Topological quantization and gauge invariance of charge transport in liquid insulators

Federico Grasselli

SISSA – Scuola Internazionale Superiore di Studi Avanzati
Trieste, Italy

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Introduction. Framework

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- 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 $\mathbf{P} \equiv \boldsymbol{\mu}/\Omega$

$$\mathbf{J}(t) = \frac{1}{\Omega}\dot{\boldsymbol{\mu}}(t) = \frac{1}{\Omega}\sum_{I=1}^{N} \mathrm{Z}_I(t)\,\mathbf{V}_I(t)$$

where

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

is the Born charge, and $\mathbf{V}_I(t) = \dot{\mathbf{R}}_I$ is the nuclear velocity

The Born tensors $\mathrm{Z}(t)$ are *strongly fluctuating with time*

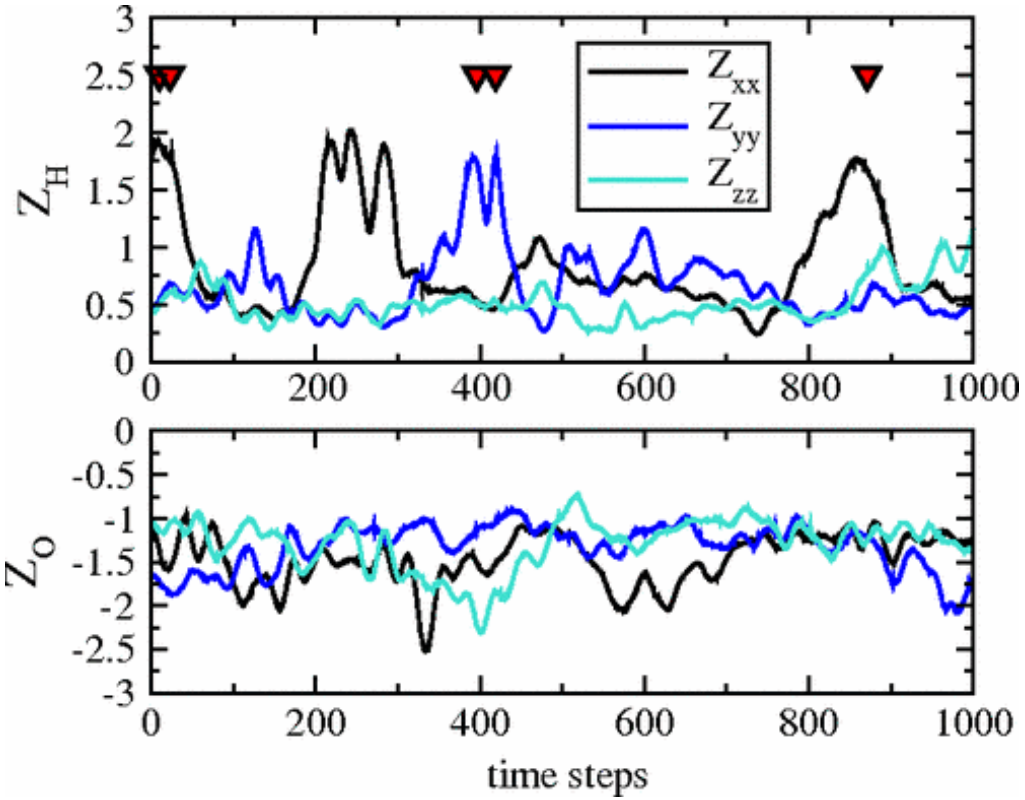

Figure: Diagonal elements of $\mathrm{Z}(t)$ for one H and O in partially dissociated water. After French, Hamel, and Redmer, PRL **107** (2011)

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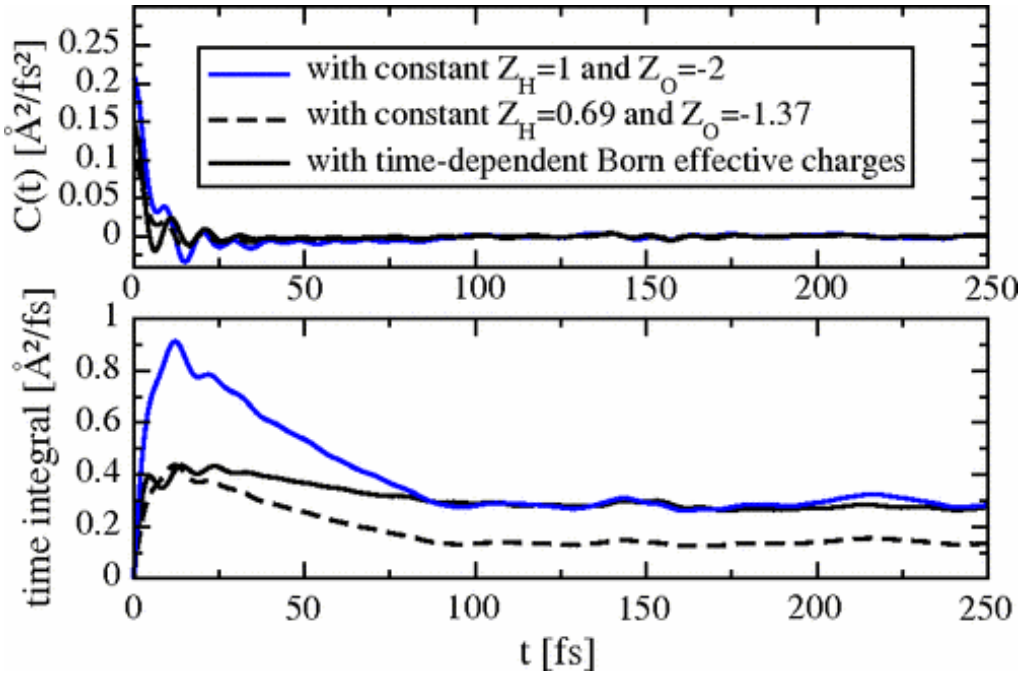

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$$\mathbf{J} = \frac{1}{\Omega} \sum_I \mathrm{Z}_I \, \mathbf{V}_I \qquad \mathbf{J}' = \frac{1}{\Omega} \sum_I q_I \mathbf{V}_I$$

"Interestingly, the use of predefined constant charges can yield the same conductivity as is found with the fully time-dependent charge tensors"

Conductivity. Gauge Invariance

Green-Kubo and Einstein formulations:

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

where the dipole displaced in a time τ is

$$\Delta \boldsymbol{\mu}(\tau) = \Omega \int_0^{\tau} \mathbf{J}(t) dt$$

[1] L. Ercole, A. Marcolongo, P. Umari, S. Baroni, J. Low Temp. Phys. (2016)
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We have the following[1,2]

Theorem (Gauge invariance)

The addition of a bounded term to $\boldsymbol{\mu}(\tau)$ does not affect σ

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Proof of gauge invariance

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

and the cross term is

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

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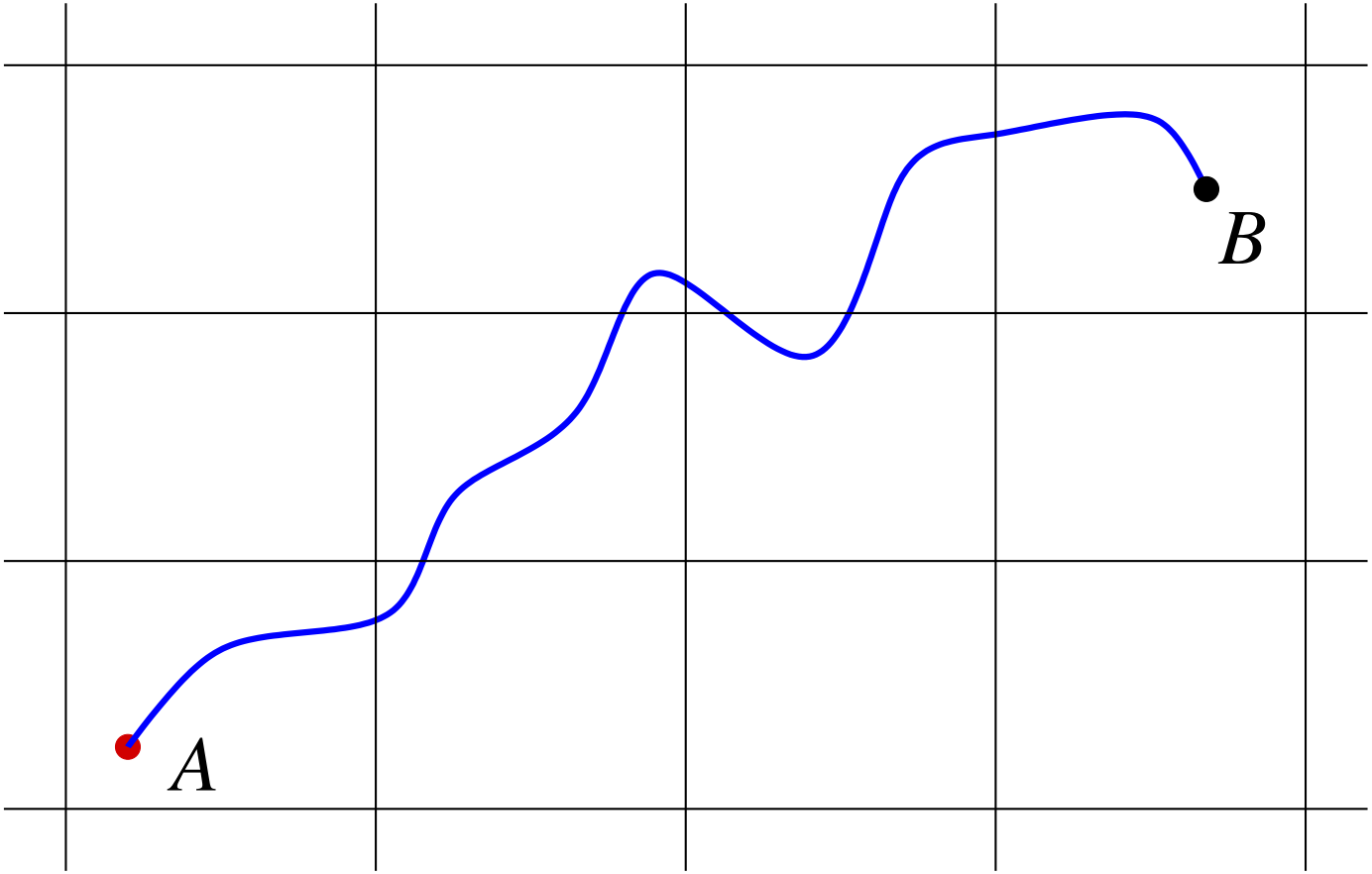

Path in the PBC-closed $3N$-dimensional nuclear configuration space

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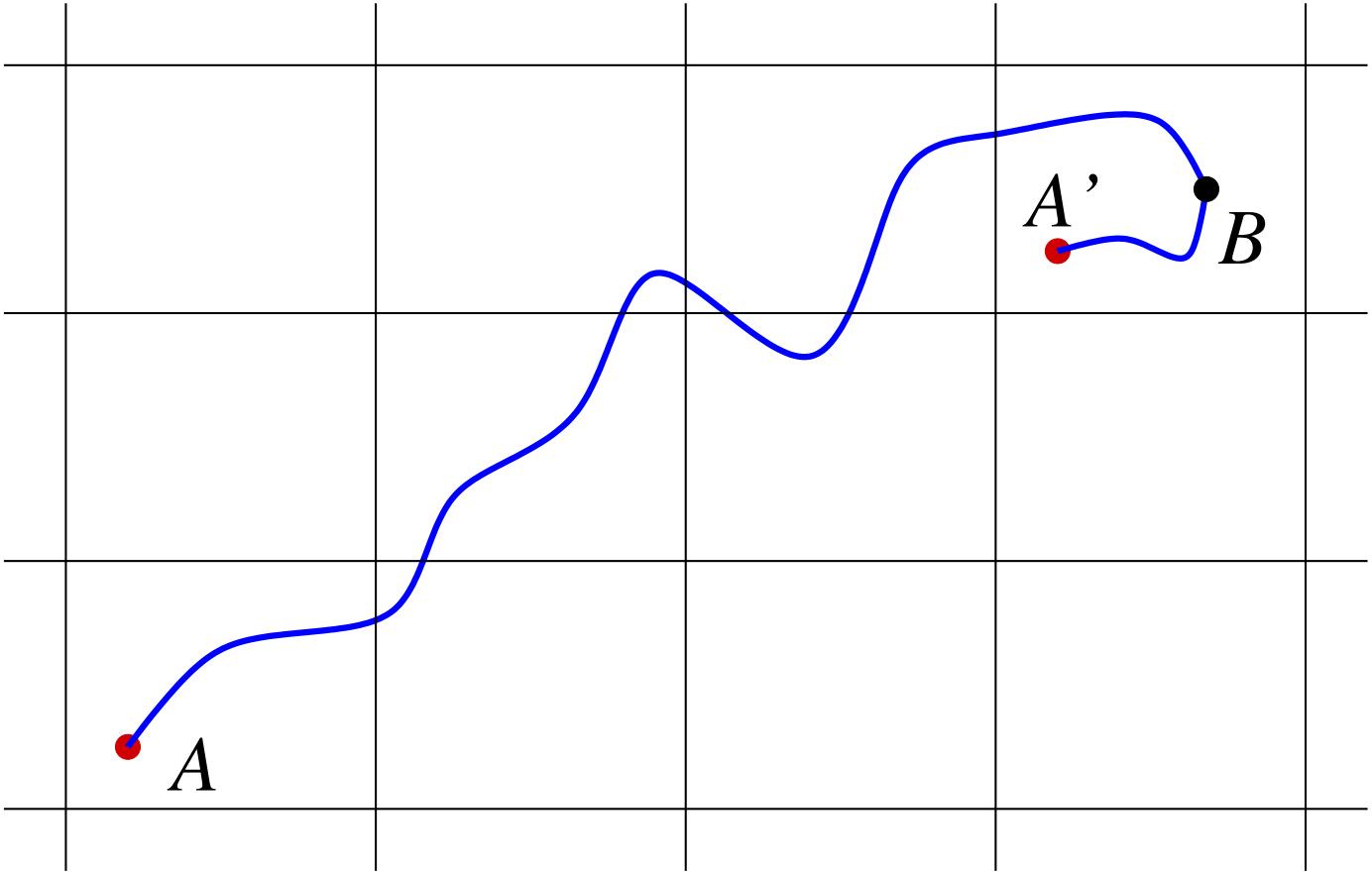

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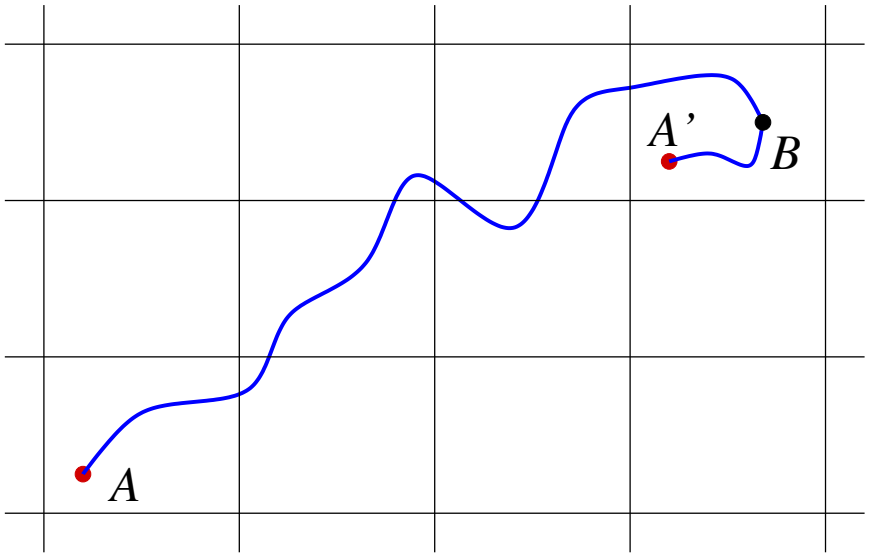

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$$= \Delta\mu_{AA'} + \Delta\mu_{A'B}$$

- 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.

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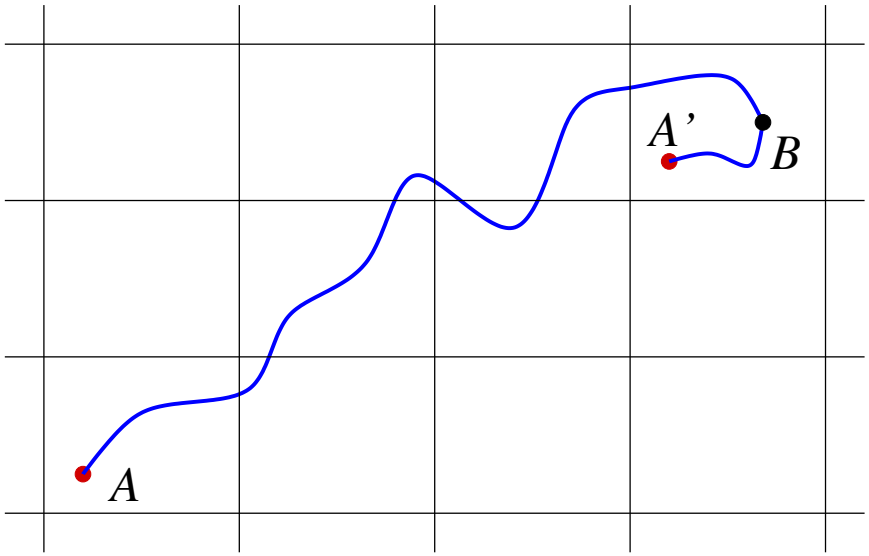

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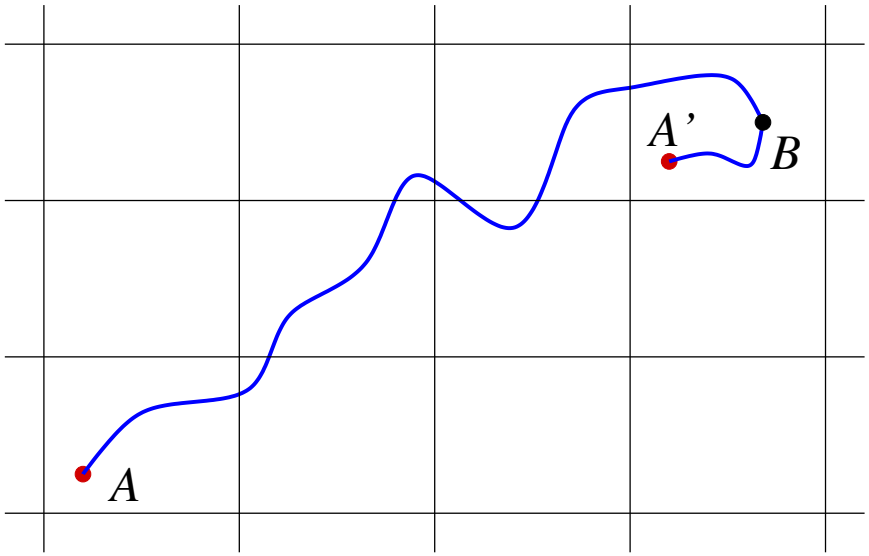

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- the open path $A'B$ **entirely belongs to one** cell.

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Therefore to evaluate σ we only need to consider

$$\Delta\boldsymbol{\mu}_{AA'} = \int_{AA'} d\boldsymbol{\mu}$$

due to the closed path from A to A':

$$\sigma \propto \lim_{\tau\to\infty} \frac{\langle|\Delta\boldsymbol{\mu}_{AB}(\tau)|^2\rangle}{2\tau} = \lim_{\tau\to\infty} \frac{\langle|\Delta\boldsymbol{\mu}_{AA'}(\tau)|^2\rangle}{2\tau}$$

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What can we know about $\Delta\boldsymbol{\mu}_{AA'}$?
$\Rightarrow$ Charge-transport quantization

Some considerations on cell size and BCs

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

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

Charge-transport quantization

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- parameter dependent electronic Hamiltonian

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- the system is *periodic* along some macroscopic direction, say i, with spatial period ℓ.

Charge-transport quantization

Theorem (Thouless (1983), King-Smith, Vanderbilt, Resta ('90s))

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,

$$Q_i \in \mathbb{Z}.$$

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$\Rightarrow$ Q_i is an **integer constant**, for any two paths connecting A and A' which can be **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 $\mathbf{n}$, where $(n_{I,i})$ indicates the number of cells spanned by atom I along direction i.

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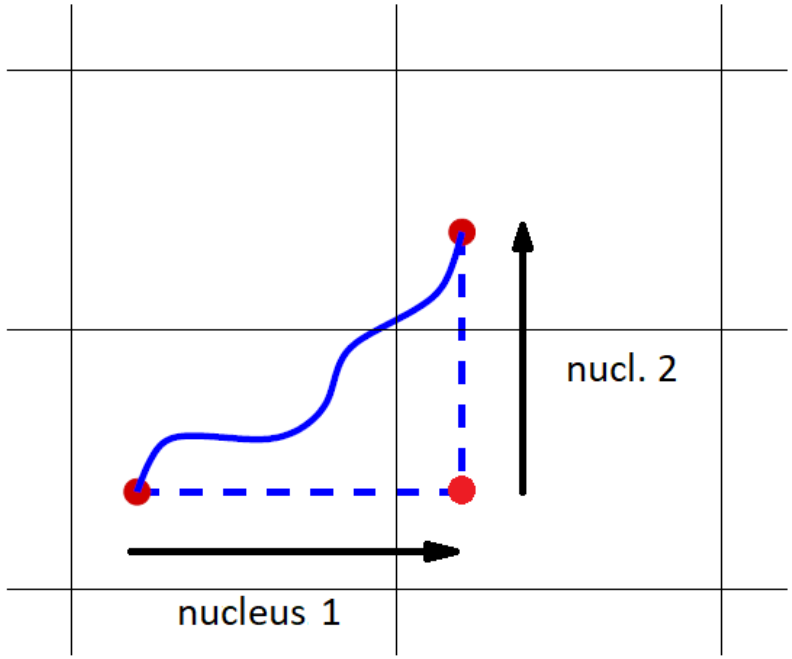

Figure: Decomposition in elementary paths for 1D, $N = 2$ nuclear configuration space: $\mathbf{n} = (1, 1)$.

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where

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

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

$$q^I = q^{S(I)}$$

Ab initio conductivity from integer (fixed) charges

$$\Delta\boldsymbol{\mu}_{AA'} = \ell \sum_{I=1}^{N} q^{S(I)} \mathbf{n}_I$$

$$\Delta\boldsymbol{\mu}'(\tau) \equiv \Omega \int_0^{\tau} \mathbf{J}'(t)dt, \text{ with } \mathbf{J}' = \frac{1}{\Omega} \sum_I q^{S(I)} \mathbf{V}_I$$

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$$\Delta\boldsymbol{\mu}'(\tau) = \Delta\boldsymbol{\mu}_{AA'}(\tau) + \underbrace{\sum_I q^{S(I)} \int_{A'}^{B} d\mathbf{R}_I(t)}_{\text{bounded}}$$

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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]

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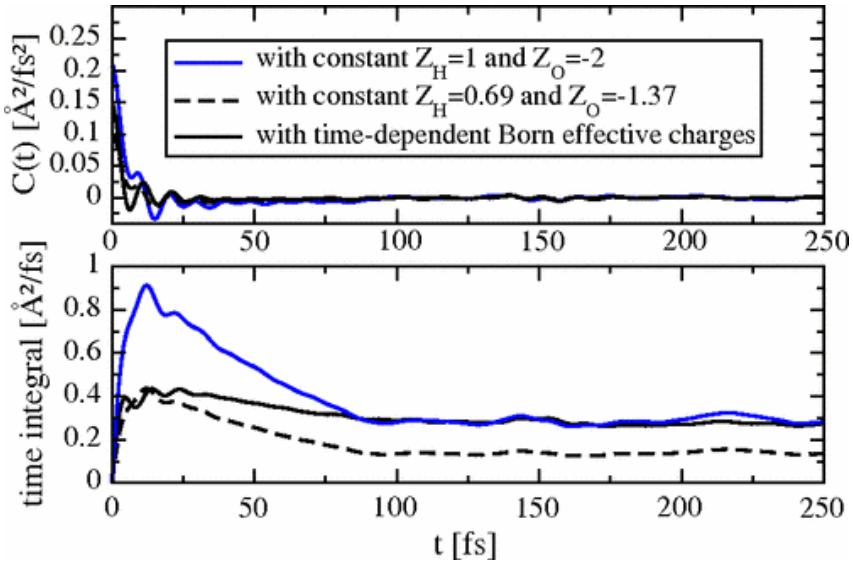

The auto-correlation functions of the fluxes differ, but their asymptotic-time integrals (i.e. the conductivities) coincide.

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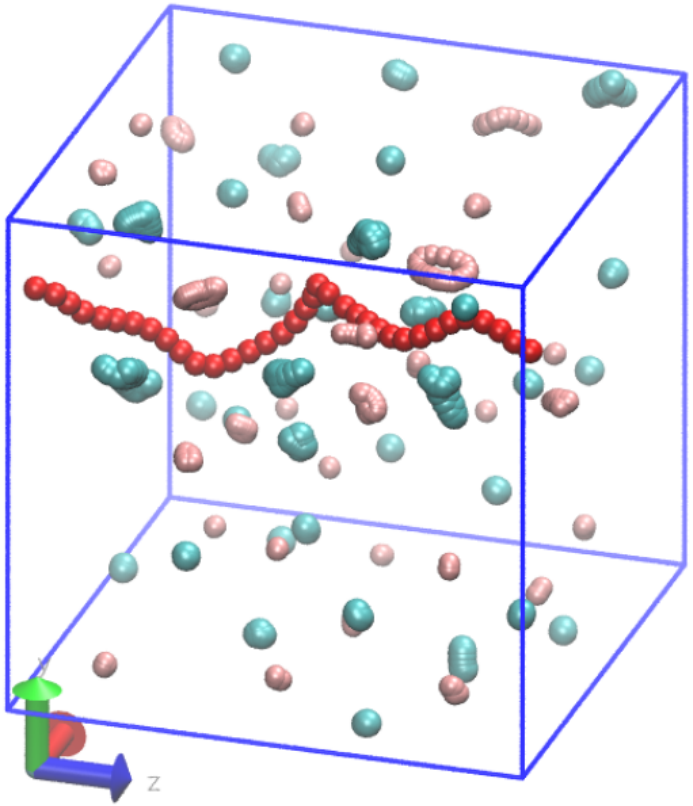
Numerical experiments

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

$$Z_{ij,I} = \left.\frac{\partial \mu_i}{\partial R_{j,I}}\right|_{\mathcal{E}=0} = \left.\frac{\partial F_{j,I}}{\partial \mathcal{E}_i}\right|_{\text{fixed nuclei}}$$

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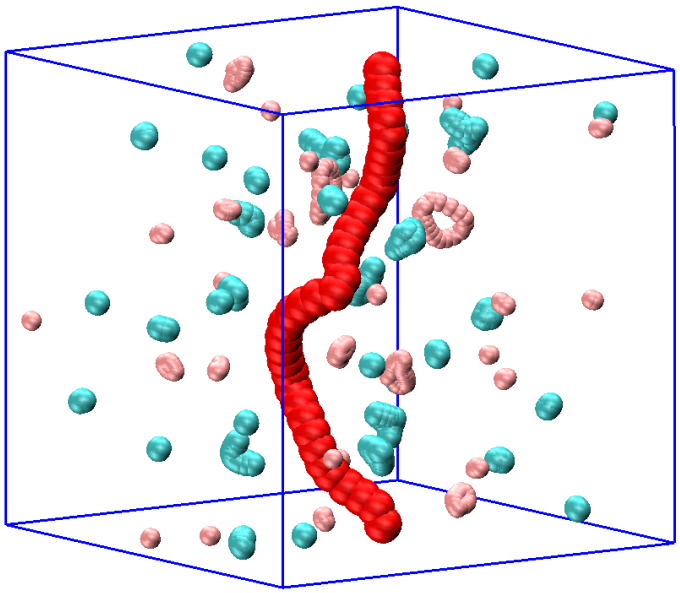
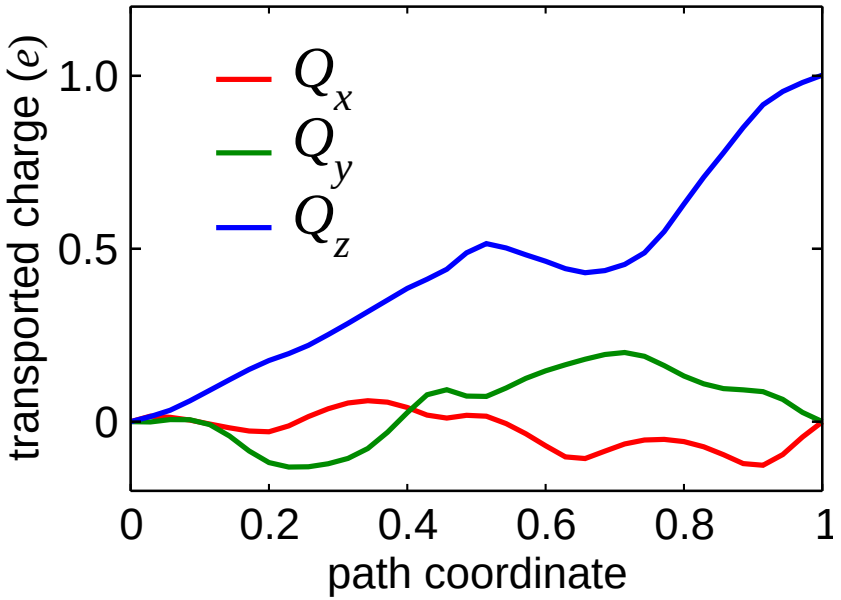
4. Integrate $d\mu_i = \sum_{I,j} Z_{ij,I} dR_{(I,j)}$ due to the path of the moving atom and divide by the cell side to get q^I

Numerical experiments





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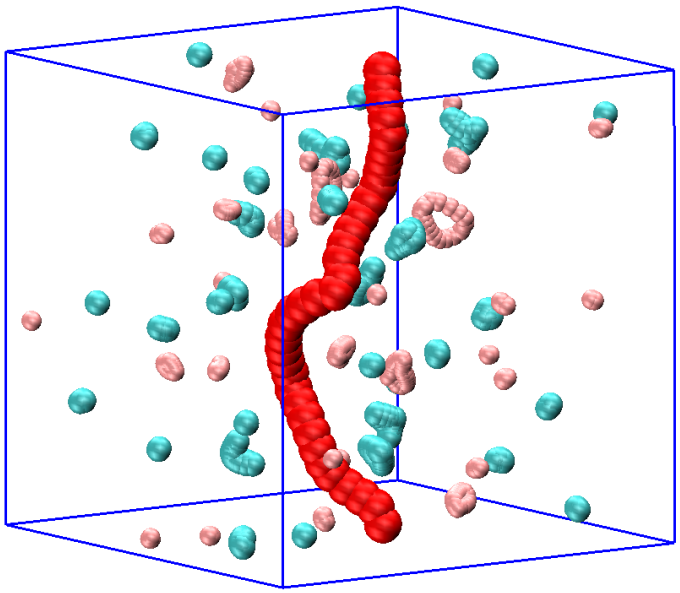

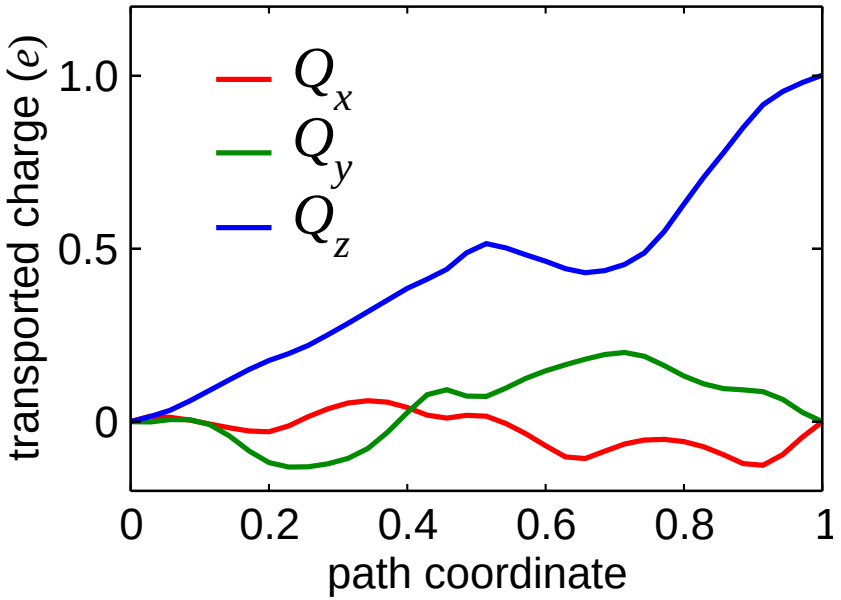

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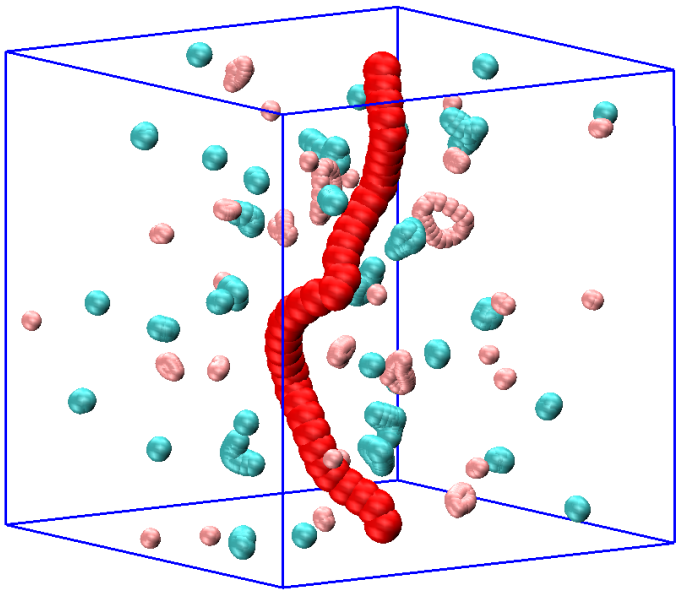
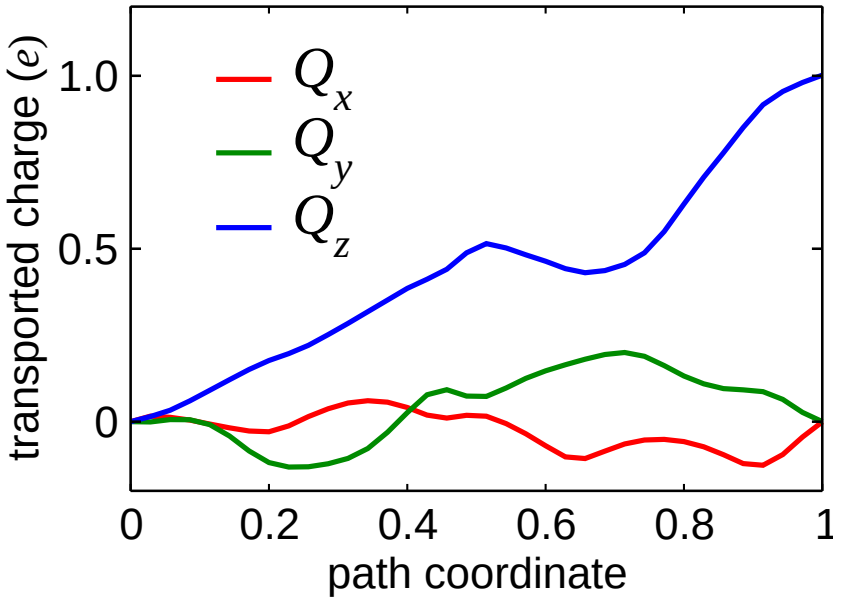




and

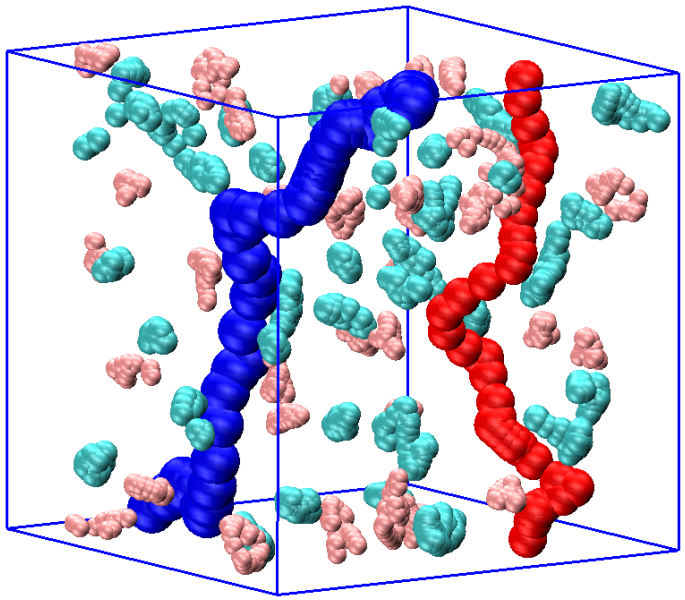
$$Q_x = -0.000(6) \qquad Q_y = 0.000(2) \qquad Q_z = 1.00(18)$$

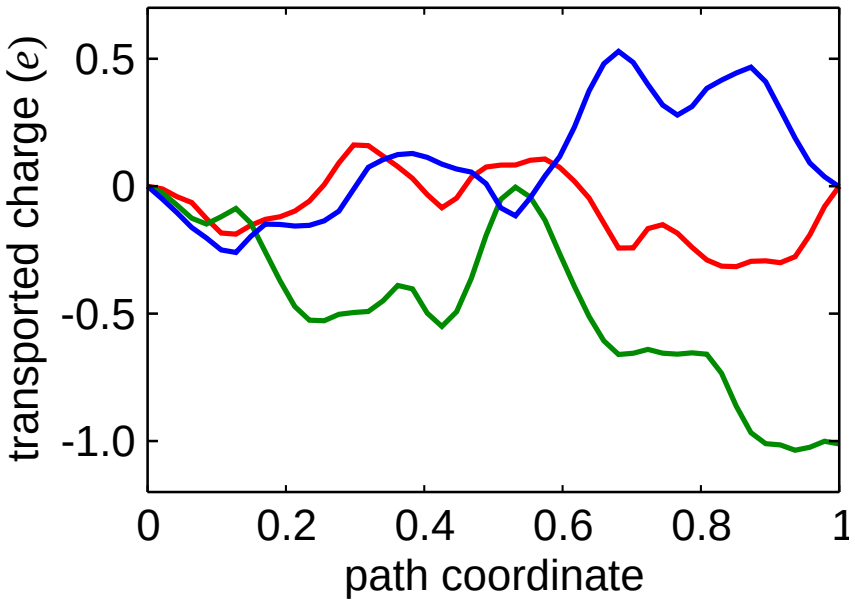
$q^{\mathrm{K}} = +1$, **charge in transit**, not a static charge[4]

[4] We recover the result in Jiang, Levchenko, Rappe, PRL (2012) on **solids**

Numerical experiments

Additivity:

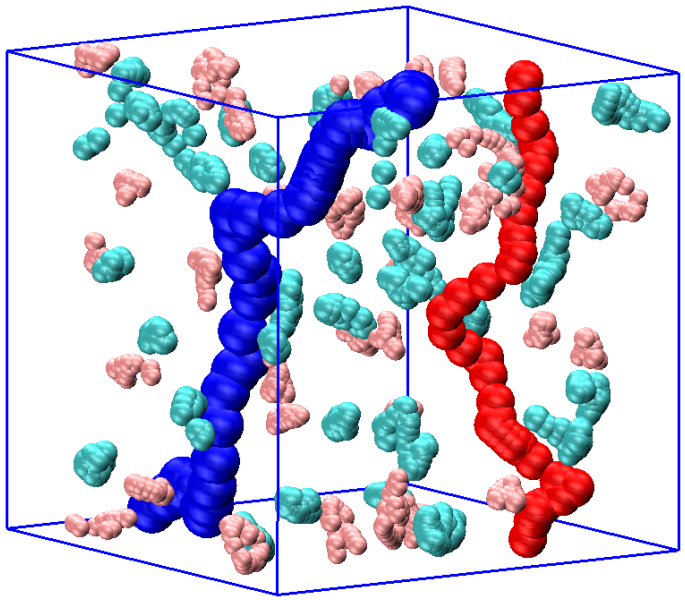


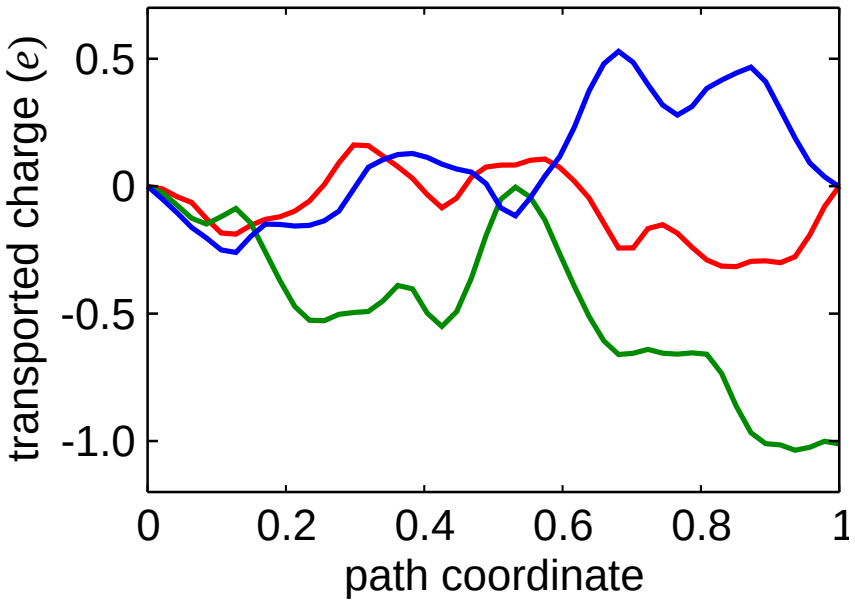


K along z, Cl along z and y

Numerical experiments

Additivity:





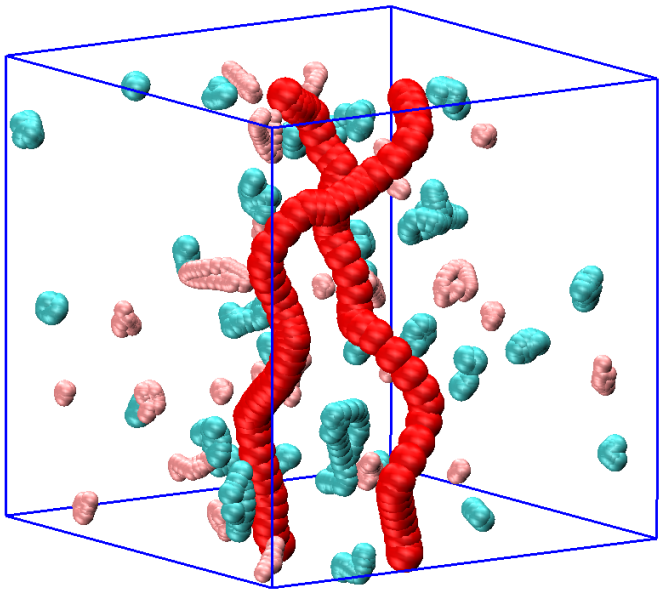
K along z, Cl along z and y

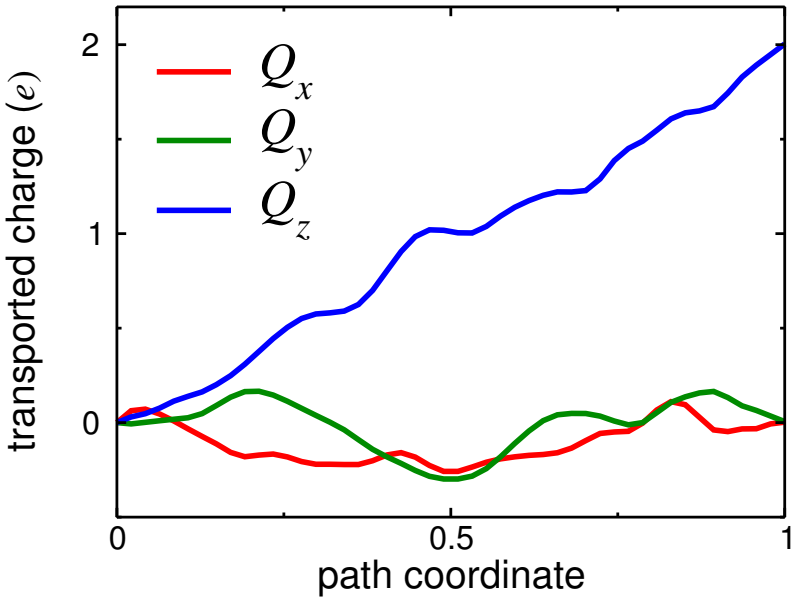
with

$$Q_x = 0 \qquad Q_y = -1 \qquad Q_z = 0$$

Numerical experiments

Exchange of two K atoms:





with

$$Q_x = 0 \qquad Q_y = 0 \qquad Q_z = +2$$

Numerical experiments

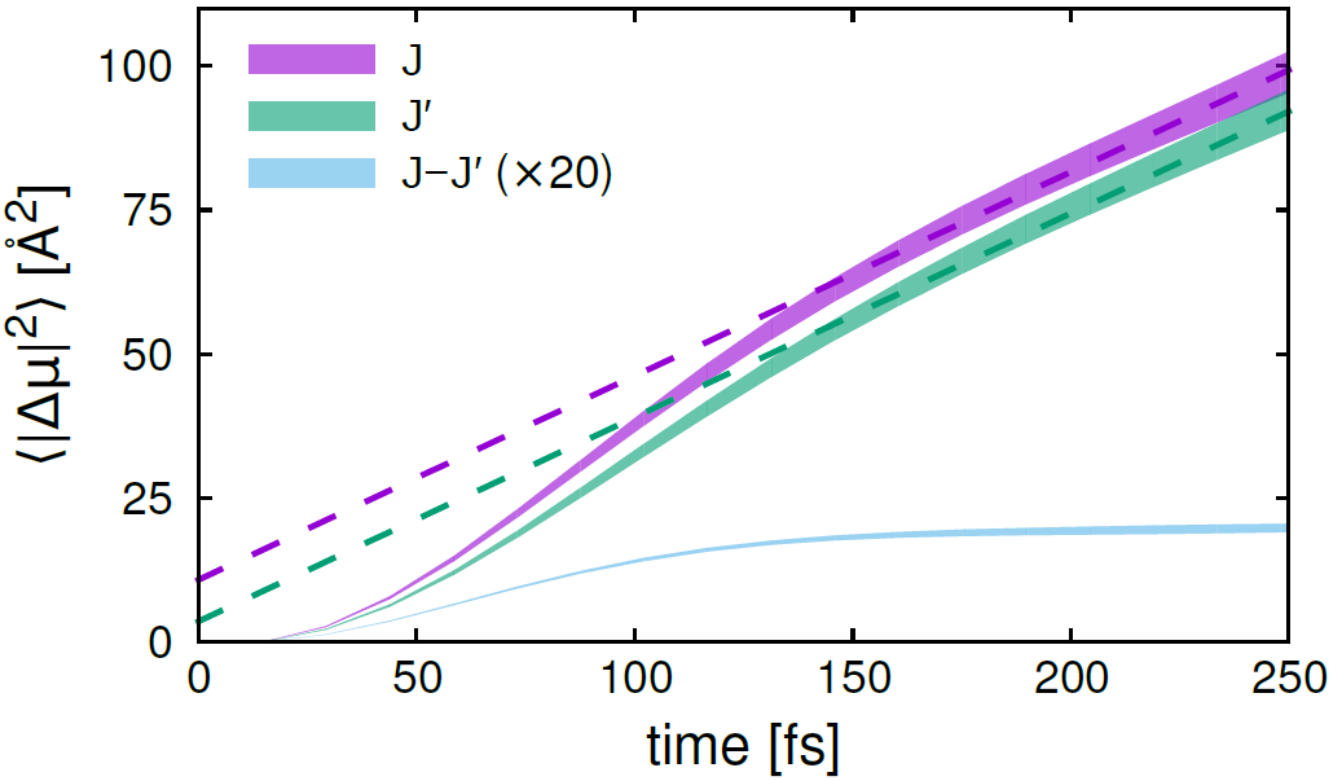


Figure: Mean square displacement of dipole vs time

Conclusions and future work

In liquid insulators

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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