6

Charge Transport in Organic Materials

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6.1 Overview of Transport Regimes

Mobility and Conductivity

- mobility μ is the proportionality constant between the electric field F charge velocity v

$$v = \mu F$$

- conductivity σ is defined via Ohm's law, with current density j

$$j = \sigma F$$

from which one obtains, with hole density p and electron density n

$$j = q(nv_e + pv_h)$$

$$\sigma = q(n\mu_e + p\mu_h)$$

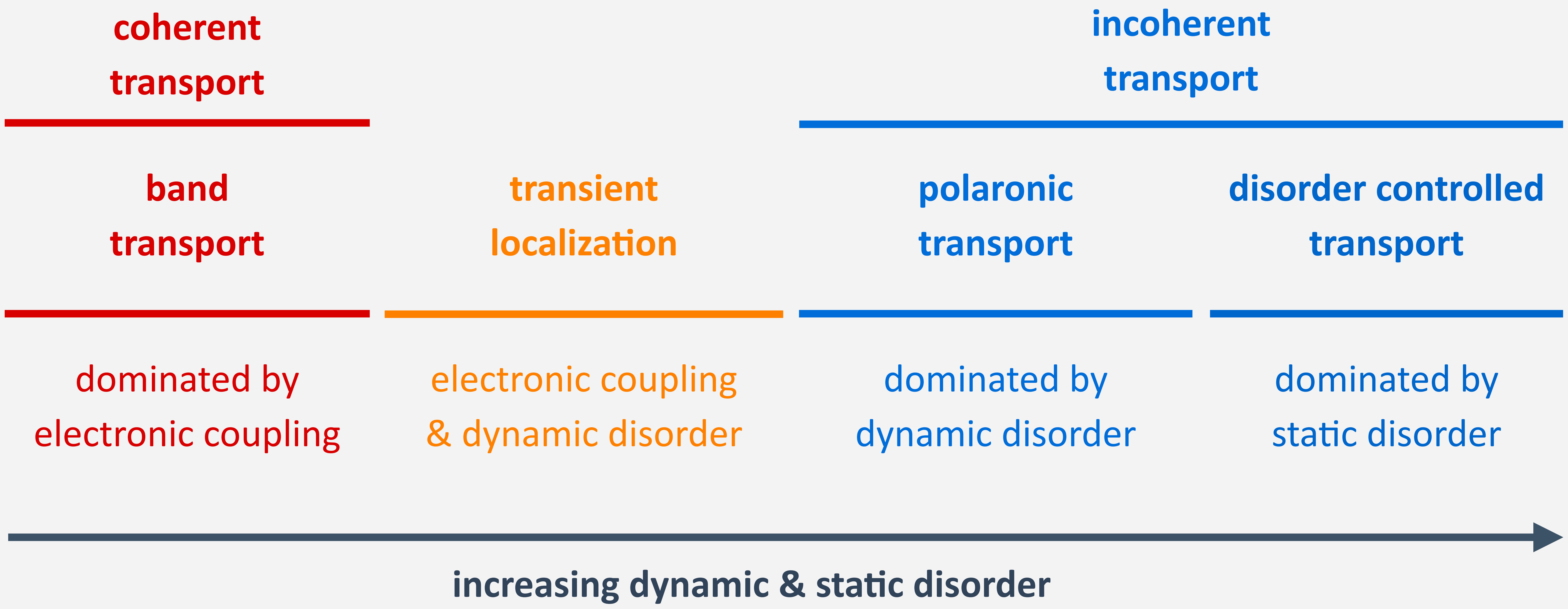
- charge mobility is also the proportionality constant between (charge) diffusion constant D and the thermal energy (Einstein–Smoluchowski relationship)

$$D = \frac{\mu}{q}\, k_B T$$

Inorganic vs Organic Materials

- **inorganic (semi)conductors**
  - electric field screening due to large dielectric constants ($\varepsilon_r > 10$)
  - weak electron-phonon coupling
  - large charge free mean paths $\lambda \gg a$ (lattice constant)
  - large mean free time τ between scattering events
  - high mobilities $\mu_{\text{inorg}} = 10\text{–}1000\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ (amorphous Si $1\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$)
- **organic (semi)conductors**
  - poor electric field screening due to small dielectric constants ($\varepsilon_r \approx 3$)
  - strong electron-phonon (vibrational) coupling
  - charge free mean path on the same order of lattice constant $\lambda \approx a$
  - $\mu_{\text{org}} = 1\text{–}40\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ for band transport or transient localization
  - $\mu_{\text{org}} = 10^{-3}\text{–}1\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ for incoherent transport
- **organic (semi)conductors are on the borderline of *coherent transport* through band-like states and *incoherent transport* through randomized charge transfer steps of charges localized on molecular sites due to polarization of the local orbital environment (polarons) and disorder**

Charge Transport Regimes in Organic Semiconductors



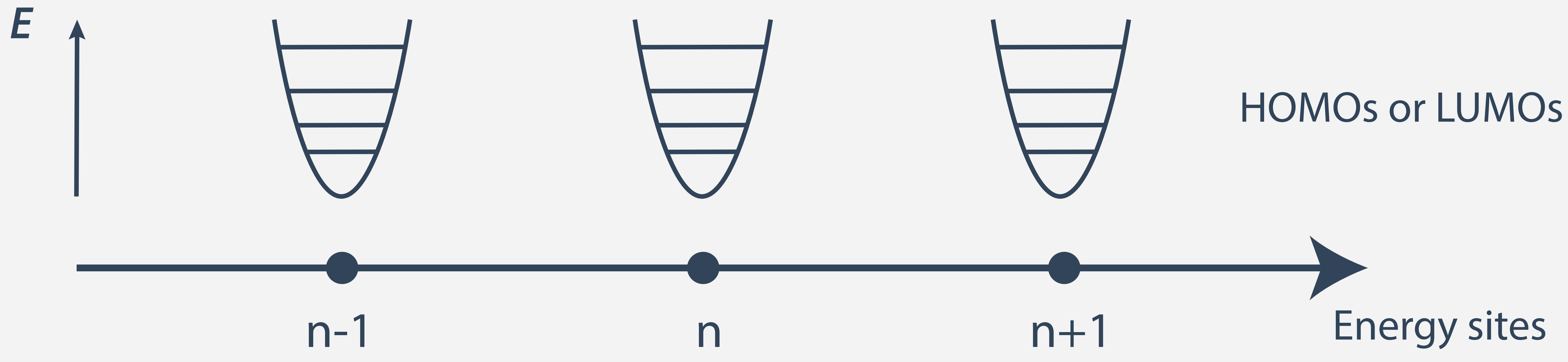
coherent transport		**incoherent transport**	
band transport	**transient localization**	**polaronic transport**	**disorder controlled transport**
dominated by electronic coupling	electronic coupling & dynamic disorder	dominated by dynamic disorder	dominated by static disorder

increasing dynamic & static disorder

- **most transport models have initially been developed for inorganic semiconductors**
- **organic semiconductors are *molecular* materials and heterogeneous**
- **transport may depend on structure and defects on different length scales**
- **different experimental techniques emphasize different aspects of transport mechanisms**

Simple Organic Semiconductor Molecular Crystal Model

- charge transport models in molecular crystals of organic semiconductors can be approximated as a 1D molecular crystal of a chain of energy sites



- **because of the intrinsically small intermolecular electronic coupling, a charged system with an excess electron (or a hole) is well described as a linear combination of the LUMOs (HOMOs) of the isolated molecules**

- **simplified approximations:**
  - one molecule per unit cell, at distance *a*
  - only one orbital per molecule (HOMO or LUMO, for hole or electron transport)
  - one effective mode of vibration included, with a harmonic oscillator potential

General One-Electron Hamiltonian for Charge Transport

- different transport regimes can be illustrated with a general one-electron Hamiltonian
- Hamiltonian includes electronic coupling, dynamic disorder, static disorder of the energy sites but assumes low carrier densities, no electron correlation or Coulomb interaction

$$H = H_0 + H_1 \quad + H_2 + H_3 \quad + H_4 + H_5$$

excitation term (intramolecular site energy)

electron transfer term (intermolecular coupling)

dynamic disorder effects (on site energies and coupling, respectively)

static disorder effects (on site energies and coupling, respectively)

- **fundamental nature of the transport process determined by the relative magnitudes of the excitation & transfer terms versus the dynamic disorder terms and the static disorder terms**

KEY CONCEPT: see A. Köhler and H. Bässler, *Electronic Processes in Organic Semiconductors*, p. 213-215

Excitation and Charge Transfer Terms

- excitation term represents total energy of an electronically and vibrationally excited system
- operators $a_n^\dagger$ (or a_n) excite (relax) an electron in an orbital on energy site ϵ_n in ideal crystal
- operators $b_\lambda^\dagger$ (or b_λ) raise (lower) a vibration by an energy quantum $\hbar\omega_\lambda$

$$\overbrace{H_0 = \underbrace{\sum_n \epsilon_n\, a_n^\dagger a_n}_{\text{electronic excitation term}} + \underbrace{\sum_\lambda \hbar\omega_\lambda \left(b_\lambda^\dagger b_\lambda + \frac{1}{2}\right)}_{\text{vibrational excitation term}}}^{\text{excitation term}}$$

$$\overbrace{H_1 = \sum_{n,m;n\neq m} J_{nm}\, a_n^\dagger a_m}^{\text{electron transfer term}}$$

- **the electron transfer term represents the electronic interaction between energy sites**
- **it defines the interaction energy J_{nm} mediating the transfer of an electron from site *m* to *n***

KEY CONCEPT: see readers for “second quantization” formalism for multiparticle systems

Dynamic Disorder Terms

- interaction of electronic and vibrational excitations captured by the dynamic disorder terms
- variations of the system parameters due to electron-phonon coupling taken into account
- strength of the electron-phonon coupling expressed by the coupling constants *g* and *f*

- **diagonal dynamic disorder term** **covers vibration-induced changes of the site energy** ϵ_n

diagonal dynamic disorder term

$$H_2 = \sum_{\lambda} \sum_{n} g_{n\lambda}^2 \, \hbar\omega_\lambda \, a_n^\dagger a_n \left(b_\lambda + b_{-\lambda}^\dagger\right)$$

- **off-diagonal dynamic disorder term** **covers vibration-induced changes of the coupling** J_{nm}

off-diagonal dynamic disorder term

$$H_3 = \sum_{n,m;n\neq m} \sum_{\lambda} f_{nm\lambda}^2 \, \hbar\omega_\lambda \, a_n^\dagger a_m \left(b_\lambda + b_{-\lambda}^\dagger\right)$$

Static Disorder Terms

- static disorder terms take effects due to structural deviations from an ideal crystal into account by introduction of a variation factor δ

- **diagonal static disorder** **introduces a distribution function $\delta\epsilon_n$ for the site energy**

diagonal static disorder term

$$H_4 = \sum_n \delta\epsilon_n \, a_n^\dagger a_n$$

- **off-diagonal static disorder** **described by a distribution function δJ_{nm} for interaction energy**

off-diagonal static disorder term

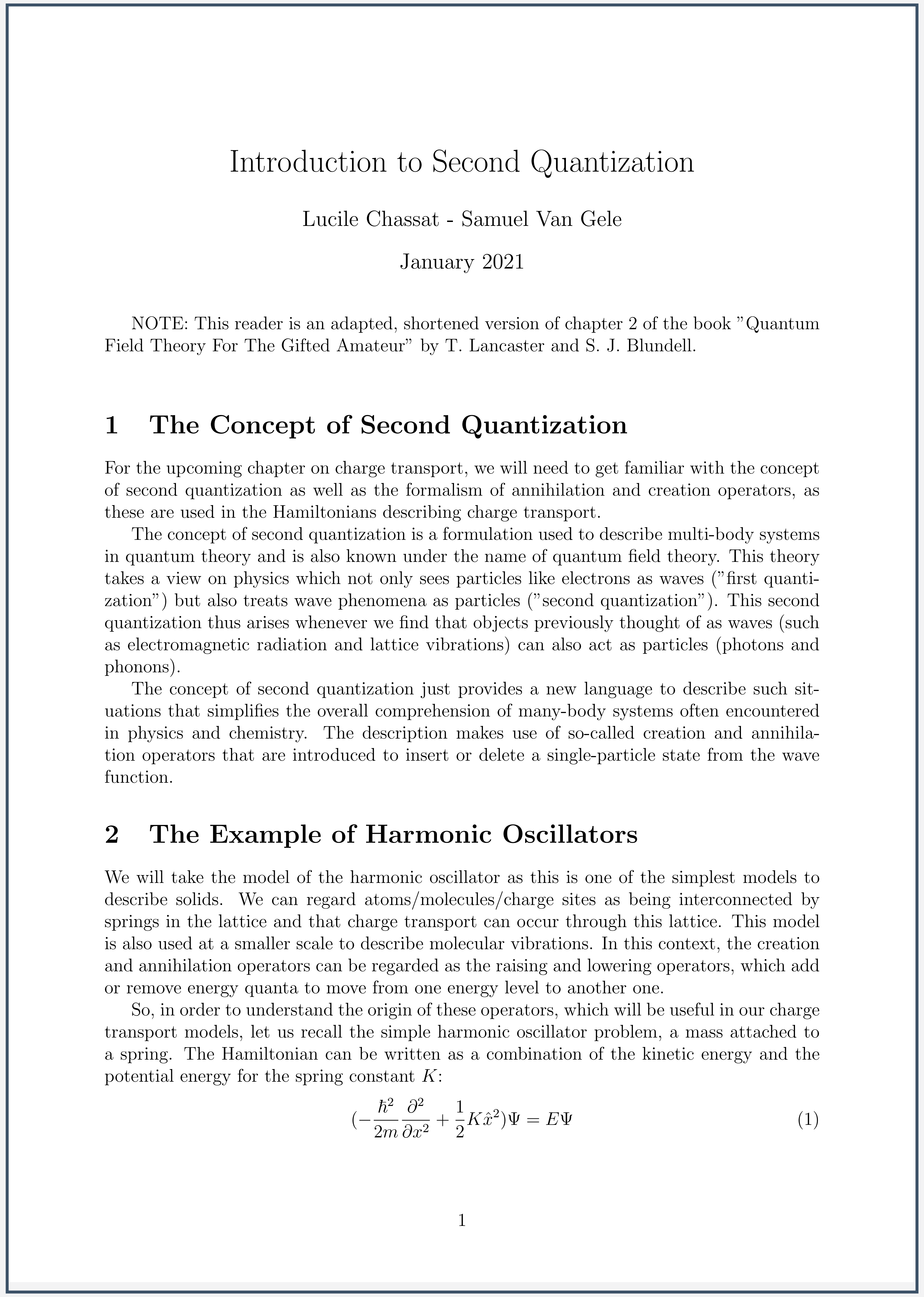
$$H_5 = \sum_{n,m;n\neq m} \delta J_{nm} \, a_n^\dagger a_m$$

Charge Transport Regimes in Organic Semiconductors

coherent transport		incoherent transport	
band transport	**transient localization**	**polaronic transport**	**disorder controlled transport**
dominated by electronic coupling	governed by electronic coupling & dynamic disorder	dominated by dynamic disorder	dominated by static disorder
$H_1(J_{nm})$	$H_1(J_{nm}) \approx H_3(f_{nm\lambda})$	$H_2(g_{n\lambda}), H_3(f_{nm\lambda})$	$H_4(\delta\epsilon_n), H_5(\delta J_{nm})$

- **different charge transport regimes can be categorised based on the relative magnitudes of**
  - the interaction energy J_{nm} between transport sites
  - the electron-phonon coupling represented through the constants $g_{n\lambda}$ and $f_{nm\lambda}$
  - the static disorder causing variations in site energy $\delta\epsilon_n$ and interaction energy δJ_{nm}

Homework and Reading Assignments



Introduction to Second Quantization

Lucile Chassat - Samuel Van Gele

January 2021

NOTE: This reader is an adapted, shortened version of chapter 2 of the book "Quantum Field Theory For The Gifted Amateur" by T. Lancaster and S. J. Blundell.

1 The Concept of Second Quantization

For the upcoming chapter on charge transport, we will need to get familiar with the concept of second quantization as well as the formalism of annihilation and creation operators, as these are used in the Hamiltonians describing charge transport.

The concept of second quantization is a formulation used to describe multi-body systems in quantum theory and is also known under the name of quantum field theory. This theory takes a view on physics which not only sees particles like electrons as waves ("first quantization") but also treats wave phenomena as particles ("second quantization"). This second quantization thus arises whenever we find that objects previously thought of as waves (such as electromagnetic radiation and lattice vibrations) can also act as particles (photons and phonons).

The concept of second quantization just provides a new language to describe such situations that simplifies the overall comprehension of many-body systems often encountered in physics and chemistry. The description makes use of so-called creation and annihilation operators that are introduced to insert or delete a single-particle state from the wave function.

2 The Example of Harmonic Oscillators

We will take the model of the harmonic oscillator as this is one of the simplest models to describe solids. We can regard atoms/molecules/charge sites as being interconnected by springs in the lattice and that charge transport can occur through this lattice. This model is also used at a smaller scale to describe molecular vibrations. In this context, the creation and annihilation operators can be regarded as the raising and lowering operators, which add or remove energy quanta to move from one energy level to another one.

So, in order to understand the origin of these operators, which will be useful in our charge transport models, let us recall the simple harmonic oscillator problem, a mass attached to a spring. The Hamiltonian can be written as a combination of the kinetic energy and the potential energy for the spring constant K:

$$(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}K\hat{x}^2)\Psi = E\Psi \tag{1}$$

Introduction to the "second quantization" formalism for non-relativistic quantum mechanics

A possible substitution for Sections 6.7 and 6.8 of Feynman's "Statistical Mechanics"

Hal Tasaki*

arXiv:1812.10732v3 [cond-mat.stat-mech] 28 Sep 2020

This is a self-contained and hopefully readable account on the method of creation and annihilation operators (also known as the Fock space representation or the "second quantization" formalism) for non-relativistic quantum mechanics of many particles.[1] Assuming knowledge only on conventional quantum mechanics in the wave function formalism, we define the creation and annihilation operators, discuss their properties, and introduce corresponding representations of states and operators of many-particle systems.[2] As the title of the note suggests, we cover most topics treated in sections 6.7 and 6.8 of Feynman's[3] "Statistical Mechanics: A Set of Lectures" (Westview Press, 1988).[4]

We note that all the contents of the present note are completely standard, and the definitions and the derivations presented here have been known to many. Although the style of the present note may be slightly more mathematical than standard physics literatures, we do not try to achieve full mathematical rigor.[5]

Contents

1 Wave functions of many particles

Single particle We start by recalling the standard quantum mechanical description of a single particle, such as an electron or an atom. A state (at an instantaneous moment) of a particle in the three dimensional space is described by a wave function $\varphi(\boldsymbol{r})$, which is a

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[1] Japanese translation is available: `https://www.gakushuin.ac.jp/~881791/pdf/2ndQNoteJ.pdf`

[2] *Note to experts:* In particular we here *derive* the (anti)commutation relations of the creation and annihilation operators, rather than simply declaring them. In this sense our approach is quite close to that of Feynman's. But we here focus on the action of creation/annihilation operators on general N body wave functions, while Feynman makes a heavy use of Slater-determinant-type states from the beginning. We hope that our presentation provides a better perspective on the formalism.

[3] A friend of mine pointed me out that this happens to be the centennial year of Richard Feynman's birth. Let me declare that this small article is to celebrate his 100th birthday!

[4] I wrote this note for undergraduate students in our group who are studying Feynman's textbook. The idea was that they can skip these two sections, which are somewhat complicated, by studying this note (and they indeed did so).

[5] The mathematically minded reader might be bothered by our heuristic treatment of the operators $\hat{\psi}(\boldsymbol{x})$ and $\hat{\mathfrak{a}}(\boldsymbol{k})$. Our treatment can be made rigorous by using suitable advanced concepts.