Transport and Thermoelectric efficiency in vibrationally assisted molecular junction

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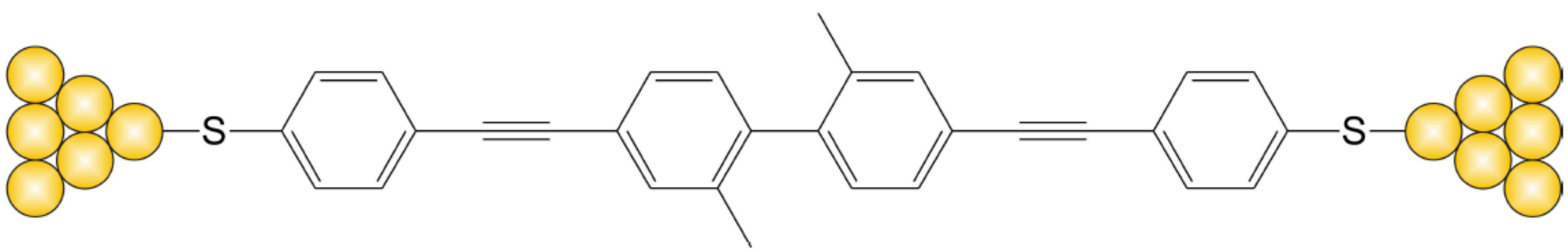


ICTS INTERNATIONAL CENTRE for THEORETICAL SCIENCES
TATA INSTITUTE OF FUNDAMENTAL RESEARCH

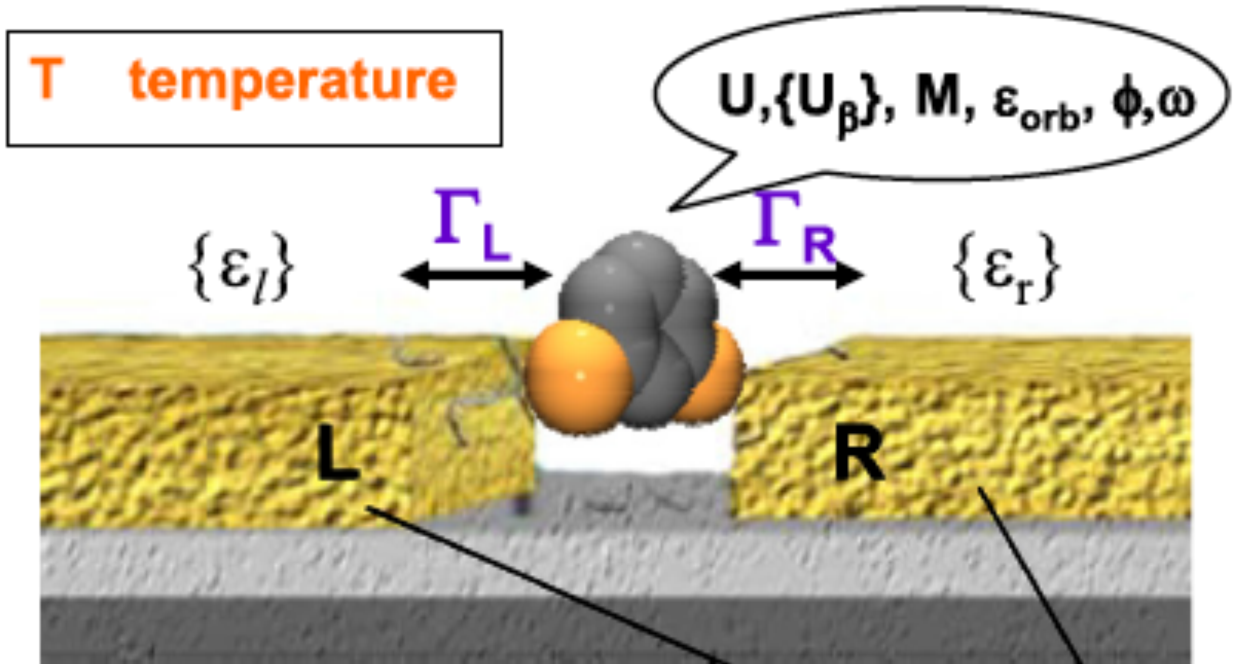
Non-Equilibrium Statistical Physics

26 Oct, 2015 - 20 Nov, 2015

Outline

- Transport and response coefficients in dimer molecular junction
- Efficiency statistics for time-reversal breaking system

Important parameters for molecular junction transport



ε_k	band states in electrode
U	electron repulsion on molecule
{U_β}	coupling to external bath modes
M	vibronic coupling on molecule
ε_{orb}	molecular orbital energies
ϕ	molecular orbitals
ω	molecular vibrational frequency
Γ	spectral density (electron-lead coupling
E_{FK}	(K=L,R) Fermi energies
Φ	bias potential

$E_{FL}=E_{FR}+|e|\Phi$

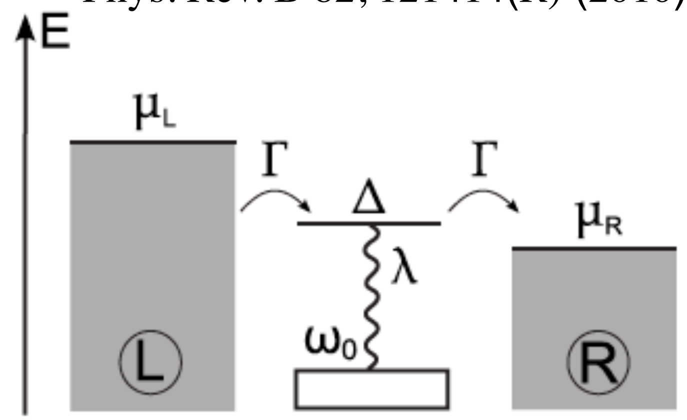
M. Galperin, M. A. Ratner, and A. Nitzan, J. Phys.: Condens. Matter 19, 103201 (2007)

Molecular electronics:

Electron-nuclei interactions are central to molecular electronic applications

Signature of molecular vibration : Inelastic electron tunneling spectroscopy

Phys. Rev. B 82, 121414(R) (2010)



Anderson-Holstein Model:
Single electron coupled to vibrational mode

Effect of vibrational mode on current, heating and cooling etc

M. Galperin, A. Nitzan, and M. A. Ratner, Phys. Rev. B 74, 075326 (2006).
M. Galperin, A. Nitzan, and M. A. Ratner, J. Chem. Phys. 121, 11965 (2004).
M. Galperin, M. A. Ratner, and A. Nitzan, J. Phys.: Condens. Matter 19, 103201 (2007). Review
R. Hartle, M. Butzin, and M. Thoss, Phys. Rev. B 87, 085422 (2013).
R. Egger and A. O. Gogolin, Phys. Rev. B 77, 113405 (2008).

Full-counting statistics

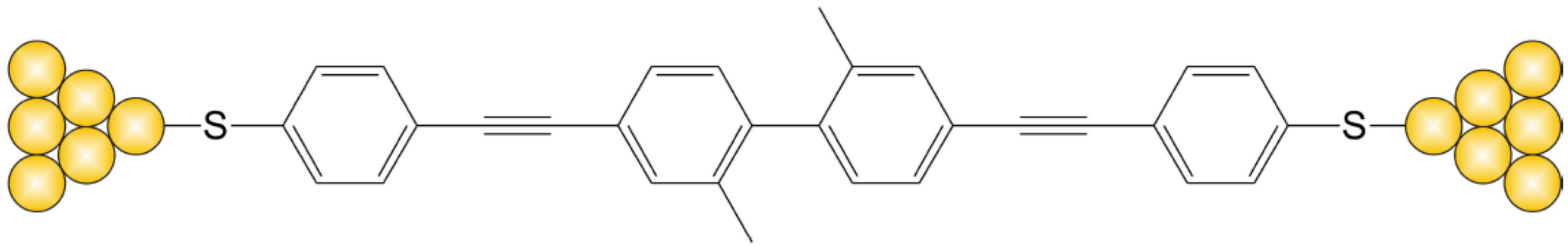
R. Avriller, and A. Levy Yeyati, Phys. Rev. B 80, 041309(R) (2009).
D. F. Urban, R. Avriller, and A. Levy Yeyati, Phys. Rev. B 82, 121414(R) (2010).
R. S. Souto et al. Phys. Rev. B 89, 085412 (2014).
T. L. Schmidt and A. Komnik, Phys. Rev. B 80, 041307(R) (2009).
Y. Utsumi et. al. Phys. Rev. B 87, 115407 (2013).

Transient study (Bistability, relaxation dynamics): exact numerical scheme

R. S Souto et. al. Phys. Rev. B 92, 125435 (2015).
Eli Y. Wilner, H. Wang, M. Thoss and E. Rabani Phys. Rev. B 89, 205129 (2014).

Molecular electronic conduction:

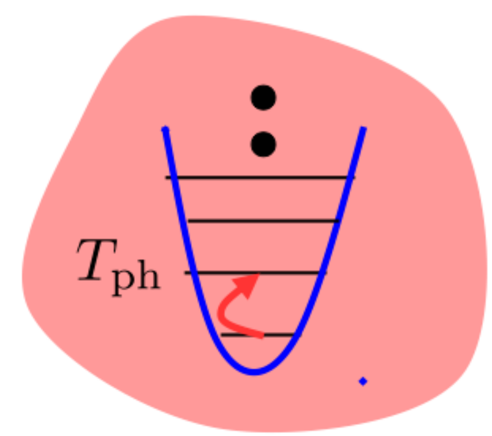
electron-vibration interaction effects



Ballman et a., Phys. Rev. Lett. 109, 056801 (2012)

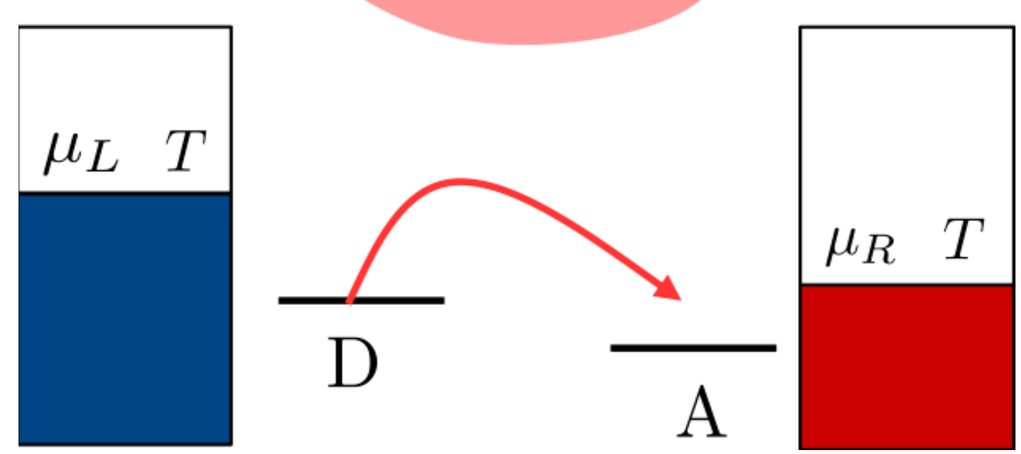
Donor-acceptor model: minimal model for building molecular diodes.

A. Aviram and M. A. Ratner, Chem. Phys. Lett. 29, 277 (1974)



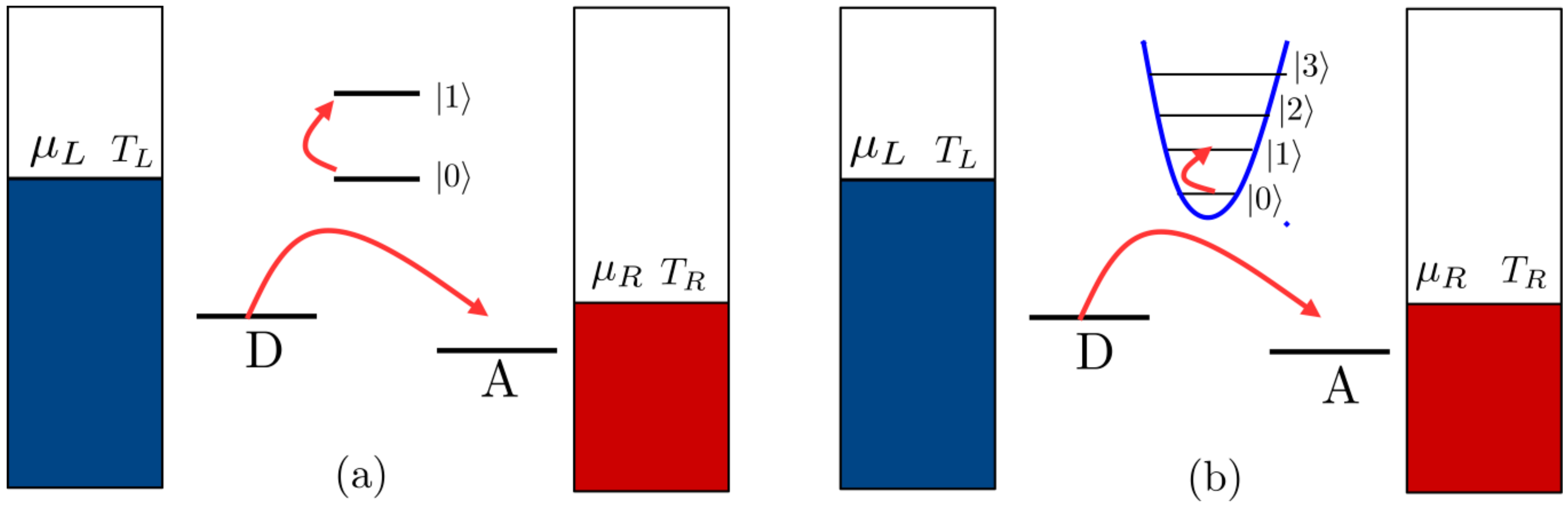
Operational questions (diode, heating effects, harmonic/anharmonic modes, thermoelectricity, three terminal system)

Building block for solar cells



Donor-Acceptor model

Model Hamiltonian : Vibrationally assisted molecular junction



$$
\begin{aligned}
H &= \epsilon_d c_d^\dagger c_d + \epsilon_a c_a^\dagger c_a + H_{vib} + H_{el-vib} \\
&+ \sum_{l \in L} \epsilon_l c_l^\dagger c_l + \sum_{r \in R} \epsilon_r c_r^\dagger c_r \\
&+ \sum_{l \in L} v_l (c_l^\dagger c_d + c_d^\dagger c_l) + \sum_{r \in R} v_r (c_r^\dagger c_a + c_a^\dagger c_r).
\end{aligned}
$$

off-diagonal coupling

Anharmonic (AH) two-state mode (DA-AH)

$$
H_{vib} = \frac{\omega_0}{2}\sigma_z \ , \ H_{el-vib} = g[c_d^\dagger c_a + c_a^\dagger c_d]\sigma_x
$$

Harmonic (HO) mode (DA-HO)

$$
H_{vib} = \omega_0 b_0^\dagger b_0, \ \ H_{el-vib} = g[c_d^\dagger c_a + c_a^\dagger c_d](b_0^\dagger + b_0)
$$

M. Esposito et. al. Rev. Mod. Phys. 81, 1665 (2009).
K. Saito and A. Dhar, Phys. Rev. Lett. 99, 180601 (2007).

Results:

$$\mathcal{Z}(\lambda_e,\lambda_p) = \left\langle e^{i\lambda_e H_R + i\lambda_p N_R}\, e^{-i\lambda_e H_R^H(t) - i\lambda_p N_R^H(t)} \right\rangle$$

2nd order in electron-phonon interaction

all order in metal-molecule strength

CGF:

Anharmonic (AH) Mode (Quantum master equation approach)

$$\mathcal{G}_{AH}(\lambda_e,\lambda_p) = -\frac{1}{2}(k_u + k_d) + \frac{1}{2}\sqrt{(k_u - k_d)^2 + 4\, k_u^\lambda k_d^\lambda}$$

Harmonic (HO) mode (Non-equilibrium Green's function approach)

$$\mathcal{G}_{HO}(\lambda_e,\lambda_p) = \frac{1}{2}(k_d - k_u) - \frac{1}{2}\sqrt{(k_u + k_d)^2 - 4k_u^\lambda k_d^\lambda}$$

Fluctuation symmetry

$$\mathcal{G}(\lambda_e,\lambda_p) = \mathcal{G}(-\lambda_e + i(\beta_L - \beta_R), -\lambda_p + i(\beta_R\mu_R - \beta_L\mu_L))$$

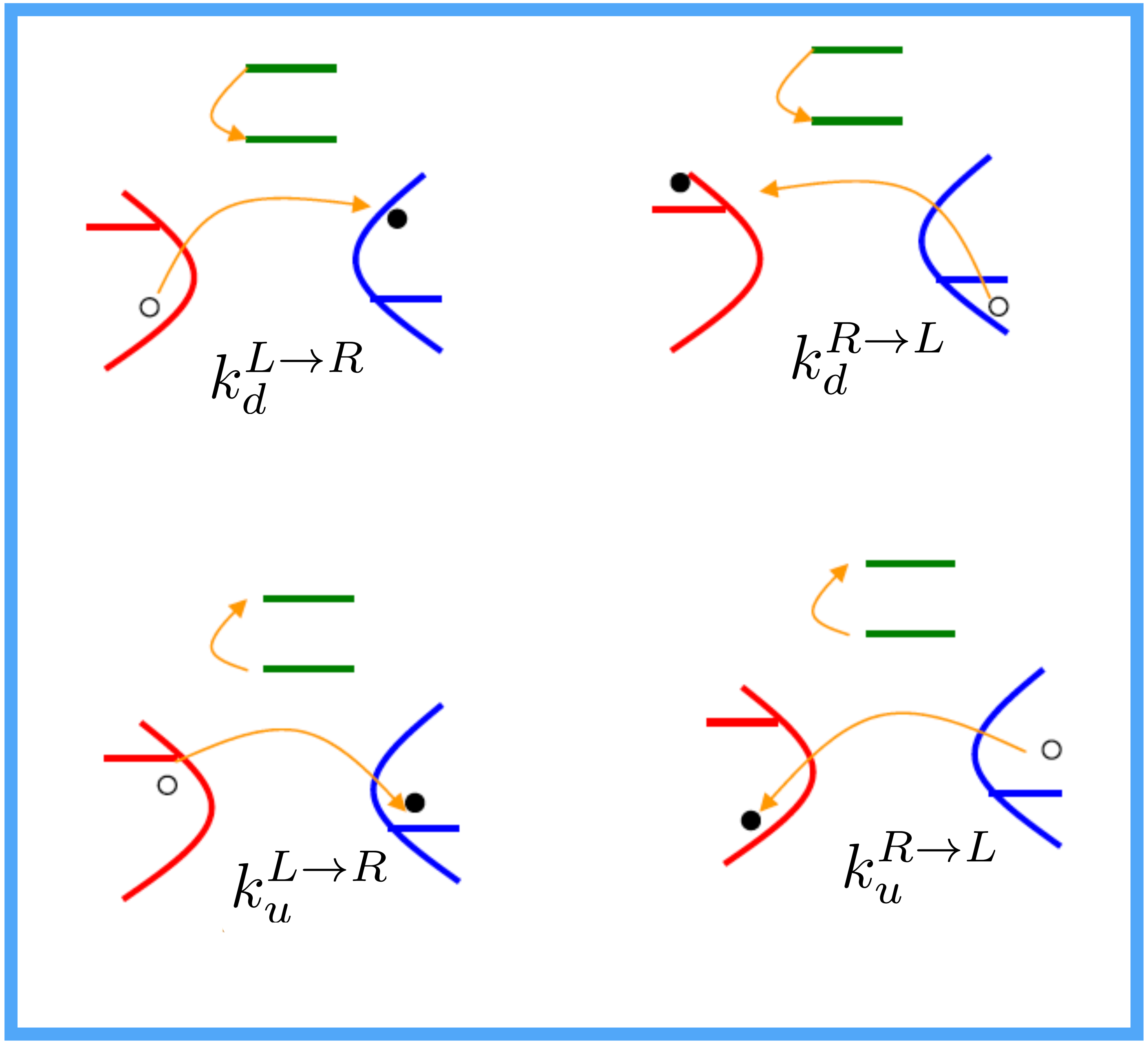
Energy-flux → $i(\beta_L - \beta_R)$; *Particle-flux* → μ_R term

B. K. Agarwalla, J.-H. Jiang, and D. Segal, Arxiv:1506.03102
B. K. Agarwalla, J.-H. Jiang, and D. Segal, Arxiv:1508.02475

$$k_d^\lambda = [k_d^\lambda]^{L\to R} + [k_d^\lambda]^{R\to L}$$

$$[k_d^\lambda]^{L\to R} = \int_{-\infty}^{\infty} \frac{d\epsilon}{2\pi} f_L(\epsilon)(1-f_R(\epsilon+\omega_0)) J_L(\epsilon) J_R(\epsilon+\omega_0)\, e^{-i\lambda_p - i(\epsilon+\omega_0)\lambda_e}$$

$$[k_d^\lambda]^{R\to L} = \int_{-\infty}^{\infty} \frac{d\epsilon}{2\pi} f_R(\epsilon)(1-f_L(\epsilon+\omega_0)) J_R(\epsilon) J_L(\epsilon+\omega_0)\, e^{i\lambda_p + i\epsilon\lambda_e}.$$



$$k_u^\lambda(\omega_0) = k_d^\lambda(\omega_0 \to -\omega_0)$$

Spectral Density

$$J_L(\epsilon) = g\frac{\Gamma_L(\epsilon)}{(\epsilon-\epsilon_d)^2 + \Gamma_L(\epsilon)^2/4}$$

$$J_R(\epsilon) = g\frac{\Gamma_R(\epsilon)}{(\epsilon-\epsilon_a)^2 + \Gamma_R(\epsilon)^2/4}$$

Currents:

$$\langle I_p \rangle = \frac{\partial \mathcal{G}(\lambda_e, \lambda_p)}{\partial (i\lambda_p)}\Big|_{\lambda_e=\lambda_p=0}$$

$$\langle I_p^{AH/HO} \rangle = 2\,\frac{k_d^{R\to L} k_u^{R\to L} - k_d^{L\to R} k_u^{L\to R}}{k_d + s k_u}$$

$s = +1$ for AH and $s = -1$ for HO

$$\langle I_e^{AH/HO} \rangle = \frac{k_d \left[\partial_{(i\lambda_e)} k_u^{\lambda}|_{\lambda_e=0}\right] + k_u \left[\partial_{(i\lambda_e)} k_d^{\lambda}|_{\lambda_e=0}\right]}{k_d + s\, k_u}$$

Sign difference reflects different steady state population normalization

$$P_0 = \frac{k_u}{k_u + k_d}$$

$$P_1 = 1 - P_0$$

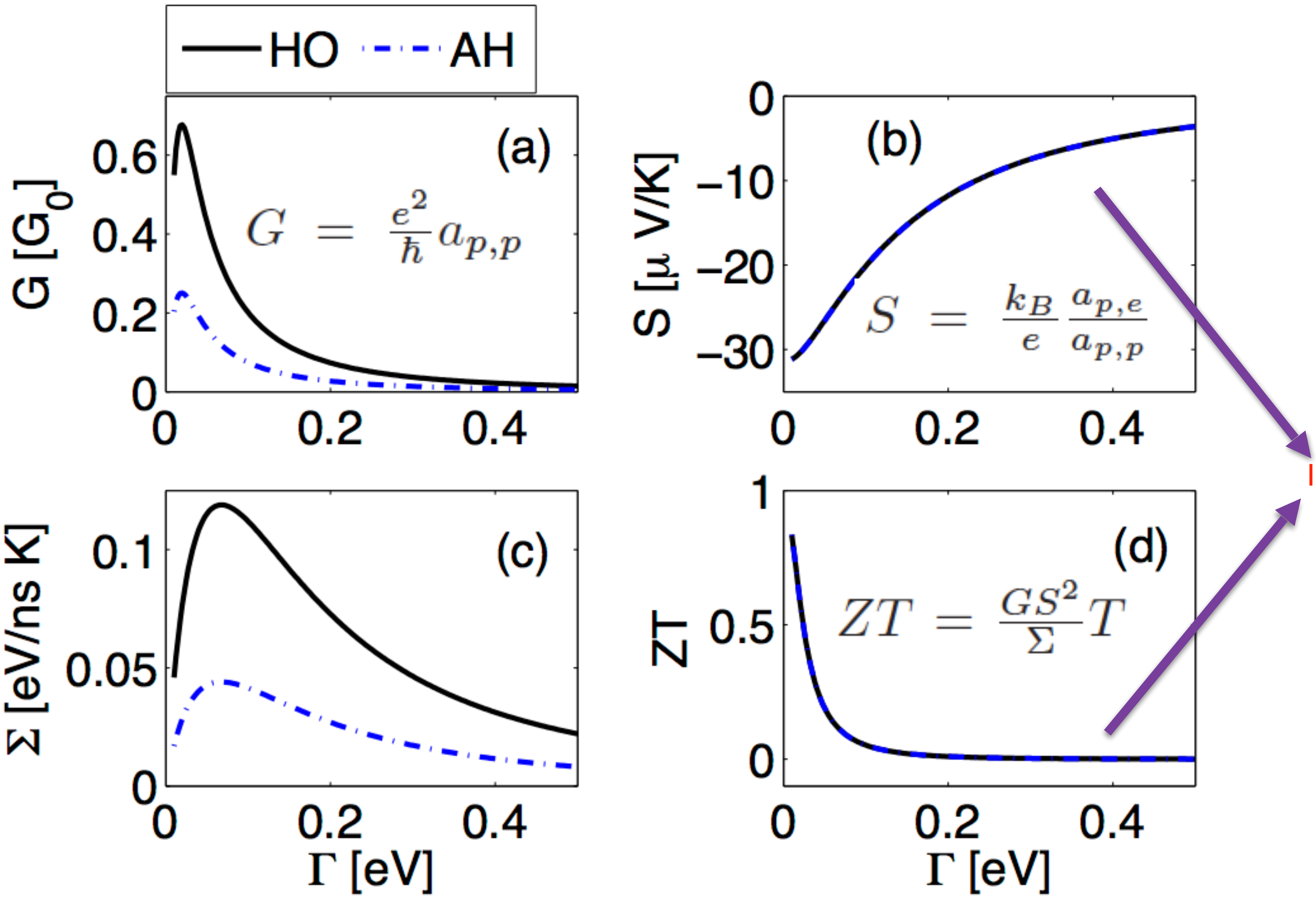
$$P_n = \left(1 - \frac{k_u}{k_d}\right)\left(\frac{k_u}{k_d}\right)^n$$

$$\langle n \rangle = \frac{k_u}{k_d - k_u}$$

Linear Response:

$$\langle I_p \rangle = \frac{e}{\hbar} a_{p,p} \Delta\mu + \frac{e}{\hbar} a_{p,e} k_B \Delta T,$$

$$\langle I_h \rangle = \frac{1}{\hbar} a_{e,p} \Delta\mu + \frac{1}{\hbar} a_{e,e} k_B \Delta T.$$



$$\Sigma = \frac{k_B}{\hbar}\left(a_{h,h} - \frac{a_{p,h} a_{h,p}}{a_{p,p}}\right)$$

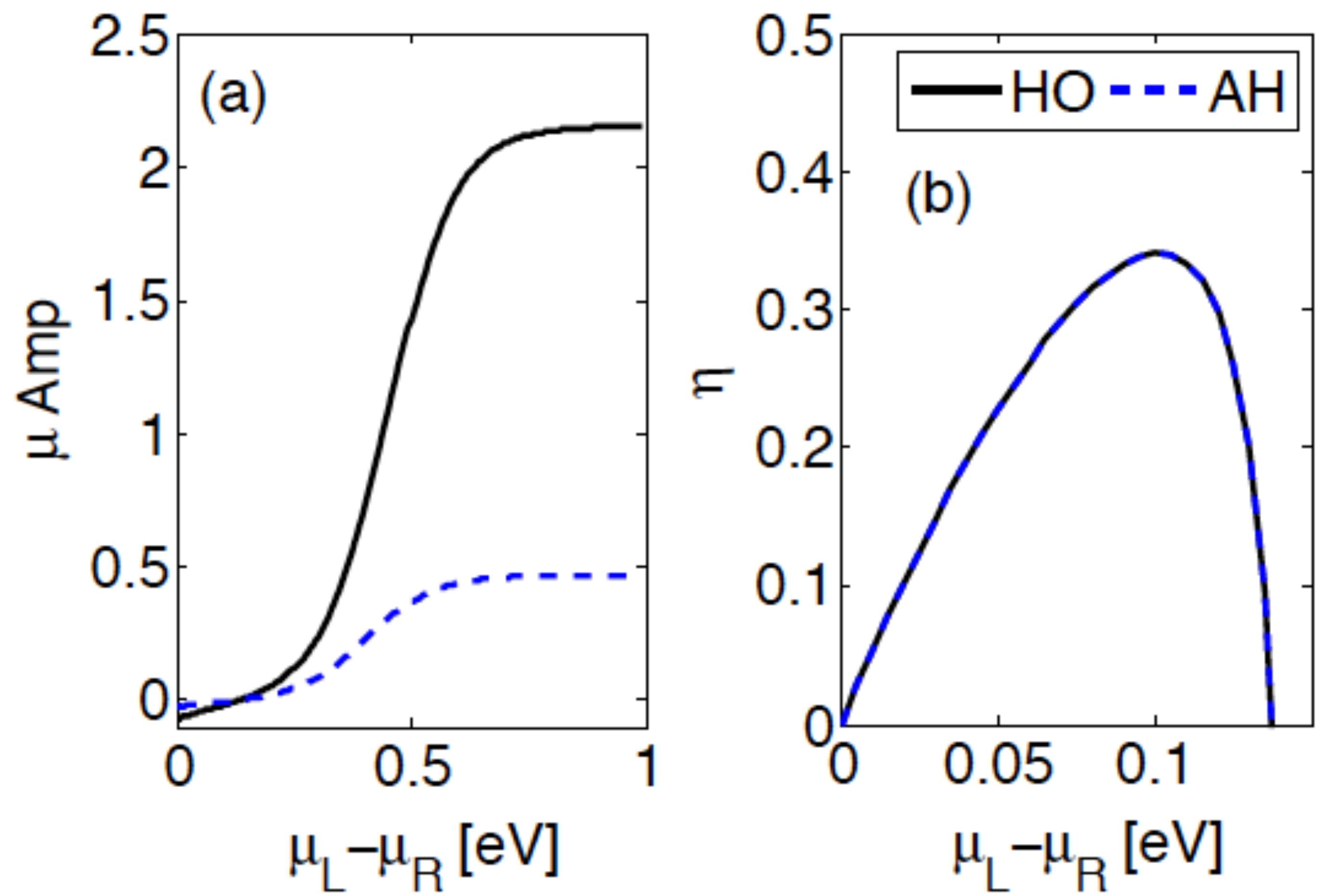
Independent of the nature of the modes

Nonlinear response for output power and efficiency

Thermoelectric device $T_L > T_R,\ \mu_L < \mu_R$

Power Output $\Rightarrow$ $$-\dot{W} \equiv (\mu_L - \mu_R)\langle I_p \rangle$$

Heat input $\Rightarrow$ $$\dot{Q} \equiv \langle I_q \rangle = \langle I_e \rangle - \mu_R \langle I_p \rangle$$

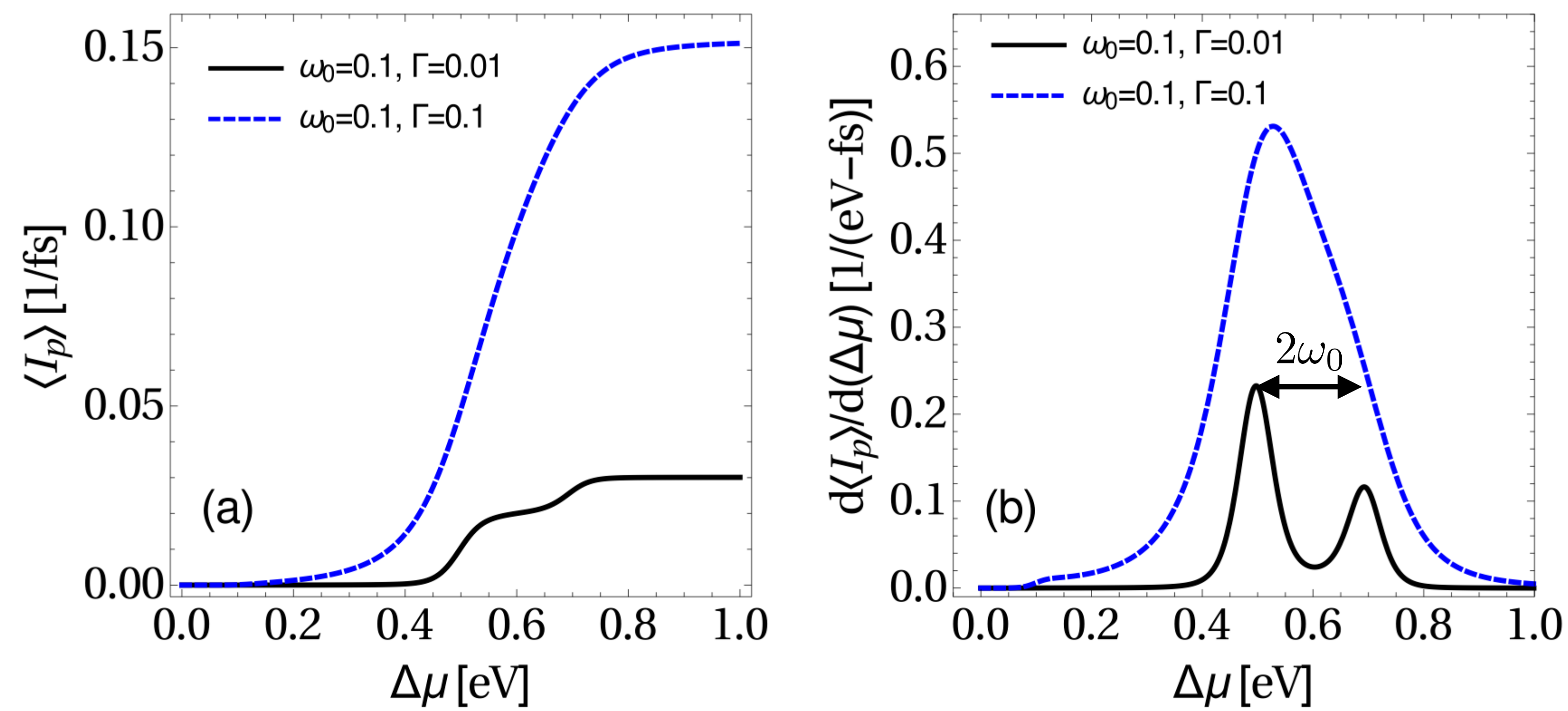


$$\eta = \frac{-W}{Q}$$

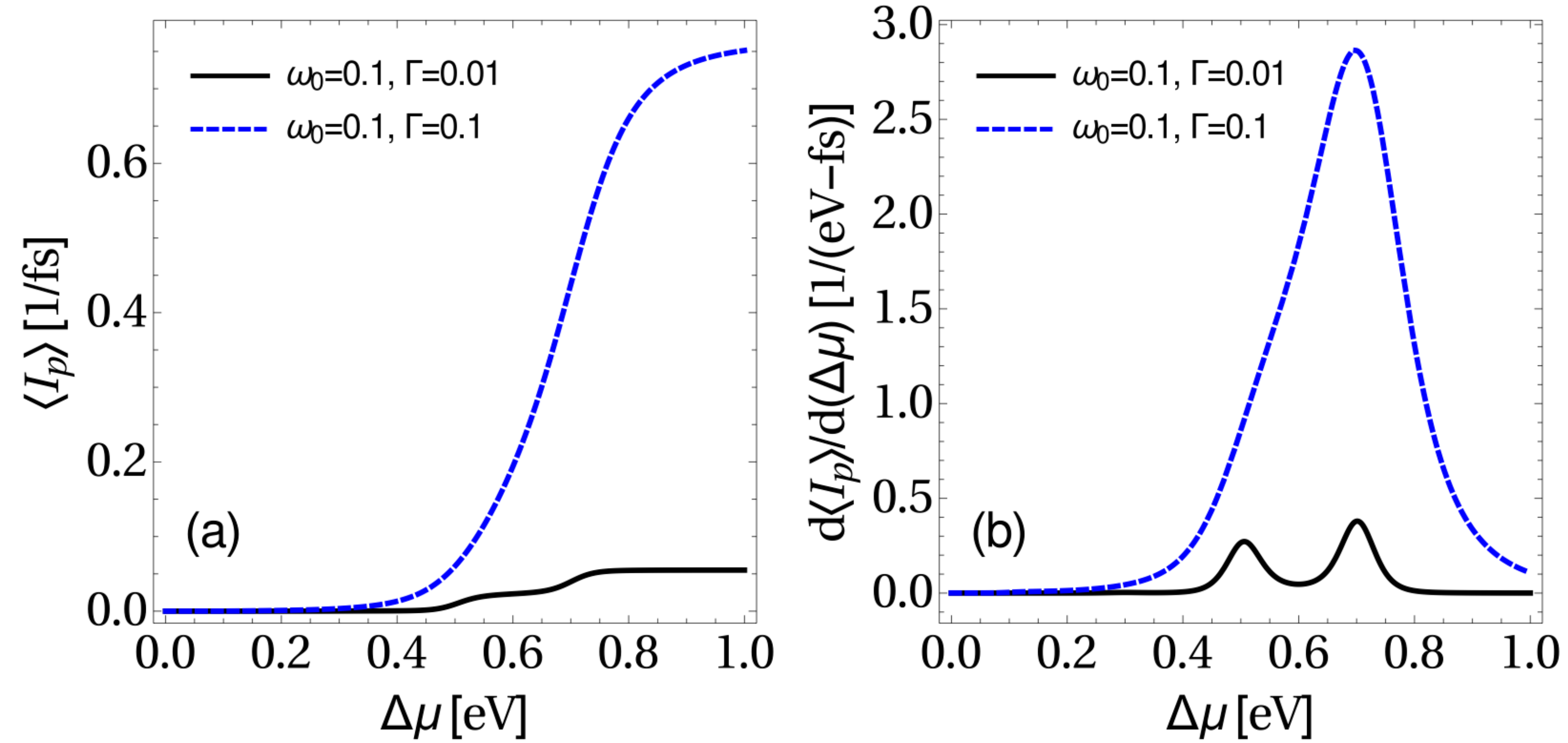
ω_0=0.02, ε_0=0.2, Γ=0.1, T_L=300, T_R=800 K
T_{ph}=300K, κ=0.01, K_d=0.002 [eV]

Current-Voltage behaviour

DA-AH



DA-HO

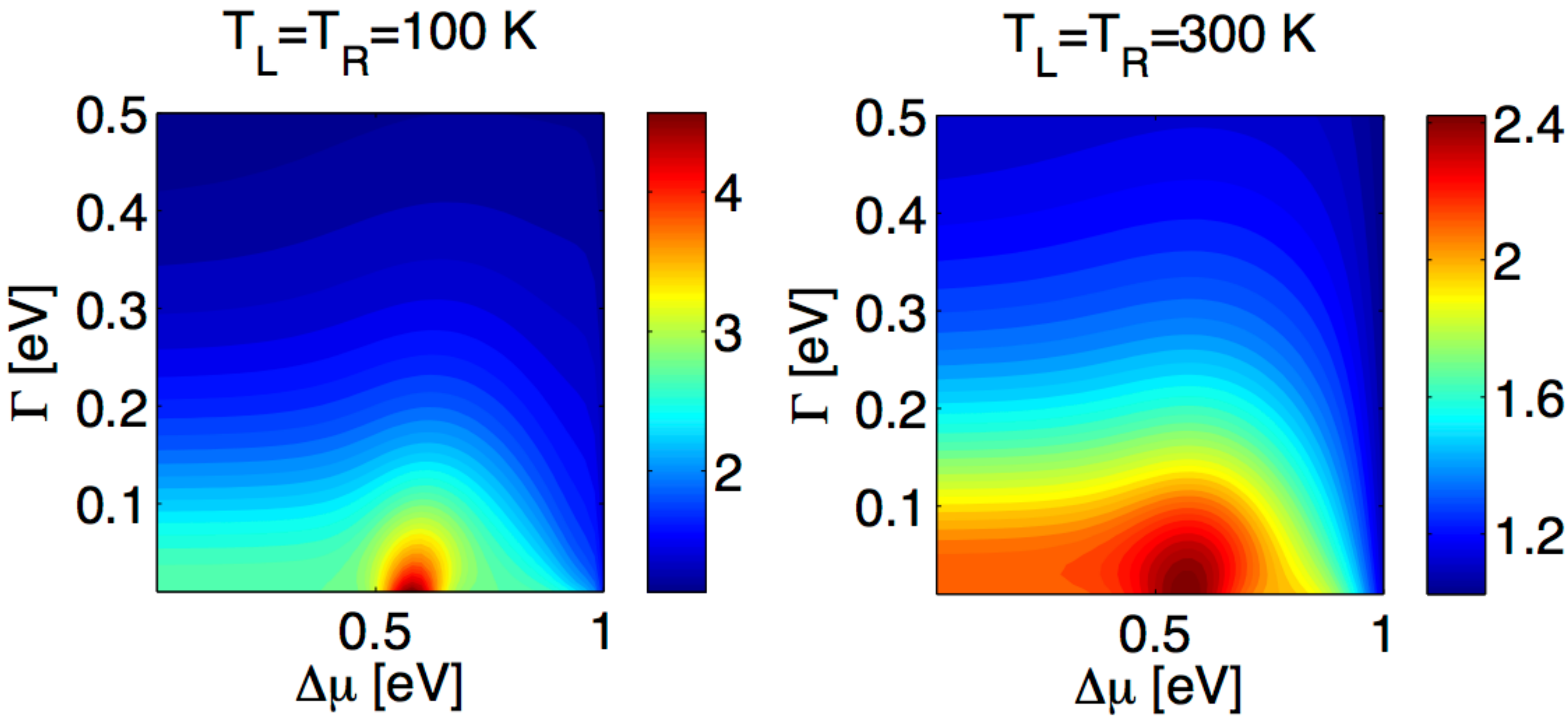


$$\epsilon_d = \epsilon_a = 0.25 \text{ eV}, \; T = T_L = T_R = 100K, \; g = 0.1 \text{ eV}$$

Rectification

$$R \equiv \frac{\langle I_p \rangle_+}{\langle I_p \rangle_-}$$

Necessary conditions :(i) spatial symmetry breaking, different energies for D and A states.
(ii) small metal-molecule hybridization energy.



$\epsilon_a = 0.2$, $\epsilon_d = 0$, $\omega_0 = 0.05$, $g = 0.01$, $\Gamma_{ph} = 0.005$ eV, $T_{ph} = 300$ K

(a) $T_L = T_R = 100$ K, and (b) $T_L = T_R = 300$ K

Scaling relations at large bias:

zero temperature, strong coupling

$$k_u \approx k_u^{R\to L} \approx \frac{\bar{g}^2\omega_0}{\Gamma_L\Gamma_R}\left(\frac{\Delta\mu}{\omega_0} - 1\right),$$

$$k_d \approx k_d^{R\to L} \approx \frac{\bar{g}^2\omega_0}{\Gamma_L\Gamma_R}\left(\frac{\Delta\mu}{\omega_0} + 1\right)$$

$$\langle I_p^{AH}\rangle = \frac{\bar{g}^2\Delta\mu}{\Gamma_L\Gamma_R}\left(1 - \frac{\omega_0^2}{\Delta\mu^2}\right)$$

$$\langle S_p^{AH}\rangle = \frac{\bar{g}^2\Delta\mu}{\Gamma_L\Gamma_R}\left(1 - \frac{\omega_0^4}{\Delta\mu^4}\right)$$

$$\langle I_p^{HO}\rangle = \frac{\bar{g}^2\omega_0}{\Gamma_L\Gamma_R}\left(\frac{\Delta\mu^2}{\omega_0^2} - 1\right)$$

$$\langle S_p^{HO}\rangle = \frac{\bar{g}^2\omega_0}{\Gamma_L\Gamma_R}\left(\frac{\Delta\mu^4}{\omega_0^4} - 1\right)$$

DA-AH $C_{n+1}/C_n \propto 1$

DA-HO $C_{n+1}/C_n \propto \Delta\mu^2/\omega_0^2$

Anderson-Holstein $C_{n+1}/C_n \propto \Delta\mu/\omega_0$

Phys. Rev. B 82, 121414(R) (2010).

Thermoelectric Efficiency and Statistics

G. Verley, T. Willaert, C. Van den Broeck, and M. Esposito, Nat. Commun. 5, 4721 (2014).
G. Verley, T. Willaert, C. Van den Broeck, and M. Esposito, Phys. Rev. E 90, 052145 (2014).

Asymptotic form $P_t(\eta) \sim e^{-t\tilde{J}(\eta)}$

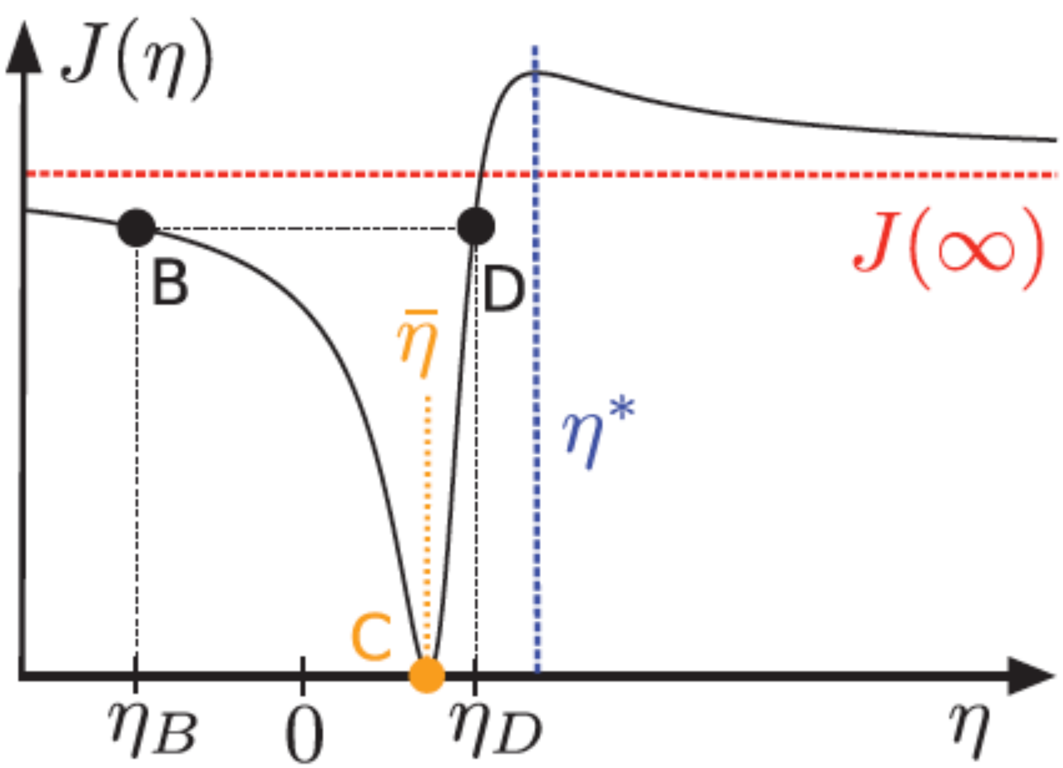
LDF $\tilde{J}(\eta) = -\min_{\lambda_w} \mathcal{G}(\lambda_w, \eta\,\eta_c\,\lambda_w)$

Analytical form in the Linear Response limit:

Expressed in terms of Onsager's coefficients

(Scaled LDF)

$$J_G(\eta) = \frac{1}{4}\frac{(\eta + \alpha^2 + \alpha d + \alpha d\eta)^2}{(1+\alpha^2+2\alpha d)(\eta^2+\alpha^2+2\alpha d\eta)}$$



$$d \equiv \frac{L_{pq}}{\sqrt{L_{pp}L_{qq}}}, \quad \alpha \equiv \frac{A_p\sqrt{L_{pp}}}{A_q\sqrt{L_{qq}}}$$

$$0 \le J_G(\eta) \le \frac{1}{4}$$

Bounded in the Gaussian limit

Efficiency Statistics for Time-reversal breaking system

Efficiency Statistics for Time-reversal breaking system

G. Benenti, K. Saito, G. Casati, PRL. 106, 230602 (2011).
K. Brandner, K. Saito, U. Seifert, PRL 110, 070603 (2013).

Linear response limit

$$P_t(\vec{I}) = \frac{t\sqrt{\det((\hat{M}^{-1})_{sym})}}{4\pi} \exp(-\frac{t}{4}\delta\vec{I}^T \cdot \hat{M}^{-1} \cdot \delta\vec{I})$$

⇩

$$\eta = \frac{-I_1 A_1}{I_2 A_2}$$

J.-H. Jiang, B. K. Agarwalla, D Segal, Phys. Rev. Lett. **115,** 040601 (2015)

$$J(\eta) \equiv \frac{\mathcal{G}(\eta)}{\bar{S}_{tot}}$$ ← (Scaled LDF)

$$\bar{S}_{tot} = \sum_i I_i A_i$$

$$= \frac{J(\eta_C)\left(\eta + \alpha^2 + \alpha q r + \alpha q \eta\right)^2}{(1 + \alpha^2 + \alpha q r + \alpha q)\left(\eta^2 + \alpha^2 + \alpha q \eta + \alpha q r \eta\right)}$$

$$J(\eta_C) \equiv \frac{4 - q^2(1+r)^2}{16(1-q^2 r)}$$ → Independent of Affinity parameter

Giuliano Benenti, Keiji Saito, and Giulio Casati

$$q \equiv \frac{L_{21}}{\sqrt{L_{22}L_{11}}}, \quad r \equiv \frac{L_{12}}{L_{21}}, \quad \alpha \equiv \frac{A_1\sqrt{L_{11}}}{A_2\sqrt{L_{22}}}$$

$$q \equiv \frac{L_{21}}{\sqrt{L_{22}L_{11}}}, \quad r \equiv \frac{L_{12}}{L_{21}}, \quad \alpha \equiv \frac{A_1\sqrt{L_{11}}}{A_2\sqrt{L_{22}}}$$

$$0 \leq J(\eta) \leq 1/4$$

$$J(\bar{\eta}) = 0 \quad \Rightarrow \quad \bar{\eta} = -\frac{\alpha(\alpha + qr)}{(\alpha q + 1)}$$

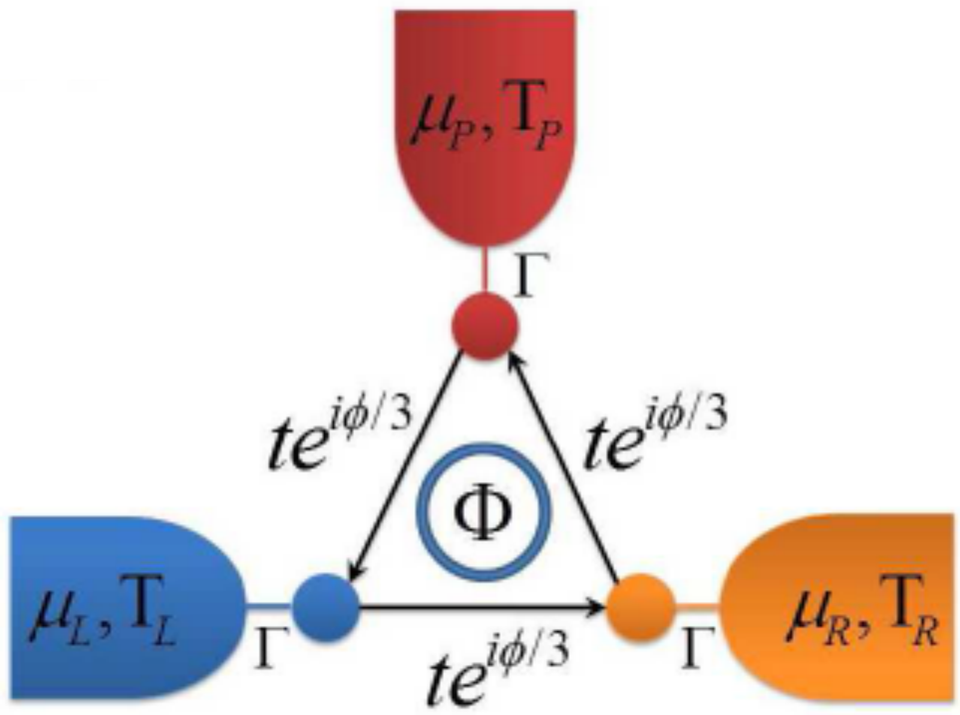
$$J(\eta^\star) = \frac{1}{4} \quad \Rightarrow \quad \eta^\star = 1 + \frac{q(r-1)(1 + \alpha q + \alpha q r + \alpha^2)}{q - qr - 2\alpha + q^2(1+r)\alpha}$$

Maximum average efficiency condition

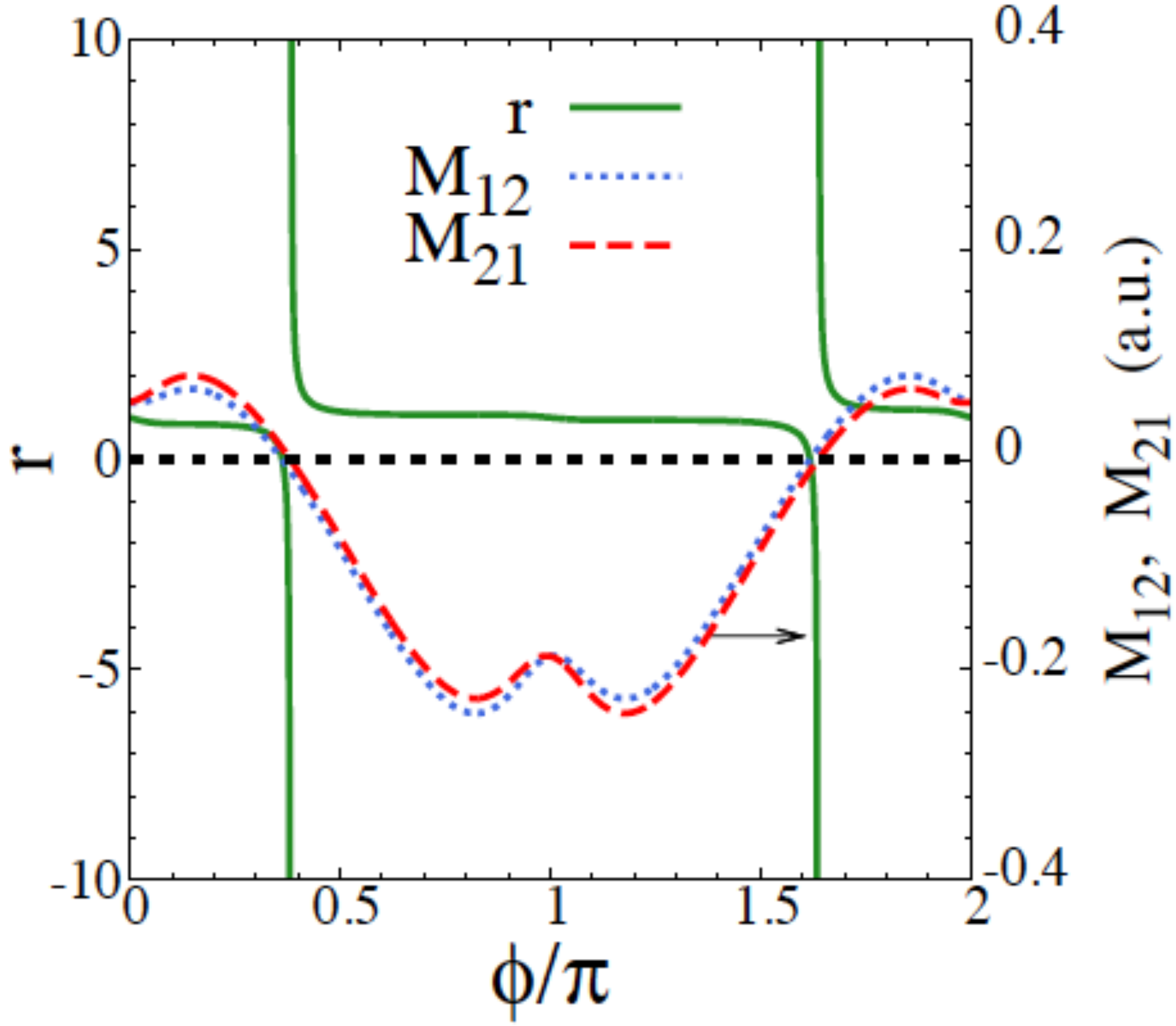
$$ZT = \frac{q^2 r}{1 - q^2 r}$$

$$\bar{\eta} = \bar{\eta}_{max} = r\frac{\sqrt{ZT+1}-1}{\sqrt{ZT+1}+1} = r\left(\frac{1-\sqrt{1-q^2r}}{1+\sqrt{1-q^2r}}\right)$$

$$\eta^\star = r$$



Triple quantum dot thermoelectric model



Onsager coefficients

$E_1 = 0.2$, $E_2 = -0.2$, $E_3 = 1$, $\Gamma = 0.5$, and $t = -1$

J.-H. Jiang, B. K. Agarwalla, D Segal, Phys. Rev. Lett. **115,** 040601 (2015)

K. Brandner, K. Saito, and U. Seifert, Phys. Rev. Lett. 110, 070603 (2013).

Efficiency fluctuation at maximum average output power

$$\bar{\eta}(W_{\max}) = \frac{rZT}{2(ZT+2)} = \frac{q^2 r^2}{4 - 2q^2 r}$$

$$\bar{\eta}_{\text{bound}}(W_{\max}) = \frac{r^2}{1+r^2}$$

$$\eta^\star = r\left(\frac{4 - 3q^2 r - q^2 r^2}{4 - 2q^2 r - 2q^2 r^2}\right)$$

Time-reversal operation

$$q \equiv \frac{L_{21}}{\sqrt{L_{22}L_{11}}}, \quad r \equiv \frac{L_{12}}{L_{21}}, \quad \alpha \equiv \frac{A_1\sqrt{L_{11}}}{A_2\sqrt{L_{22}}}$$

$$r(-\phi) \to \frac{1}{r}$$

$$q(-\phi) \to qr$$

$$J(\eta) - \tilde{J}(\eta) = \frac{J(\eta_C)}{1+\alpha^2+\alpha qr+\alpha q}\frac{\alpha^2 q^2(r^2-1)(1-\eta^2)+2(\alpha^2+\eta)\alpha q(r-1)(1-\eta)}{\alpha^2+\alpha q\eta+\alpha qr\eta+\eta^2}$$

Summary:

- We focused on donor-acceptor junction in which electron transfer is assisted by a particular mode, harmonic or anharmonic.

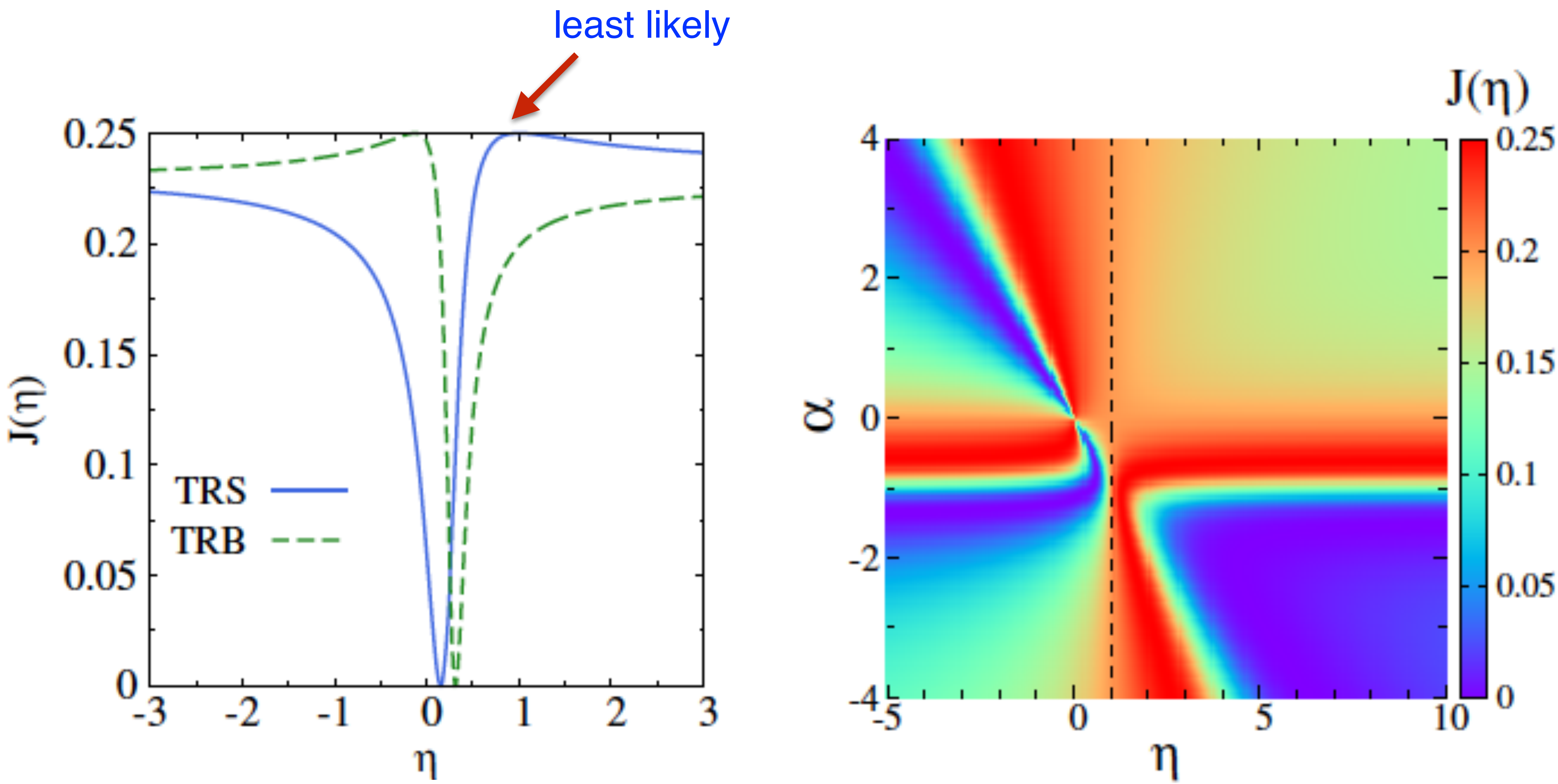
- Charge and energy currents are sensitive to the nature of the modes while S, ZT and average efficiency are insensitive.

- It can also be shown that for n-state truncated HO would provide same figure of merit.

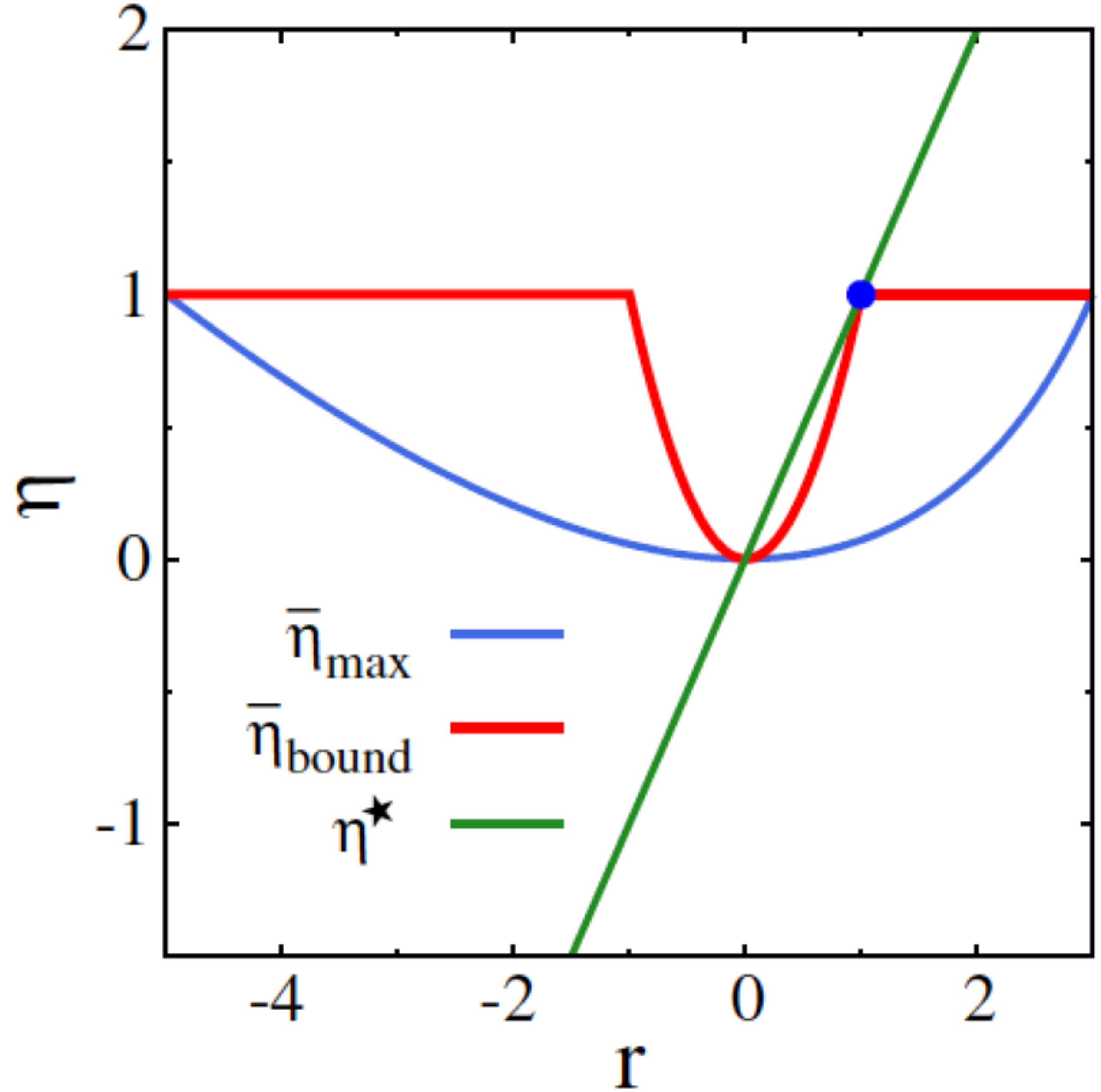
- Efficiency statistics for time-reversal breaking system is studied in the linear response limit,

- Least likely efficiency depends on asymmetry coefficient in the maximum average efficiency condition.

Thank You


least likely
J(η)
η
TRS
TRB
0.25
0.2
0.15
0.1
0.05
0
-3
-2
-1
0
1
2
3
J(η)
α
η
4
2
0
-2
-4
-5
0
5
10
0.25
0.2
0.15
0.1
0.05
0

Maximum average efficiency condition



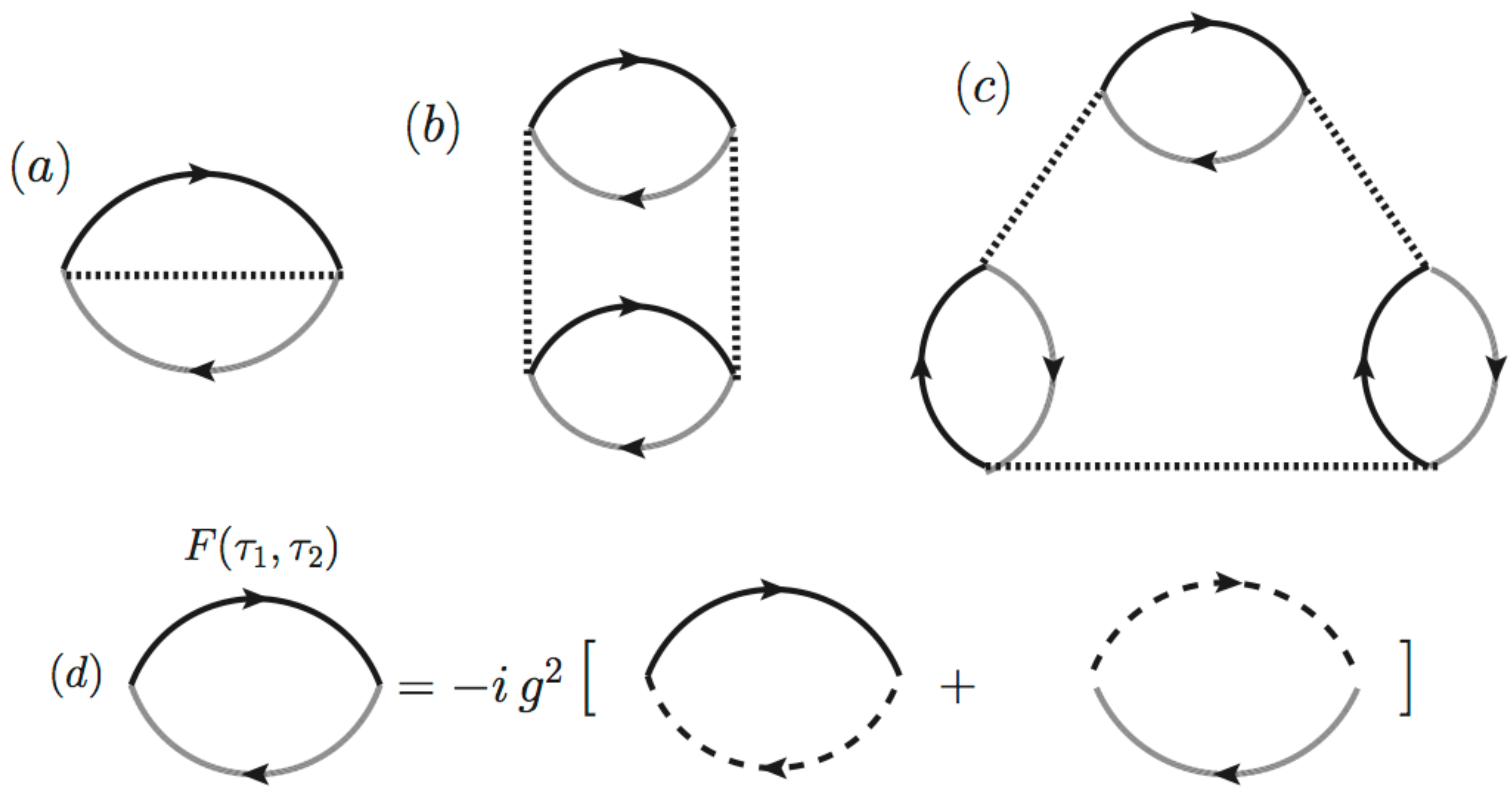
$$\bar{\eta}_{max} = r\,\frac{\sqrt{ZT+1}-1}{\sqrt{ZT+1}+1}$$

$$\bar{\eta}_{bound} = \min\{r^2, 1\}$$

$$\eta^{\star} = r$$

NEGF

$$\mathcal{G}(\lambda_e, \lambda_p) = \ln \mathcal{Z}_{\mathrm{RPA}}(\lambda_e, \lambda_p)$$
$$= -\frac{1}{2} \mathrm{Tr}_\tau \ \ln \left[I - D_0(\tau, \tau') \tilde{F}(\tau', \tau) \right]$$



Ring type Feynman diagrams in contour time. Diagrams (a) second-order (b) fourth-order and (c) sixth-order in the electron-phonon coupling. The dotted line is the phonon Green's function. Closed loops are the electron-hole propagator which is a sum of the two diagrams (d) consisting of free electron left (solid) and right (dashed) Green's functions.

Thermoelectric Efficiency and Statistics

Fluctuation symmetry

$$\mathcal{G}(\lambda_e, \lambda_p) = \mathcal{G}(-\lambda_e + i(\beta_L - \beta_R), -\lambda_p + i(\beta_R \mu_R - \beta_L \mu_L))$$

Energy-flux *Particle-flux*

Thermoelectric device $T_L > T_R, \ \mu_L < \mu_R$

Power Output ⇨ $-\dot{W} \equiv (\mu_L - \mu_R)\langle I_p \rangle$

Heat input ⇨ $\dot{Q} \equiv \langle I_q \rangle = \langle I_e \rangle - \mu_R \langle I_p \rangle$

$$\mathcal{G}(\lambda_w, \lambda_q) = \mathcal{G}(-\lambda_w + i\beta_L, -\lambda_q + i(\beta_L - \beta_R))$$

$$\left\langle \exp\left[-\frac{w}{T_L} - \left(\frac{1}{T_L} - \frac{1}{T_R}\right) q \right] \right\rangle = 1$$

Jensen's inequality $\eta \leq \eta_c$ Upper bound of efficiency

Asymptotic form $P_t(\eta) \sim e^{-t\tilde{J}(\eta)}$

LDF $\tilde{J}(\eta) = -\min_{\lambda_w} \mathcal{G}(\lambda_w, \eta\,\eta_c\,\lambda_w)$

Analytical form in the Linear Response limit:

Expressed in terms of Onsager's coefficients

$$J_G(\eta) = \frac{1}{4}\frac{(\eta + \alpha^2 + \alpha d + \alpha d\eta)^2}{(1 + \alpha^2 + 2\alpha d)(\eta^2 + \alpha^2 + 2\alpha d\eta)}$$

$$d \equiv \frac{L_{pq}}{\sqrt{L_{pp}L_{qq}}}, \qquad \alpha \equiv \frac{A_p\sqrt{L_{pp}}}{A_q\sqrt{L_{qq}}}$$

$$0 \leq J_G(\eta) \leq \frac{1}{4}$$

Bounded in the Gaussian limit

G. Verley, T. Willaert, C. Van den Broeck, and M. Esposito, Nat. Commun. 5, 4721 (2014).
G. Verley, T. Willaert, C. Van den Broeck, and M. Esposito, Phys. Rev. E 90, 052145 (2014).