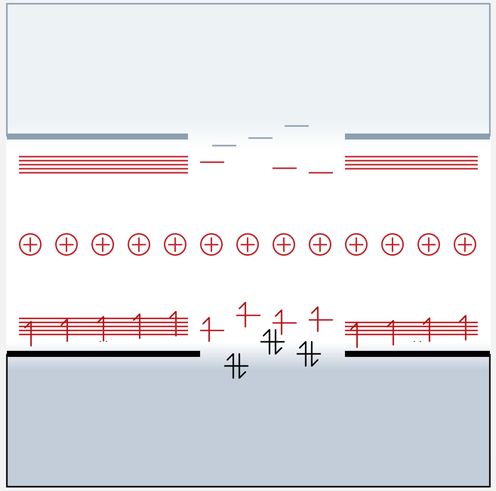
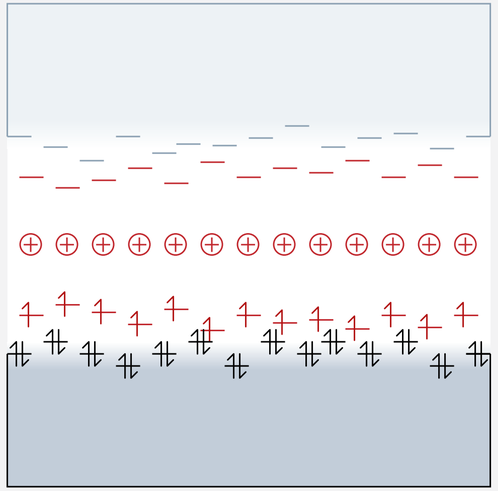
6.3 Polaronic Transport

Incoherent Transport in Disordered Organic Solids

- static disorder slow on the time scale of charge transport, results in energetic heterogeneity
- dynamic disorder causes fluctuations of coupling constant *J* on the order of *J* itself



polycrystalline solid



amorphous solid

- **premises for band transport usually not fulfilled in partially ordered organic solids**
- **even in crystalline solids, molecular motions destroy translational symmetry**

Criteria for Polaronic Transport and Disorder-Controlled Transport

- **incoherent transport prevails if any energy present due to dynamic disorder and/or static disorder is larger than the interaction energy between neighboring sites**

$$H_1 \ll H_2, H_3, H_4, H_5$$

- **charge carriers become localized at individual sites and proceed by a sequence of non-coherent transfer events**

- **polaronic transport if dynamic disorder dominates in an otherwise highly ordered crystal**

$$H_1 \ll H_2, H_3, \quad H_4 = H_5 = 0$$

  - polarons are charged molecules with a changed geometry & lattice distortion
  - “self-localization” due to intramolecular / intermolecular geometric changes
  - transport takes place via thermal activated inter-site hopping

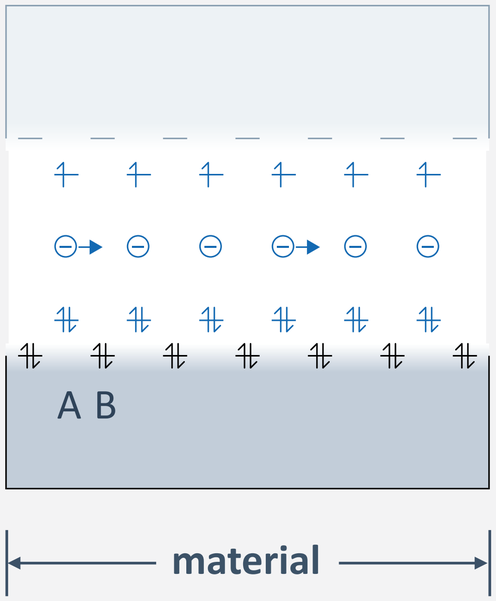
- **disorder-controlled if static disorder dominates in non-crystalline systems**

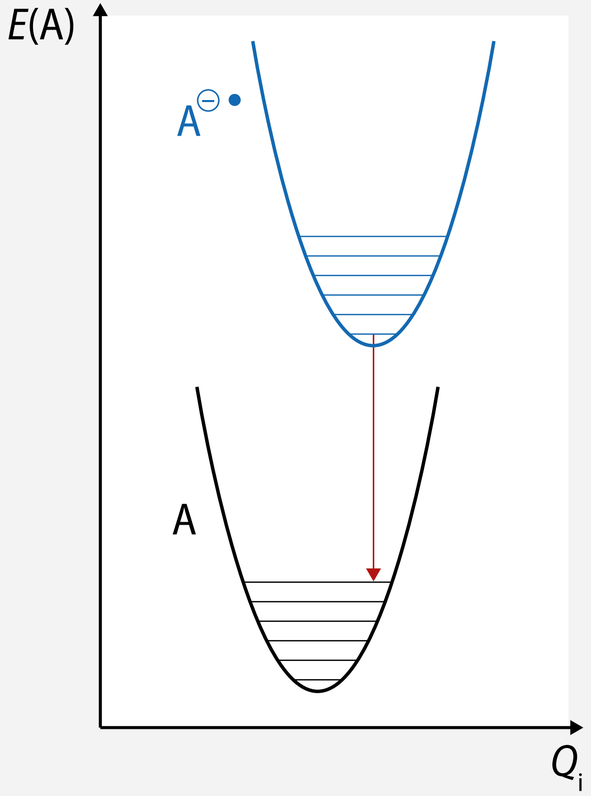
$$H_1 \ll H_4, H_5, \quad H_2 = H_3 = 0$$

- **transport is random walk by “hopping” between neighboring sites with different energies**

Charge Transfer from One Molecule to a Neighbor

- all site energies are (in first approximation) equal, but fluctuation of transfer integral
- charge carriers localized due to intramolecular and intermolecular vibrations





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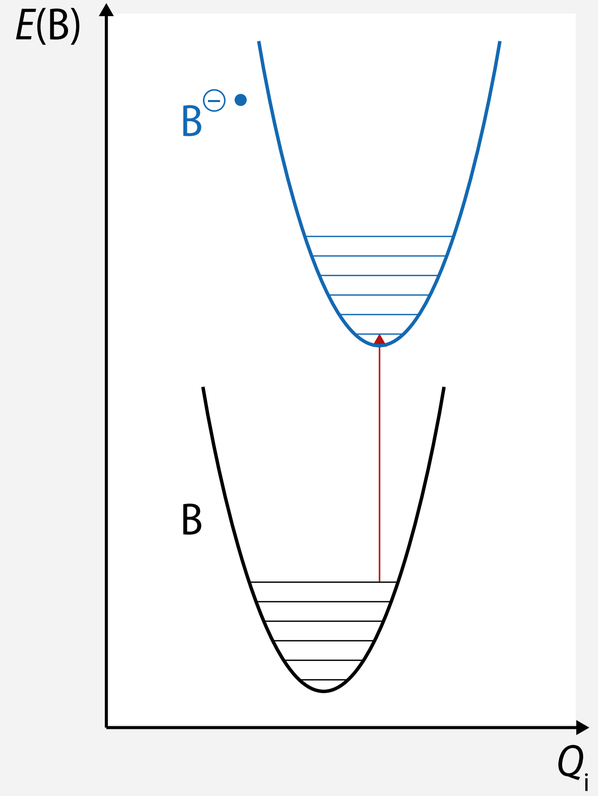
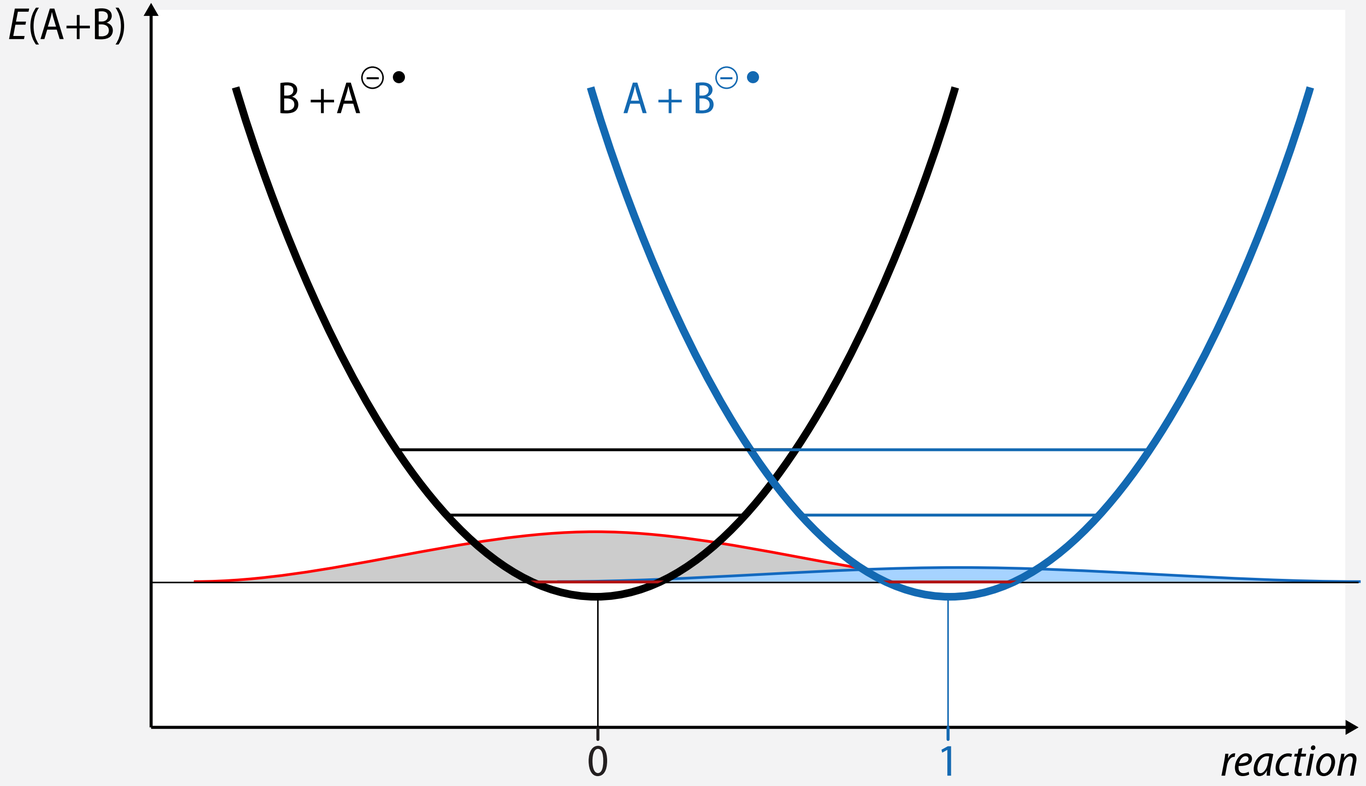


- **charge transport takes place by an incoherent sequence of charge transfer events**
- **transfer step involves simultaneous excitation of a molecule and relaxation of a neighbor**

Charge Transport by Quantum-Mechanical Tunneling

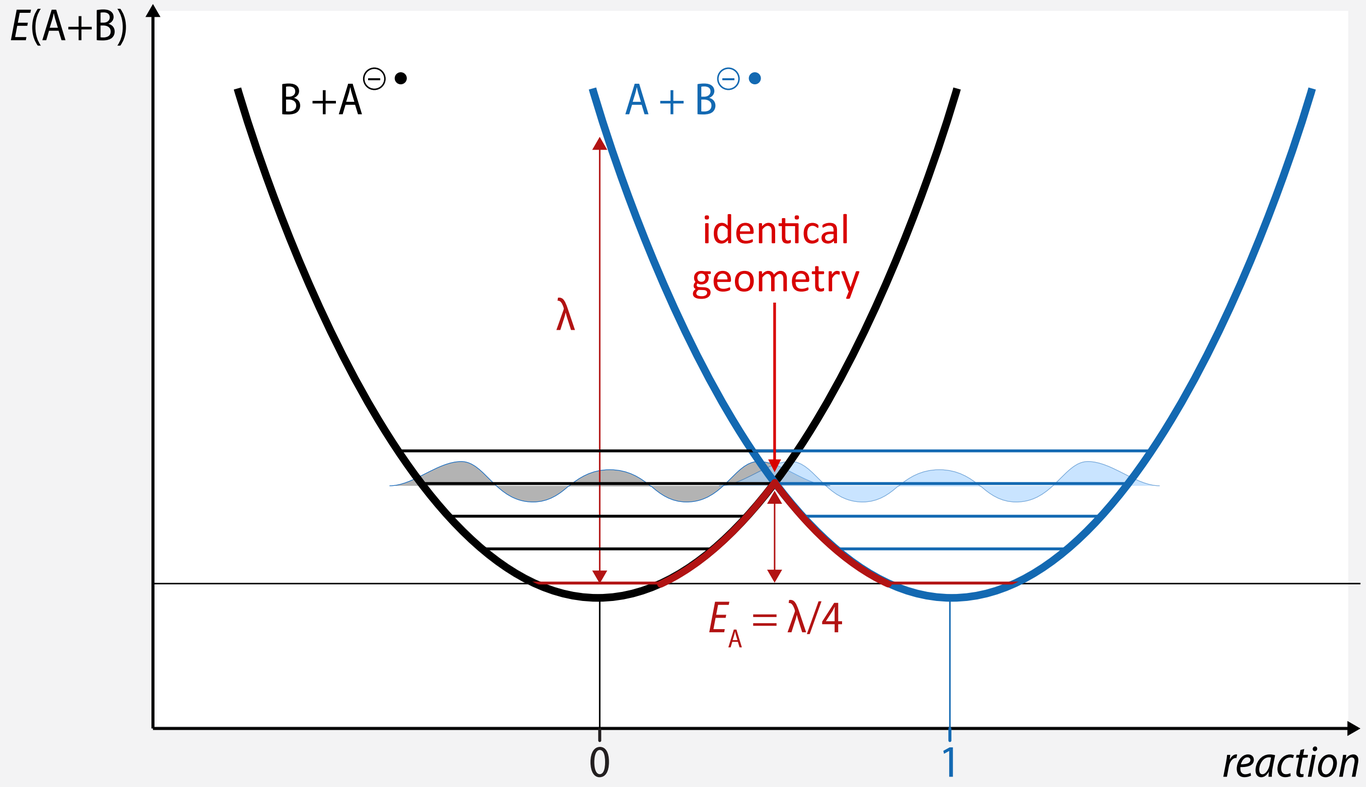
- finite potential well results in certain probability to find electron outside the well
- tunneling to nearby molecules if energy levels identical (required for “resonant exchange”)



- **probability for tunneling decreases exponentially with distance**
- **process itself has no temperature dependence, but one observes $\mu \propto T^{-n}$ due to dynamic disorder**

A Single Thermally Activated Hopping Step

- thermally activated hopping, for a given reorganization energy $\lambda = \lambda_{inner} + \lambda_{outer}$
- polaron binding energy E_{pol}: $\lambda_{inner} \approx \lambda_A + \lambda_B = 2E_{pol}$



- **reorganization energy confines charge to an energy site (molecule or group of molecules)**
- **polaron is called “self-localized charge carrier”, trapped in its own lattice distortion**

Temperature Dependence of Macroscopic Polaronic Transport

- **Holstein model with transfer rate k_t for weak coupling J (in the rate law $r_T = k_T [A]$ for transfer)**

$$k_T = \frac{J^2}{\hbar} \sqrt{\frac{\pi}{\lambda k T}} \, e^{-\frac{\lambda}{4kT}} \quad \text{or} \quad k_T = \frac{J^2}{\hbar} \sqrt{\frac{4\pi}{E_A k T}} \, e^{-\frac{E_A}{kT}}$$

  - no transfer in case of coupling constant $J = 0$
  - for small J, model corresponds to Marcus theory for charge transfer

- **charge carrier mobility μ according to Einstein diffusion law**

$$\mu = \frac{eD}{k_B T}$$ with diffusion coefficient $$D = \frac{1}{2n} k_T a^2$$, dimensionality n, lattice constant a

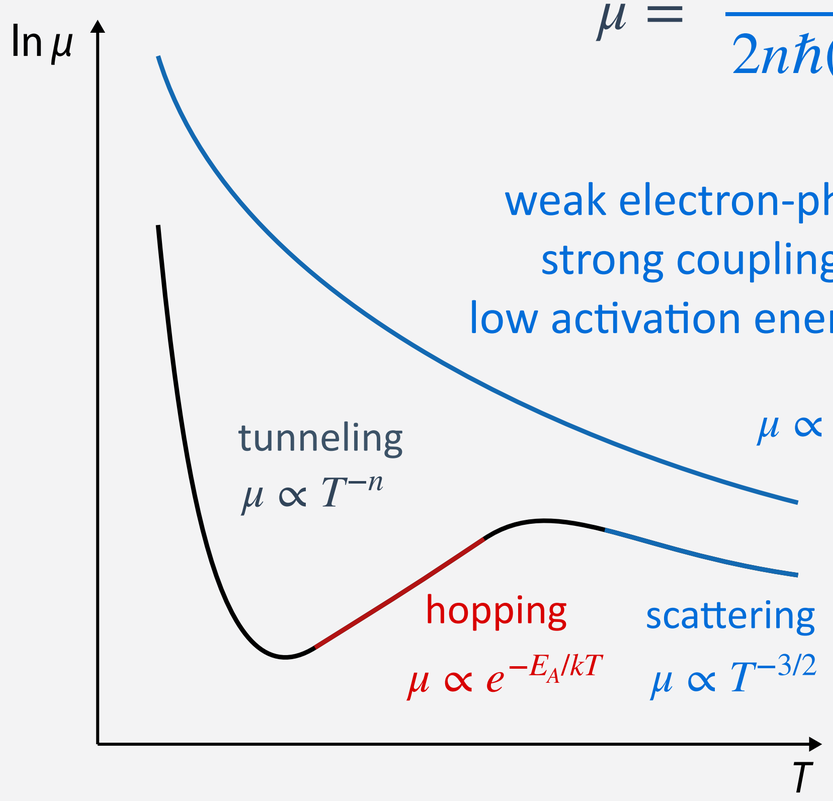
$$\mu = \frac{e a^2 J^2}{2n\hbar (kT)^{3/2}} \sqrt{\frac{\pi}{\lambda}} \, e^{-\frac{\lambda}{4kT}}$$

- **well-defined thermally activated hopping rate determines average mobility**

Temperature Dependence of Charge Transport

- charge mobility μ can be described by different regimes:

$$\mu = \frac{ea^2J^2}{2n\hbar(kT)^{3/2}}\sqrt{\frac{\pi}{\lambda}}\, e^{-\frac{\lambda}{4kT}}$$



weak electron-phonon coupling
strong coupling J > 200 meV **band transport**
low activation energy E_A < 100 meV

strong electron-phonon coupling
weak coupling J < 50 meV **polaron transport**
activation energy E_A ≥ 100 meV

- **temperature dependence depends on reorganization energy (molecular rigidity) and coupling constant (size of the π-system, packing)**