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

Coherent (ballistic) transport

Sequential tunneling (TIH)

$g = \frac{1}{R} \propto \exp(-\beta L)$

Independent of temperature

Analytical theory of length dependence of conductance (coherent)

\[ g \approx \frac{4\pi^2 t_L^4 \rho_{\text{electrode}}}{|\lambda_1 + \Sigma'|^2} \left| \frac{\lambda_1 - \lambda_2}{\sqrt{\lambda_1}} \right|^2 \exp\left(-2 |\Delta_F|/2t + \sqrt{(\Delta_F/2t)^2 - 1} \right) (N - 1) \]

\[ \rightarrow \exp(-\beta N) \]

\[ \beta = 2 \ln(|\Delta_F|/t) \]

Resonant (coherent) tunneling

\[ \chi = \Delta_F/2t \leq 1 \]

Off-resonant (coherent) tunneling

\[ \chi = \Delta_F/2t > 1 \]

Sequential tunneling (hopping transport)

Decoherence: electron-phonon, Coulomb blockade, etc

Rate equation (FGR) approach between hopping sites

\[ H = \mathcal{E}_0 c^\dagger c + \sum_{\mu} \mathcal{E}_k c^\dagger_k c_k + \sum_k (V c^\dagger_k c_k + H.C) + M \Omega_0 (b + b^\dagger) c^\dagger_k c_k + b^\dagger b \]

Lang-Firsov transformation

\[ \rightarrow \overline{H} = \exp\left(\frac{M}{\Omega_0} c^\dagger c(b^\dagger - b)\right) H \exp\left(-\frac{M}{\Omega_0} c^\dagger c(b^\dagger - b)\right) \]

\[ = \left(\mathcal{E}_0 - \frac{M^2}{\Omega_0}\right) c^\dagger c + \sum_{\mu} \mathcal{E}_k c^\dagger_k c_k + \sum_k (V c^\dagger_k c_k + H.C) \]
Transition from "i" to "f"

\[
\Gamma = \frac{\Gamma_i \Gamma_f}{\Gamma_i + \Gamma_f} \rightarrow 2\pi |H_{fi}|^2 \delta(\epsilon - \epsilon_i)
\]

Decoherence → FGR

\[
k_{ET} = -2 |H_{fi}|^2 \text{Im} G^r(\epsilon_i)
\]

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

In high temperature limit:

\[
I_n(x) \rightarrow \frac{\exp(x - n^2 / 2x)}{\sqrt{2\pi x}}
\]

Features: Temperature dependence

Marcus Theory

Features: Temperature dependence

: Arrhenius plot
—NEGF Formalism for transport in nano-contact—
\[ H = \sum_{\mu}(\varepsilon_{\mu} + \varphi(t))d^{\dagger}_{\mu}d_{\mu} + \sum_{k}(\varepsilon_{k} + \varphi(t))c^{\dagger}_{k}c_{k} + \sum_{\mu k}(V_{\mu k}d^{\dagger}_{\mu}c_{k} + H.C) \]

\[ + U_{ij,kl}d^{\dagger}_{i}d^{\dagger}_{j}d^{\dagger}_{k}d^{\dagger}_{l} + \sum_{\alpha}\Omega_{\alpha}b^{\dagger}_{\alpha}b_{\alpha} + \sum_{\mu,\alpha}M_{\alpha}(b^{\dagger}_{\alpha} + b_{\alpha})d^{\dagger}_{\mu}d_{\mu} \]

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

**Green’s function (correlation function)**

\[ G^{<}_{12}(t_{1},t_{2}) = i\left\langle d^{\dagger}_{2}(t_{2})d_{1}(t_{1}) \right\rangle \]

\[ G^{>}_{12}(t_{1},t_{2}) = -i\left\langle d_{1}(t_{1})d^{\dagger}_{2}(t_{2}) \right\rangle \]

**Contour-ordered Green’s function**

\[ G_{12}(\tau_{1},\tau_{2}) = -i\left\langle \hat{\rho}_{t_{0}}T_{C}[d_{1}(t_{1})d^{\dagger}_{2}(t_{2})] \right\rangle \]

\[ d_{1}(\tau_{1}) = U(t_{0},\tau_{1})d_{1}U(\tau_{1},t_{0}) \]
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

\[
G(\tau_1, \tau_2) = G_0(\tau_1, \tau_2) + \int d\tau d\tau' G_0(\tau_1, \tau) \Sigma(\tau, \tau') G(\tau', \tau_2)
\]

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

\[ g_{surf,L/R}^< (E) = -f_{L/R} (E) \left( g_{surf,L/R}^r - g_{surf,L/R}^a \right) \]

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

\[ g_k^r (E) \xrightarrow{\text{semi-infinite boundary condition}} g_{surf}^r (E) \]

Let us define electric current as flux on the left electrode

\[ I = \frac{i}{2\pi} \int d\varepsilon \text{Tr} \left\{ \Gamma_L (\varepsilon - \varphi_L) \left[ G^<(\varepsilon) + f_L (\varepsilon - \varphi_L) (G^r (\varepsilon) - G (\varepsilon)) \right] \right\} \]

\[ \Gamma_L (\varepsilon) = i \left( \Sigma_L (\varepsilon) - \Sigma_L^\dagger (\varepsilon) \right) \]

\[ \Sigma_L (\varepsilon) = V g_{surf:L}^r (\varepsilon) V^* \]

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

Landauer formula

\[ I (V_b) = \int d\varepsilon \text{Tr} \left[ \Gamma_L (\varepsilon + V_b/2) G^r (\varepsilon) \Gamma_R (\varepsilon - V_b/2) G^a (\varepsilon) \right] \{ f (\varepsilon : \varepsilon_F + V_b/2) - f (\varepsilon : \varepsilon_F - V_b/2) \} \]
Electron-pathway by NEGF

Observable quantity $I = \text{flux of electron}$

How electron passes in the conductor (molecule) ?

$$J_{\mu \rightarrow \nu} = g_0 V \text{Im} \left\{ H_{\mu \nu}^* \left( G_{L} G_{\dagger} \right)_{\mu \nu} - H_{\mu \nu}^* \left( G_{R} G_{\dagger} \right)_{\mu \nu} \right\}$$

$$\bar{J}_A = g_0 V \sum_{B \neq A} \sum_{\mu \in A, \nu \in B} J_{\mu \rightarrow \nu} \bar{u}_{AB}$$
—Cross-over of NEGF and scattering theory —
in ballistic transport
✓ Electronic structure of the molecular junction is **not** same with intrinsic property of “free” molecular system.

Orbital engineering + Contact chemistry = **rigorous** Conducting orbital?

![Diagram showing relationships between orbital engineering, contact chemistry, and electronic properties](image)

- **Conducting Orbital Engineering**
  - MO theory (Quantum chemistry)
  - Contact Chemistry
  - Orbital Engineering
  - Energy level and phase of molecular orbital
  - Hybridization of electronic states in semi-infinite-electrode, charge up
  - Effect of applied bias voltage
How can we identify quantitative "conducting orbital"?

\[(E - H) \Psi_I = 0 \rightarrow \Psi_I = \chi^+_L(E) + \sum_{\alpha} S_{\alpha\beta}^{}(E) \chi_\beta^{}(E)\]

\[S(E) = \exp(i\Delta(E)) = \exp(iX^\dagger X)\]

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

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

\[P + Q = P + Q_L + Q_R = \text{device}(+\text{semi-infinite})\]

\[P = \{\varphi_\mu\} \text{ MOs or AOs in the molecule}\]

\[Q_L = \{\chi_L(E)\} \text{ left channel states}\]

\[Q_R = \{\chi_R(E)\} \text{ right channel states}\]
What we want is “conducting orbital” = MO projected on the $P$ space “dressed” by surface/electrodes electronic sates

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

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

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

PMO Correction terms (“dressed part”) = Orbital Engineering = Contact Engineering

small (~0)

$H^\text{eff}_{PP} = H_{PP} + H_{PQ_L}\mathbf{G}_{QQ}^r(E)H_{Q_LP}$

MPSH

Diagonalize of MPSH $\rightarrow$ PMO

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

intrisic electronic coupling with $L$

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

intrisic electronic coupling with $R$

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

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

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.
IETS is a finger print of molecule (vibron) and local heating process!!
Very short survey of c-LOE formalism

\[ G^\leq = G^r \Sigma^\leq G^a \]

\[ D^\leq (\omega) = D^r (\omega) \Pi^\leq (\omega) D^a (\omega) \]

\[
I (V) = \frac{1}{2\pi} \int dE \text{Tr} \left[ \Sigma^\leq (E,V) G^> (E,V) - \Sigma^> (E,V) G^\leq (E,V) \right] = \int dEi (E) 
\]

\[
J_{\text{ph}}^{\text{th}} (V) = \frac{1}{2\pi} \int d\omega \omega \text{Tr} \left[ \Pi^\leq (\omega) D^> (\omega) + \Pi^> (\omega) D^\leq (\omega) \right] = \int d\omega \omega j (\omega) 
\]

Self-energy terms of electron-phonon interaction

\[
\Sigma^\leq (E) = \Sigma^\leq [E; G^\leq, D^\leq] 
\]

\[
\Sigma^r (E) = \Sigma^r [E; G^{\leq/>, G^r, D^\leq, D^a] 
\]

\[
\Pi^\leq (\omega) = \Pi^\leq [\omega; G^{\leq/>}] 
\]

\[
\Pi^r (\omega) = \Pi^r [\omega; G^{\leq/>}, G^r] 
\]
Rigorous LOE

\[ G_{LOE}^r = G_{DFT}^r + G_{DFT}^r \sum_{\text{eph}} G_{DFT}^r \quad G_{LOE}^\prec = G_{LOE}^r \left( \Sigma^{<}_L + \Sigma^{<}_R \right) G_{LOE}^a + G_{DFT}^r \sum_{\text{eph}} G_{DFT}^a \]

\[ D^r(\omega) = \sum_\alpha D_{0\alpha}^r(\omega) = \sum_\alpha \frac{2\Omega^\alpha}{\omega^2 - \Omega^2_\alpha + i\eta^\alpha} \quad D^\prec(\omega) = D^r \left[ i\eta(\omega/\Omega)N_{BE} \right] D^a + D^r \Pi^\prec_{\text{eph}} D^a \]

self-energy of lead phonon \( \Pi^r_{L/R}(\omega) \) \quad heat dissipation to electrodes: \( \Pi^\prec_{L/R}(\omega) \)

\[ \Sigma_{\text{eph}}^\prec(E) = \Sigma_{\text{eph}}^\prec[E; G_{DFT}^\prec, D^\prec] \quad \Pi_{\text{eph}}^\prec(\omega) = \Pi_{\text{eph}}^\prec[\omega; G_{DFT}^{\prec>] \]

\[ \rightarrow \text{partially 4th order of electron-phonon couplings} \]

Conventional LOE

Rigorous LOE formulation then

\[ \int dEA(E \pm \Omega)B(E \pm \Omega) \sim \int dEA(E)B(E \pm \Omega) \]

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

\[ \int_{E_0 + \Omega^\alpha}^{E_0 + \Omega^\alpha} dEA(E) \sim 2A(E_0)\Omega^\alpha \]

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 \( \frac{d^2I}{dV^2} \)

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

No contribution to “heating”

(2) Inelastic current term

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

Symmetric \( \frac{d^2I}{dV^2} \)

Local heating: (energy-exchange)

(3) Asymmetric correction term

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

Asymmetric \( \frac{d^2I}{dV^2} \)

Signal from off-resonant to resonant (band-like) transport
Nonequilibrium phonon distribution (vibrational heating)

\[
D^<(\omega = \Omega_\alpha) \rightarrow N_\alpha = \frac{T^\text{in}_\alpha(E_F)F_\alpha(V,T) + \left\{ T^\text{inl}_\alpha(E_F) + T^\text{inR}_\alpha(E_F) \right\}\Omega_\alpha N_{BE}(\Omega_\alpha, T) + 2\eta N_{BE}(\Omega_\alpha, T)}{4(T^d_\alpha(E_F)\Omega_\alpha + \eta/2)}
\]

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

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

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

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

**electron-hole damping terms**

\[
T^d_\alpha(E, V) = \text{Tr}[M^\alpha \text{Im}G(E)M^\alpha \text{Im}G]
\]

**dissipation to bulk electrodes**

\(\eta\): local phonon (vibron) –electrode phonon coupling

\(\eta \rightarrow 0\): undamped limit (completely nonthermalized)

\(\eta \rightarrow \text{inf}\): (external) damped limit (thermalized)
Vibronic-pathway as an analogue of electron-pathway

Observable quantity $I = \text{flux of electron}$

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

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

$$J^{bal}_{\mu \rightarrow \nu} = g_0 V \text{Im} \left\{ H^*_{\mu \nu} \left( \frac{G_L G}{G_R} \right)_{\mu \nu} - H^*_{\mu \nu} \left( \frac{G_R G}{G_L} \right)_{\mu \nu} \right\}$$

$$J^{inel}_{\mu \rightarrow \nu} = g_0 V (2N_{\alpha} + 1) \{ \text{Im} \, H^*_{\mu \nu} \left( \frac{G_{\alpha} G_L G}{G_R} \right) + \text{Im} \, H^*_{\mu \nu} \left( \frac{G_{\alpha} G_R G}{G_L} \right) \} \Theta(V - \Omega_{\alpha})$$
(2) Current induced force (classical ion dynamics)

\[ H = \sum_{\mu} (\varepsilon_{\mu} + \varphi) d^{\dagger}_\mu d_\mu + \sum_{k} (\varepsilon_{k} + \varphi) c^{\dagger}_k c_k + \sum_{\mu k} (V_{\mu k} d^{\dagger}_\mu c_k + H.C) \]

\[ + U_{ij,kl} d^{\dagger}_i d^{\dagger}_j d_k d_l + \sum_{\mu,\nu} d^{\dagger}_\mu \left[ H_e (X) \right]_{\mu \nu} d_\nu \]

\[ X(t) = (\vec{R}_1, \vec{R}_2, \cdots \vec{R}_N) \]

electron energy

time of ion motion

\[ A(t_1, t_2) = A\left(\frac{t_1 - t_2}{2}, \frac{t_1 + t_2}{2}\right) \rightarrow A(E, t) \]

Force act on ion \( l \):  \[ F_l (X(t)) \equiv \frac{i}{2\pi} \int dE \text{Tr} \left[ \frac{\partial H_e}{\partial R_l} G^{<} (E,t) \right] \]

\[ G^{<} (E,t) \approx G^{<} (E : X) + \mathcal{Z} \left[ G^{<} (E : X), \frac{dX}{dt} \right] \]
Mean force (Ehrenfest force)

\[ F_{\text{MF}}^I (X) = \frac{i}{2\pi} \int dE \text{Tr} \left[ \frac{\partial H_e}{\partial R_I} G^< (E : X) \right] \]

\[ = F_{\text{BO}}^{\text{ust}} + \left\{ \frac{i}{2\pi} \int dE \text{Tr} \left[ \frac{\partial H_e}{\partial R_I} (G^< - G^<_{eq}) \right] - F_{\text{ext}}^\text{ext} (V_{bias}) \right\} + F_{\text{ext}}^\text{ext} \]

Dissipation force

\[ F_{\text{dss}}^I (X) = \frac{i}{2\pi} \int dE \text{Tr} \left[ \frac{\partial H_e}{\partial R_I} \Im \left[ G^< (E : X), \frac{dX}{dt} \right] \right] \]

Quantum heating/dissipation

\[ N_\alpha = \frac{T_{\text{in}}^\alpha (E_F) F_\alpha (V,T) + \left\{ T_{\text{in}}^{\text{L}} (E_F) + T_{\text{in}}^{\text{R}} (E_F) \right\} \Omega_\alpha N_{\text{BE}} (\Omega_\alpha, T) + 2\eta N_{\text{BE}} (\Omega_\alpha, T)}{4(T_{\text{d}}^\alpha (E_F) \Omega_\alpha + \eta/2)} \]
—Notes of First Principles NEGF: NEGF-DFT —
Classification of electric transport and our focus

\[
\frac{\text{MFP length}}{\text{conductor length}}
\]

Ballistic transport + \begin{tabular}{l}
 electron-phonon scattering \\
 electron-phonon induced force \\
 Thermal induced hopping (TIH)
\end{tabular}

Ballistic transport + \begin{tabular}{l}
 NEGF + perturbation \\
 Noneq. BO (Ehrenfest) Dynamics \\
 Holstein polaron / TIH
\end{tabular}

Weak \rightarrow Strong

Electron-phonon couplings

Fast \rightarrow Slow

dissipation of electron energy to ion kinetic motion

Realm of Marcus theory

Nonadiabatic \rightarrow Adiabatic

NEGF + perturbation

NEGF + Noneq. BO (Ehrenfest) Dynamics

Thermal induced hopping (TIH)

Holstein polaron / TIH
Example of “Contact Chemistry” (Electrode-dependence)

I-V characteristics of PTCDA 3 ML film by first principles calculations

Ag electrodes

Al electrodes

T. Ohoto, K. Yamashita, and H. Nakamura
Out line of NEGF-DFT

Bulk DFT + boundary condition

\[ \Sigma^r = V_H + V_{XC} + V_{ext} + \Sigma^r_L + \Sigma^r_R \]
\[ \Sigma^< = 0 + \Sigma^<_{L} + \Sigma^<_{R} \]

uniform electric field

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

Shift chemical potential \( \pm V_{bias}/2 \)

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

\[ G^r(E) = (E - H_0 - \Sigma^r_L - \Sigma^r_R - V_H[\rho] - V_{XC}[\rho])^{-1} \]

\[ G^< = G^r \Sigma^< G^a \]

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

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”. $\rightarrow$ Dynamical matrix

(2) Select normal modes $Q$ localized on molecular conductor ($\Gamma$-point)

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

(4) NEGF-DFT $\rightarrow$ c-LOE

$$\frac{\partial H_{KS}(k_{//})}{\partial Q_{\alpha}}$$
Out line of first principles current-induced force

\[ F_{I}^{MF} (X) = \frac{i}{2\pi} \int dE \text{Tr} \left[ \frac{\partial H_{e}}{\partial R_{I}} G^{<} (E : X) \right] \]

\[ F_{I}^{MF} (X) = -\frac{\partial \langle \Psi | H | \Psi \rangle}{\partial R_{I}} \]

\( \Psi \) steady state (scattering state)

Assuming the same expression of \( E_{KS}^{tot} \) and \( \frac{\partial E_{KS}^{tot}}{\partial R_{I}} \),

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 \( \Psi \) ) is not determined by variational principle under bias voltage.

Additional terms is required to calculate \( \langle \Psi | \frac{\partial H}{\partial R_{I}} | \Psi \rangle \)?
— 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

...
Aviram-Ratner (AR)

\[ D = \text{electron rich} \rightarrow p \]
\[ A = \text{electron deficient} \rightarrow n \]

Favorite direction \( p \rightarrow n \)

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

\[ M[D - \sigma - A]M \rightarrow M^-[D^+ - \sigma - A^-]M^+ \]
\[ M^-[D^+ - \sigma - A^-]M^+ \rightarrow M^-[D - \sigma - A]M^+ \]
Ellenbogen-Love (EL)

\[ D = \text{electron rich} \rightarrow p \]
\[ A = \text{electron deficient} \rightarrow n \]

**Favorite direction**  \( n \rightarrow p \)

**“intrinsic” response** of HOMO/LUMO to bias

HOMO(D) and LUMO(A) responses to bias based on each redox potential

MO energy

A(LUMO)

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

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

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D−σ−A structure molecule is basically EL type diode, i.e., n→p direction
pn-resemble diblock molecular diode

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

Experiment


rectifying direction = $p \rightarrow n$ !!
First principles calculation (NEGF-DFT)

Conductance-rectification parameter

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

biprydiminyl-biphenyl (Exp.)

biprydiminyl-biphenyl (Thoery)

tetraphenyl (Exp.)

tetraphenyl (Theory)


rectifying direction = \( p \rightarrow n \) !!
Resonance Structure of Conductance

\[ \tau_\alpha \sim \frac{4\gamma_L\gamma_R}{\left\{ E - (E_{0\alpha} + \Delta E) \right\}^2 + (\gamma_L + \gamma_R)^2} \]

Important for **quantitative** analysis

\[ E_\alpha = E_\alpha (E, V) \rightarrow E_\alpha (E_F, V) \neq E_\alpha (E_{0\alpha}, V) \]

\[ \gamma_{L/R} = \gamma_{L/R} (E, V) \rightarrow \gamma_{L/R} (E_F, V) \neq \gamma_{L/R} (E_F, V) \neq \gamma_{L/R} (E_{0\alpha}, V) \]

**Key of Rectification by conducting orbital!!**

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

\[ \gamma_L (V)\gamma_R (V) \ll \left( \frac{\gamma_L (V) + \gamma_R (V)}{2} \right)^2 \]

\[ \gamma_L (-V)\gamma_R (-V) \ll \gamma_L (V)\gamma_R (V) \]
**Rectification by Switch of “Conducting Orbital”**

*Including terminal –S*

Diode (bipyridiminyl-biphenyl)

<table>
<thead>
<tr>
<th>Bias (Volt)</th>
<th>$E_{H-2}$ (eV)</th>
<th>$\sqrt{\gamma_L\gamma_R}$</th>
<th>$E_{H-1}$</th>
<th>$\sqrt{\gamma_L\gamma_R}$</th>
<th>$E_H$</th>
<th>$\sqrt{\gamma_L\gamma_R}$</th>
<th>$E_L$</th>
<th>$\sqrt{\gamma_L\gamma_R}$</th>
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<tbody>
<tr>
<td>-0.8</td>
<td>-1.56</td>
<td>0.135</td>
<td>-1.41</td>
<td>0.285</td>
<td>-1.00</td>
<td>0.011</td>
<td>1.63</td>
<td>0.071</td>
</tr>
<tr>
<td>-0.4</td>
<td>-1.76</td>
<td>0.089</td>
<td>-1.31</td>
<td>0.152</td>
<td>-1.21</td>
<td>0.044</td>
<td>1.60</td>
<td>0.042</td>
</tr>
</tbody>
</table>

Switching of “conducting MO” by bias-induced asymmetric electronic coupling

<table>
<thead>
<tr>
<th>Bias (Volt)</th>
<th>$E_{H-2}$ (eV)</th>
<th>$\sqrt{\gamma_L\gamma_R}$</th>
<th>$E_{H-1}$</th>
<th>$\sqrt{\gamma_L\gamma_R}$</th>
<th>$E_H$</th>
<th>$\sqrt{\gamma_L\gamma_R}$</th>
<th>$E_L$</th>
<th>$\sqrt{\gamma_L\gamma_R}$</th>
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<tbody>
<tr>
<td>0.4</td>
<td>-2.08</td>
<td>0.302</td>
<td>-1.42</td>
<td>0.018</td>
<td>-1.18</td>
<td>0.106</td>
<td>1.44</td>
<td>0.038</td>
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<tr>
<td>0.8</td>
<td>-2.07</td>
<td>0.424</td>
<td>-1.50</td>
<td>0.048</td>
<td>-1.09</td>
<td>0.144</td>
<td>1.35</td>
<td>0.065</td>
</tr>
</tbody>
</table>

Tetraphenyl

<table>
<thead>
<tr>
<th>Bias (Volt)</th>
<th>$E_{H-2}$ (eV)</th>
<th>$\sqrt{\gamma_L\gamma_R}$</th>
<th>$E_{H-1}$</th>
<th>$\sqrt{\gamma_L\gamma_R}$</th>
<th>$E_H$</th>
<th>$\sqrt{\gamma_L\gamma_R}$</th>
<th>$E_L$</th>
<th>$\sqrt{\gamma_L\gamma_R}$</th>
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</thead>
<tbody>
<tr>
<td>-0.8</td>
<td>-1.88</td>
<td>0.003</td>
<td>-1.90</td>
<td>0.433</td>
<td>-0.97</td>
<td>0.162</td>
<td>2.01</td>
<td>0.090</td>
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<tr>
<td>-0.4</td>
<td>-2.71</td>
<td>0.437</td>
<td>-1.72</td>
<td>0.331</td>
<td>-1.05</td>
<td>0.142</td>
<td>2.01</td>
<td>0.062</td>
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<tr>
<td>0.4</td>
<td>-2.81</td>
<td>0.466</td>
<td>-1.84</td>
<td>0.358</td>
<td>-1.02</td>
<td>0.143</td>
<td>2.08</td>
<td>0.071</td>
</tr>
<tr>
<td>0.8</td>
<td>-1.82</td>
<td>0.628</td>
<td>-1.80</td>
<td>0.489</td>
<td>-0.99</td>
<td>0.166</td>
<td>1.95</td>
<td>0.113</td>
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</table>
Crossover of views in molecular diode and pn junctions

\[ H_{PP}^{\text{eff}} = \left( \mathbf{H}_{ij}^{\text{eff}} \right) = \begin{pmatrix} H_{11}^{\text{eff}} & \cdots & \cdots & H_{14}^{\text{eff}} \\ \vdots & H_{22}^{\text{eff}} & \ddots & \vdots \\ \vdots & \ddots & H_{33}^{\text{eff}} & \vdots \\ H_{41}^{\text{eff}} & \cdots & \cdots & H_{44}^{\text{eff}} \end{pmatrix} \]

\[ \tilde{H}_{PP}^{\text{eff}} = \left( \text{diag}(U_j) \right)^{\dagger} \left( \mathbf{H}_{ij}^{\text{eff}} \right) \left( \text{diag}(U_j) \right) \]

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!

Diagram of molecular site energy alignment
Why EL mechanism (opposite directional rectification) did not work?

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)  

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

0.5 rule

Off-set: heating effect
Dissipation: suppress off-set
Au atomic wire

IETS active modes: longitudinal mode

Dominated by elastic scattering

$\Omega_1 = 62.9 \text{cm}^{-1}$ (ABL)

$\Omega_2 = 108.5 \text{cm}^{-1}$ (non ABL)

$\Omega_3 = 111.3 \text{cm}^{-1}$ (ABL)
Comparison of mode selectivity of IR and Raman

Benzene-dithiol junction

<table>
<thead>
<tr>
<th>Mode</th>
<th>$I_{IR}$</th>
<th>$I_{Raman}$</th>
<th>$\bar{T}_{ec}$</th>
<th>$\bar{T}_{ecSym}$</th>
<th>$\bar{T}_{in}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B2G$^1$</td>
<td>0.000</td>
<td>0.000</td>
<td>1.070</td>
<td>-0.030</td>
<td>0.294</td>
</tr>
<tr>
<td>AG$^2$</td>
<td>0.000</td>
<td>0.196</td>
<td>0.822</td>
<td>-0.030</td>
<td>0.472</td>
</tr>
<tr>
<td>AU$^3$</td>
<td>0.000</td>
<td>0.000</td>
<td>0.502</td>
<td>-0.018</td>
<td>0.385</td>
</tr>
<tr>
<td>B3U$^4$</td>
<td>0.164</td>
<td>0.014</td>
<td>0.426</td>
<td>-0.008</td>
<td>0.104</td>
</tr>
<tr>
<td>B2G$^5$</td>
<td>0.000</td>
<td>0.028</td>
<td>-0.035</td>
<td>-0.003</td>
<td>0.061</td>
</tr>
<tr>
<td>B1G$^6$</td>
<td>0.000</td>
<td>0.023</td>
<td>0.497</td>
<td>-0.004</td>
<td>0.132</td>
</tr>
<tr>
<td>AG$^7$</td>
<td>0.000</td>
<td>0.063</td>
<td>-0.045</td>
<td>-0.024</td>
<td>0.231</td>
</tr>
<tr>
<td>AG$^8$</td>
<td>0.000</td>
<td>0.036</td>
<td>0.271</td>
<td>-0.014</td>
<td>0.214</td>
</tr>
<tr>
<td>AG$^9$</td>
<td>0.000</td>
<td>1.000</td>
<td>0.695</td>
<td>-0.055</td>
<td>0.816</td>
</tr>
<tr>
<td>AG$^{10}$</td>
<td>0.000</td>
<td>0.936</td>
<td>1.139</td>
<td>-0.062</td>
<td>1.000</td>
</tr>
</tbody>
</table>
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.

\[
\frac{d^2I}{dV^2} \rightarrow N_{BE}(\Omega_\alpha, T_{\alpha}^{\text{eff}}(V))
\]

How each mode is heated?

Electron-phonon coupling

In the projected MO

<table>
<thead>
<tr>
<th></th>
<th>BDT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{3u}^{(1)}$</td>
<td></td>
</tr>
<tr>
<td>$\pi^{(1)}\pi^{(1)}$</td>
<td>0.00</td>
</tr>
<tr>
<td>$\pi^{(2)}\pi^{(2)}$</td>
<td>0.00</td>
</tr>
<tr>
<td>$\sigma\pi^{(2)}$</td>
<td>0.00</td>
</tr>
<tr>
<td>$\pi^{(1)}\pi^{(2)}$</td>
<td>0.00</td>
</tr>
<tr>
<td>$\sigma\pi^{(1)}$</td>
<td>0.18</td>
</tr>
</tbody>
</table>
Local heating is also asymmetric in Molecular Diode?

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

$$I_{\alpha}^{\text{inel}} (V)/I_{\alpha}^{\text{inel}} (-V) \propto \left\{ I(V)/I(-V) \right\}^2 \cdots ?$$

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

Inelastic current and local heating are not necessarily enhanced by rectification.
Include effects of “intrinsic” contact-asymmetry to single conducting orbital model

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

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

Universal function of temperature, $V$, and $\Omega$

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

\[ D^\prec(\omega) = D^r \left[ i \eta(\omega/\Omega) N^\text{BE} \right] D^a + D^r \Pi^\prec \Pi^\prec \]

\[ \rightarrow \Pi^\prec_L + \Pi^\prec_R \]

(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)

\[ \frac{1}{\sqrt{2\Omega_\alpha}} \langle \mu | \frac{\partial H}{\partial Q_a} | \nu \rangle \]
Open question (2) local temperature?

Local temperature = measurement of local heating of “device”

Naïve extension

\[ N_\alpha (V) \rightarrow N_{BE} (\Omega_\alpha, T_{eff} (V)) \]
\[ \rightarrow \min \sum_{\alpha \subseteq \text{all}} \left| N_\alpha (V) - N_{BE} (\Omega_\alpha, T_{eff} (V)) \right|^2 \]

This is not observable “temperature”.

Local temperature defined by break of “bond”

\[ k(T_{eff}) = k_0 \exp(-\frac{E_a}{k_BT_{eff}}) \]
\[ \tau_{\text{break}} = 1/k \]

Observable by changing time-scale of “pulling”

\[ \tau_{\text{break}} \sim \frac{E_a}{Q_{\text{inside}}} \]
\[ Q_{\text{inside}} = \sum_{\alpha} \frac{1}{2\pi} \int dEE \text{Tr} \left[ \Sigma_{\text{eph}}^c G^\succ - \Sigma_{\text{eph}}^\succ G^c \right] \]
\[ + \sum_{\alpha} \frac{1}{2\pi} \int d\omega \omega \text{Tr} \left[ \Pi_{\text{eph}}^c D^\succ + \Pi_{\text{eph}}^\succ D^c \right] \]
Electron correlation in nonequilibrium transport
Hybrid XC functional: B3LYP, HSE

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

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.

\[ G^{r} = G_{DFT}^{r} + G_{DFT}^{r} \sum_{ee} G^{r} \quad G^{<} = G^{r} \left( \Sigma_{L}^{<} + \Sigma_{R}^{<} + \Sigma_{ee}^{<} \right) G^{a} \]

e-e scattering effect in conductor

0-bias: \( \Sigma_{ee}^{r} \) corrects HOMO-LUMO gap just as use of improved XC

Nonequilibrium case (non 0-bias) ?