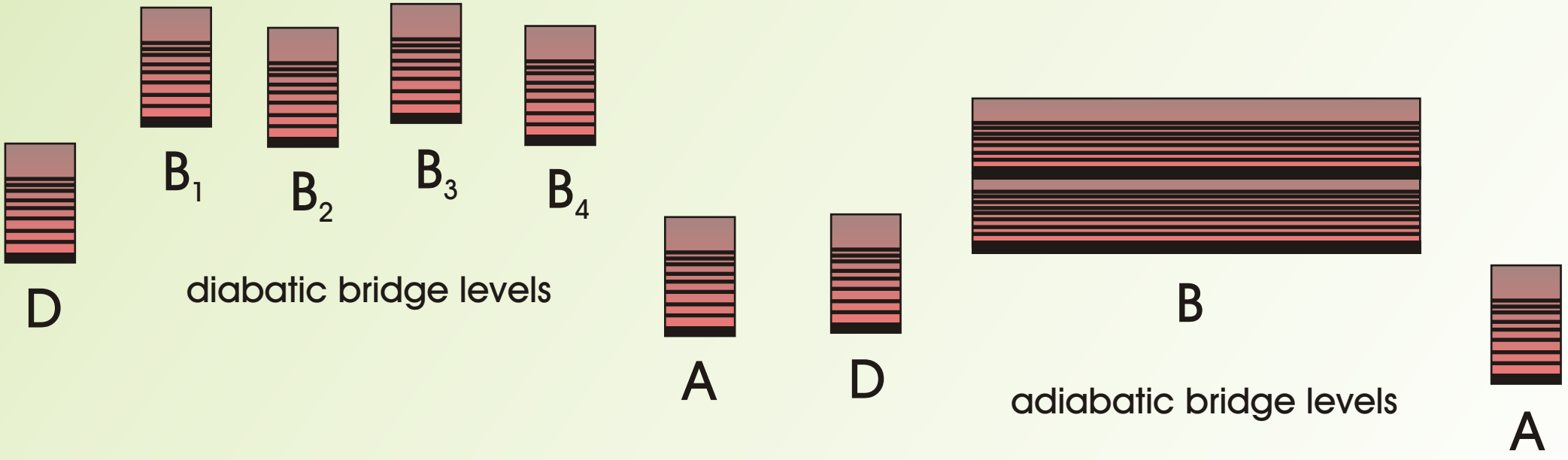
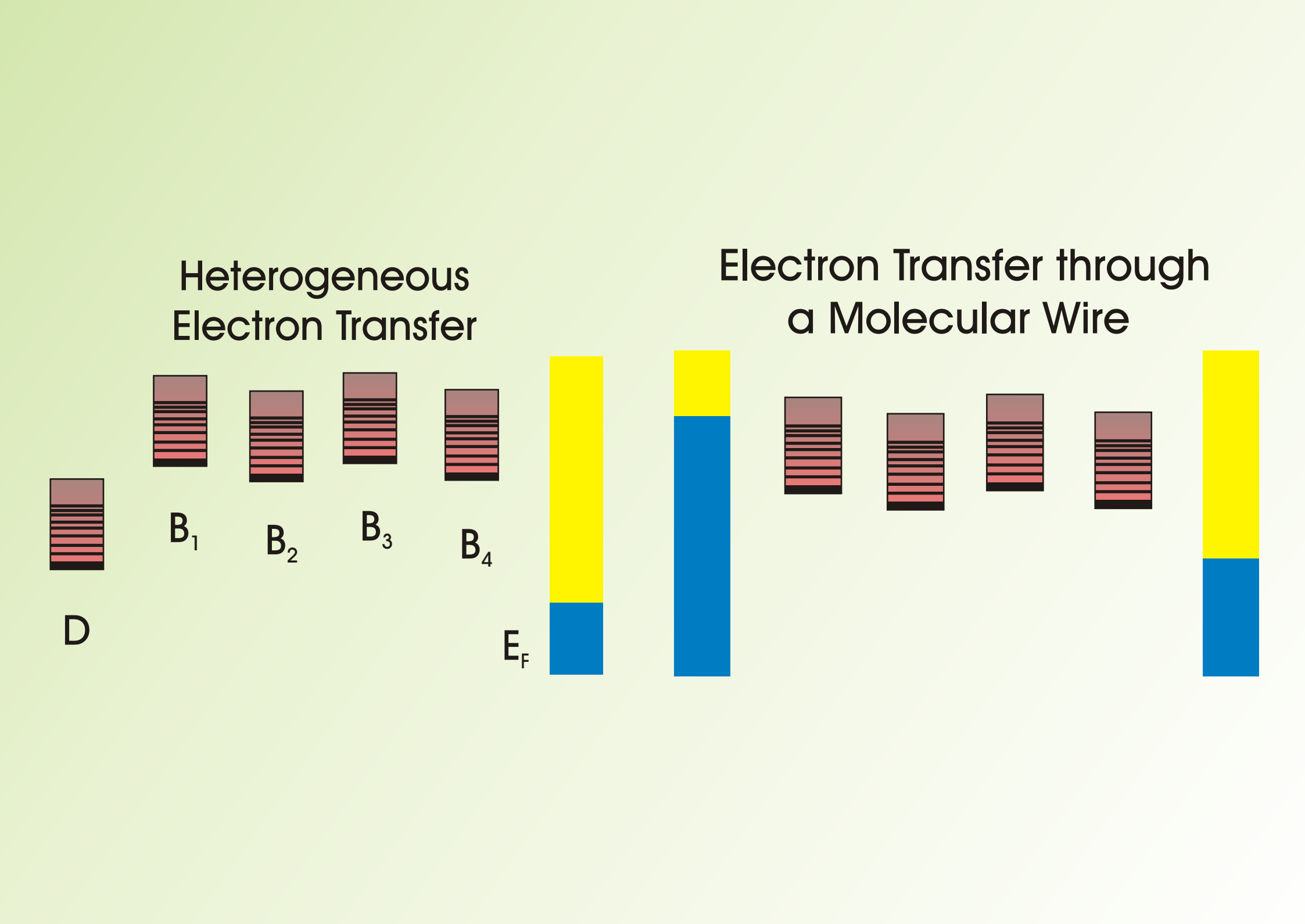
Unified Theory of Bridge Mediated Electron Transfer

Volkhard May

Institute of Physics
Humboldt-University
at Berlin

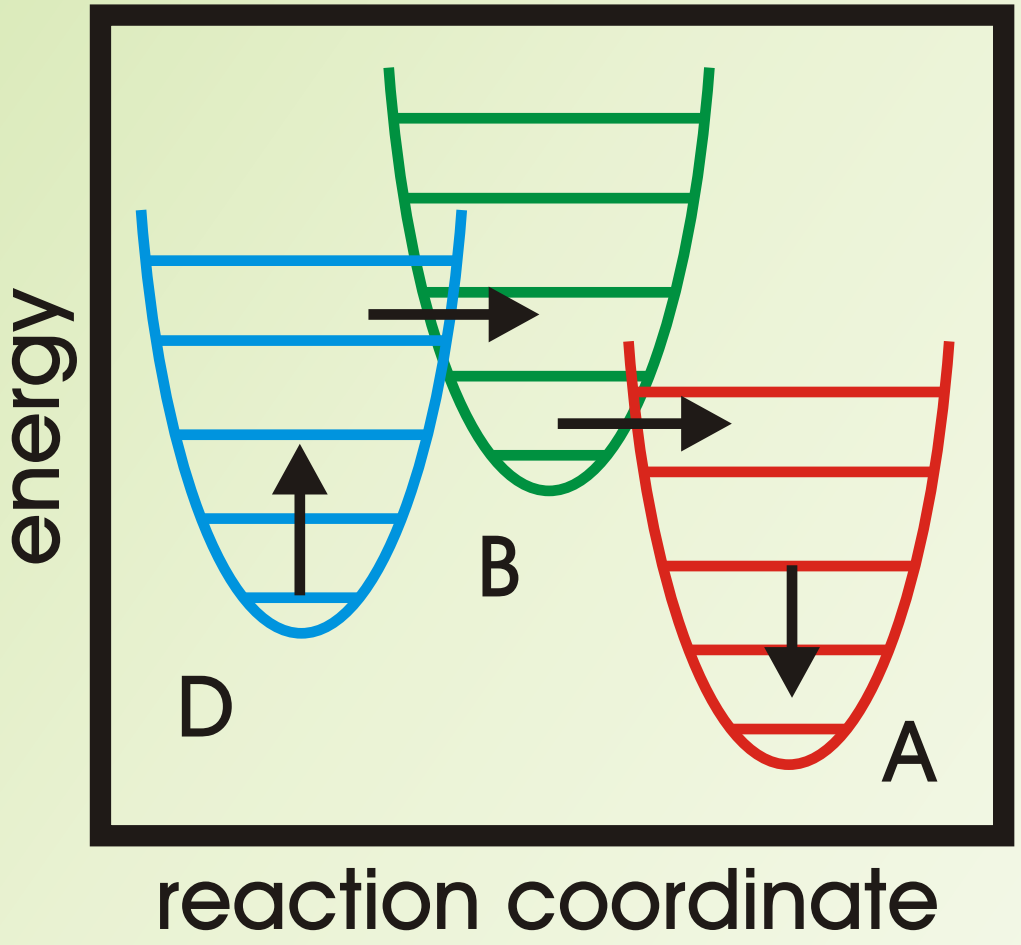
Bridge Mediated Donor-Acceptor Electron Transfer




Heterogeneous
Electron Transfer
D
B1
B2
B3
B4
EF
Electron Transfer through
a Molecular Wire

Basic Theoretical Description of Electron Transfer

Energetics



Dynamics

Electron-Vibrational Density Matrix

$$r_{m\{M\},n\{N\}}$$

ET on a fs-timescale

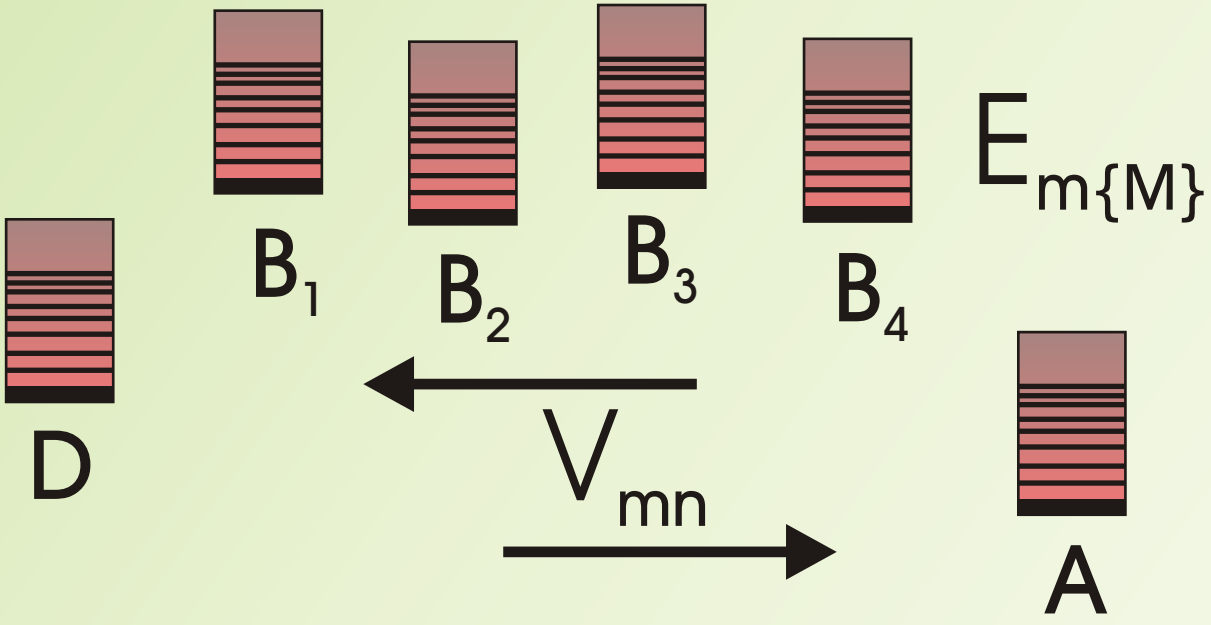
electron and vibrational coherences

ET on a ns-timescale

electron populations

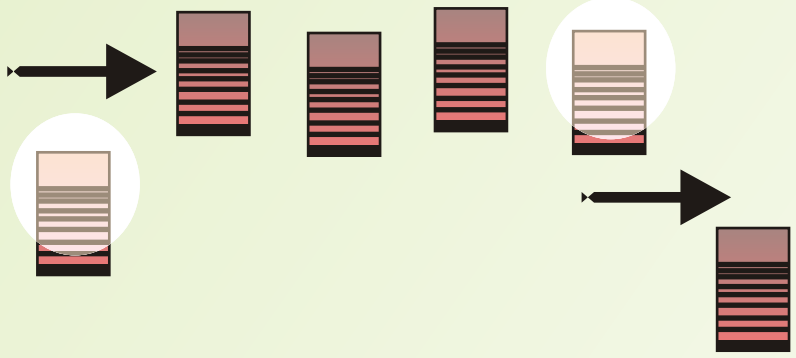
Electron Transfer in Donor-Acceptor Complexes

Standard Scheme of Bridge Mediated Nonadiabatic Electron Transfer

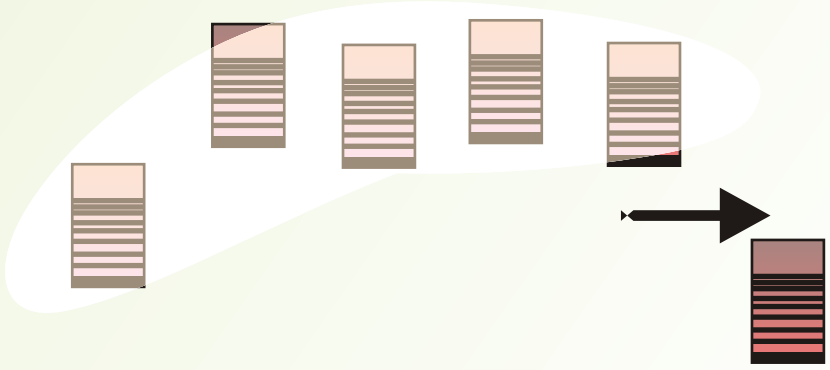


- diabatic electronic states
- electronic interstate coupling
- finite lifetime of vibrational levels

Sequential ET



Superexchange ET



Rate Equations for State Populations

$$\frac{\partial}{\partial t}P_m(t) = -\sum_n \left(k_{m\to n}P_m(t) - k_{n\to m}P_n(t)\right)$$

Interstate Coupling Expansion

$$k_{m\to n} = k^{(2)}_{m\to n} + k^{(4)}_{m\to n} + k^{(6)}_{m\to n} + \ldots$$

N´th-order expression

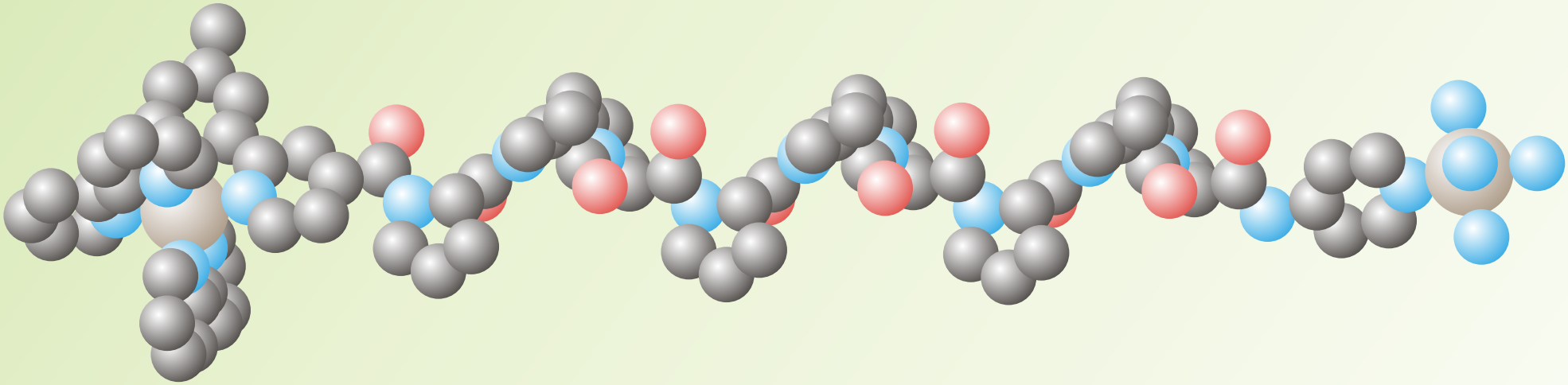
$$k^{(N)}_{m\to n} = -i\mathrm{tr}_{\mathrm{el-vib}}\{|\varphi_n\rangle\langle\varphi_n|\ \mathcal{V}\cdot\mathcal{G}(\omega=0)\mathcal{V}\cdot\mathcal{G}(\omega=0)\mathcal{V}\cdot\ldots\cdot\mathcal{G}(\omega=0)\mathcal{V}\cdot\hat{R}_m|\varphi_m\rangle\langle\varphi_m|\}$$

motion within a given electronic state

coupling between different electronic states

vibrational equilibrium in electronic state m

Polyproline Mediated Electron Transfer



Experiments:
Isied, Ogawa, and Wishart, Chem. Rev. 92, 381 (1992).

Theory:
Petrov, Shevchenko, Teslenko, and May, J. Chem. Phys. 115, 7107 (2001).
Petrov and May, J. Phys. Chem. A 105, 10176 (2001).
Petrov, Shevchenko, and May, Chem. Phys. 288, 269 (2003).
Bade, Petrov, and May, (in press).

Rate Expressions for Nonadiabatic ET

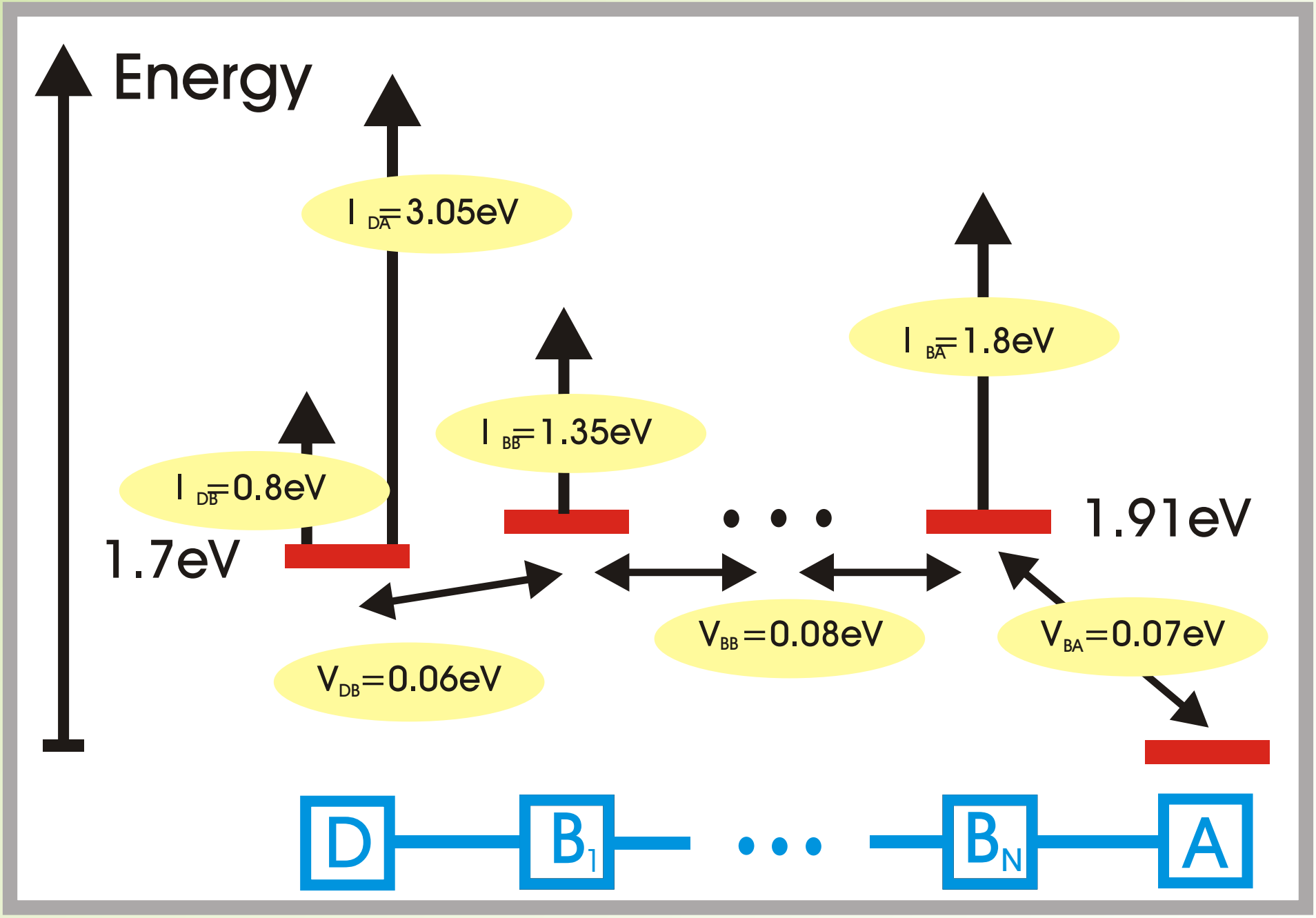
$$k_{m\to n}^{(\mathrm{seq})} = \frac{2\pi}{\hbar}|V_{mn}|^2 \mathcal{D}_{mn}(\Delta E_{mn}) \qquad k_{D\to A}^{(\mathrm{super})} = \frac{2\pi}{\hbar}|T_{DA}|^2 \mathcal{D}_{DA}(\Delta E_{DA})$$

Franck-Condon weighted and thermally averaged combined DOS: high-temperature limit

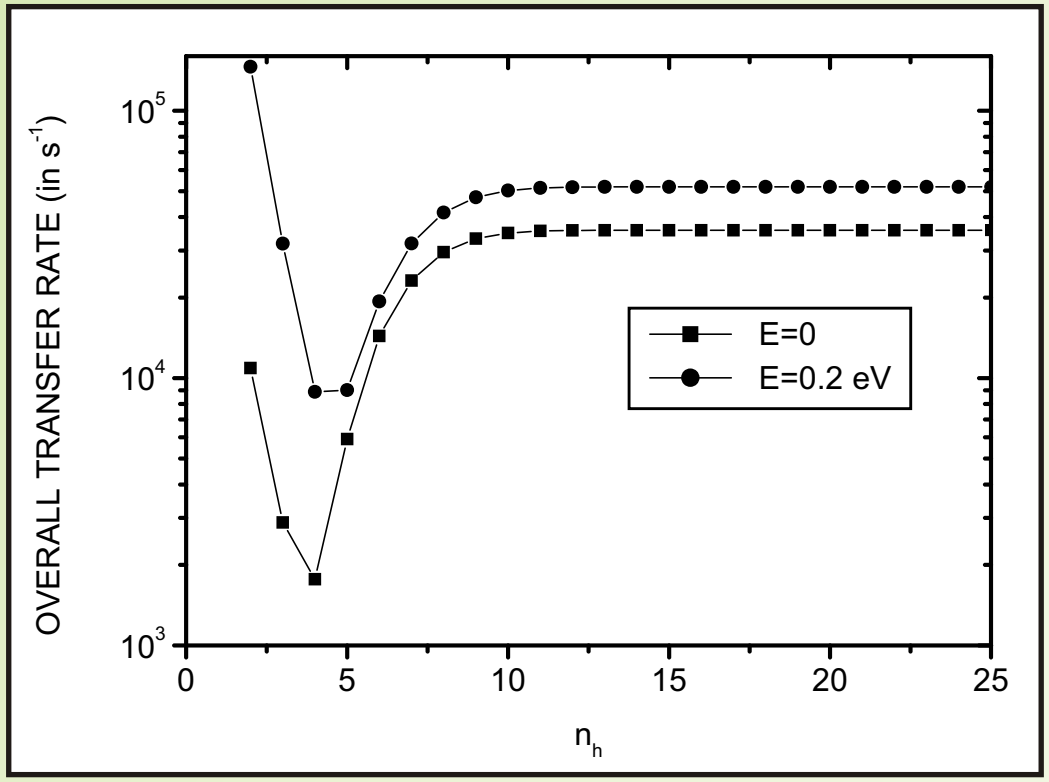
$$\mathcal{D}_{mn}(\Delta E_{mn}) = \frac{1}{\sqrt{4\pi\lambda_{mn}k_B T}} \exp\{-\frac{(\Delta E_{mn}-\lambda_{mn})^2}{4\lambda_{mn}k_{\mathrm{B}}T}\}$$

transfer integral of the superexchange mechanism

$$T_{DA} = \frac{V_{D,1}V_{1,2}\ldots V_{N-1,N}V_{N,A}}{\sqrt{\Delta E_{1D}\Delta E_{1A}\Delta E_{2D}\Delta E_{2A}\ldots\Delta E_{ND}\Delta E_{NA}}}$$


Energy
I DA=3.05eV
I DB=0.8eV
I BB=1.35eV
I BA=1.8eV
1.7eV
1.91eV
V DB=0.06eV
V BB=0.08eV
V BA=0.07eV
D
B1
BN
A

Thermally Activated versus Superexchange ET



$$|V_{mn}|/h > 1/t_{rel}$$

I~1eV, V = 0.02eV,
DE_{DB} =1.64eV, V_B=0.72eV

$$k_{\mathrm{ET}} = k_{\mathrm{ET}}^{(\mathrm{fw})} + k_{\mathrm{ET}}^{(\mathrm{bw})} = \{1 + e^{-\Delta E/k_{\mathrm{B}}T}\}\ \{k_{D\to A}^{(\mathrm{super})} + \frac{k_{D\to B}^{(\mathrm{act})} k_{B\to A}^{(\mathrm{act})}}{k_{B\to D}^{(\mathrm{act})} + k_{B\to A}^{(\mathrm{act})}}\}$$

$$k_{\mathrm{ET}}^{(\mathrm{fw})} \approx k_{\mathrm{ref}}^{(\mathrm{sup})} e^{-\alpha(N_{\mathrm{B}}-1)} + \frac{2k_{\mathrm{ref}}^{(\mathrm{sup})}}{N_{\mathrm{B}}+1} \sin^2[\frac{\pi}{N_{\mathrm{B}}+1}]\ e^{2\xi \cos[\frac{\pi}{N_{\mathrm{B}}+1}]}$$

Effects of Structural and Energetic Disorder

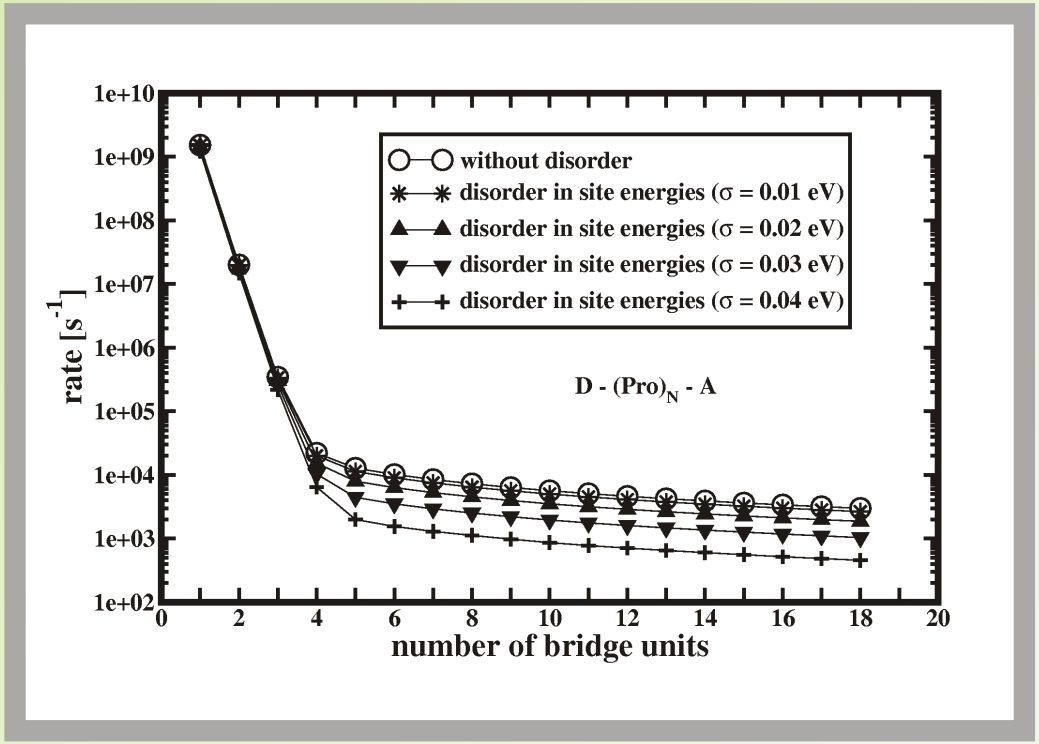
disorder (ensemble) averaged donor population

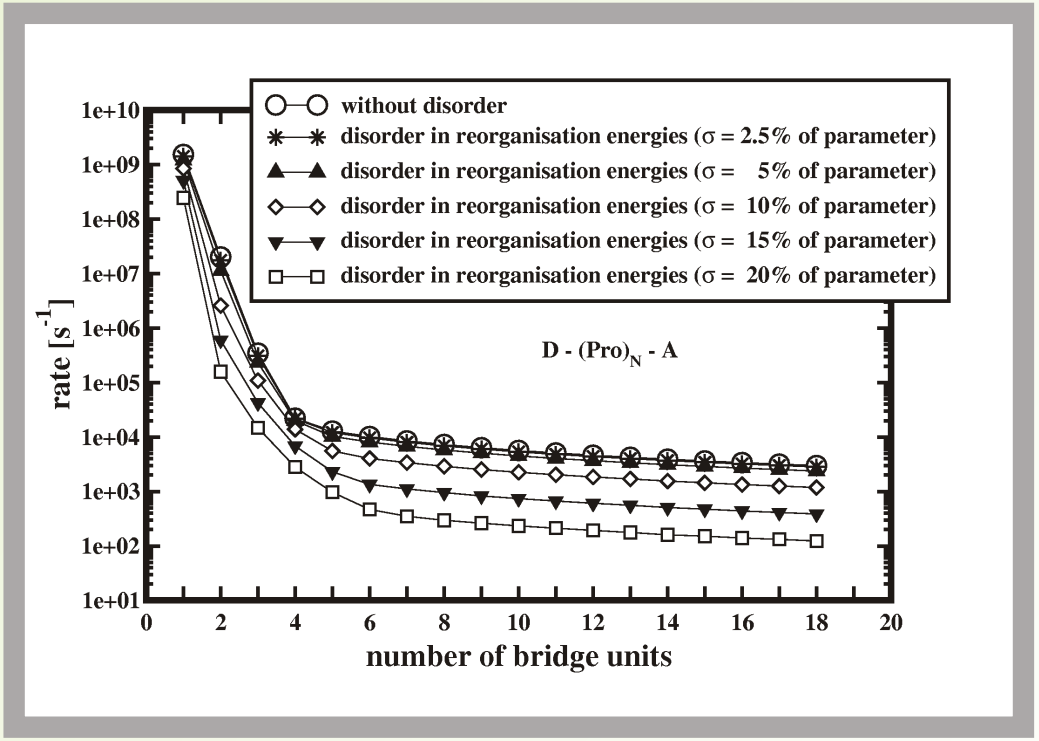
$$\langle P_D(t)\rangle = \langle P_D(\infty)\rangle + (1 - \langle P_D(\infty)\rangle)\exp(-k_{\mathrm{ET}}^{(\mathrm{eff})}t)$$

effective electron transfer rate

$$\frac{1}{k_{\mathrm{ET}}^{(\mathrm{eff})}} = \int_0^\infty dt\, \frac{\langle P_D(t)\rangle - \langle P_D(\infty)\rangle}{1 - \langle P_D(\infty)\rangle}$$

Influence of Static Disorder





Acknowledgements

E. G. Petrov, Ye. V. Shevchenko,
and Ya. R. Zelinsky
(Bogolyubov Institute
for Theoretical Physics, Kiev)

Volkswagen-Stiftung
(Germany)