi x}}$

$$k_{ET} = 2\,|\,H_{fi}\,|^2\, \frac{\exp\{-\beta/4\lambda(\Delta - \lambda)^2\}}{\sqrt{4\pi\lambda/\beta}}$$

Features : Temperature dependence
      : Arrhenius plot

Marcus Theory

Initial State

Final State

ε_0

$\lambda = \dfrac{M^2}{\Omega_0}$

E_i

λ

Δ

$\varepsilon_0 - \lambda = \bar{\varepsilon}_0$
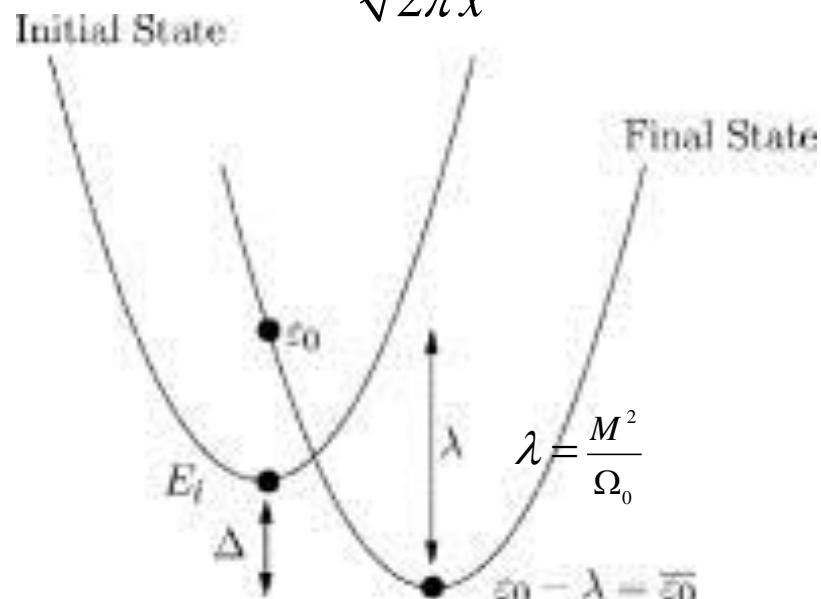
－**NEGF Formalism for transport in nano-contact**－

$$H = \sum_{\mu}(\varepsilon_{\mu} + \varphi(t))d_{\mu}^{\dagger}d_{\mu} + \sum_{k}(\varepsilon_{k} + \varphi(t))c_{k}^{\dagger}c_{k} + \sum_{\mu k}(V_{\mu k}d_{\mu}^{\dagger}c_{k} + H.C)$$

$$+U_{ij,kl}d_{i}^{\dagger}d_{j}^{\dagger}d_{k}^{\dagger}d_{l}^{\dagger} + \sum_{\alpha}\Omega_{\alpha}b_{\alpha}^{\dagger}b_{\alpha} + \sum_{\mu,\alpha}M_{\alpha}(b_{\alpha}^{\dagger} + b_{\alpha})d_{\mu}^{\dagger}d_{\mu}$$

electric current → one-particle property → one-particle density matrix

Green's function (correlation function)

$$G_{12}^{<}(t_1,t_2) = i\left\langle d_2^{\dagger}(t_2)d_1(t_1)\right\rangle$$

$$G_{12}^{>}(t_1,t_2) = -i\left\langle d_1(t_1)d_2^{\dagger}(t_2)\right\rangle$$

Contour-ordered Green's function

(a)
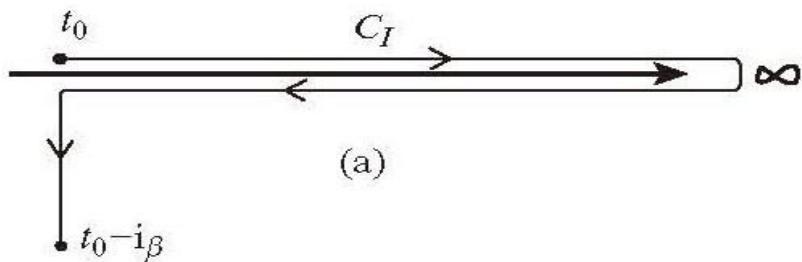
$$G_{12}(\tau_1,\tau_2) = -i\left\langle \hat{\rho}_{t_0}T_C[d_1(t_1)d_2^{\dagger}(t_2)]\right\rangle$$

$$d_1(\tau_1) = U(t_0,\tau_1)d_1 U(\tau_1,t_0)$$

Ground state (Eq. state) : T order $\rightarrow$ Non Eq. state: Keldysh contour T_C
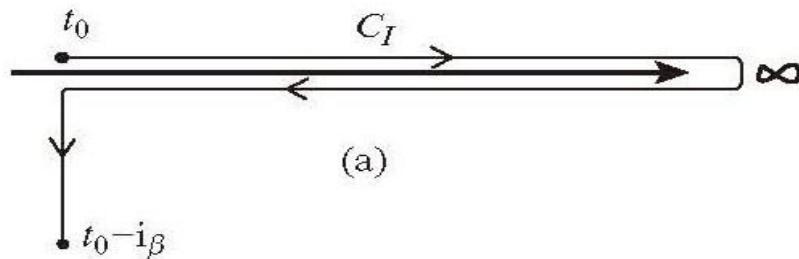
Contour-ordered GF satisfies the SAME equation with the standard GF

$$G(\tau_1, \tau_2) = G_0(\tau_1, \tau_2) + \int_C d\tau d\tau' G_0(\tau_1, \tau) \Sigma(\tau, \tau') G(\tau', \tau_2)$$

Possible to apply the same Feynman diagram approach etc.

However, integral along contour time loop is necessary.

$G^<(t_1, t_2) : t_1, t_2$ must be on the different axis.

$G^T(t_1, t_2) : t_1, t_2$ must be on the same axis.

$$A(\tau_1, \tau_2) = \int_c d\tau \, B_0(\tau_1, \tau) C(\tau, \tau_2)$$

On real time axis

$$A^<(t_1, t_2) = \int dt (B^r(t_1, t) C^r(t, t_2) + B^<(t_1, t) C^a(t, t_2))$$

$$A^r(t_1, t_2) = \int dt B^r(t_1, t) C^r(t, t_2)$$

EOM $\rightarrow$

$$\left[i\frac{\partial}{\partial t} - \varepsilon \right] G^<(t_1, t_2) = \int_{-\infty}^{t_1} dt' \Sigma^r(t_1, t') G^<(t', t_2) + \int_{-\infty}^{t_2} dt' \Sigma^<(t_1, t') G^a(t', t_2)$$

Dyson equation
(time or Energy domain)

$$G^< = G^r \Sigma^< G^a + (1 + G^r \Sigma^r) G_0^< (1 + G^a \Sigma^a)$$

$$(1 + G^r \Sigma^r) G_0^< (1 + G^a \Sigma^a) \approx \left(G_0^r \right)^{-1} - \left(G_0^a \right)^{-1} \rightarrow 0$$

Electric current by Jauho-Wingreen-Meir formula

Ansatz: Electrodes are non interacting system and thermerized, i.e, equilibrium

$$g^{<}_{surf,L/R}(E) = -f_{L/R}(E)\left(g^{r}_{surf,L/R} - g^{a}_{surf,L/R}\right)$$

$$\Sigma^{<}_{L/R}(E) = if_{L/R}(E)\Gamma_{L/R}(E)$$

$$g^{r}_{k}(E) \xrightarrow[\substack{\text{semi-infinite boundary condition} \\ \text{(termination of bulk)}}]{} g^{r}_{surf}(E)$$

Let us define electric current as *flux* on the left electrode

$$I = \tfrac{i}{2\pi}\int d\varepsilon \operatorname{Tr}\left\{\Gamma_{L}(\varepsilon-\varphi_{L})\left[G^{<}(\varepsilon)+f_{L}(\varepsilon-\varphi_{L})\left(G^{r}(\varepsilon)-G(\varepsilon)\right)\right]\right\}$$

$$\Gamma_{L}(\varepsilon) = i\left(\Sigma_{L}(\varepsilon)-\Sigma^{\dagger}_{L}(\varepsilon)\right) \quad \Sigma_{L}(\varepsilon) = Vg^{r}_{surf:L}(\varepsilon)V^{*}$$

$$\rightarrow I(V_b) = \frac{1}{2\pi}\int dE \operatorname{Tr}\left[\Sigma^{<}_{L}(E,V_b)G^{>}(E,V_b) - \Sigma^{>}_{L}(E,V_b)G^{<}(E,V_b)\right]$$

Landauer formula

$$I(V_b) = \int d\varepsilon \operatorname{Tr}\left[\Gamma_{L}(\varepsilon+V_b/2)G^{r}(\varepsilon)\Gamma_{R}(\varepsilon-V_b/2)G^{a}(\varepsilon)\right]\left\{f(\varepsilon:\varepsilon_F+V_b/2)-f(\varepsilon:\varepsilon_F-V_b/2)\right\}$$

Electron-pathway by NEGF

Observable quantity I = *flux* of electron

How electron passes in the conductor (molecule) ?

$$J_{\mu \to \nu} = g_0 V \operatorname{Im} \left\{ H_{\mu\nu}^* \left(\overline{\mathbf{G}\mathbf{\Gamma}_L \mathbf{G}^\dagger} \right)_{\mu\nu} - H_{\mu\nu}^* \left(\overline{\mathbf{G}\mathbf{\Gamma}_R \mathbf{G}^\dagger} \right)_{\mu\nu} \right\}$$

$$\vec{J}_A = g_0 V \sum_{B \neq A} \sum_{\mu \in A, \nu \in B} J_{\mu \to \nu} \vec{u}_{AB}$$

in ballistic transport

－Cross-over of NEGF and scattering theory －

✓ **Electronic structure of the molecular junction is *not* same with intrinsic property of "free" molecular system.**

Orbital engineering + Contact chemistry = _rigorous_ Conducting orbital ?

Conducting Orbital Engineering

MO theory (Quantum chemistry)

Surface physics

Orbital Engineering

Contact Chemistry

Energy level and **phase** of molecular orbital

(1) **Hybridization of electronic states in semi-infinite-electrode, charge up**

(2) **Effect of applied bias voltage**
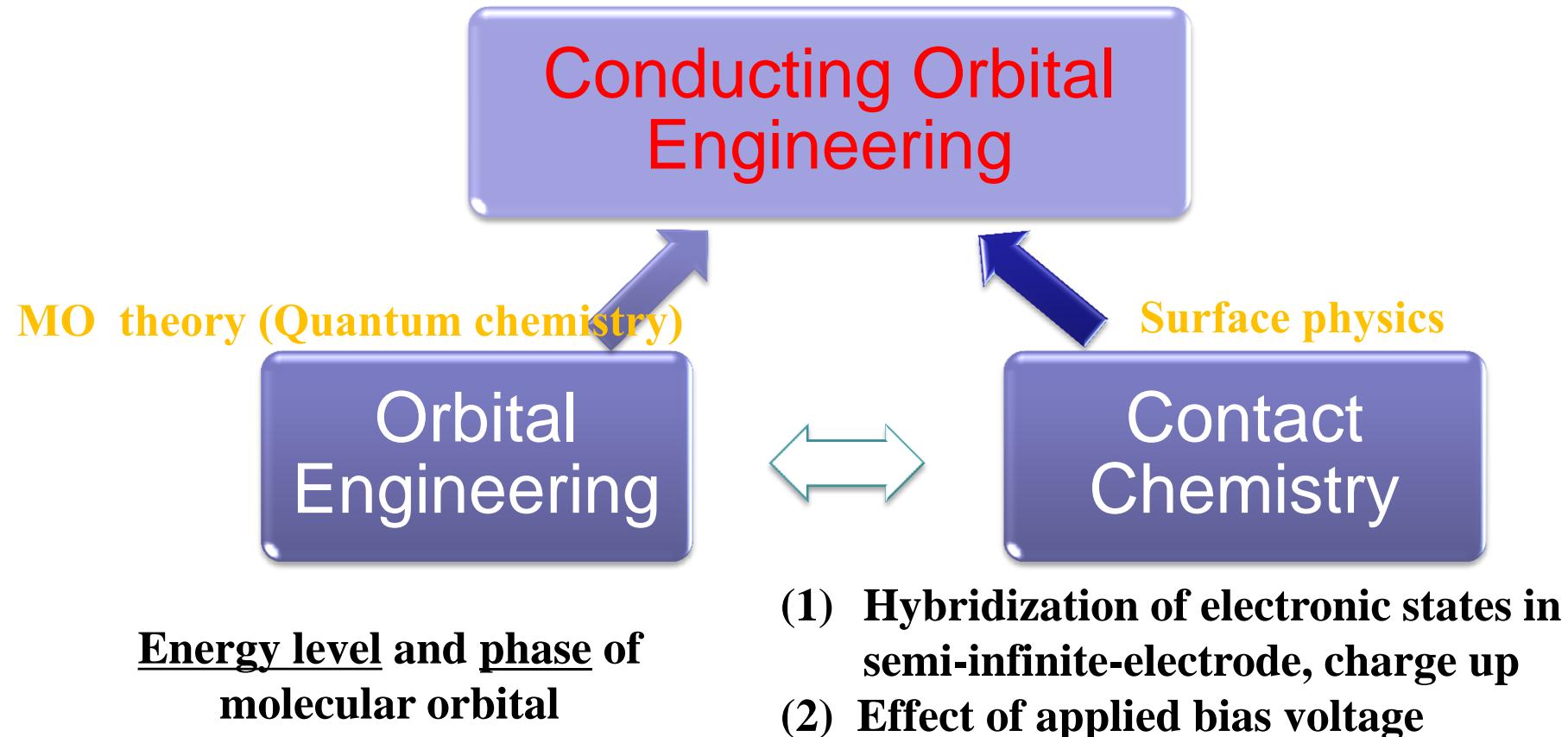
# How can we identify quantitative "*conducting orbital*" ?

$$(E - H)\Psi_I = 0 \rightarrow \Psi_I = \chi_L^+(E) + \sum_\alpha S_{\alpha\beta}(E)\chi_\beta(E)$$

S-matrix

$$\mathbf{S}(E) = \exp(i\Delta(E)) = \exp(i\mathbf{X}^\dagger\boldsymbol{\delta}(E)\mathbf{X})$$

resonance structure: $\sin^2(\delta/2)$

More strictly, we need only *reactive part* of S matrix since we focus on "current"

semi-infinite electrode   semi-infinite electrode

Q_L *P*-space Q_R
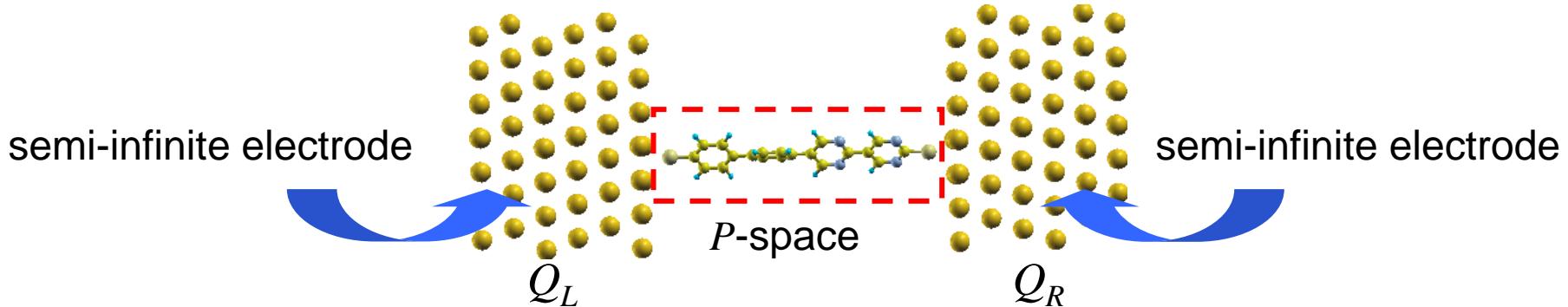
$P+Q = P+Q_L+Q_R = $ device$(+$*semi-infinite*$)$

$P = \{\varphi_\mu\}$ MOs or AOs in the molecule

$Q_L = \{\chi_L(E)\}$ left channel states

$Q_R = \{\chi_R(E)\}$ right channel states

What we want is "conducting orbital" = MO projected on the **P** space "dressed" by surface/electrodes electronic sates

$$(E-H)\Psi_I = 0 \rightarrow (E - H_{PP}^{eff})\sum_\mu a_\mu \varphi_\mu = 0$$

$$\Psi_\alpha(E) = \sum_\mu a_{\mu\alpha}\varphi_\mu + \sum_c d_{\alpha,cL}\chi_{cL}(E) + \sum_c d_{\alpha,cR}\chi_{cR}(E)$$

$$\approx \psi_\alpha + \sum_c d_{\alpha,cL}\chi_{cL}(E) + \sum_c d_{\alpha,cR}\chi_{cR}(E)$$

PMO   **Correction terms ("dressed part")**

= Orbital Engineering   = Contact Engineering

small (~0)

$$H_{PP}^{eff} = H_{PP} + H_{PQ_L}G_{QQ}^r(E)H_{Q_LP} + H_{PQ_L}G_{QQ}^r(E)H_{Q_LP} + H_{PQ_L}G_{QQ}^r(E)H_{Q_RP} + H_{PQ_E}G_{QQ}^r(E)H_{Q_LP}$$

MPSH

Diagonalize of MPSH →PMO

$E_{0\alpha}, |\psi_\alpha>$

intrinsic electronic coupling with *L*

$$<\alpha|\cdots|\alpha> = \Delta E_L + i\gamma_L$$

intrinsic electronic coupling with *R*

$$<\alpha|\cdots|\alpha> = \Delta E_R + i\gamma_R$$
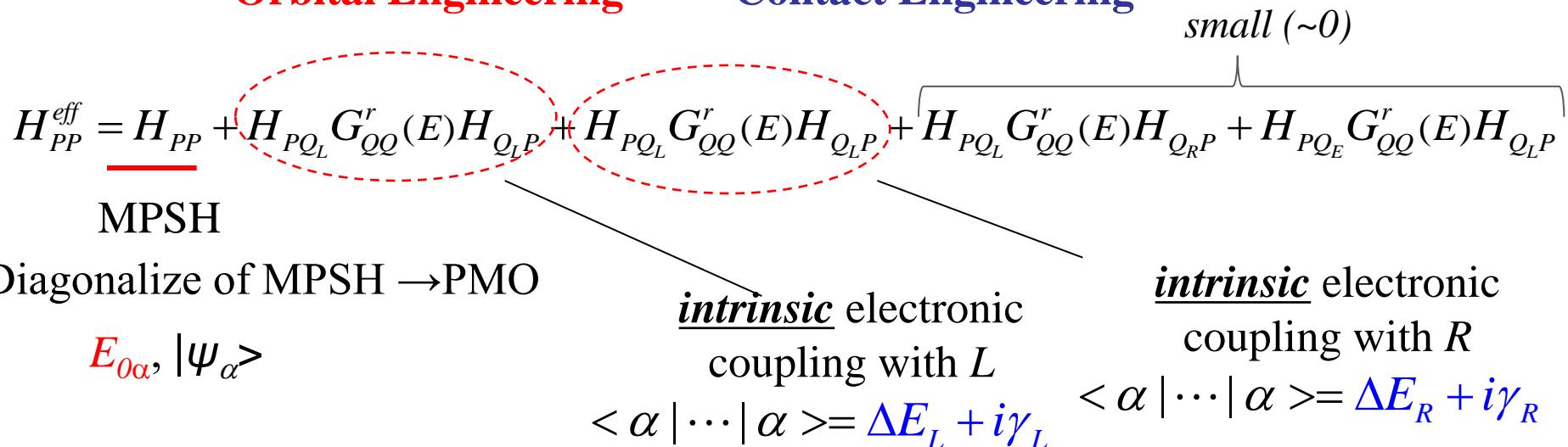
Resonance Structure of Conductance by Breit-Wigner form

$$\tau = \sum_{\alpha} \tau_{\alpha}, \ \tau_{\alpha} \sim \frac{4\gamma_L \gamma_R}{\{E - \underbrace{(E_{0\alpha} + \Delta E)}_{E_{\alpha}}\}^2 + (\gamma_L + \gamma_R)^2}$$

If $\tau_{\alpha}(E \approx E_F)$ is large, it is "conducting orbital".

Identify "conducting MO" rigorously in *any bias-voltage* based on NEGF-DFT

— **Interaction of electron and ion motions** —

(1) Inelastic transport by electron-phonon (vibron) interactions

$$H = \sum_{\mu} (\varepsilon_{\mu} + \varphi(t)) d_{\mu}^{\dagger} d_{\mu} + \sum_{k} (\varepsilon_{k} + \varphi(t)) c_{k}^{\dagger} c_{k} + \sum_{\mu k} (V_{\mu k} d_{\mu}^{\dagger} c_{k} + H.C)$$

$$+ U_{ij,kl} d_{i}^{\dagger} d_{j}^{\dagger} d_{k} d_{l} + \sum_{\alpha} \Omega_{\alpha} b_{\alpha}^{\dagger} b_{\alpha} + \sum_{\mu,\alpha} M_{\alpha} (b_{\alpha}^{\dagger} + b_{\alpha}) d_{\mu}^{\dagger} d_{\mu}$$

✓ **Interaction with localized phonon in conductor (molecular vibration: vibron), joule heating and local temperature**

Viibron can be well-defined when conductor is atomic wire or organic molecules…
For electrode, we already assume thermilized electrodes for ions of electrodes.
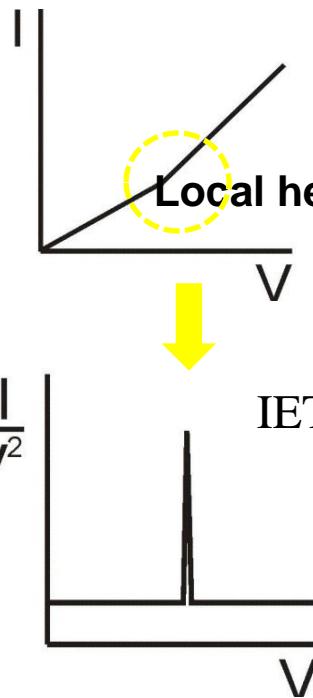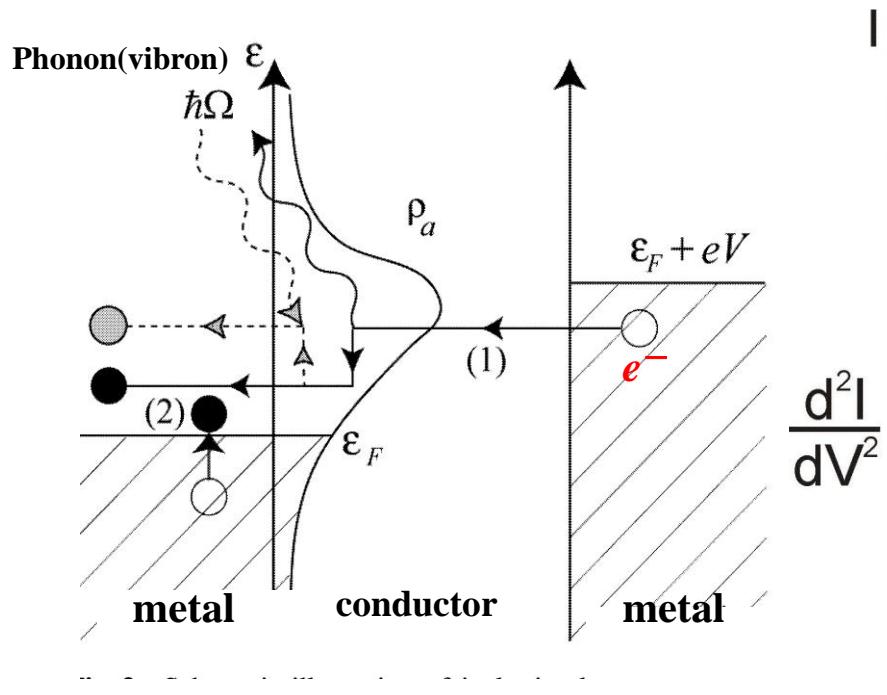
Local heating of vibron by electric current

IETS=**finger print of molecule and local heating of device**

IETS is a finger print of molecule (vibron) and local heating process !!

Very short survey of c-LOE formalism

$$G^< = G^r \Sigma^< G^a$$

$$D^<(\omega) = D^r(\omega) \Pi^<(\omega) D^a(\omega)$$

$$I(V) = \frac{1}{2\pi} \int dE \, \mathrm{Tr}\left[\Sigma_L^<(E,V) G^>(E,V) - \Sigma_L^>(E,V) G^<(E,V) \right] = \int dE \, i(E)$$

$$J_{th}^{ph}(V) = \frac{1}{2\pi} \int d\omega \, \omega \, \mathrm{Tr}\left[\Pi_L^<(\omega) D^>(\omega) + \Pi_L^>(\omega) D^<(\omega) \right] = \int d\omega \, \omega \, j(\omega)$$

Self-energy terms of electron-phonon interaction
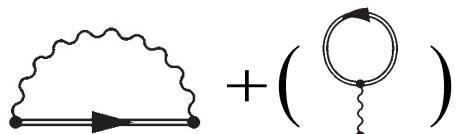
$$\Sigma^<(E) = \Sigma^<[E; G^<, D^<]$$

$$\Sigma^r(E) = \Sigma^r[E; G^{</>}, G^r, D^<, D^a]$$
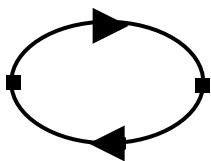
$$\Pi^<(\omega) = \Pi^<[\omega; G^{</>}]$$

$$\Pi^r(\omega) = \Pi^r[\omega; G^{</>}, G^r]$$

Rigorous LOE

$$G_{LOE}^r = G_{DFT}^r + G_{DFT}^r \Sigma_{eph}^r G_{DFT}^r \qquad G_{LOE}^< = G_{LOE}^r \left(\Sigma_L^< + \Sigma_R^< \right) G_{LOE}^a + G_{DFT}^r \Sigma_{eph}^< G_{DFT}^a$$

$$D^r(\omega) = \sum_\alpha D_{0\alpha}^r(\omega) = \sum \frac{2\Omega_\alpha}{\omega^2 - \Omega_\alpha^2 + i\eta_\alpha} \qquad D^<(\omega) = D^r \left[i\eta \left(\omega/\Omega \right) N_{BE} \right] D^a + D^r \Pi_{eph}^< D^a$$

self-energy of lead phonon $\Pi_{L/R}^r(\omega)$ heat dissipation to electrodes: $\Pi_{L/R}^<(\omega)$

$$\Sigma_{eph}^<(E) = \Sigma_{eph}^< [E; G_{DFT}^<, D^<] \qquad\qquad \Pi_{eph}^<(\omega) = \Pi_{eph}^< [\omega; G_{DFT}^{</>}]$$

→ partially 4th order of electron-phonon couplings

Conventional LOE

Rigorous LOE formulation then $\quad \int dE A(E \pm \Omega) B(E \pm \Omega) \sim \int dE A(E) B(E \pm \Omega)$

Slow varying for energy-scale of vibration   Rapid function of energy

$$\int_{E_0 - \Omega_\alpha}^{E_0 + \Omega_\alpha} dE A(E) \sim 2 A(E_0) \Omega_\alpha$$

H. Nakamura, et al. *Phys. Rev.* B., **78**, 235420 (2008)

Electric current terms by electron-phonon scatterings

$$i(E) = i^{\text{bal}} + i_\alpha^{\text{ec}} + i_\alpha^{\text{ecL}} + i_\alpha^{\text{ecR}} + i_\alpha^{\text{inel}} + i_\alpha^{\text{asymL}} + i_\alpha^{\text{asymR}}$$

(1) Elastic correction terms

$$i_\alpha^{\text{ec}}(E) = g_0 T_\alpha^{\text{ec}}(E)(2N_\alpha + 1)(f_L - f_R)$$

Symmetric $\dfrac{d^2I}{dV^2}$

$$i_\alpha^{\text{ecL/R}}(E) = g_0 T_\alpha^{\text{ecL/R}}(E)(f_{L/R+} - f_{L/R-})(f_L - f_R)$$

No contribution to "heating"

(2) Inelastic current term

$$i_\alpha^{\text{inel}}(E) = g_0 T^{\text{in}}(E)\left\{2N_\alpha(f_L - f_R) - f_{R+}(1 - f_L) + f_L(1 - f_{R-})\right\}$$

Symmetric $\dfrac{d^2I}{dV^2}$

Local heating: (energy-exchange)

(3) asymmetric correction term

$$i_\alpha^{\text{asymL/R}} = g_0 \int d\omega \, \text{Re}[D(\omega)]T^{\text{asymL/R}}(E)f_{L/R-}(f_L - f_R)$$

Asymmetric $\dfrac{d^2I}{dV^2}$

Signal from off-resonant to resonant (band-like) transport

Nonequilibrium phonon distribution (vibrational heating)

$$D_\alpha^<(\omega = \Omega_\alpha) \to N_\alpha = \frac{T_\alpha^{in}(E_F)F_\alpha(V,T) + \{T_\alpha^{inL}(E_F) + T_\alpha^{inR}(E_F)\}\Omega_\alpha N_{BE}(\Omega_\alpha,T) + 2\eta N_{BE}(\Omega_\alpha,T)}{4(T_\alpha^d(E_F)\Omega_\alpha + \eta/2)}$$

$F_\alpha(\Omega_\alpha, V, T)$: independent of electronic structure

Heating terms by inelastic current and electron-hole ex. processes)

$$T_\alpha^{in}(E,V) = \text{Tr}[M^\alpha G(E)\Gamma_R(E)G^\dagger(E)M^\alpha G^\dagger(E)\Gamma_L(E)G(E)]$$

$$T_\alpha^{inL/R}(E,V) = \text{Tr}[M^\alpha G(E)\Gamma_{L/R}(E)G^\dagger(E)M^\alpha G^\dagger(E)\Gamma_{L/R}(E)G(E)]$$

electron-hole damping terms

$$T_\alpha^d(E,V) = \text{Tr}[M^\alpha \, \text{Im}\, G(E) M^\alpha \, \text{Im}\, G]$$

dissipation to bulk electrodes

η : local phonon (vibron) –electrode phonon coupling

$\eta \to$ 0 : undamped limit （completely nonthermalized)

     inf : (external) damped limit (thermalized)

Vibronic-pathway as an analogue of electron-pathway

Observable quantity I = *flux* of electron

$$I^{bal} + \left(I^{ec} + I^{ecL} + I^{ecR} \right) + I^{inel}$$

How an electron *scattered inelastically* passes in the conductor (molecule) ?

$$J^{bal}_{\mu \to v} = g_0 V \, \mathrm{Im} \left\{ H^*_{\mu v} \left(\overline{\mathbf{G}\mathbf{\Gamma}_L \mathbf{G}^\dagger} \right)_{\mu v} - H^*_{\mu v} \left(\overline{\mathbf{G}\mathbf{\Gamma}_R \mathbf{G}^\dagger} \right)_{\mu v} \right\}$$

$$J^{inel}_{\mu \to v} = g_0 V (2N_\alpha + 1) \{ \mathrm{Im}\, H^*_{\mu v} \left(\overline{\mathbf{G}\mathbf{M}^\alpha \mathbf{G}\mathbf{\Gamma}_L \mathbf{G}^\dagger \mathbf{M}^\alpha \mathbf{G}^\dagger} \right)_{\mu v} - \mathrm{Im}\, H^*_{\mu v} \left(\overline{\mathbf{G}\mathbf{M}^\alpha \mathbf{G}\mathbf{\Gamma}_R \mathbf{G}^\dagger \mathbf{M}^\alpha \mathbf{G}^\dagger} \right)_{\mu v} \} \Theta(V - \Omega_\alpha)$$

(2) Current induced force (classical ion dynamics)

$$H = \sum_{\mu}(\varepsilon_{\mu} + \varphi)d_{\mu}^{\dagger}d_{\mu} + \sum_{k}(\varepsilon_k + \varphi)c_k^{\dagger}c_k + \sum_{\mu k}(V_{\mu k}d_{\mu}^{\dagger}c_k + H.C)$$

$$+U_{ij,kl}d_i^{\dagger}d_j^{\dagger}d_k d_l + \sum_{\mu,\nu}d_{\mu}^{\dagger}\left[H_e(\mathbf{X})\right]_{\mu\nu}d_{\nu}$$

$$\mathbf{X}(t) = (\vec{R}_1, \vec{R}_2, \cdots \vec{R}_N)$$

electron energy

$$A(t_1, t_2) = A(\frac{t_1 - t_2}{2}, \frac{t_1 + t_2}{2}) \rightarrow A(E, t)$$

time of ion motion

Force act on ion I :
$$F_I(X(t)) \equiv \frac{i}{2\pi}\int dE \mathrm{Tr}\left[\frac{\partial H_e}{\partial R_I}G^<(E,t)\right]$$

$$G^<(E,t) \approx G^<(E:\mathbf{X}) + \Im\left[G^<(E:\mathbf{X}), \frac{d\mathbf{X}}{dt}\right]$$

Mean force (Ehrenfest force)
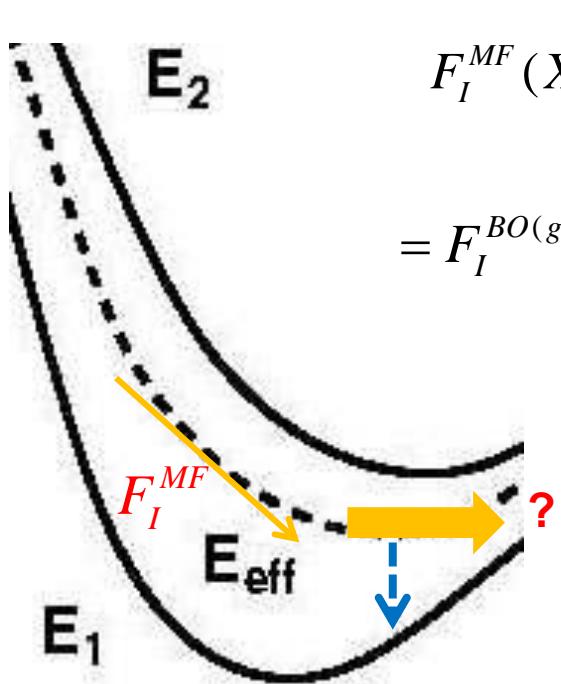
$$F_I^{MF}(X) = \frac{i}{2\pi} \int dE \, \mathrm{Tr}\left[\frac{\partial H_e}{\partial R_I} G^<(E:\mathbf{X}) \right]$$

$$= F_I^{BO(gst)} + \left\{ \frac{i}{2\pi} \int dE \, \mathrm{Tr}\left[\frac{\partial H_e}{\partial R_I} \left(G^< - G_{eq}^<\right) \right] - F^{ext}(V_{bias}) \right\} + F^{ext}$$

E_2

F_I^{MF}

E_{eff} **?**

E_1

Dissipation force

$$F_I^{dss}(X) = \frac{i}{2\pi} \int dE \, \mathrm{Tr}\left[\frac{\partial H_e}{\partial R_I} \Im\left[G^<(E:\mathbf{X}), \ \frac{d\mathbf{X}}{dt} \right] \right]$$

Quantum heating/dissipation

$$N_\alpha = \frac{T_\alpha^{in}(E_F)F_\alpha(V,T) + \left\{T_\alpha^{inL}(E_F) + T_\alpha^{inR}(E_F)\right\}\Omega_\alpha N_{BE}(\Omega_\alpha,T) + 2\eta N_{BE}(\Omega_\alpha,T)}{4(T_\alpha^d(E_F)\Omega_\alpha + \eta/2)}$$

－Notes of First Principles NEGF: NEGF-DFT －

Classification of electric transport and our focus
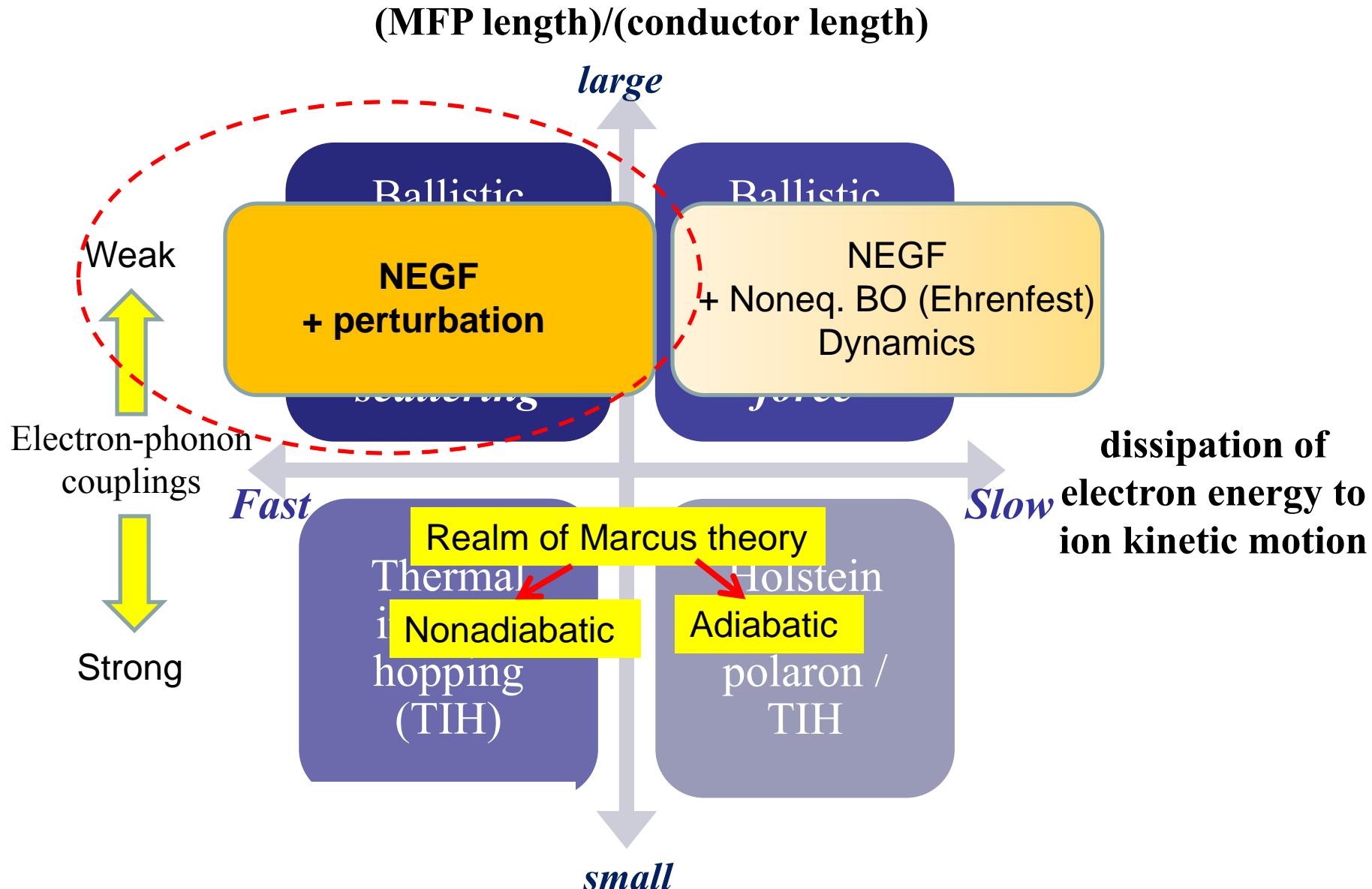
Example of "Contact Chemistry" (Electrode-dependence)

PTCDA

PTCDA

π - bond

Ag-O bond

charge donation

Ag(111)
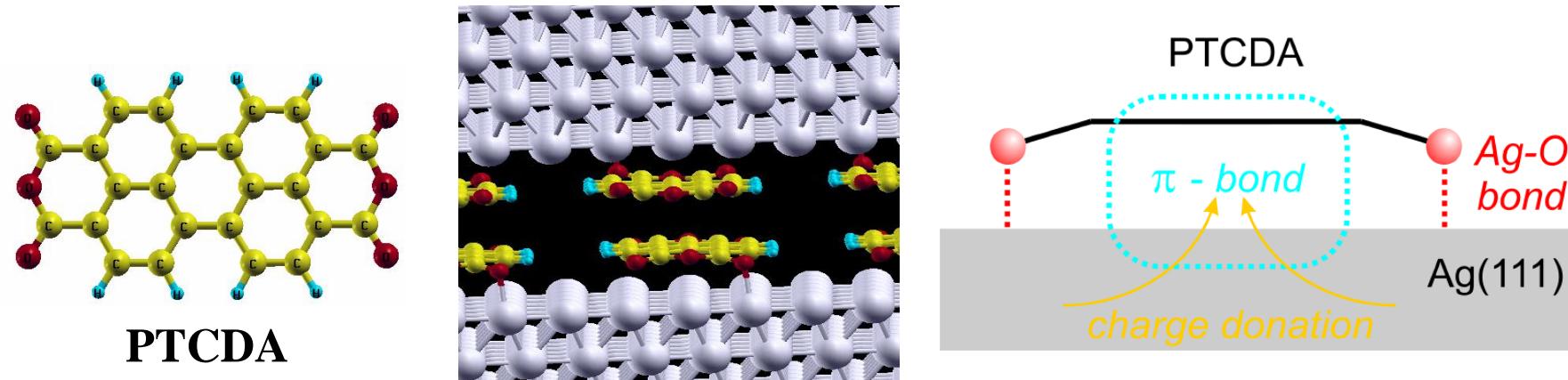
I-V characteristics of PTCDA 3 ML film by first principles calculations

Ag electrodes

I (micro Ampere)

eV

Al electrodes

I (MicroAmpere)

Al-O: ~ Aauminium oxide

V (eV)
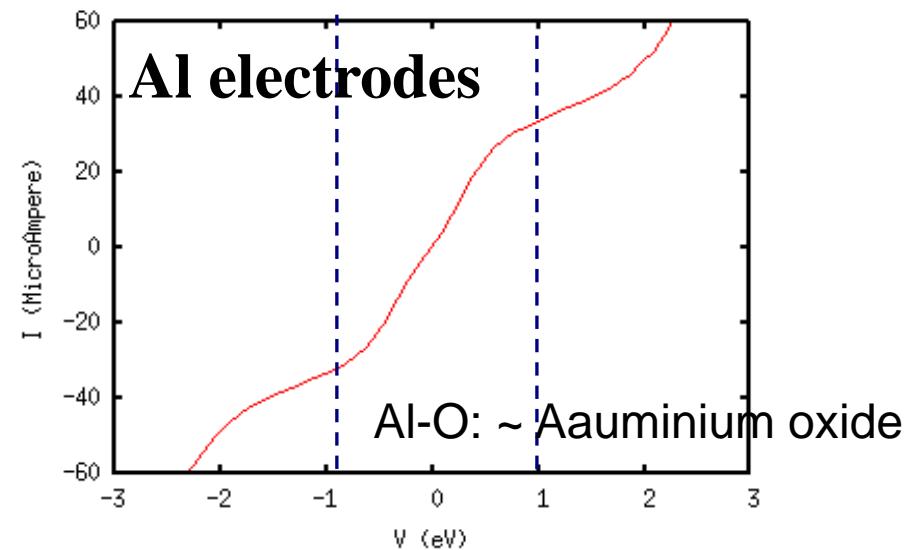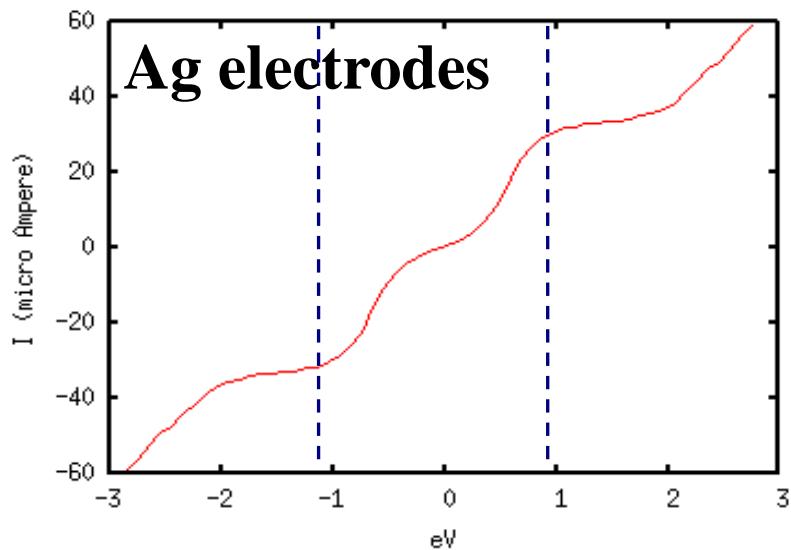
T. Ohoto , K. Yamashita, and H. Nakamura*Phys. Rev. B* **84**, 045417 (2011)

Out line of NEGF-DFT
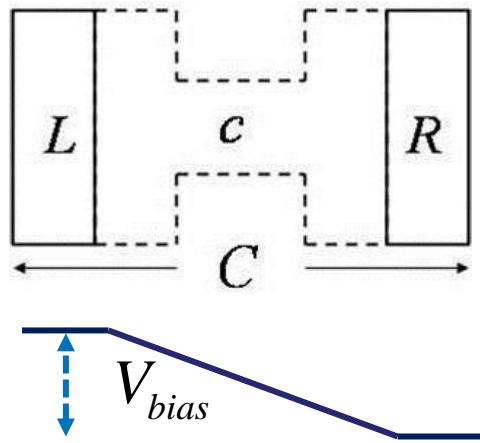
Bulk DFT + boundary condition

$$\Sigma^r = V_H + V_{XC} + V_{ext} + \Sigma_L^r + \Sigma_R^r \qquad \Sigma^< = 0 + \Sigma_L^< + \Sigma_R^<$$

uniform electric field

V_{bias}

$$\Sigma_{L/R}^<(E) = i f_{L/R}(E) \Gamma_{L/R}(E)$$

Shift chemical potential $\pm V_{bias}/2$

skeleton H+V_{ext} of "c" and KS-H of L/R

$$G^r(E) = (E - H_0 - \Sigma_L^r - \Sigma_R^r - V_H[\rho] - V_{XC}[\rho])^{-1}$$

$$G^< = G^r \Sigma^< G^a$$

$$\rho = \frac{-i}{2\pi} \int d\varepsilon\, G^<(\varepsilon) \rightarrow V_H + V_{XC}$$

update

$$G^< = G^r \Sigma^< G^a$$
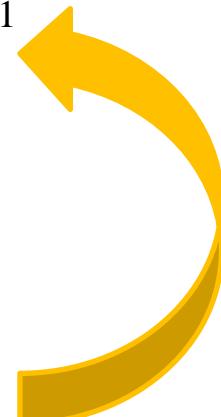
Out line of first principles *c*-LOE
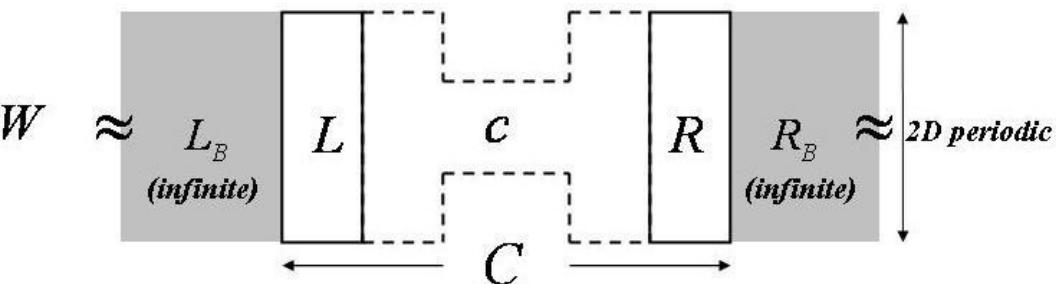
Assumption:

If sufficient number of buffer layers are taken, KS-SCF should give reliable DM, V_{KS} on C
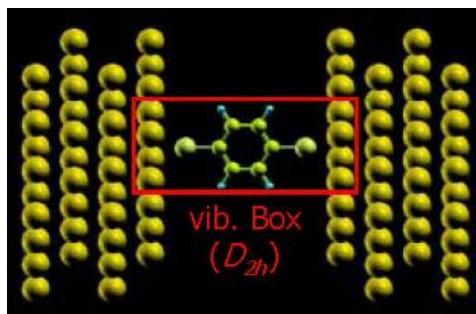
(1) Relax only atoms in *"vib box"* . → *Dynamical matrix*

(2) Select normal modes Q localized on molecular conductor (Γ-point)

(3) Calculate coupling using $\dfrac{\partial H_{KS}(\vec{k}_{//})}{\partial R}$ then transform to Helzberg-Teller (non local Holstein) coupling $\dfrac{\partial H_{KS}(\vec{k}_{//})}{\partial Q_\alpha}$

(4) NEGF-DFT → c-LOE

$$\frac{\partial H_{KS}(\vec{k}_{//})}{\partial Q_\alpha}$$

Out line of first principles current-induced force

$$F_I^{MF}(X) = \frac{i}{2\pi}\int dE \mathrm{Tr}\left[\frac{\partial H_e}{\partial R_I}G^<(E:\mathbf{X})\right] \longleftrightarrow F_I^{MF}(X) = -\frac{\partial\langle\Psi|H|\Psi\rangle}{\partial R_I}$$

Ψ steady state (scattering state)

Assuming the same expression of E_{KS}^{tot} and $\dfrac{\partial E_{KS}^{tot}}{\partial R_I}$,

Replace density matrix to that of NEGF result

Technical issues:
if you use AO basis, Pulay correction term should be modified.

Open questions:
(1) Mean force is not strictly conservative force.
(2) Even if we accept HF force, NEGF (and Ψ) is not determined by variational
    principle under bias voltage.

Additional terms is required to calculate $\left\langle\Psi\left|\dfrac{\partial H}{\partial R_I}\right|\Psi\right\rangle$?

－**Application to real systems**－

(1) Molecular Diode

"Unimolecular rectifier"

"They (Aviram and Ratner) proposed rectifying molecule was designed so that electrical conduction within it would be favored from the electron-rich subunit or moiety (electron donor) to an electron-poor moiety (electron acceptor), but disfavored (by several electron Volts) in the reverse direction "

(From Wikipedia, "Unimolecular rectifier")
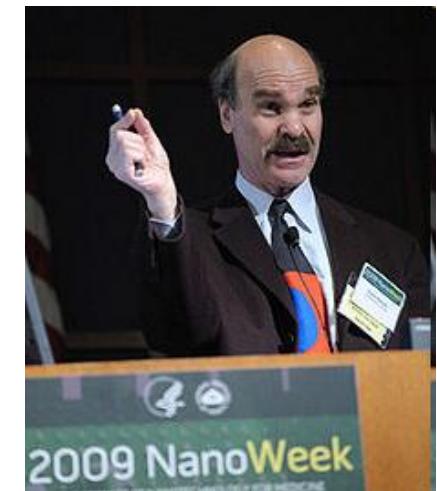
Two proposed mechanisms : AR and EL

MOLECULAR RECTIFIERS

Arieh AVIRAM
*IBM Thomas J. Watson Research Center,
Yorktown Heights, New York 10598, USA*

and

Mark A. RATNER*
*Department of Chemistry, New York University,
New York, New York 10003, USA*

Received 10 June 1974

The construction of a very simple electronic device, a rectifier, based on the use of a single organic molecule is discussed. The molecular rectifier consists of a donor pi system and an acceptor pi system, separated by a sigma-bonded (methylene) tunnelling bridge. The response of such a molecule to an applied field is calculated, and rectifier properties indeed appear.

Architectures for Molecular Electronic Computers: 1. Logic Structures and an Adder Designed from Molecular Electronic Diodes

JAMES C. ELLENBOGEN AND J. CHRISTOPHER LOVE

Recently, there have been significant advances in the fabrication and demonstration of individual molecular electronic wires and diode switches. This paper reviews those developments and shows how demonstrated molecular devices might be combined to design molecular-scale electronic digital computer logic. The design for the demonstrated rectifying molecular diode switches is refined and made more compatible with the demonstrated wires through the introduction of intramolecular dopant groups chemically bonded to modified molecular wires. Quantum mechanical calculations are

others [16]–[19] in the field of nanoelectronics suggest that it might be possible to build and to demonstrate somewhat more complex molecular electronic structures that would include two or three molecular electronic diodes and that would perform as digital logic circuits.

It is the purpose of this paper to provide and to explain novel designs for several such simple molecular electronic

NATIONAL INSTITUTE OF **ADVANCED INDUSTRIAL SCIENCE AND TECHNOLOGY (AIST)**

Aviram-Ratner (AR)
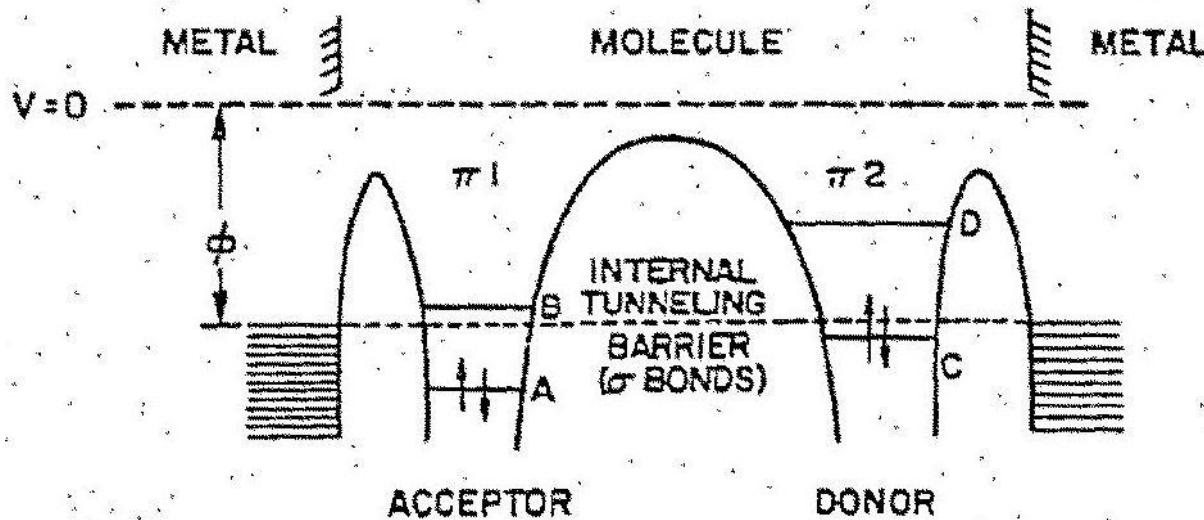
D = electron rich $\rightarrow$ p
A = electron deficient $\rightarrow$ n

Favorite direction p $\longrightarrow$ n

Energy-alignment: E_F ($\pm V/2$), HOMO(D), LUMO(A)

$$M\left[D-\sigma-A\right]M \rightarrow M^{-}\left[D^{+}-\sigma-A^{-}\right]M^{+}$$

$$M^{-}\left[D^{+}-\sigma-A^{-}\right]M^{+} \rightarrow M^{-}\left[D-\sigma-A\right]M^{+}$$
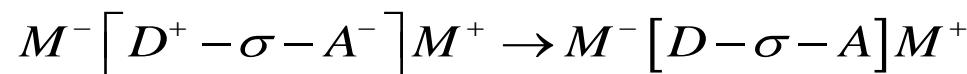
Ellenbogen-Love (EL)

D = electron rich $\rightarrow$ p
A = electron deficient $\rightarrow$ n

MO energy

Favorite direction n ——————> p

A(LUMO)

"intrinsic" response of HOMO/LUMO to bias

<u>HOMO(D)</u> and <u>LUMO(A)</u> responses to bias
based on each redox potential

D(HOMO)
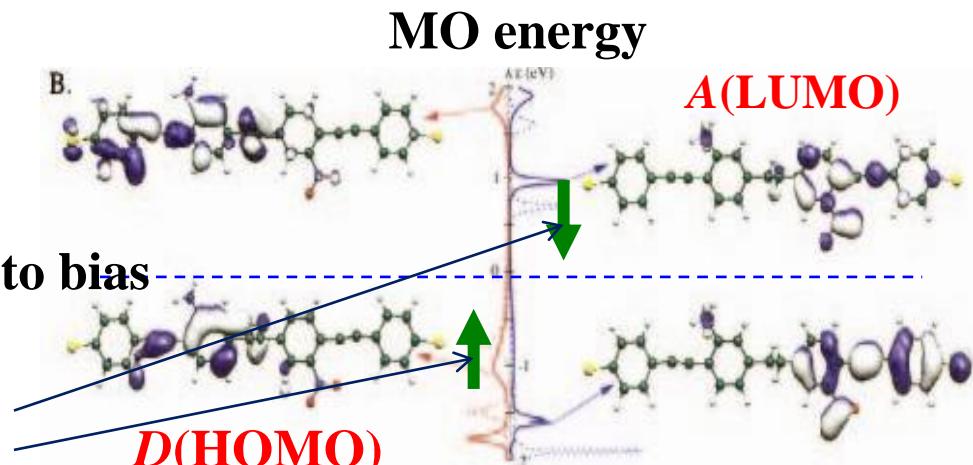
AR or EL ?

The transport properties of D-σ-A molecules: A strikingly opposite directional rectification

J. B. Pan, Z. H. Zhang,[a] X. Q. Deng, M. Qiu, and C. Guo
Institute of Nanomaterial and Nanostructure, Changsha University of Science and Technology, Changsha 410004, People's Republic of China

J|A|C|S
COMMUNICATIONS

Do Aviram−Ratner Diodes Rectify?
Kurt Stokbro,* Jeremy Taylor, and Mads Brandbyge
Mikroelektronik Centret (MIC), Technical University of Denmark, Building 345E, DK-2800 Lyngby, Denmark

$D - \sigma - A$ **structure molecule is basically EL type diode, i.e., $n \rightarrow p$ direction**

pn-resemble diblock molecular diode

Evidence of *low-voltage* (*off-resonant* tunneling) rectification

Experiment

tetraphenyl

biphenyl | bipyrimidinyl
e− rich (n) | e−deficient (p)

**biphenyl-bipyrimidinyl**
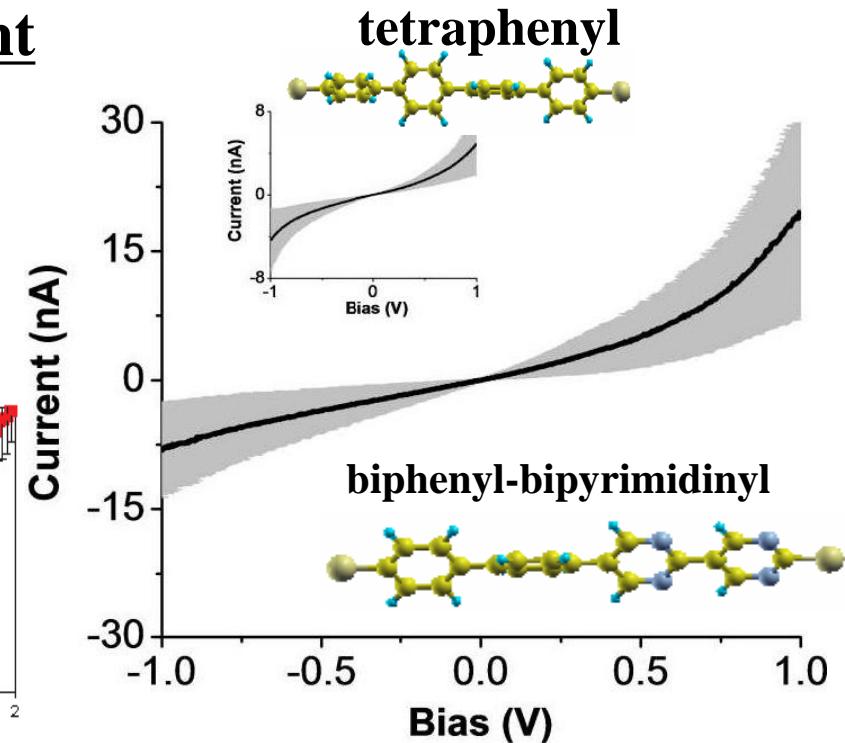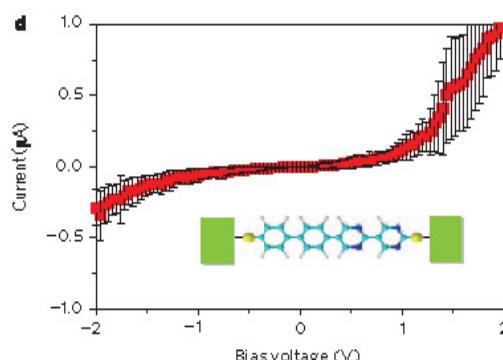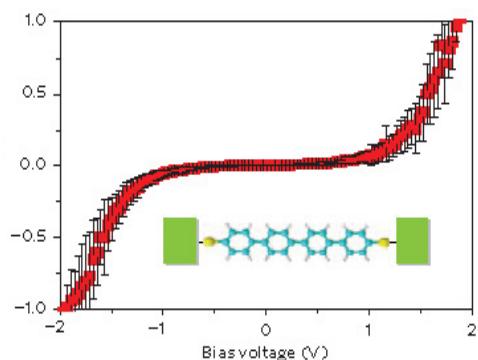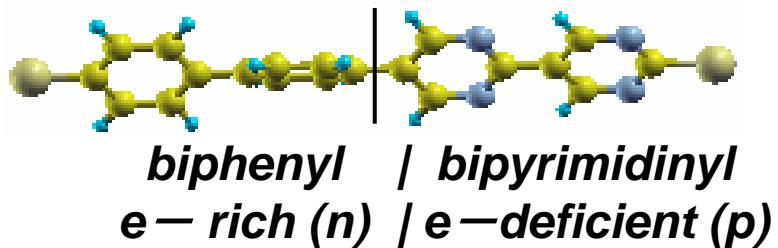
I. Diez-Perez *et.al*   *Nature Chemistry* **1** 635 (2009) H. Hihath *et a*l *ACS Nano* **5**, 8331 (2011)

rectifying direction = *p→n !!*

First principles calculation (NEGF-DFT)

$$\eta(V) = \frac{I(V)}{I(-V)} = 1.34 @ 0.5\text{Volt}$$

Conductance-rectification parameter

$$\kappa(V) = \left(\frac{dI}{dV}(V) - \frac{dI}{dV}(-V)\right) \bigg/ \frac{dI}{dV}(0)$$

biprydiminyl-biphenyl (Exp.)

biprydiminyl-biphenyl (Thoery)

tetraphenyl (Exp.)

tetraphenyl (Theory)
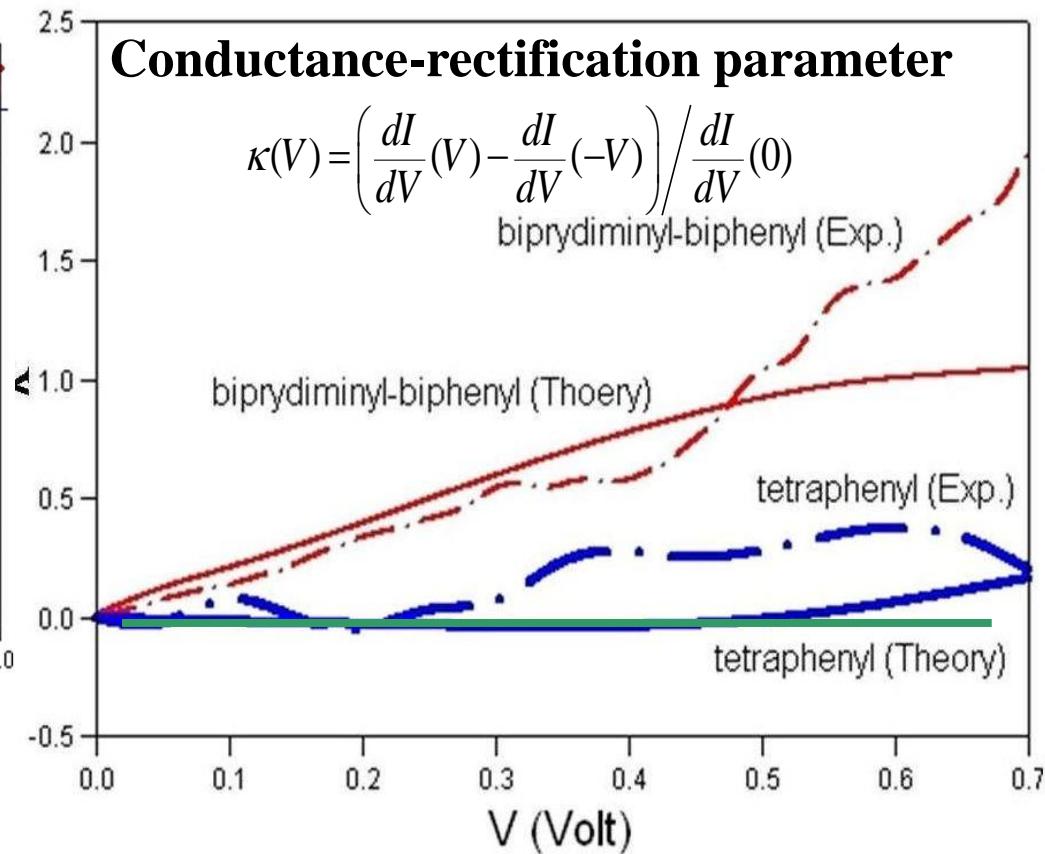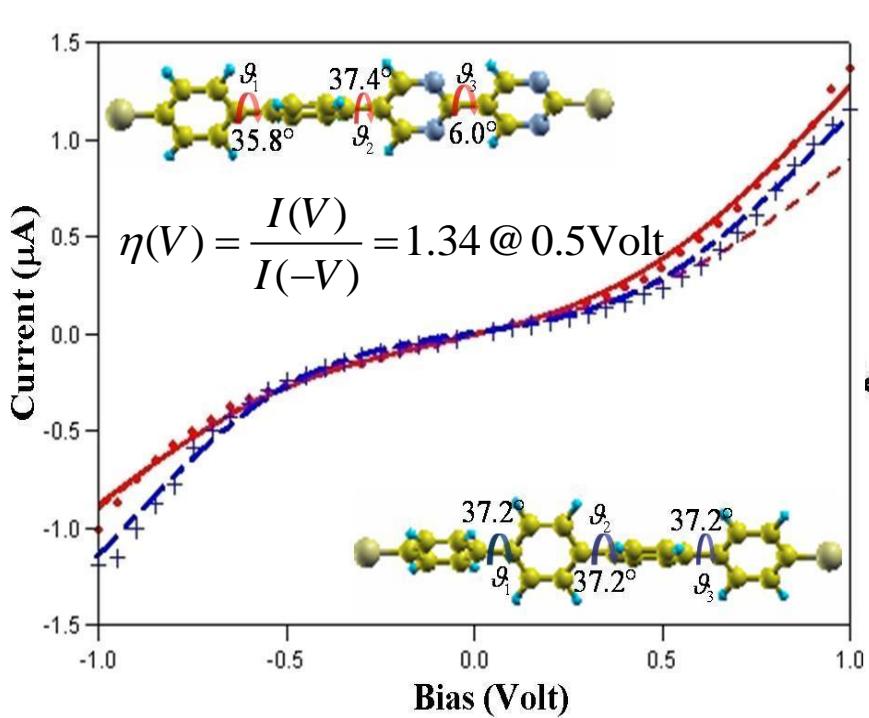
H. Nakamura *et al. J. Phys Chem C.* **115** 11931 (2011)

rectifying direction = *p→n !!*

Why it works in low-voltage
Why not EL ?
Really AR mechanism ?

Resonance Structure of Conductance

$$\tau_\alpha \sim \frac{4\gamma_L\gamma_R}{\{E-(\underbrace{E_{0\alpha}+\Delta E)}_{E_\alpha}\}^2+(\gamma_L+\gamma_R)^2}$$

Important for *quantitative* analysis $E_\alpha = E_\alpha(E,V) \to E_\alpha(E_F,V) \neq E_\alpha(E_{0\alpha},V)$

$$\gamma_{L/R} = \gamma_{L/R}(E,V) \to \gamma_{L/R}(E_F,V) \neq \gamma_{L/R}(E_F,V) \neq \gamma_{L/R}(E_{0\alpha},V)$$

Key of Rectification by conducting orbital!!

Bias-induced *intrinsic electronic* contact-asymmetry
(*not* local contact/anchoring structure!!)

$$\gamma_L(V)\gamma_R(V) << \left(\frac{\gamma_L(V)+\gamma_R(V)}{2}\right)^2 \qquad \gamma_L(-V)\gamma_R(-V) << \gamma_L(V)\gamma_R(V)$$

Rectification by Switch of "Conducting Orbital"

* Including terminal –S

Diode (bipyridiminyl-biphenyl)

Bias (Volt)	E_{H-2} (eV)	$\sqrt{\gamma_L \gamma_R}$	E_{H-1}	$\sqrt{\gamma_L \gamma_R}$	E_H	$\sqrt{\gamma_L \gamma_R}$	E_L	$\sqrt{\gamma_L \gamma_R}$
−0.8	-1.56	0.135	-1.41	0.285	-1.00	0.011	1.63	0.071
−0.4	-1.76	0.089	-1.31	0.152	-1.21	0.044	1.60	0.042
0.4	-2.08	0.302	-1.42	0.018	-1.18	0.106	1.44	0.038
0.8	-2.07	0.424	-1.50	0.048	-1.09	0.144	1.35	0.065

Switching of "conducting MO" by bias-induced asymmetric electronic coupling

Tetraphenyl

Bias (Volt)	E_{H-2} (eV)	$\sqrt{\gamma_L \gamma_R}$	E_{H-1}	$\sqrt{\gamma_L \gamma_R}$	E_H	$\sqrt{\gamma_L \gamma_R}$	E_L	$\sqrt{\gamma_L \gamma_R}$
−0.8	-1.88	0.003	-1.90	0.433	-0.97	0.162	2.01	0.090
−0.4	-2.71	0.437	-1.72	0.331	-1.05	0.142	2.01	0.062
0.4	-2.81	0.466	-1.84	0.358	-1.02	0.143	2.08	0.071
0.8	-1.82	0.628	-1.80	0.489	-0.99	0.166	1.95	0.113

Crossover of views in molecular diode and pn junctions

$$H_{PP}^{eff} = \left(\mathbf{H}_{ij}^{eff} \right) = \begin{pmatrix} \mathbf{H}_{11}^{eff} & \cdots & \cdots & \mathbf{H}_{14}^{eff} \\ \vdots & \mathbf{H}_{22}^{eff} & \ddots & \vdots \\ \vdots & \ddots & \mathbf{H}_{33}^{eff} & \vdots \\ \mathbf{H}_{41}^{eff} & \cdots & \cdots & \mathbf{H}_{44}^{eff} \end{pmatrix} \qquad \tilde{H}_{PP}^{eff} = \left(\mathrm{diag}(\mathbf{U}_j) \right)^{\dagger} \left(\mathbf{H}_{ij}^{eff} \right) \left(\mathrm{diag}(\mathbf{U}_j) \right)$$

We also have "rigorous" site (= atomic site, molecular fragment site etc) model from fully self-consistent NEGF.

Now, we see cross-over between languages of semiconductor physics and chemistry!

A (*n*-type)   D (*p*-type)

— **Biased along p→n direction**   - - - **Biased along n→p direction**
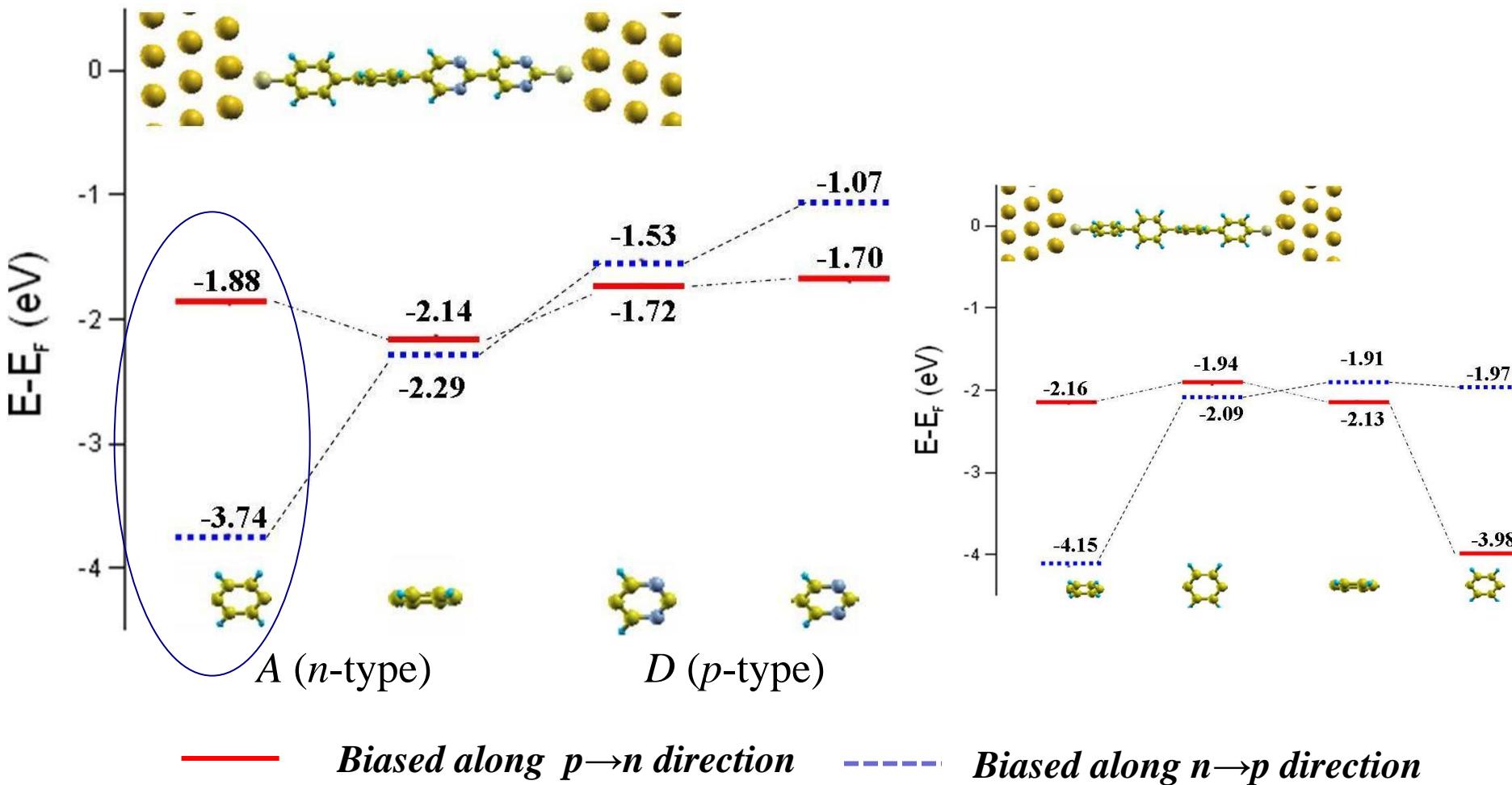
Diagram of molecular site energy alignment

Why EL mechanism (opposite directional rectification) did not work ?

LUMO(A) 1.6 eV

EL: LUMO(D)

EL: HOMO(A)

E-E$_F$ (eV)

-1.88   -2.14   -1.53   -1.07
         -2.29   -1.72   -1.70
-3.74

A (n-type)   *D (p-type)*
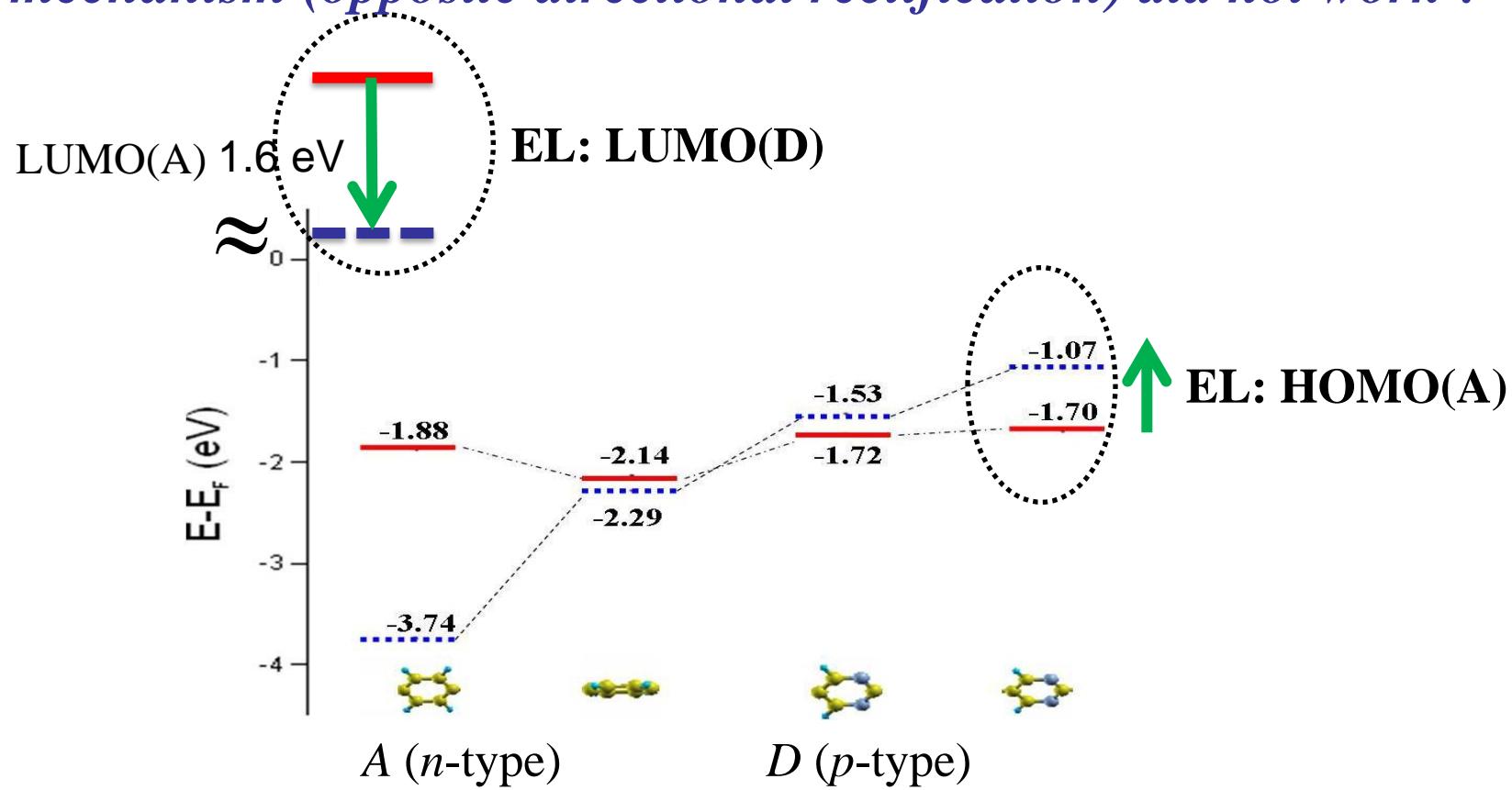
However, this LUMO (A) pathway is frustrated by strong *electric* contact-asymmetry

$$\frac{\gamma^A_{\text{LUMO}}}{\gamma^A_{\text{HOMO}}} \approx 0.007 \ @ \text{EL-favorite bias (opposite to } pn)$$

(2) IETS and local heating

IETS peak/dip and off-set by "heating"

Single level model (or single conducting orbital model)   nearly symmetric contact

$$I_\alpha^{\mathrm{ec}} + (I_\alpha^{\mathrm{ecL}} + I_\alpha^{\mathrm{ecR}}) + I_\alpha^{\mathrm{inel}} + (I_\alpha^{\mathrm{asymL}} + {}_\alpha^{\mathrm{asymR}}) \sim T^2(1-2T)$$

0.5 rule

**Off-set: heating effect**

Dissipation：suppress off-set

Au atomic wire
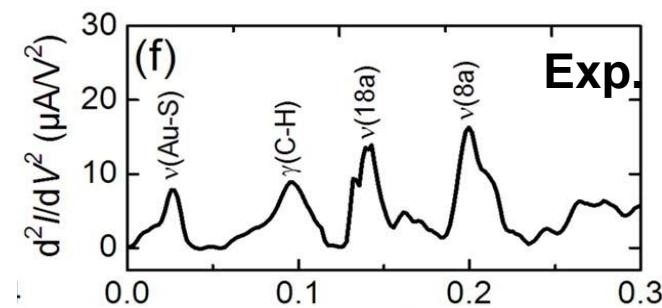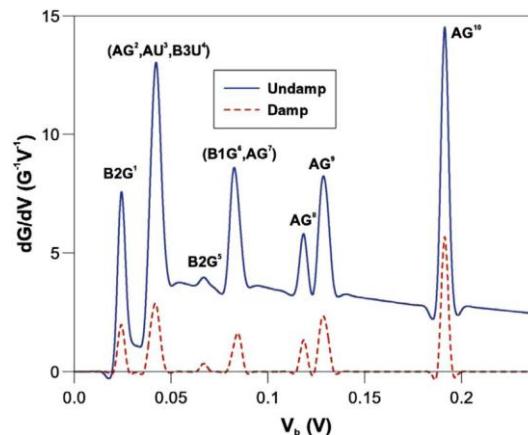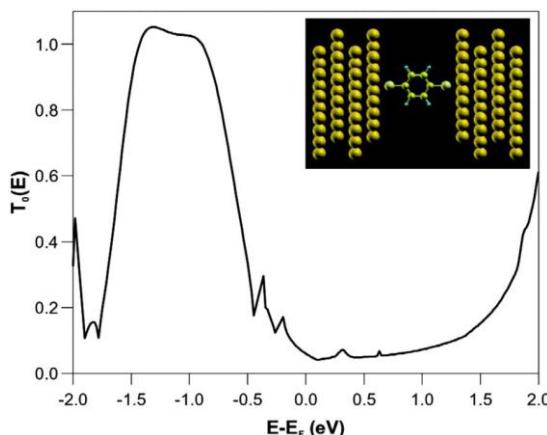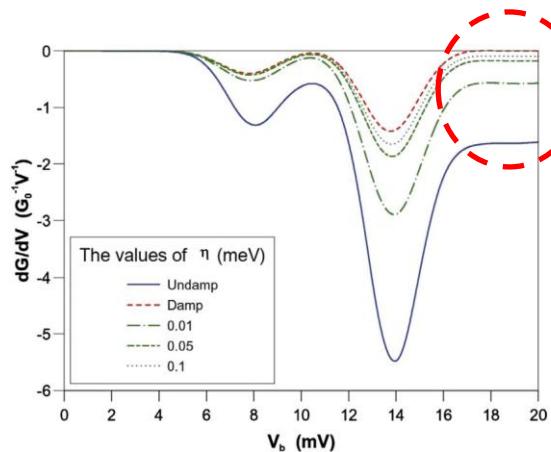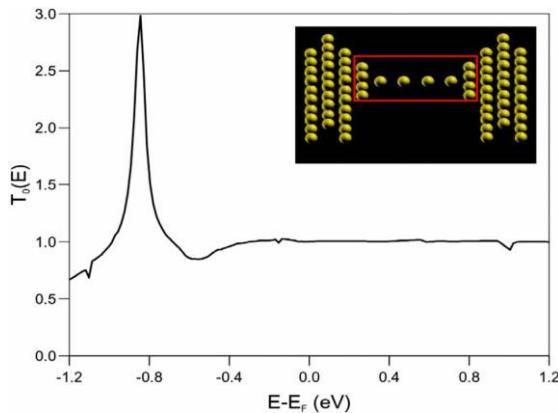
Dominated by elastic scattering

IETS active modes: longitudinal mode
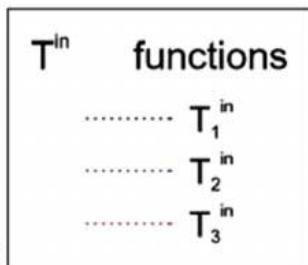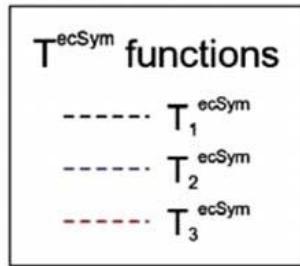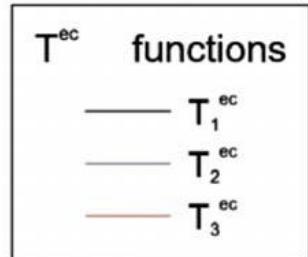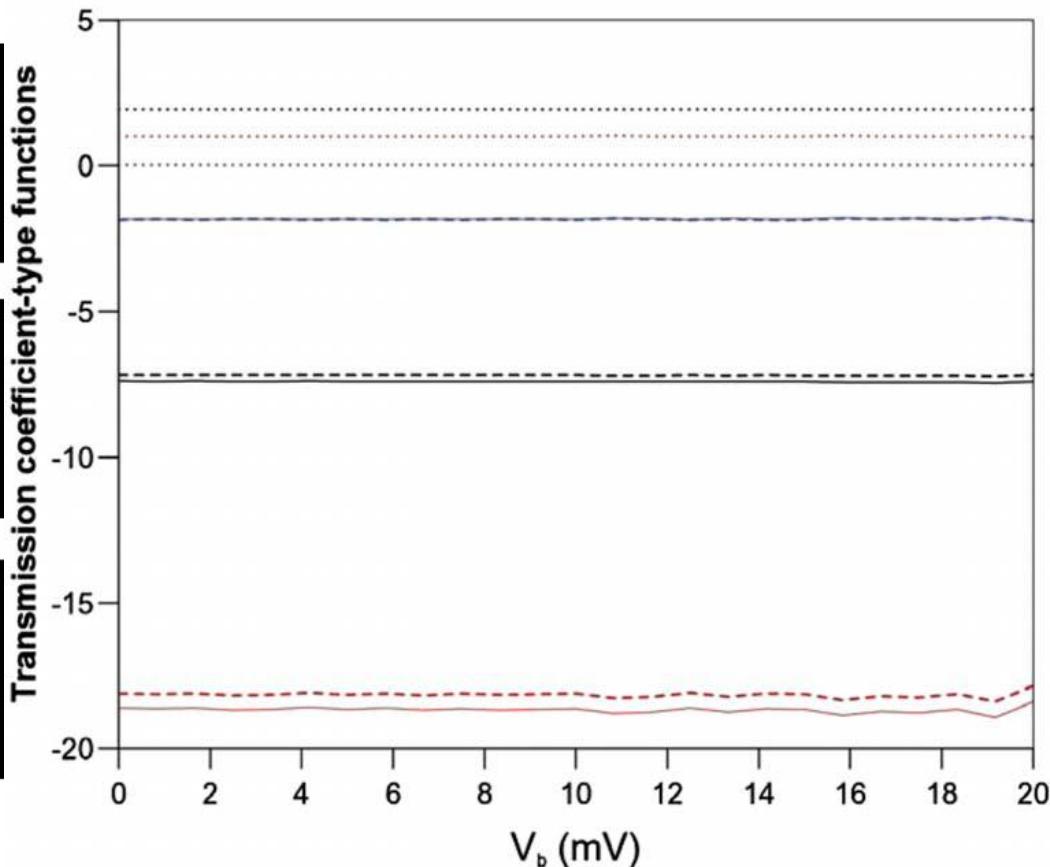
Comparison of mode selectivity of IR and Raman

Benzene-dithiol junction
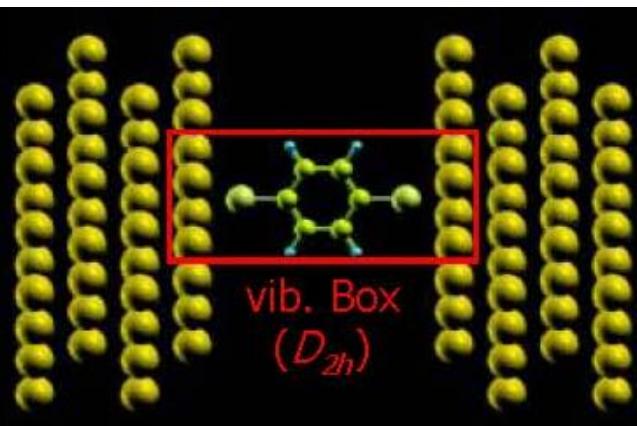
| Mode	I_{IR}	I_{Raman}	$\overline{T}^{ec}$	$\overline{T}^{ecSym}$	$\overline{T}^{in}$
$B2G^1$	0.000	0.000	1.070	-0.030	0.294
AG^2	0.000	0.196	0.822	-0.030	0.472
AU^3	0.000	0.000	0.502	-0.018	0.385
$B3U^4$	0.164	0.014	0.426	-0.008	0.104
$B2G^5$	0.000	0.028	-0.035	-0.003	0.061
$B1G^6$	0.000	0.023	0.497	-0.004	0.132
AG^7	0.000	0.063	-0.045	-0.024	0.231
AG^8	0.000	0.036	0.271	-0.014	0.214
AG^9	0.000	1.000	0.695	-0.055	0.816
AG^{10}	0.000	0.936	1.139	-0.062	1.000

Propensity of IETS (= heated modes)

(Q1.) Is there any propensity in IETS active modes ?
(A1.) Yes. Propensity relates to correlation of electron-pathway and displacement
vector of normal mode.

(Q2.) Is there any relation or similarity to selection rules of IR or Raman ?
(A2.) Simplified IETS theory (current+site charge *model*) tells IETS rules should be
similar with Raman., but this is not correct.
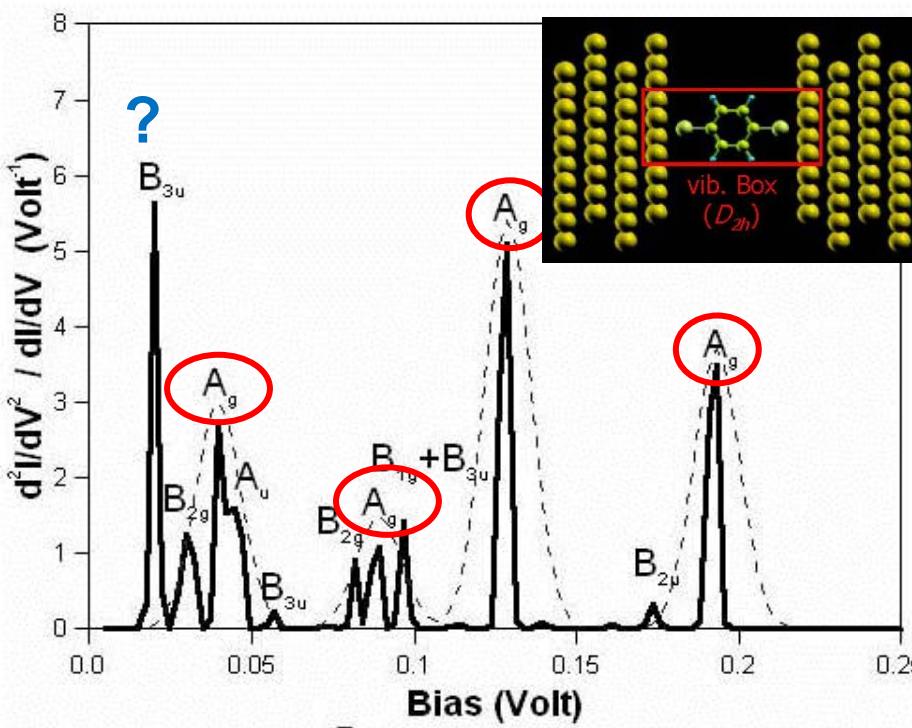
How each mode is heated ?

$$N_\alpha(V) \rightarrow N_{BE}(\Omega_\alpha, T_\alpha^{eff}(V))$$
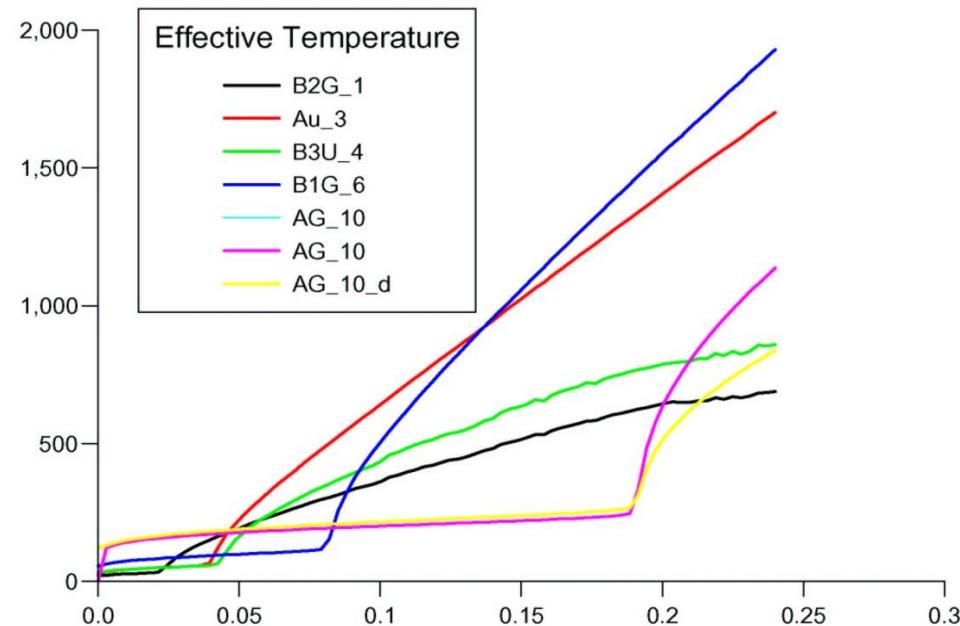
H. Nakamura *et al*, *Phys. Rev. B* **78**, 235420(2010).

electron-pathway

$A_g^{(5)}$

B_{3u}

vibronic-pathway
$A_g^{(5)}$

vironic-pathway
B_{3u}
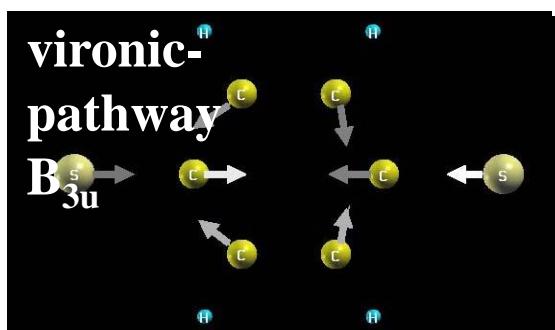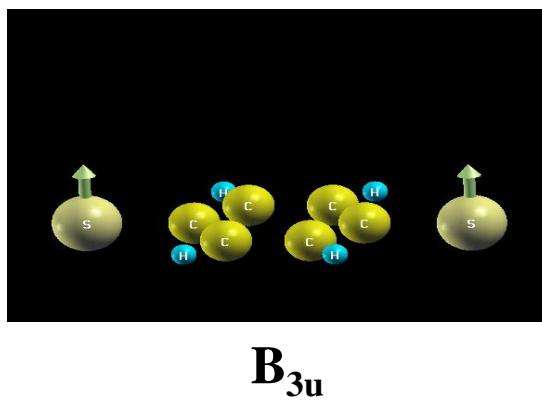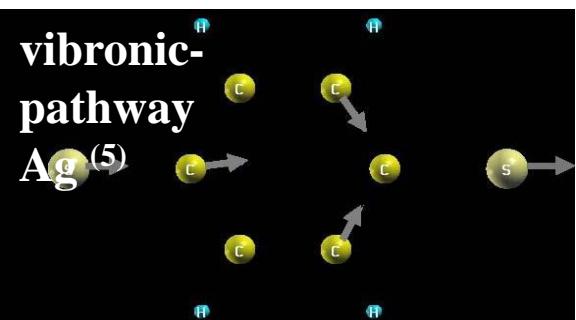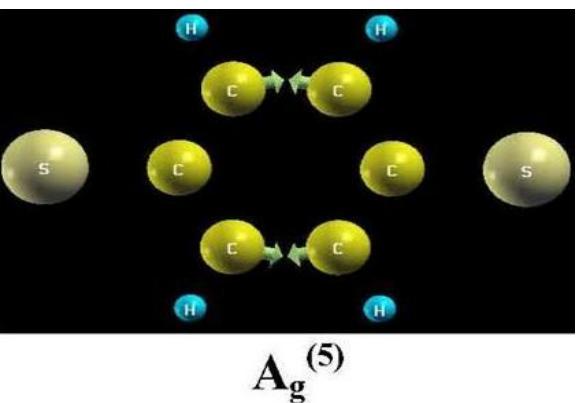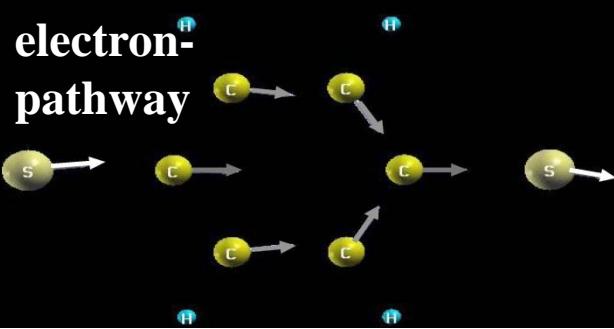
Electron-phonon coupling
In the projected MO

	BDT
	$B_{3u}^{(1)}$
$\pi^{(1)}\pi^{(1)}$	0.00
$\pi^{(2)}\pi^{(2)}$	0.00
$\sigma\pi^{(2)}$	0.00
$\pi^{(1)}\pi^{(2)}$	0.00
$\sigma\pi^{(1)}$	0.18

Local heating is also asymmetric in Molecular Diode ?

Symmetric and single conducting orbital model tells $I_\alpha^{\mathrm{inel}} \sim T^2(1-2T) \sim T^2$

$$I_\alpha^{\mathrm{inel}}(V) \Big/ I_\alpha^{\mathrm{inel}}(-V) \propto \{I(V)\big/I(-V)\}^2 \ \cdots?$$

Experiment V.S First principles   Bias-polarity dependence of IETS

biphenyl-bipyrimidinyl

Vibron as finger print
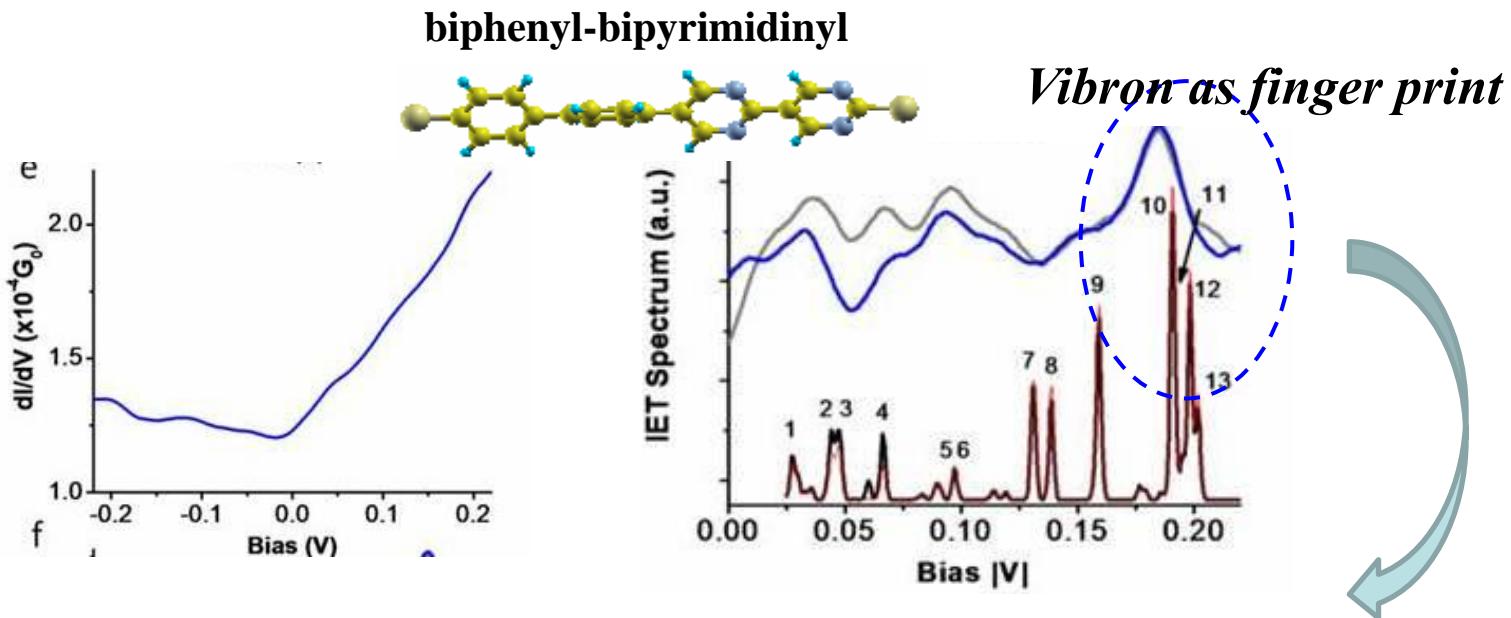
H. Hihath *et al* *ACS Nano* **5**, 8331 (2011)

Inelastic current and local heating are not necessarily enhanced by rectification.

Include effects of "intrinsic" contact-asymmetry to single conducting orbital model

$$\frac{d^2(\delta I)}{dV^2} = |<\psi_\alpha | \frac{\partial H}{\partial Q} | \psi_\alpha >|^2 \frac{(E_F - E_\alpha)^2 - (\gamma_L + \gamma_R)^2/4}{\{(E_F - E_\alpha)^2 + (\gamma_L + \gamma_R)^2/4\}^2} T \frac{d^2 F}{dV^2}$$

$$= M^2 \chi T \frac{d^2 F}{dV^2}$$

Universal function of temperature, V, and Ω

Coupling of phonon and conducting orbital

$$\psi_\alpha(V) \neq \psi_\alpha(-V)$$
$$M(V)/M(-V) \sim 0.9 < 1.0$$

"sum" of intrinsic molecule-lead coupling

$$\gamma_L(V) + \gamma_R(V) \neq \gamma_L(-V) + \gamma_R(-V)$$

$$\chi(V)/\chi(-V) \sim 0.95 < 1.0$$

"product of intrinsic molecule-lead coupling

$$\gamma_L(V)\gamma_R(V) \neq \gamma_L(-V)\gamma_R(-V)$$

$$1.0 < T(V)/T(-V)$$
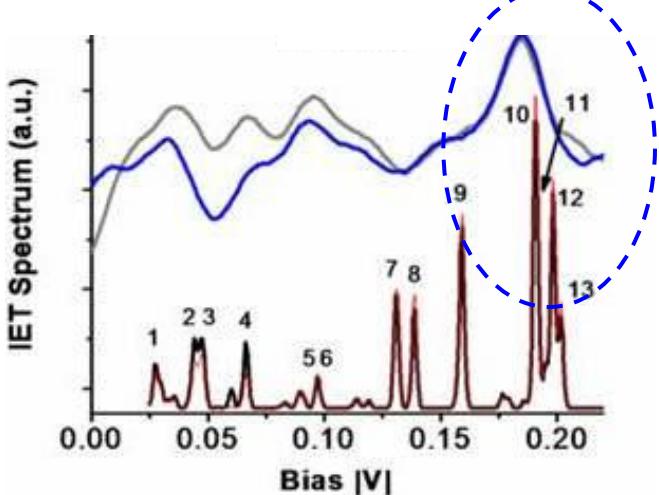
With weak bias-dependence of phonon DOS, rectification of inelastic current was suppressed..
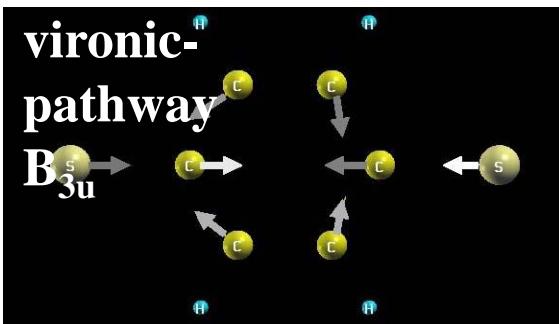
> Further development and Open question

(1) Thermal transport should be included in the same level calculations for heat dissipation

$$D^<(\omega) = D^r\left[i\eta(\omega/\Omega)N_{BE}\right]D^a + D^r\Pi^<_{eph}D^a$$

$$\rightarrow \Pi^<_L + \Pi^<_R$$

(2) In most of first principles NEGF of inelastic process, vibron Q_a is diagonalized by only Hessian of "extended molecule".

$$D^r(\omega) = \sum_\alpha D^r_\alpha(\omega) \rightarrow \text{real space approach} \quad \neq \sum_\alpha D^r_\alpha(\omega)$$

(3) How electron-phonon coupling at electrodes should be truncated ?

Herzberg-Teller (nonlocal Holstein) $\qquad \frac{1}{\sqrt{2\Omega_\alpha}}\left\langle \mu \mid \frac{\partial H}{\partial Q_\alpha} \mid \nu \right\rangle$

➢ Open question (2) local temperature ?

local temperature = measurement of local heating of "device"
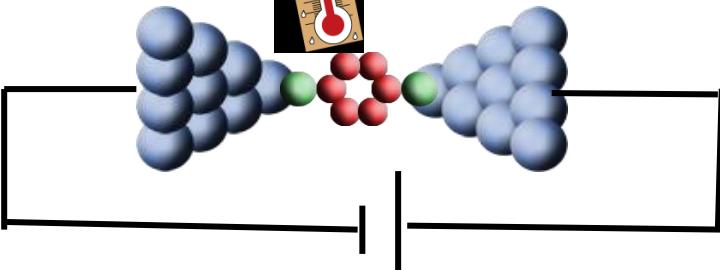
Naïve extension

$$N_\alpha(V) \to N_{BE}(\Omega_\alpha, T_\alpha^{eff}(V))$$

$$\to \min \sum_{\alpha \subset all} \left| N_\alpha(V) - N_{BE}(\Omega_\alpha, T^{eff}(V)) \right|^2$$

This is not observable "temperature".

Local temperature defined by break of "bond"

$$k(T^{eff}) = k_0 \exp(-\frac{E_a}{k_B T^{eff}})$$

$$\tau_{break} = 1/k$$

$$\tau_{break} \sim E_a / Q_{inside}$$

Observable by changing time-scale of "pulling"

$$Q_{inside} = \sum_\alpha \frac{1}{2\pi} \int dE E \mathrm{Tr}\left[\Sigma_{eph}^< G^> - \Sigma_{eph}^> G^< \right]$$

$$+ \sum_\alpha \frac{1}{2\pi} \int d\omega \omega \mathrm{Tr}\left[\Pi_{eph}^< D^> + \Pi_{eph}^> D^< \right]$$

－Electron correlation in nonequilibrium transport－

$$H = \sum_{\mu}(\varepsilon_{\mu} + \varphi)d_{\mu}^{\dagger}d_{\mu} + \sum_{k}(\varepsilon_{k} + \varphi)c_{k}^{\dagger}c_{k} + \sum_{\mu k}(V_{\mu k}d_{\mu}^{\dagger}c_{k} + H.C) + U_{ij,kl}d_{i}^{\dagger}d_{j}^{\dagger}d_{k}d_{l}$$

Hybrid XC functional: B3LYP, HSE → Band gap of electrodes

HOMO-LUMO gap of conductor

Improve conductance in 0-bias limit

In NEGF scheme (Meir-Wingreen-Jauho), electrodes are non-interacting systems.

$$G^{r} = G_{DFT}^{r} + G_{DFT}^{r}\Sigma_{ee}^{r}G^{r} \qquad G^{<} = G^{r}\left(\Sigma_{L}^{<} + \Sigma_{R}^{<} + \Sigma_{ee}^{<}\right)G^{a}$$

e-e scattering effect *in conductor*

0-bias: Σ_{ee}^{r} corrects HOMO-LUMO gap just as use of improved XC

Nonequilibrium case (non 0-bias) ?