Topological quantization and gauge invariance of charge transport in liquid insulators

Federico Grasselli

SISSA – Scuola Internazionale Superiore di Studi Avanzati
Trieste, Italy
Electrical conductivity

\[ J^{n.e.} = -\sigma \nabla V \]
Electrical conductivity

\[ J^{n.e.} = -\sigma \nabla V \]

- Ab initio approach to charge transport in electronic insulators (e.g. ionic liquids: NaCl, KCl, part. dissoc. water, etc.)
Electrical conductivity

\[ \mathbf{J}^{n.e.} = -\sigma \nabla V \]

- Ab initio approach to charge transport in electronic insulators (e.g. ionic liquids: NaCl, KCl, part. dissoc. water, etc.)
- Linear Response (Green-Kubo) formalism: conductivity from equilibrium molecular dynamics simulations

\[ \sigma \propto \int_0^\infty \langle \mathbf{J}(t) \cdot \mathbf{J}(0) \rangle \, dt \]
Charge flux defined as time derivative of polarization $P \equiv \mu/\Omega$

$$J(t) = \frac{1}{\Omega} \dot{\mu}(t) = \frac{1}{\Omega} \sum_{I=1}^{N} Z_{iI}(t) V_I(t)$$

where

$$Z_{ij,I}(t) \equiv \frac{\partial \mu_i}{\partial R_{j,I}}$$

is the Born charge, and $V_I(t) = \dot{R}_I$ is the nuclear velocity.
The Born tensors $Z(t)$ are strongly fluctuating with time.

**Figure:** Diagonal elements of $Z(t)$ for one H and O in partially dissociated water. After French, Hamel, and Redmer, PRL 107 (2011)
Interestingly, the use of predefined constant charges can yield the same conductivity as is found with the fully time-dependent charge tensors.

\[
\mathbf{J} = \frac{1}{\Omega} \sum_i Z_i \mathbf{V}_i, \quad \mathbf{J}' = \frac{1}{\Omega} \sum_i q_i \mathbf{V}_i
\]
Conductivity. Gauge Invariance

Green-Kubo and Einstein formulations:

\[ \sigma \propto \int_0^\infty \langle J(t) \cdot J(0) \rangle dt \propto \lim_{\tau \to +\infty} \frac{\langle |\Delta \mu(\tau)|^2 \rangle}{2\tau} \]

where the dipole displaced in a time \( \tau \) is

\[ \Delta \mu(\tau) = \Omega \int_0^\tau J(t) dt \]

---

Conductivity. Gauge Invariance

Green-Kubo and Einstein formulations:

\[ \sigma \propto \int_0^\infty \langle J(t) \cdot J(0) \rangle dt \propto \lim_{\tau \to +\infty} \frac{\langle |\Delta \mu(\tau)|^2 \rangle}{2\tau} \]

where the dipole displaced in a time \( \tau \) is

\[ \Delta \mu(\tau) = \Omega \int_0^\tau J(t) dt \]

We have the following\(^1,^2\)

**Theorem (Gauge invariance)**

The addition of a **bounded term** to \( \mu(\tau) \) does not affect \( \sigma \)

---


Proof of gauge invariance

Take an additional term $b(t)$, and consider $\mu'(t) = \mu(t) + b(t)$.
Proof of gauge invariance

Take an additional term \( b(t) \), and consider \( \mu'(t) = \mu(t) + b(t) \)

\[
\sigma_{\mu'\mu'} = \sigma_{\mu\mu} + \sigma_{bb} + 2\sigma_{b\mu}
\]

where

\[
\sigma_{bb} = \lim_{\tau \to \infty} \frac{\langle |b(\tau) - b(0)|^2 \rangle}{2\tau}
\]

and the cross term is

\[
\sigma_{b\mu} \equiv \lim_{\tau \to \infty} \frac{\langle [b(\tau) - b(0)] \cdot [\mu(\tau) - \mu(0)] \rangle}{2\tau}.
\]
Proof of gauge invariance

Take an additional term \( b(t) \), and consider \( \mu'(t) = \mu(t) + b(t) \)

\[
\sigma_{\mu'\mu'} = \sigma_{\mu\mu} + \sigma_{bb} + 2\sigma_{b\mu}
\]

where

\[
\sigma_{bb} = \lim_{\tau \to \infty} \frac{\langle |b(\tau) - b(0)|^2 \rangle}{2\tau}
\]

and the cross term is

\[
\sigma_{b\mu} \equiv \lim_{\tau \to \infty} \frac{\langle [b(\tau) - b(0)] \cdot [\mu(\tau) - \mu(0)] \rangle}{2\tau}.
\]

The following Schwarz inequality holds

\[
\sigma_{b\mu} \leq \sqrt{\sigma_{bb}\sigma_{\mu\mu}}
\]
Proof of gauge invariance

Take an additional term $b(t)$, and consider $\mu'(t) = \mu(t) + b(t)$

$$\sigma_{\mu'\mu'} = \sigma_{\mu\mu} + \sigma_{bb} + 2\sigma_{b\mu}$$

where

$$\sigma_{bb} = \lim_{\tau \to \infty} \frac{\langle |b(\tau) - b(0)|^2 \rangle}{2\tau}$$

and the cross term is

$$\sigma_{b\mu} \equiv \lim_{\tau \to \infty} \frac{\langle [b(\tau) - b(0)] \cdot [\mu(\tau) - \mu(0)] \rangle}{2\tau}.$$  

The following Schwarz inequality holds

$$\sigma_{b\mu} \leq \sqrt{\sigma_{bb}\sigma_{\mu\mu}}$$

If $b$ is bounded, then $\sigma_{bb} = 0$, hence $\sigma_{b\mu} = 0$
Proof of gauge invariance

Take an additional term $\mathbf{b}(t)$, and consider $\mathbf{\mu}'(t) = \mathbf{\mu}(t) + \mathbf{b}(t)$

$$\sigma_{\mathbf{\mu}'\mathbf{\mu}'} = \sigma_{\mathbf{\mu}\mathbf{\mu}} + \sigma_{\mathbf{b}\mathbf{b}} + 2\sigma_{\mathbf{b}\mathbf{\mu}}$$

where

$$\sigma_{\mathbf{b}\mathbf{b}} = \lim_{\tau \to \infty} \frac{\langle |\mathbf{b}(\tau) - \mathbf{b}(0)|^2 \rangle}{2\tau}$$

and the cross term is

$$\sigma_{\mathbf{b}\mathbf{\mu}} \equiv \lim_{\tau \to \infty} \frac{\langle [\mathbf{b}(\tau) - \mathbf{b}(0)] \cdot [\mathbf{\mu}(\tau) - \mathbf{\mu}(0)] \rangle}{2\tau}.$$ 

The following Schwarz inequality holds

$$\sigma_{\mathbf{b}\mathbf{\mu}} \leq \sqrt{\sigma_{\mathbf{b}\mathbf{b}}\sigma_{\mathbf{\mu}\mathbf{\mu}}}$$

If $\mathbf{b}$ is bounded, then $\sigma_{\mathbf{b}\mathbf{b}} = 0$, hence $\sigma_{\mathbf{b}\mathbf{\mu}} = 0$

$$\sigma_{\mathbf{\mu}'\mathbf{\mu}'} = \sigma_{\mathbf{\mu}\mathbf{\mu}}$$
Path in the PBC-closed $3N$-dimensional nuclear configuration space
Path in the PBC-closed $3N$-dimensional nuclear configuration space
Conductivity. Gauge Invariance

The point $A'$ is the replica (periodic image) of the initial point $A$ sharing with the point $B$ the same cell of the nuclear configuration space.

$$\Delta \mu_{AB} \equiv \int_{AB} d\mu$$
$$= \Delta \mu_{AA'} + \Delta \mu_{A'B}$$
The point $A'$ is the replica (periodic image) of the initial point $A$ sharing with the point $B$ the same cell of the nuclear configuration space.

⇒ When we wrap the trajectory in PBCs, the path connecting $A$ and $A'$ is closed (loop).

\[
\Delta \mu_{AB} \equiv \int_{AB} d\mu = \Delta \mu_{AA'} + \Delta \mu_{A'B}
\]
the point $A'$ is the replica (periodic image) of the initial point $A$ sharing with the point $B$ the same cell of the nuclear configuration space.

⇒ When we *wrap* the trajectory in PBCs, the path connecting $A$ and $A'$ is **closed** (*loop*).

- the open path $A'B$ **entirely belongs to one** cell.

\[
\Delta \mu_{AB} \equiv \int_{\mathcal{B}_{AB}} d\mu = \Delta \mu_{AA'} + \Delta \mu_{A'B}
\]
\[ \Delta \mu_{A'B} \text{ is bounded.} \]
\( \Delta \mu_{A'B} \) is bounded.

Therefore to evaluate \( \sigma \) we only need to consider

\[
\Delta \mu_{AA'} = \int_{AA'} d\mu
\]

due to the closed path from \( A \) to \( A' \):

\[
\sigma \propto \lim_{\tau \to \infty} \frac{\langle |\Delta \mu_{AB}(\tau)|^2 \rangle}{2\tau} = \lim_{\tau \to \infty} \frac{\langle |\Delta \mu_{AA'}(\tau)|^2 \rangle}{2\tau}
\]
\[ \Delta \mu_{A'B} \text{ is bounded}. \]

Therefore to evaluate \( \sigma \) we only need to consider

\[ \Delta \mu_{AA'} = \int_{AA'} d\mu \]

due to the closed path from \( A \) to \( A' \):

\[ \sigma \propto \lim_{\tau \to \infty} \frac{\langle |\Delta \mu_{AB}(\tau)|^2 \rangle}{2\tau} = \lim_{\tau \to \infty} \frac{\langle |\Delta \mu_{AA'}(\tau)|^2 \rangle}{2\tau} \]

What can we know about \( \Delta \mu_{AA'} \)?
\[ \Rightarrow \text{Charge-transport quantization} \]
Some considerations on cell size and BCs

- The system size has to be larger than the relevant correlation/diffusion lengths
  
  ⇒ Equilibrium properties are independent of specific BCs adopted in the simulation
Some considerations on cell size and BCs

- The system size has to be larger than the relevant correlation/diffusion lengths
  ⇒ Equilibrium properties are independent of specific BCs adopted in the simulation
- PBCs chosen since they
  - minimize size effects
Some considerations on cell size and BCs

- The system size has to be larger than the relevant correlation/diffusion lengths

⇒ Equilibrium properties are independent of specific BCs adopted in the simulation

- PBCs chosen since they
  - minimize size effects
  - the $\tau \to \infty$ limit of Einstein’s formula commutes with thermodynamic limit (not true in open BCs)
The system size has to be larger than the relevant correlation/diffusion lengths.

Equilibrium properties are independent of specific BCs adopted in the simulation.

PBCs chosen since they minimize size effects.

the $\tau \to \infty$ limit of Einstein’s formula commutes with thermodynamic limit (not true in open BCs).

We argue that our conclusions do not depend on the system size, and hold in the thermodynamic limit.
Suppose

- parameter dependent electronic Hamiltonian

\[ \hat{H}^{R(t)}, \quad R(t) \equiv (R_1(t), \ldots, R_N(t)) \]
Suppose

- parameter dependent electronic Hamiltonian

\[ \hat{H}^{R(t)}, \quad R(t) \equiv (R_1(t), \ldots, R_N(t)) \]

- \( \hat{H} \) is cyclic, i.e. \( \hat{H}^{R(0)} = \hat{H}^{R(T)} \) for some \( T \)
Suppose

- parameter dependent electronic Hamiltonian

\[ \hat{H}^{\mathbf{R}(t)}, \quad \mathbf{R}(t) \equiv (\mathbf{R}_1(t), \ldots, \mathbf{R}_N(t)) \]

- \( \hat{H} \) is cyclic, i.e. \( \hat{H}^{\mathbf{R}(0)} = \hat{H}^{\mathbf{R}(T)} \) for some \( T \)

- the evolution satisfies the hypotheses of the adiabatic theorem (slow, gapped, non degenerate ground state)
Charge-transport quantization

Suppose

- parameter dependent electronic Hamiltonian

\[ \hat{H}^{R(t)}, \quad R(t) \equiv (R_1(t), \ldots, R_N(t)) \]

- \( \hat{H} \) is cyclic, i.e. \( \hat{H}^{R(0)} = \hat{H}^{R(T)} \) for some \( T \)

- the evolution satisfies the hypotheses of the adiabatic theorem
  (slow, gapped, non degenerate ground state)

- the system is periodic along some macroscopic direction, say \( i \), with spatial period \( \ell \).
The total transported charge along $i$ in a closed path $AA'$ in nuclear configuration space with PBCs:

$$Q_i \equiv \frac{1}{\ell} \int_{AA'} d\mu_i = \frac{\Delta \mu_{AA'} i}{\ell}$$

is an integer number,

$$Q_i \in \mathbb{Z}.$$
$Q_i$ is a continuous functional of the path connecting $A$ and $A'$.
$Q$ is an integer constant

- $Q_i$ is a **continuous** functional of the path connecting $A$ and $A'$
- $Q_i$ is **integer**
$Q$ is an integer \textit{constant}.

- $Q_i$ is a \textit{continuous} functional of the path connecting $A$ and $A'$.
- $Q_i$ is \textit{integer}.

$\Rightarrow$ $Q_i$ is an \textit{integer constant}, for any two paths connecting $A$ and $A'$ which can be \textit{continuously deformed into one another}.
Equivalent paths and separability of $Q_i$

PBC-closed nuclear config space isomorphic to $\mathbb{Z}^{3N}$: each path $AA'$ expressed uniquely via the $3N$-integer tuple $n$, where $(n_{I,i})$ indicates the number of cells spanned by atom $I$ along direction $i$. 

Figure: Decomposition in elementary paths for 1D, $N=2$ nuclear configuration space: $n=(1,1)$. 

F. Grasselli  
Electrical conductivity of liquid insulators
Equivalent paths and separability of $Q_i$

PBC-closed nuclear config space isomorphic to $\mathbb{Z}^{3N}$: each path $AA'$ expressed uniquely via the $3N$-integer tuple $\mathbf{n}$, where $(n_{I,i})$ indicates the number of cells spanned by atom $I$ along direction $i$.

Figure: Decomposition in elementary paths for 1D, $N = 2$ nuclear configuration space: $\mathbf{n} = (1, 1)$.
Separability of $Q_i$ in atomic contributions

We assume that all trivial loops ($A' \equiv A$) can be shrunk to a point without closing the electronic gap.

$$Q_i = \sum_{I=1}^{N} \sum_{j=1}^{n} (I, j) q(I, j)$$

where

$$q(I, j)_{i} = Q_i [n = (0, \ldots, 1, \ldots, 0) \in \mathbb{Z}$$

The hypothesis above also implies that the $q$s are scalars:

$$q(I, j)_{i} = q_I \delta_{ij}$$

If we further assume that the exchange of atoms of same species $S$ can be performed without closing the electronic gap, then $q_I = q_S (I)$. 

F. Grasselli  Electrical conductivity of liquid insulators
Separability of $Q_i$ in atomic contributions

We assume that all trivial loops ($A' \equiv A$) can be shrunk to a point without closing the electronic gap.

$$Q_i = \sum_{l=1}^{N} \sum_{j=1}^{3} n(l,j) q_{i}^{(l,j)}$$

where

$$q_{i}^{(l,j)} = Q_i[n = (0, \ldots, \underbrace{1}_{\text{atom } l \text{ along } j}, 0, \ldots, 0)] \in \mathbb{Z}$$
Separability of $Q_i$ in atomic contributions

We assume that all trivial loops ($A' \equiv A$) can be shrunk to a point without closing the electronic gap.

$$Q_i = \sum_{l=1}^{N} \sum_{j=1}^{3} n_{(l,j)} q_{i}^{(l,j)}$$

where

$$q_{i}^{(l,j)} = Q_i[n = (0, \ldots, \underbrace{1}_{\text{atom } l \text{ along } j}, 0, \ldots, 0)] \in \mathbb{Z}$$

The hypothesis above also implies that the $q$s are scalars:

$$q_{i}^{(l,j)} = q^l \delta_{ij}$$
Separeability of $Q_i$ in atomic contributions

We assume that all trivial loops ($A' \equiv A$) can be shrunk to a point without closing the electronic gap.

$$Q_i = \sum_{i=1}^{N} \sum_{j=1}^{3} n_{(i,j)} q_i^{(i,j)}$$

where

$$q_i^{(i,j)} = Q_i[n = (0, \ldots, 1, 0, \ldots, 0)] \in \mathbb{Z}$$

The hypothesis above also implies that the $q$s are scalars:

$$q_i^{(i,j)} = q^l \delta_{ij}$$

If we further assume that the exchange of atoms of same species $S$ can be performed without closing the electronic gap, then

$$q^l = q^{S(l)}$$
Ab initio conductivity from integer (fixed) charges

\[ \Delta \mu_{AA'} = \ell \sum_{l=1}^{N} q^{S(l)} n_l \]

\[ \Delta \mu'(\tau) \equiv \Omega \int_{0}^{T} J'(t) dt, \text{ with } J' = \frac{1}{\Omega} \sum_{l} q^{S(l)} v_l \]
Ab initio conductivity from integer (fixed) charges

\[ \Delta \mu_{AA'} = \ell \sum_{l=1}^{N} q^{S(l)} n_{l} \]

\[ \Delta \mu'(\tau) \equiv \Omega \int_{0}^{\tau} J'(t) dt, \text{ with } J' = \frac{1}{\Omega} \sum_{l} q^{S(l)} V_{l} \]

Evidently, we have

\[ \Delta \mu'(\tau) = \Delta \mu_{AA'}(\tau) + \sum_{l} q^{S(l)} \int_{A'}^{B} dR_{l}(t) \]

bounded
Ab initio conductivity from integer (fixed) charges

\[ \Delta \mu_{AA'} = \ell \sum_{I=1}^{N} q^{S(I)} n_I \]

\[ \Delta \mu'(\tau) \equiv \Omega \int_{0}^{\tau} J'(t) dt, \text{ with } J' = \frac{1}{\Omega} \sum_{I} q^{S(I)} V_I \]

Evidently, we have

\[ \Delta \mu'(\tau) = \Delta \mu_{AA'}(\tau) + \sum_{l} q^{S(l)} \int_{A'}^{B} dR_l(t) \]

\[ \lim_{\tau \to \infty} \frac{\langle |\Delta \mu(\tau)|^2 \rangle}{2\tau} = \lim_{\tau \to \infty} \frac{\langle |\Delta \mu_{AA'}(\tau)|^2 \rangle}{2\tau} = \lim_{\tau \to \infty} \frac{\langle |\Delta \mu'(\tau)|^2 \rangle}{2\tau} \]
The ab initio conductivity can be obtained by replacing, for each atom, its time-dependent, real-valued, Born charge tensor with an integer, time-independent number.\(^3\)

\(^3\)FG and Stefano Baroni, arXiv:1902.07256 accepted by *Nature Phys.*
The ab initio conductivity can be obtained by replacing, for each atom, its time-dependent, real-valued, Born charge tensor with an integer, time-independent number.\(^3\)

The auto-correlation functions of the fluxes differ, but their asymptotic-time integrals (i.e. the conductivities) coincide.

Numerical experiments

Performed via QUANTUM ESPRESSO

1. Take a snapshot of liquid KCl AIMD simulation
2. Generate a loop for one nucleus (say K), discretized as a set of different images (neb.x)
3. Compute Born charge tensors for each atom

\[ Z_{ij,l} = \frac{\partial \mu_i}{\partial R_{j,l}} \bigg|_{\varepsilon=0} = \frac{\partial F_{j,l}}{\partial \varepsilon_i} \bigg|_{\text{fixed nuclei}} \]

at each image of the path.
3. Compute Born charge tensors for each atom

\[ Z_{ij,l} = \frac{\partial \mu_i}{\partial R_{j,l}} \bigg|_{\varepsilon=0} = \frac{\partial F_{j,l}}{\partial \varepsilon_i} \bigg|_{\text{fixed nuclei}} \]

at each image of the path.

DFPT (phcg.x) and Berry’s phase formulation of polarization (via CG in cp.x) yield same results.
3. Compute Born charge tensors for each atom

\[ Z_{ij,l} = \frac{\partial \mu_i}{\partial R_{j,l}} \bigg|_{\varepsilon=0} = \frac{\partial F_{j,l}}{\partial \varepsilon_i} \bigg|_{\text{fixed nuclei}} \]

at each image of the path.

DFPT (phcg.x) and Berry’s phase formulation of polarization (via CG in cp.x) yield same results.

4. Integrate \( d\mu_i = \sum_{I,j} Z_{ij,l} dR_{(I,j)} \) due to the path of the moving atom and divide by the cell side to get \( q^I \)
Numerical experiments

\[ Q_x = -0.000 \] \hspace{1cm} \[ Q_y = 0.000 \] \hspace{1cm} \[ Q_z = 1.00 \] \hspace{1cm} \[ \text{transported charge (e)} \]

\[ q_K = +1, \text{ charge in transit, not a static charge} \]

\[ \text{We recover the result in Jiang, Levchenko, Rappe, PRL (2012) on \textbf{solids}} \]
Numerical experiments

\[ Q_x = -0.000(6) \quad Q_y = 0.000(2) \quad Q_z = 1.00(18) \]

\(^4\)We recover the result in Jiang, Levchenko, Rappe, PRL (2012) on solids
Numerical experiments

and

\[ Q_x = -0.000(6) \quad Q_y = 0.000(2) \quad Q_z = 1.00(18) \]

\[ q^K = +1, \textbf{charge in transit}, \textit{not a static charge}^4 \]

\[^4\text{We recover the result in Jiang, Levchenko, Rappe, PRL (2012) on solids}\]
Numerical experiments

Additivity:

K along z, Cl along z and y

transported charge (e)

path coordinate
Numerical experiments

Additivity:

\[ K \text{ along } z, \quad Cl \text{ along } z \text{ and } y \]

with

\[ Q_x = 0 \quad Q_y = -1 \quad Q_z = 0 \]
Numerical experiments

Exchange of two K atoms:

with

\[ Q_x = 0 \quad Q_y = 0 \quad Q_z = +2 \]
Figure: Mean square displacement of dipole vs time
Conclusions and future work

In liquid insulators

- **gauge invariance** of transport coefficient and **charge-transport quantization** arguments can be directly applied to study charge transport

Current/next steps (with Paolo Pegolo)

- investigate systems where charge transport occurs without ionic core (mass) transport
- investigate systems where atoms of the same species are present in different oxidation states
In liquid insulators

- **gauge invariance** of transport coefficient and **charge-transport quantization** arguments can be directly applied to study charge transport

- ab initio $\sigma$ can be obtained by substituting Born tensors with **integer charges**, classically associated (oxidation states) to ions

Current/next steps (with Paolo Pegolo)

◦ investigate systems where charge transport occurs without ionic core (mass) transport

◦ investigate systems where atoms of the same species are present in different oxidation states
Conclusions and future work

In liquid insulators

- **gauge invariance** of transport coefficient and **charge-transport quantization** arguments can be directly applied to study charge transport.

- ab initio $\sigma$ can be obtained by substituting Born tensors with **integer charges**, classically associated (oxidation states) to ions.

- only **good trajectories** (velocities) of atoms are needed: correct forces via AIMD or neural networks (Linfeng’s talk).

Current/next steps (with Paolo Pegolo)
- investigate systems where charge transport occurs without ionic core (mass) transport.
- investigate systems where atoms of the same species are present in different oxidation states.
Conclusions and future work

In liquid insulators

- **gauge invariance** of transport coefficient and **charge-transport quantization** arguments can be directly applied to study charge transport

- ab initio $\sigma$ can be obtained by substituting Born tensors with **integer charges**, classically associated (oxidation states) to ions

- only **good trajectories** (velocities) of atoms are needed: correct forces via AIMD or neural networks (Linfeng’s talk).

Current/next steps (with Paolo Pegolo)

- investigate systems where charge transport occurs without ionic core (mass) transport

- investigate systems where atoms of the same species are present in different oxidation states