A mathematical model for Mott's Variable Range Hopping

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Main References

N. F. Mott,
J. Non-Crystal. Solids, **1**, 1 (1968).

B. Shklovskii, A. Efros,
Electronic properties of doped semiconductors,
Springer, Berlin, 1984.

A. Faggionato, H. Schulz-Baldes, D. Spehner,
Mott law as lower bound for a random walk in a random environment,
Commun. Math. Phys., **263**, 21-64, (2006).

G. Androulakis, J. Bellissard, C. Sadel,
A mathematical model for Mott's variable range hopping,
in preparation, 2009.

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I - Physics: background

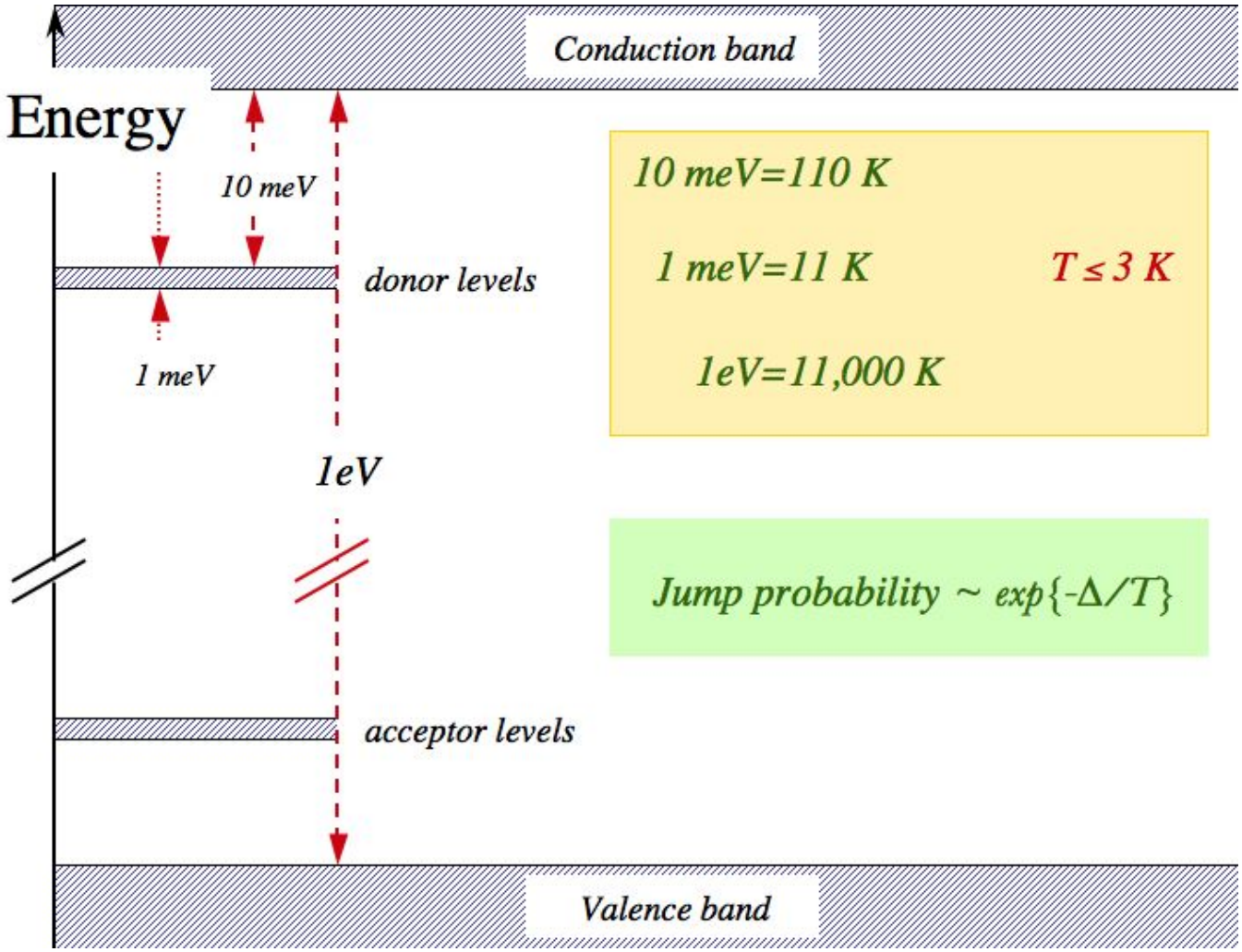
B. Shklovskii, A. Efros, *Electronic properties of doped semiconductors*, Springer, Berlin, 1984.

Semi-conductors

- Semi-conductors like *Si, Ga As*, have a diamond crystal structure: atoms are located on a *perfectly periodic lattice* $\mathcal{L}$ endowed with a $\mathbb{Z}^d$*-action*

$$x \in \mathcal{L} \mapsto x + a \in \mathcal{L}\,, \qquad a \in \mathbb{Z}^d\,.$$

- Electron-electron interaction on site induces a large gap at the Fermi level: *without impurities, perfect insulators*.
- Light dopping: impurities are randomly distributed, with a *concentration* of $O(10^{-9})$.
- At room temperature, impurity electrons jump in the conduction band leading to *"large" conductivity*.
- At very low temperature, electrons are confined on the impurity sites: electrons see only a *random sub-lattice* $\mathcal{L}_\omega \subset \mathcal{L}$.



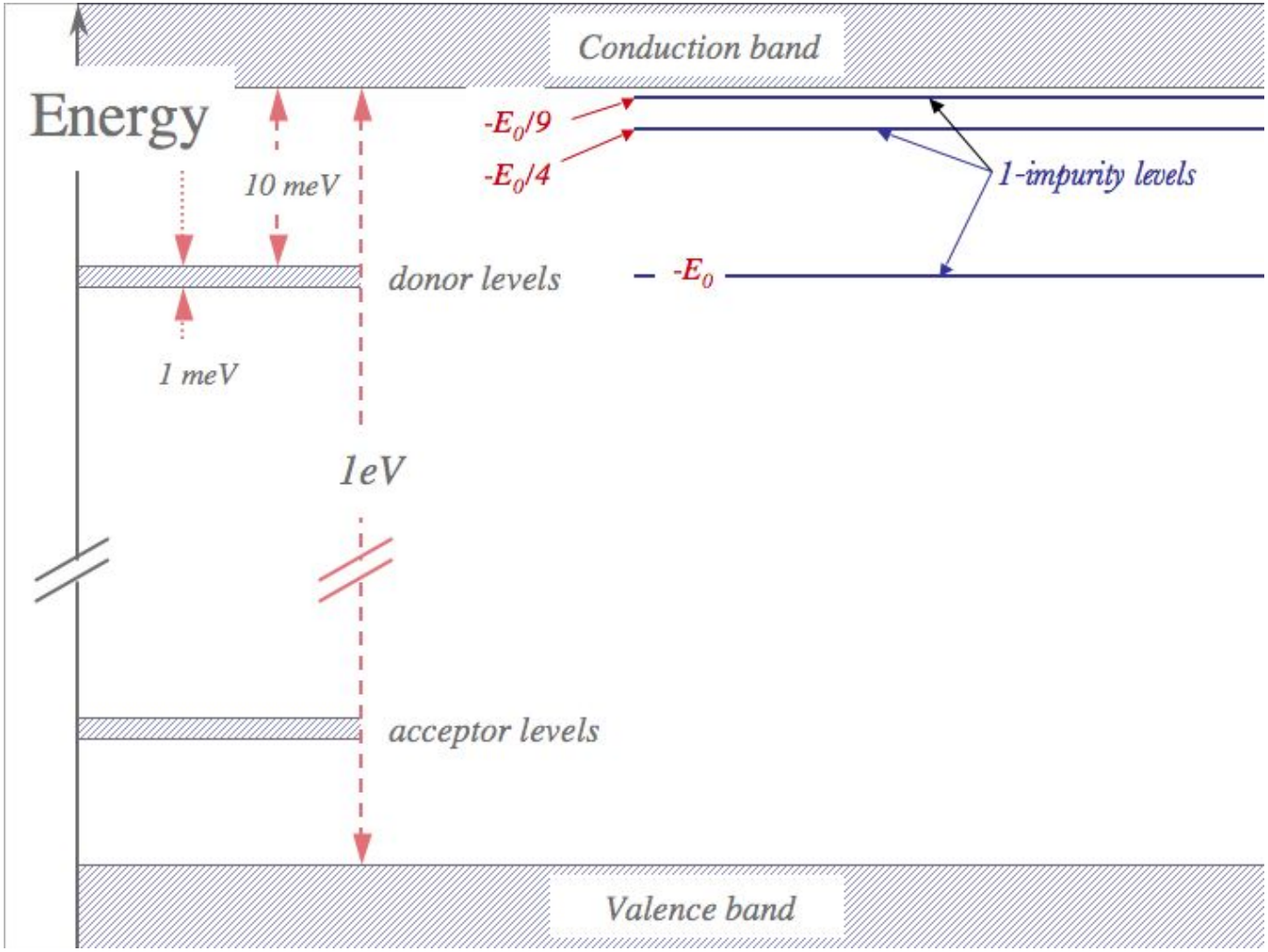
- Bands and gaps in semi-conductors -

Impurities

- An isolated impurity can be a *donor* (one electron in excess) or an *acceptor* (one missing electron). Acceptors attracts electrons in excess to create a *negative ion*, whereas donors gives their excess electron, leading to a *positive ion*.

- The semi-conductor is *compensate* if there are impurities of both types. In this talk *donors will be the majority (n-type)*, so that some of donor electrons stay in the donor level, filling the donor band partially.

- Each isolated donor site, behaves like a *hydrogen atom*, with Bohr radius $a_B \simeq 100$ Å. The ground state and the first excited state of this atom are $-E_0 \simeq -10meV$ and $-E_0/4$ below the conduction band.

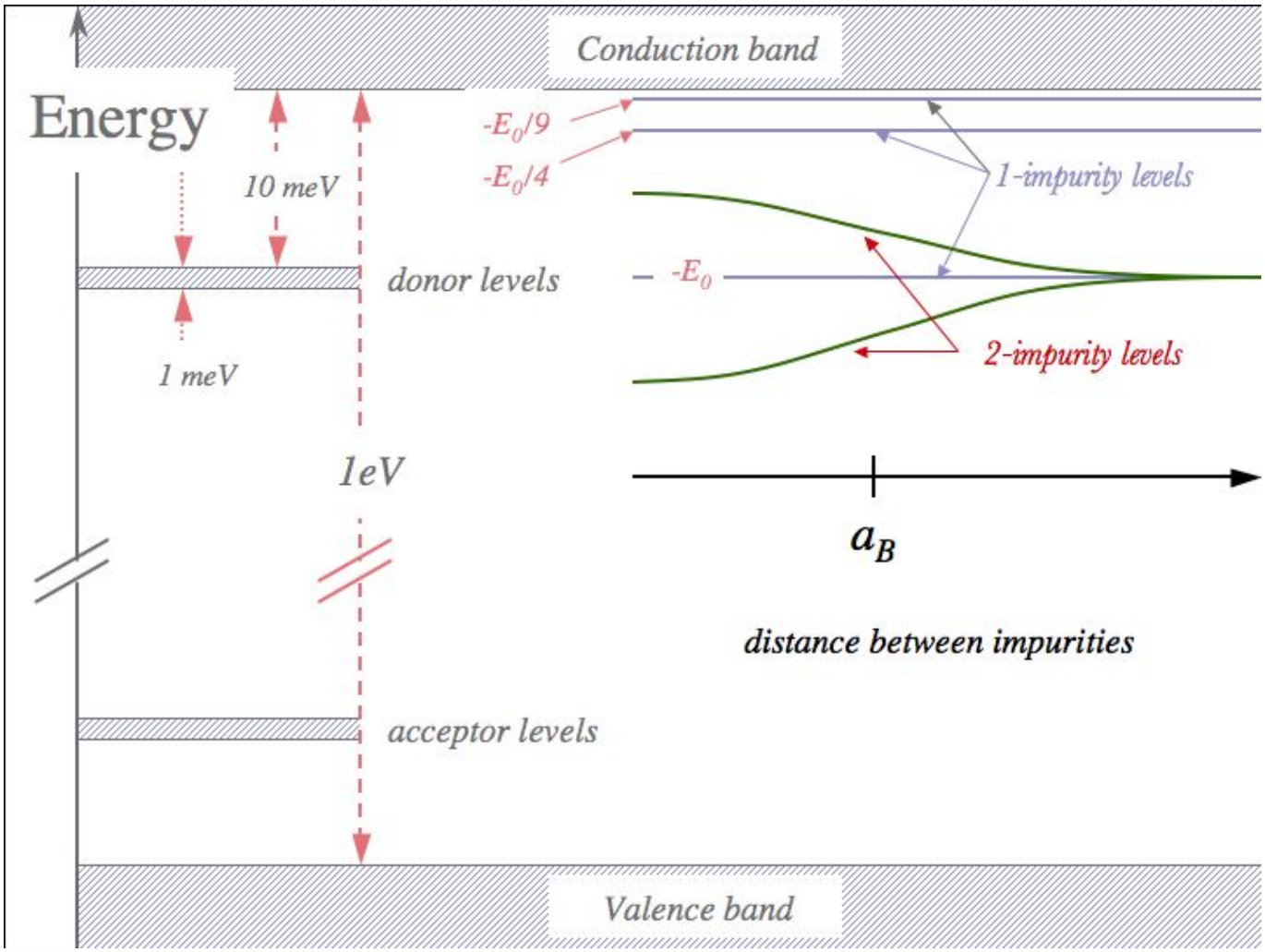


- Impurity levels -

- At temperature low enough ($T \leq 10\,K$), all donor electrons are confined in the ground state.

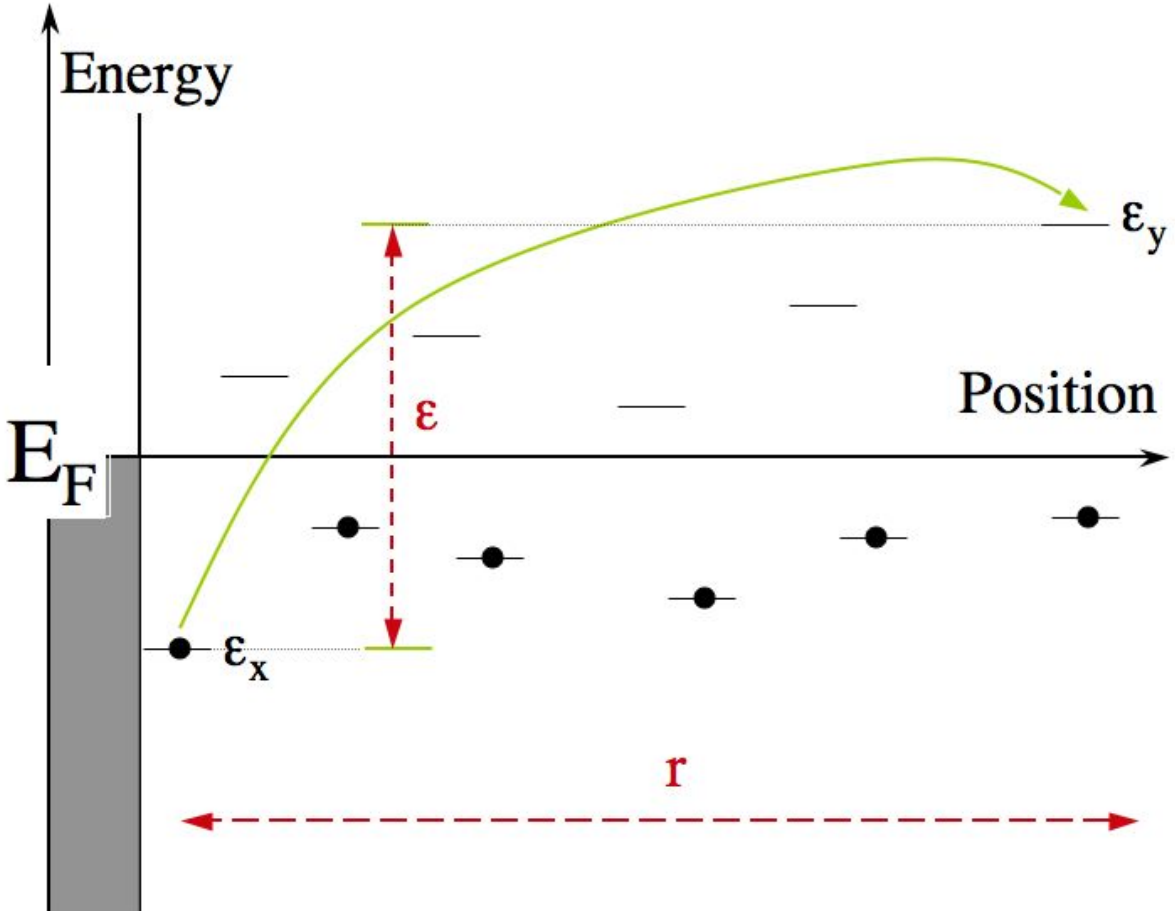
- If two impurities come close, they behave like a molecule H_2, and the groundstate splits into a *pair of levels* with energies way away from the main impurity band *(level repulsion)*.

- *The positions of the impurity sites are random, the positions of impurities occupied by a donor electron are random, the Coulomb potential produced by various ions is also random.*



- Two-impurity levels -

Mott's variable range hopping



- Strongly localized regime, dimension *d*
- Low electronic DOS, Low temperature

- Absorption-emission of a phonon of energy ε

$$\text{Prob} \propto e^{-\varepsilon/k_B T}$$

- Tunnelling probability at distance r

$$\text{Prob} \propto e^{-r/\xi}$$

- Density of state at Fermi level n_F, *(level splitting in impurity clusters)*

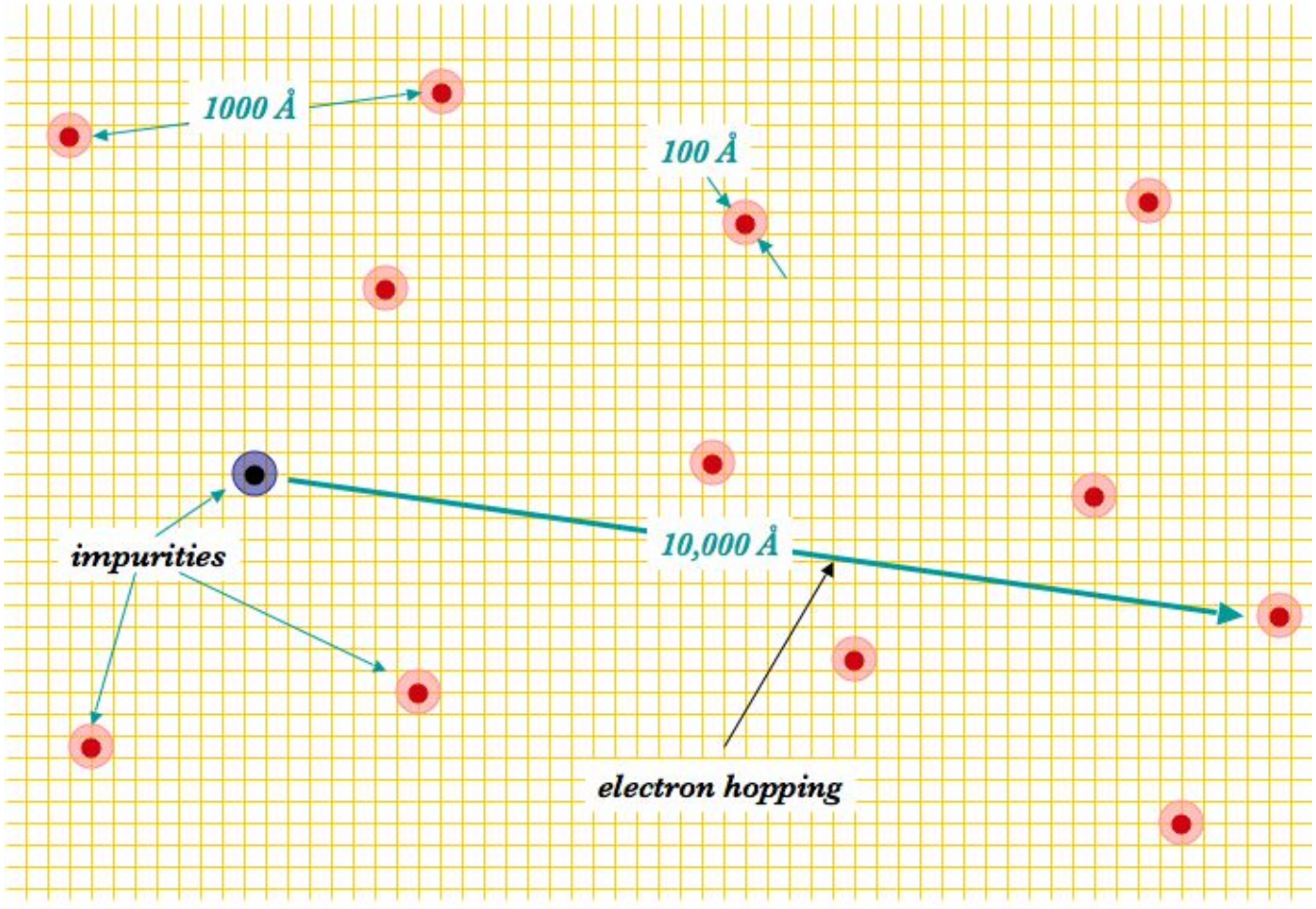
$$\varepsilon \, n_F \, r^d \geq 1$$

- Optimizing, the conductivity satisfies

$$\sigma \propto e^{-(T_0/T)^{1/d+1}}$$ **Mott's law**

- Optimal energy $\varepsilon_{opt} \sim T^{d/(d+1)} \gg T$

- Optimal distance $r_{opt} \sim 1/T^{1/(d+1)} \gg \xi$



- Typical length scales for electron hopping -

II - Electronic States & Observables

Electronic states

- Let $s = (s_x)_{x \in \mathcal{L}}$, $s_x \in \{0, 1\}$ be a family of random variables such that $s_x = 1$ if and only if an electronic state is *available at* x.

- If the level repulsion is ignored, s coincides with the distribution of impurities, namely *the* s_x *are i.i.d.'s*, with common distribution

$$\text{Prob}\{s_x = 1\} = c \qquad \text{Prob}\{s_x = 0\} = 1 - c$$

- At each site the electron energy is a random variable ϵ_x uniformly distributed in the impurity band

$$\Delta = [E_0 - \frac{W}{2}, E_0 + \frac{W}{2}]$$

- The set Ω of families (s, ϵ) with $s = (s_x)_{x \in \mathcal{L}}$ and $\epsilon = (\epsilon_x)_{x \in \mathcal{L}, s_x = 1}$, is *compact*.

- Due to level repulsion electronic states $s_x = s_y = 1$ are cut-off if $|\epsilon_x - \epsilon_y||x - y|$ is too small.

Theorem 1 *There is an $\mathbb{R}^d$-invariant ergodic probability distribution $\mathbb{P}$ on Ω such that the condition $s_x = s_y = 1$ implies*

$$|\epsilon_x - \epsilon_y| \geq C|x - y|^{-d} e^{-|x-y|/\xi}$$

$\mathbb{P}$-almost surely and the density of states is almost constant on Δ,

(A result by Dobrushin and Lanford is used here)

Fermion Algebra

Electrons are described by *fermion creation-annihilation* operators $a_x, a_x^\dagger$ located on the set $\mathcal{L}_\omega = \{x \in \mathcal{L}\,;\, s_x = 1, \epsilon_x \in \Delta\}$

$$a_x a_y + a_y a_x = 0\,, \qquad (a_x)^* = a_x^\dagger\,, \qquad a_x a_y^\dagger + a_y^\dagger a_x = \delta_{xy}\,.$$

For $\Lambda \subset \mathcal{L}$ a finite subset, let $\mathfrak{A}_\Lambda(\omega)$ be the C*-algebra generated by $\{a_x, a_x^\dagger\,;\, x \in \Lambda \cap \mathcal{L}_\omega\}$ and

$$\mathfrak{A}_{loc}(\omega) = \bigcup_{\Lambda\ finite} \mathfrak{A}_\Lambda(\omega)\,, \qquad \mathfrak{A}(\omega) = \overline{\mathfrak{A}_{loc}(\omega)}\,.$$

Each $\mathfrak{A}(\omega)$ is $\mathbb{Z}_2$-graded with

$$\sigma \in \mathrm{Aut}(\mathfrak{A}(\omega))\,, \qquad \sigma(a_x) = -a_x\,, \quad \forall x \in \mathcal{L}_\omega\,.$$

Covariance

The set $\Gamma_\Omega = \Omega \rtimes \mathbb{Z}^d$ is a *locally compact groupoid*

1. Range and Source maps:
   $r : (\omega, a) \in \Gamma_\Omega \mapsto \omega \in \Omega\,, \qquad s : (\omega, a) \in \Gamma_\Omega \mapsto \tau^{-a}\omega \in \Omega$
2. Product: $(\omega, a) \circ (\tau^{-a}\omega, b) = (\omega, a + b)$
3. Inverse: $(\omega, a)^{-1} = (\tau^{-a}\omega, -a)$.
4. Product topology.

There is a Γ_Ω-action on the field $\mathfrak{A} = (\mathfrak{A}(\omega))_{\omega\in\Omega}$ by $*$-isomorphisms,

$$\eta_{(\omega,a)} : \mathfrak{A}(\tau^{-a}\omega) \mapsto \mathfrak{A}(\omega)\,, \qquad \eta_{(\omega,a)}(a_x) = a_{x+a}\,, \qquad x \in \mathcal{L}_\omega - a\,.$$

Theorem 2 $\mathfrak{A}$ *is endowed with a structure of continuous* Γ_Ω*-covariant field of* C^**-algebras with reference continuous sections given by polynomials in the creation-annihilation operators with coefficients in* $C(\Omega)$*.*

A field $\theta = (\theta_\omega)_{\omega\in\Omega}$ of $*$*-homorphisms* from $\mathfrak{A}$ into itself is

- Continuous: if it transforms continuous sections into continuous sections
- Covariant: if

$$\eta_{(\omega,a)} \circ \theta_{\mathrm{T}^{-a}\omega} = \theta_\omega \circ \eta_{(\omega,a)}$$

Gibbs Dynamics

The electron *number* operator and the *Hamiltonian* are

$$N_\Lambda(\omega) = \sum_{x \in \mathcal{L}_\omega \cap \Lambda} a_x^\dagger a_x \,, \qquad H_\Lambda(\omega) = \sum_{x \in \mathcal{L}_\omega \cap \Lambda} \epsilon_x \, a_x^\dagger a_x \,.$$

For $A \in \mathfrak{A}(\omega)$ the *Gibbs dynamics* is defined by

$$\alpha_t^{(\omega)}(A) \;=\; \lim_{\Lambda \uparrow \mathcal{L}} \, e^{\imath t (H_\Lambda(\omega) - \mu N_\Lambda(\omega))} \; A \; e^{-\imath t (H_\Lambda(\omega) - \mu N_\Lambda(\omega))} \,.$$

where μ is the *chemical potential*.

The field $\alpha_t = \left(\alpha_t^{(\omega)}\right)_{\omega \in \Omega}$ *of* $*$*-automorphism, is continuous and covariant. The map* $t \mapsto \alpha_t$ *is norm pointwise continuous.*

Equilibrium

The Gibbs construction for thermal equilibrium leads to a unique field of *β-KMS states* $(\rho_\omega)_{\omega\in\Omega}$, where $\beta = 1/k_{_B}T$ is the inverse temperature. It is given $\mathbb{P}$-almost surely by

$$\rho_\omega(a_x) = \rho_\omega(a_x^\dagger) = 0\,, \qquad \rho_\omega(a_x^\dagger a_x) = \frac{1}{1+e^{\beta(\epsilon_x-\mu)}}$$

$$\rho_\omega(AB) = \rho_\omega(A)\rho_\omega(B)\,, \quad \text{if} \quad A\in\mathfrak{A}_\Lambda\,,\ B\in\mathfrak{A}_{\Lambda'} \quad \text{and} \quad \Lambda\cap\Lambda' = \emptyset$$

Then ρ satisfies the KMS-condition

$$\rho_\omega(AB) = \rho_\omega\left(\alpha^{(\omega)}_{-\imath\beta}(B)A\right).$$

GNS-representation

Using the *GNS-construction*, leads to

- A continuous field of *graded* Hilbert spaces $\mathcal{H} = (\mathcal{H}_\omega)_{\omega\in\Omega}$, together with a *unitary representation* of Γ_Ω
- A continuous field of *unit vectors* $\xi = (\xi_\omega)_{\omega\in\Omega}$
- A (strongly) continuous covariant field of *representations* $\pi = (\pi_\omega)_{\omega\in\Omega}$ of $\mathfrak{A}$ in $\mathcal{H}$, for which ξ is *cyclic*
- A (strong-resolvent) continuous covariant field of *selfadjoint* operators $F = (F_\omega)_{\omega\in\Omega}$ implementing the dynamics α and defining the *Tomita-Takesaki modular* operators
- A continuous covariant field of *positive Araki-Connes cones* $\mathcal{H}_+ = (\mathcal{H}_{\omega,+})_{\omega\in\Omega}$, which are self-dual, homogeneous and oriented, with $\xi \in \mathcal{H}_+$

III - Dissipative Dynamics

Dissipative Dynamics

A dissipative dynamics is described by *a continuous covariant field of Markov semi-groups* on $\mathfrak{A}$. Its generator will be given through a continuous covariant family of *(infinite dimensional, unbounded) Lindblad* operators.

The first dynamics is the one that describes the *return to equilibrium*, and should satisfy the *detailed balance condition*.

The other ones describes the electron dynamics when submitted to an *external electric field* putting the system slightly out of equilibrium in order to justify the *linear response theory* and to give a rigorous proof of the *Green-Kubo's formulae*.

The generator will always have the form

$$\mathfrak{L}_\omega(A) = \lim_{\Lambda\uparrow\mathcal{L}} \imath[H_\Lambda(\omega), A] + \mathfrak{D}_\omega(A)\,,$$

with

$$\mathfrak{D}_\omega(A) = \sum_{\gamma\in\mathcal{J}} \left(\frac{1}{2}\left\{ L_\gamma(\omega)^* L_\gamma(\omega), A \right\} - (-1)^{d_{L_\gamma} d_A} L_\gamma(\omega)^* A L_\gamma(\omega) \right)$$

- here $A \in \mathfrak{A}_{loc}(\omega)$ and d_A denotes the $\mathbb{Z}_2$-*degree* of A
- the set $\mathcal{J}$ is countable and $\gamma \in \mathcal{J}$ is called a *jump*

The Kinetic Part

Mott's argument can be modeled with

- Jumps are between *two impurity sites* $x \to y$ on $\mathcal{L}_\omega$.
- then

$$L_{x\to y}(\omega) = \sqrt{\Gamma_{x\to y}(\omega)}\ a_y^\dagger\, a_x$$

- The *jump rate* is given by

$$\Gamma_{x\to y}(\omega) = \Gamma_0\, s_x\, s_y\, \frac{e^{-|x-y|/\xi}}{Z}\, \frac{1}{1+e^{\beta(\epsilon_y-\epsilon_x)}}$$

- The contribution of these jumps to the sum defining $\mathfrak{D}$ is denoted by $\mathfrak{D}_\omega^{kin}$

Facts:

- The field of Lindblad operator defined by $\mathfrak{D}_{kin}$ is *well defined* on $\mathfrak{A}$, generates a continuous covariant field of Markov semi-groups

- It *models correctly* the main argument of Mott concerning the jump rates of electrons between impurities

- $\mathfrak{D}^{kin}$ *conserves the electrons number*, so that it admits *several inequivalent invariant states* obtained by changing the chemical potential

- In particular it *not sufficient* to describe the return to equilibrium.

The Thermal Bath

To force the return to equilibrium, coupling the system to a thermal bath is required to *break the conservation of electron number*

- Due to electron-phonon collisions on site, electrons *thermalizes* with the crystal (the electron energy is not conserved)
- During the collision process, electrons can *come in-or-out* the energy band Δ
- Electron can be *expelled from* or *added to* the region in which the system is described

- New jumps are added of the form $x \to x_\star$ or $x_\star \to x$, with

$$x \in \mathcal{L}_\omega \qquad\qquad x_\star \in \mathcal{L}$$

The sites $x_\star$ represent the *position* where the *electron-phonon interaction* takes place. It can be *anywhere* in the crystal, even out of impurity sites.

- then

$$L_{x\to x_\star}(\omega) = \sqrt{\Gamma_{x\to x_\star}(\omega)}\ a_x \qquad L_{x_\star\to x}(\omega) = \sqrt{\Gamma_{x_\star\to x}(\omega)}\ a_x^\dagger$$

- The jump rates are given by

$$\Gamma_{x\to x_\star}(\omega) = \Gamma_\star\ s_x\ \frac{e^{-|x-x_\star|/\xi}}{Z_\star}\ \frac{1}{1+e^{\beta(\mu-\epsilon_x)}}, \quad \Gamma_{x_\star\to x}(\omega) = \Gamma_\star\ s_x\ \frac{e^{-|x-x_\star|/\xi}}{Z_\star}\ \frac{1}{1+e^{\beta(\epsilon_x-\mu)}}$$

The final model is described by

$$\mathfrak{L}_\omega(A) = \lim_{\Lambda\uparrow\mathcal{L}} \imath[H_\Lambda(\omega), A] + \mathfrak{D}^{kin}_\omega(A) + \mathfrak{D}^{\star}_\omega(A)\,, \qquad A \in \mathfrak{A}_{loc}(\omega)$$

with $\mathfrak{D}^\star$ denoting the contribution of the thermal bath

Theorem 3 *(i)- The field of Lindblad operators $\mathfrak{L}_\omega$ defines a continuous covariant field of Markov semi-groups on $\mathfrak{A}$.*

(ii)- This field admits $\rho = (\rho_\omega)_{\omega\in\Omega}$ as a unique invariant state and the return to equilibrium occurs exponentially fast in time.

(iii)- It implements a completely positive semi-group of contraction in the GNS representation with a generator having a spectral gap bounded form below by $\Gamma_\star$, uniformly in $\omega \in \Omega$.

IV - Conductivity

Currents

Formally, the current is defined as the product of the *charge* of the charge carriers by the *time derivative of the position* operator R, namely

$$J = -e\, \mathfrak{L}_\omega(R)$$

Because of the infinite volume limit, such a definition leads to some delicate problems. However the result of this analysis is the following: there is a *current-density operator* defined by (for electrons)

$$J_x(\omega) = \frac{-e}{2} \sum_{y \in \mathcal{L}_\omega} (y-x)\, \left\{ \Gamma_{x\to y}(\omega)\, n_x\, (1-n_y) - \Gamma_{y\to x}(\omega)\, (1-n_x)\, n_y \right\}$$

where $n_x = a_x^\dagger a_x$, $(1-n_x) = a_x\, a_x^\dagger$

Remark: The contribution of the thermal bath to the current *vanishes* in the infinite volume limit. Only the kinetic part of the dissipation participates to the current. This is because the current is produced by the electron-phonon interaction, pushing the electron out of impurity sites.

Theorem 4 *(i)- The current-density defines a covariant continuous field of operators.*

(ii)- At equilibrium the thermal average of the current vanishes

Consequently to *produce a nontrivial macroscopic current*, the system must be put *out of equilibrium*.

Non Equilibrium Dissipative Dynamics

Only the effect of a *uniform static electric field* will be investigated here, namely $\nabla\mu = -e\mathcal{E}$. On a *mesoscopic length scale* the chemical potential should be replaced by

$$\mu \to \mu - e\mathcal{E}\cdot(x - x_0)$$

where x_0 will be chosen in each term as a natural origin. Such a change affects

1. The *coherent dynamics*, namely the Hamiltonian
2. The *kinetic part* of the dissipation namely
   $\epsilon_x - \epsilon_y \;\to\; \epsilon_x - \epsilon_y + e\mathcal{E}\cdot(x - y)$
3. The *thermal part* of the dissipation also
   $\epsilon_x - \mu \;\to\; \epsilon_x - \mu + e\mathcal{E}\cdot(x - x_\star)$

Let $\mathfrak{L}^{\varepsilon}_{\omega}$ denotes the corresponding Linblad generator

Theorem 5 *(i)- $\mathfrak{L}^{\varepsilon}_{\omega}$ is well defined on $\mathfrak{A}_{loc}(\omega)$ and generates a continuous covariant field of Markov semi-groups on $\mathfrak{A}$.*

(ii)- This semigroup admits a continuous covariant field of stationary state ρ^{ε}.

(iii)- the averaged current density defines a function $j^{\varepsilon}_{\omega} \in \mathbb{R}^d$ such that $\rho^{\varepsilon}_{\omega}(J_x(\omega)) = j^{\varepsilon}_{\mathrm{T}^{-x}\omega}$.

(iv)- The disorder average of this local current defines the experimental current-density $j_{exp}(\mathcal{E})$ which is smooth w.r.t. $\mathcal{E}$ near $\mathcal{E} = 0$.

In other words, the *linear response theory* is valid within this model !

The Kubo Formula

As a result

$$j_{exp}(\mathcal{E}) = \sigma\mathcal{E} + O(\mathcal{E}^2)$$

where σ is the conductivity tensor which is given by

$$\sigma = \beta \int_\Omega d\mathbb{P}(\omega) \sum_{x\in\mathcal{L}} \langle J_x(\omega)|\frac{1}{\mathcal{D}_\omega} J_0(\omega)\rangle \qquad \textbf{[Kubo]}$$

- The inner product is defined by the *GNS representation of the equilibrium state*
- The formula restricts to the sub-Hilbert space $\mathcal{K}_\omega$ contained in $\{\xi_\omega\}^\perp$ and spanned by the $\{n_{x_1}\cdots n_{x_k}\xi_\omega\,;\, x_i \in \mathcal{L}_\omega\}$.
- $\mathcal{D}_\omega$ is the positive operator induced on $\mathcal{K}_\omega$ by $\mathfrak{D}$.

Estimates

- The operator $\mathcal{D}_\omega$ satisfies

$$\mathcal{D}_\omega \;\geq\; \Gamma_\star \, \mathbf{1}_{\mathcal{K}_\omega}$$

- *a more complicated upper bound is available*

- Various positivity properties implies

$$\sigma \leq \frac{\beta}{\Gamma_\star} \int_\Omega d\mathbb{P}(\omega) \sum_{x \in \mathcal{L}_\omega} \langle J_x(\omega) | J_0(\omega) \rangle$$

- The *r.h.s.* can be computed explicitly in terms of the transition rates $\Gamma_{x \to y}$ and lead to expressions similar to the ones obtained in the Mott argument.

- A lower bound is in principle possible.

- Consequence: there are constant $C > 0$, $T_0 > 0$ such that

$$\sigma \leq C \exp\left\{\left(\frac{T_0}{T}\right)^{1/d+1}\right\} \qquad \textbf{[Mott's law]}$$

It is *expected* that there are constant $C_- > 0$, $T_1 > 0$, $\alpha \leq 1$ such that

$$\sigma \geq C_- \exp\left\{\left(\frac{T_1}{T}\right)^{\alpha/d+1}\right\}$$

V - To conclude

A long arduous way

- Describing electrons in a semi-conductor at very low temperature requires to use a random environment provided by the sub-lattice of impurities.
- In Mott's argument, level repulsion for impurities too close from each other is an essential ingredient and lead to the definition of a probability measure for the electronic states. An old argument by Dobrushin is used here.
- A formalism of second quantization is required to take into account statistical correlations. It leads to a covariant field of C^*-algebras. As a consequence the mathematics becomes heavy and painful.

- However, using the full strength of Tomita-Takesaki theory, the use of the Araki-Connes positive cones, gives the right mathematical framework through which the Mott model can be described.
- The Mott model is given in terms of a Lindblad operator generating a Markov semi-group.
- Then the formalism behind the Non-equilibrium Statistical Mechanics, leads (i) to distinguish various time scales, length scales, energy scales (ii) to define the notion of local equilibrium (iii) to a logical way to define mesoscopic currents.
- It becomes possible to prove rigorously the validity of the linear response theory and the Kubo formula.
- Thanks to the positivity properties emphasized by the formalism, it is possible to estimate rigorously the conductivity in terms of the temperature leading to Mott's law.

Thanks for your patience !