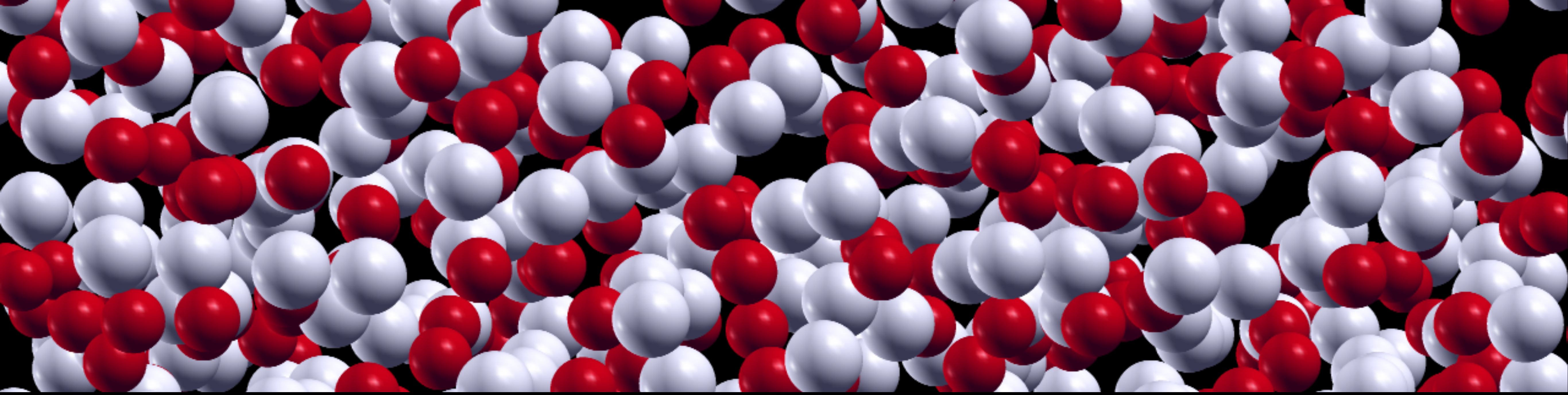
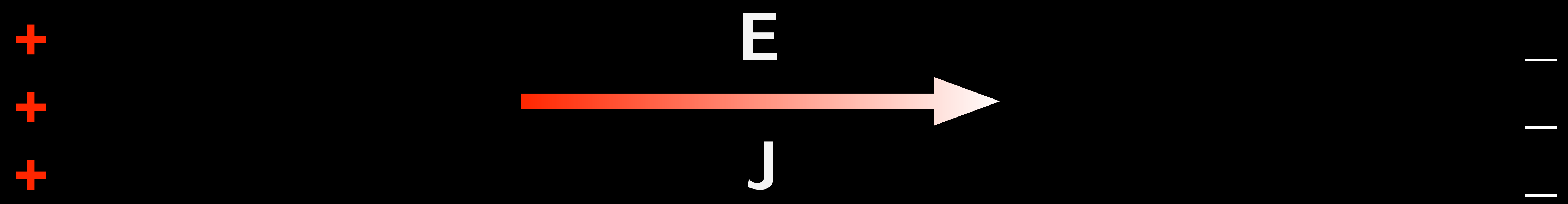
quantum topological effects in the transport properties of ionic conductors

Stefano Baroni
Scuola Internazionale Superiore di Studi Avanzati
Trieste — Italy

semi-plenary talk given at the CMD28 / 2020GEFES on-line conference, Universidad Autónoma de Madrid, September 2, 2020





$$\mathbf{J} = \sigma \mathbf{E}$$

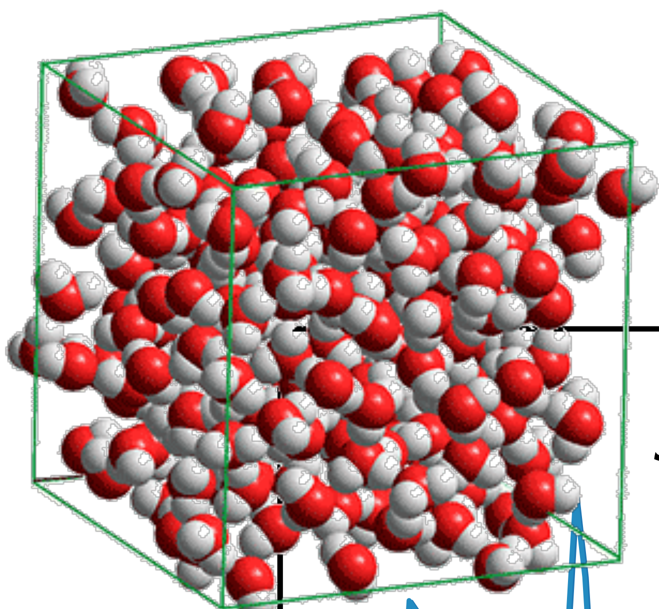
$$\mathbf{J} = \frac{1}{\Omega} \sum_i \mathbf{Z}^*_i \cdot \mathbf{v}_i \qquad Z^*_{i\alpha\beta} = \frac{\partial \mu_\alpha}{\partial u_{i\beta}}$$

$$\sigma = \frac{\Omega}{3 k_B T} \left\langle |\mathbf{J}|^2 \right\rangle \times \tau_J$$

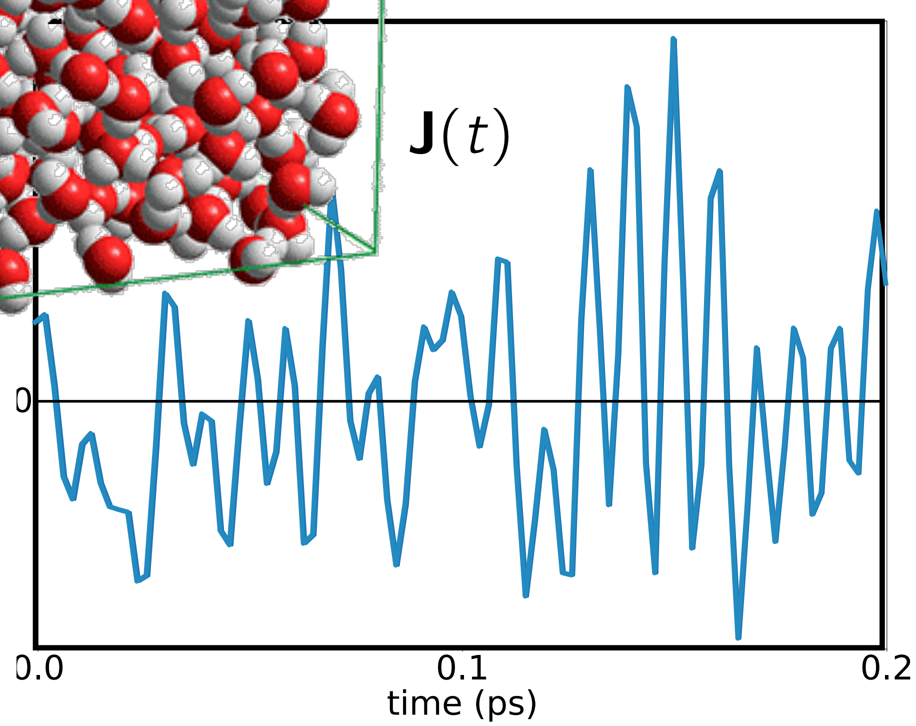
the conundrum

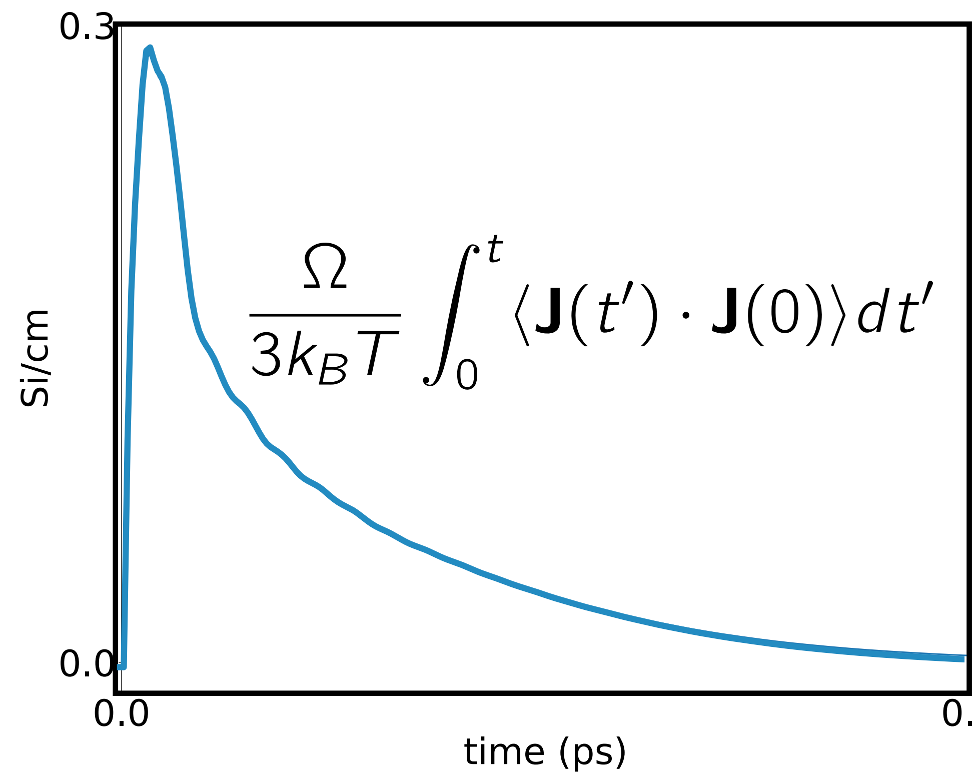
$$\mathbf{J} = \frac{1}{\Omega} \sum_i \mathbf{Z}_i^* \cdot \mathbf{v}_i$$

$$\sigma = \frac{\Omega}{3k_B T} \left\langle |\mathbf{J}|^2 \right\rangle \times \tau_J$$



molecular H_2O





the conundrum

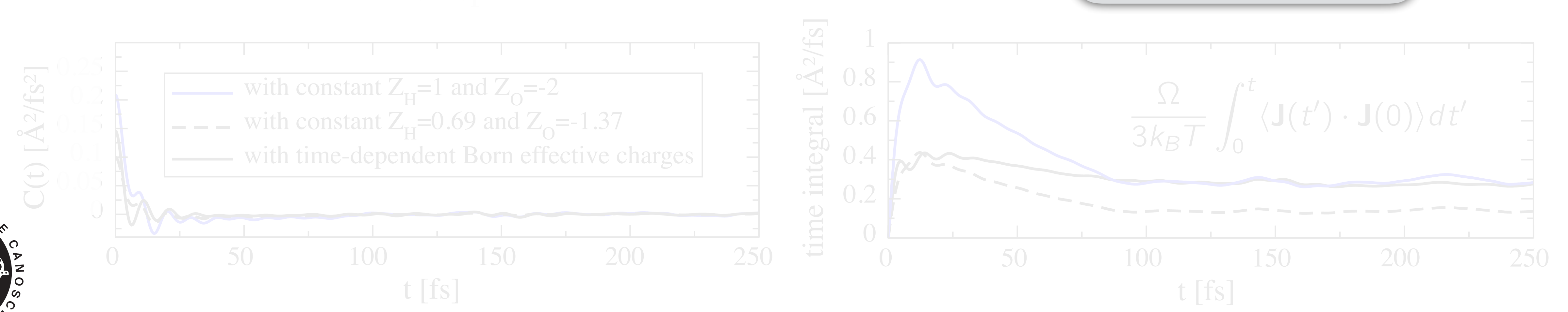
PRL 107, 185901 (2011) PHYSICAL REVIEW LETTERS week ending 28 OCTOBER 2011

Dynamical Screening and Ionic Conductivity in Water from *Ab Initio* Simulations

Martin French,[1] Sebastien Hamel,[2] and Ronald Redmer[1]

"*Interestingly, the use of predefined constant charges can yield the same conductivity as is found with the fully time-dependent charge tensors, but only if they have values of Z_H=1 and Z_O=-2.*"

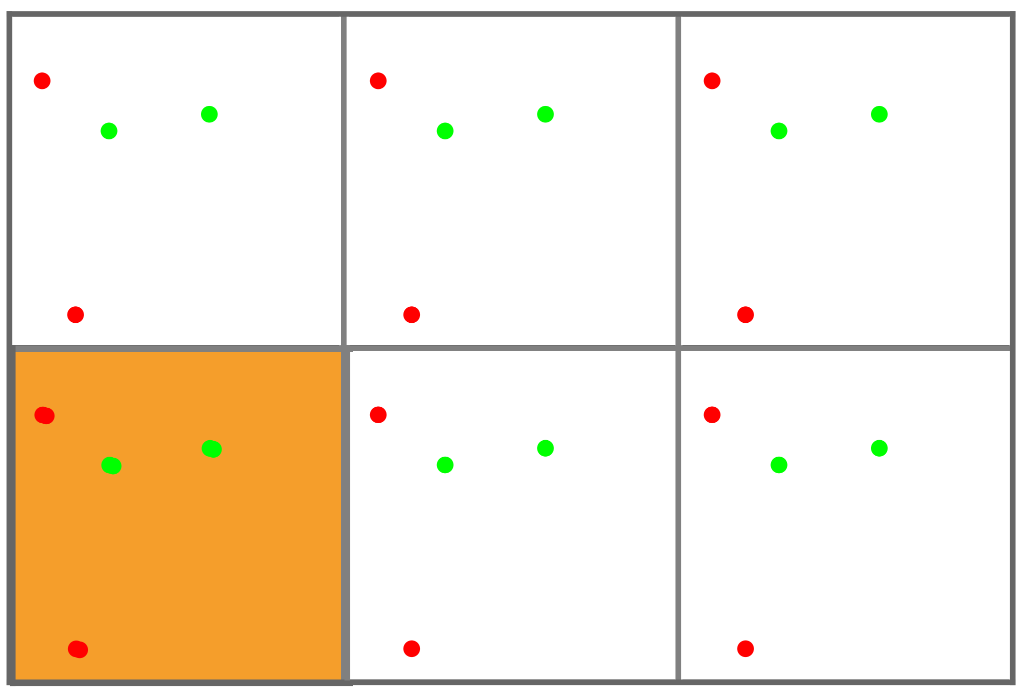
atomic *oxidation states*

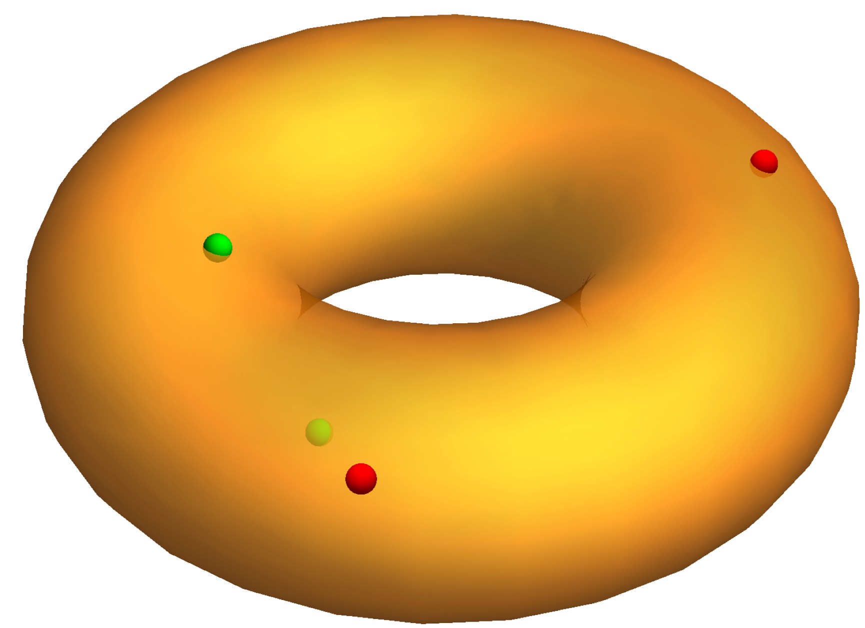


how come?

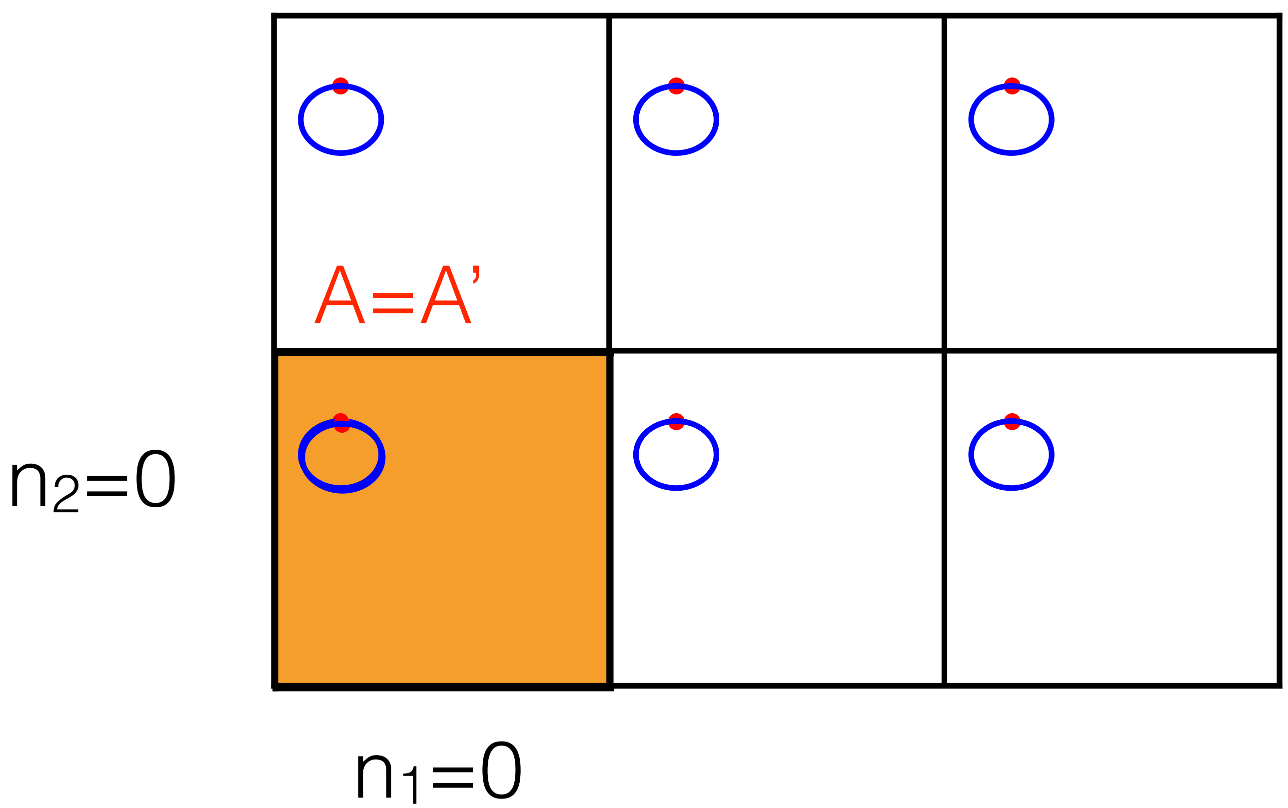
what are oxidation states, in the first place?

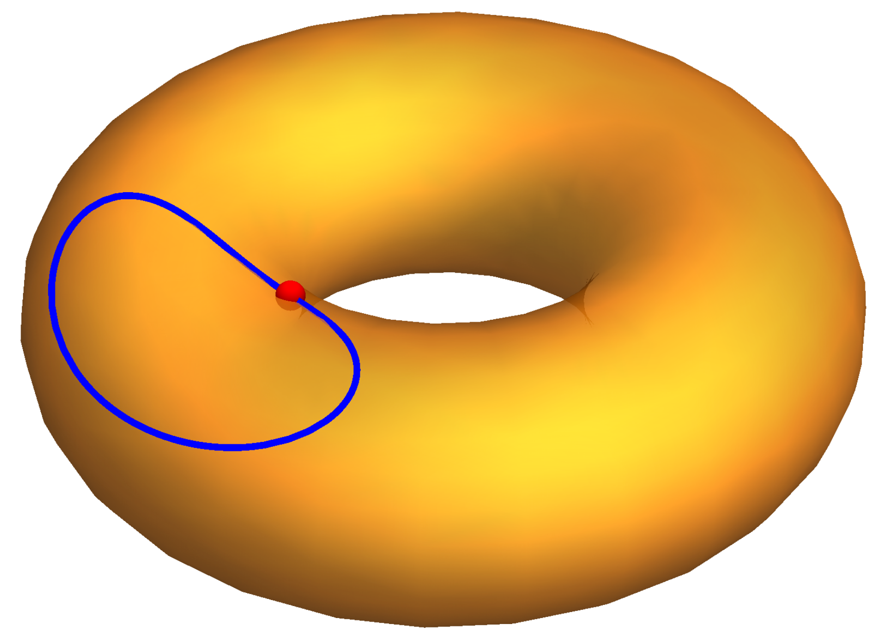
what are oxidation states, in the first place?



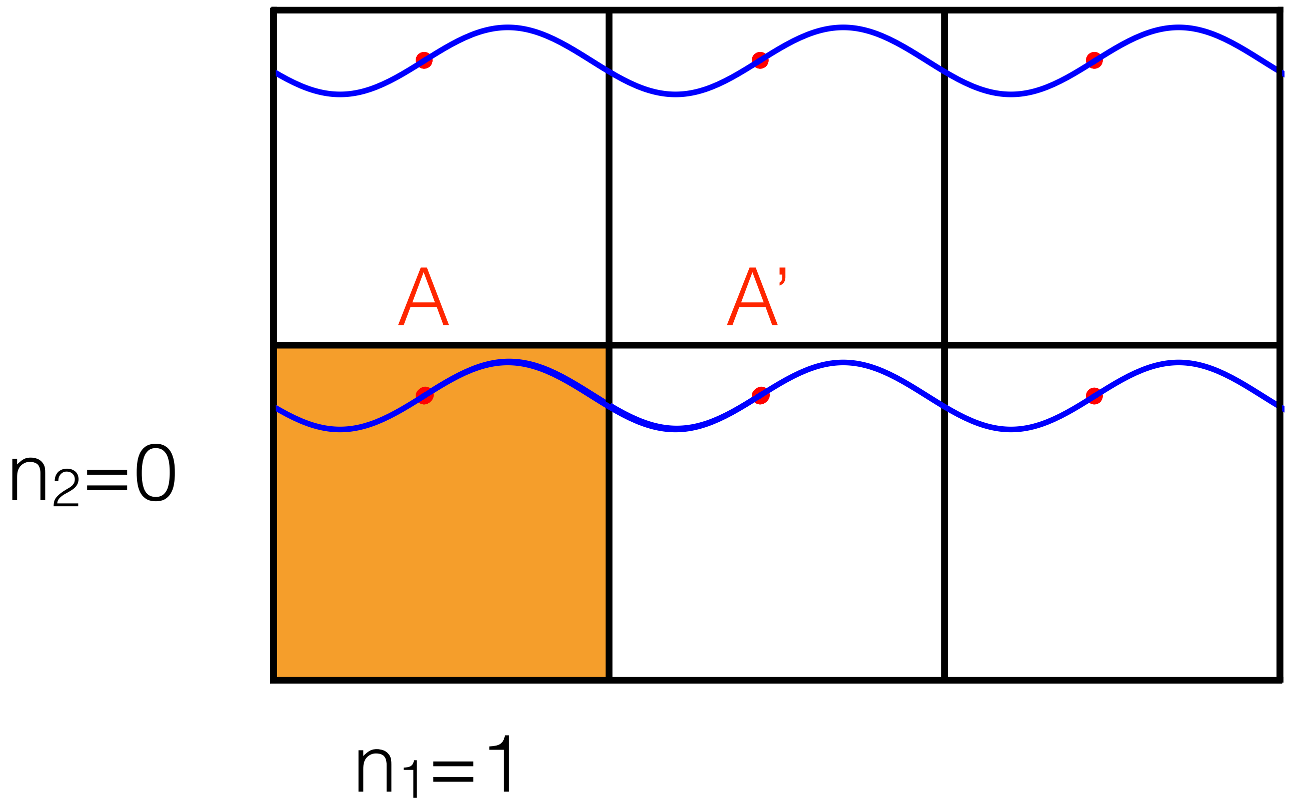


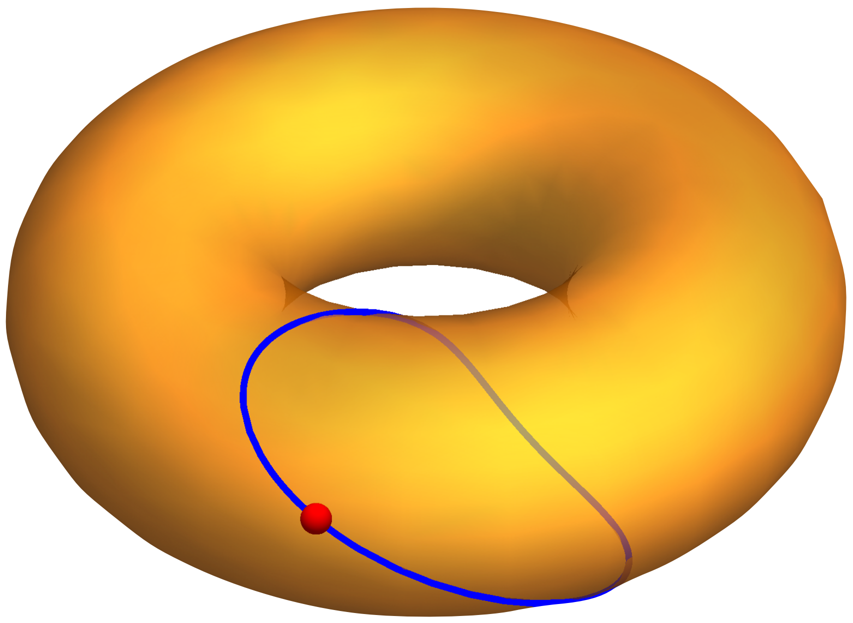
what are oxidation states, in the first place?



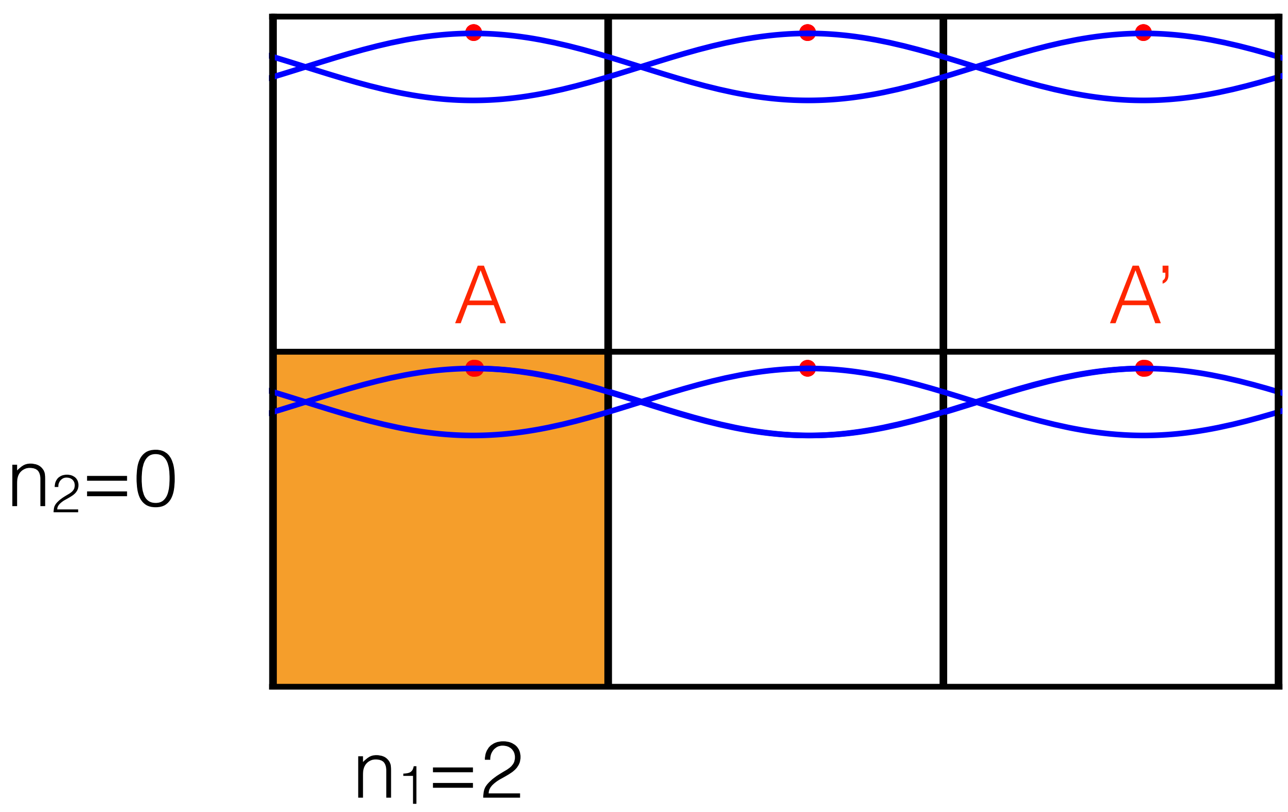


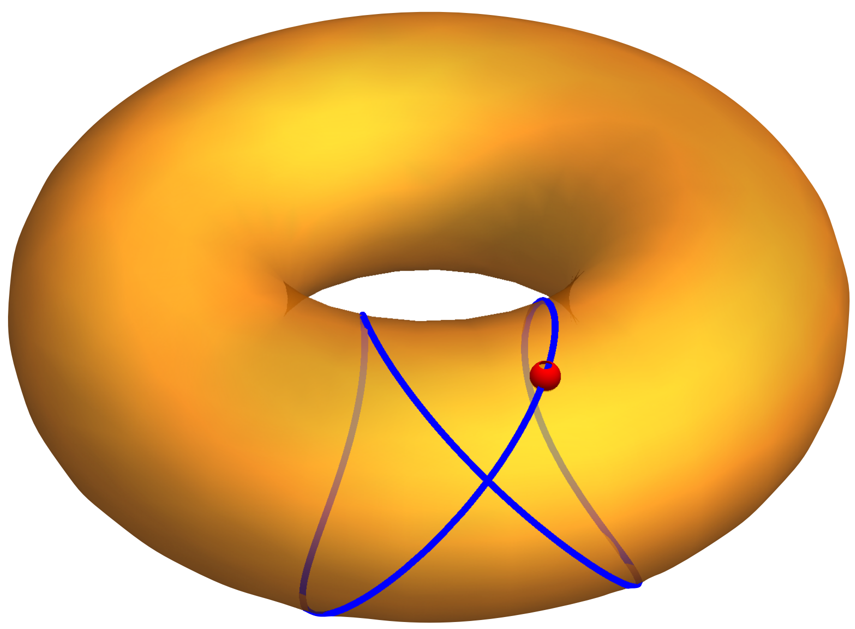
what are oxidation states, in the first place?



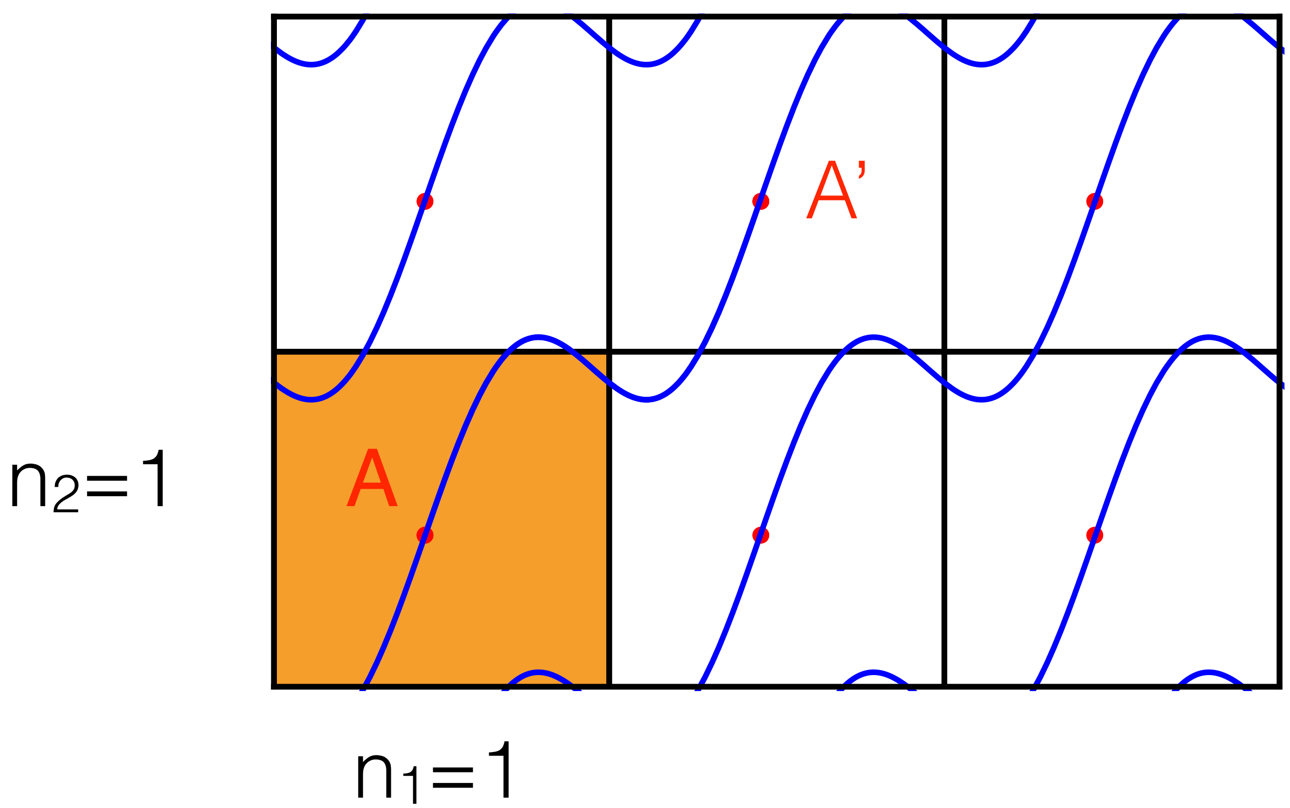


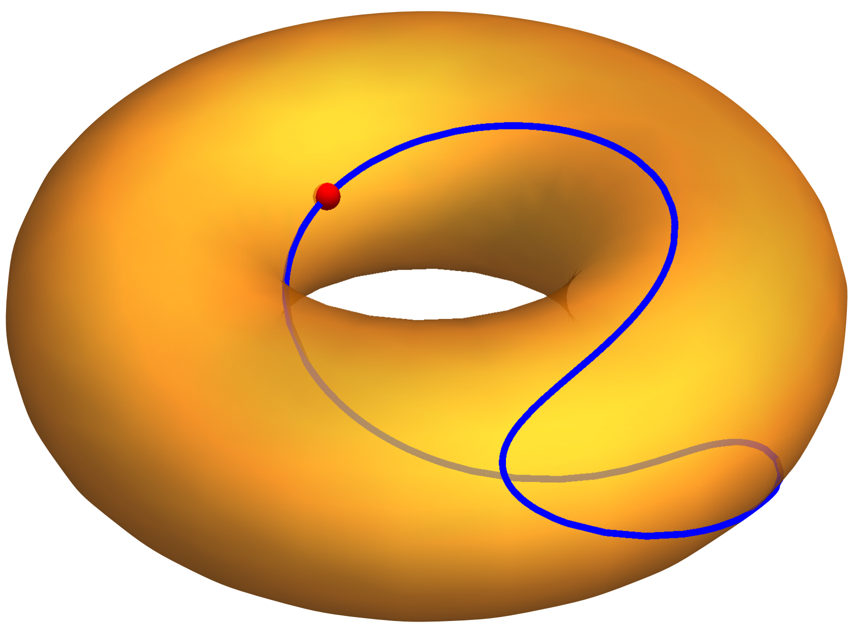
what are oxidation states, in the first place?



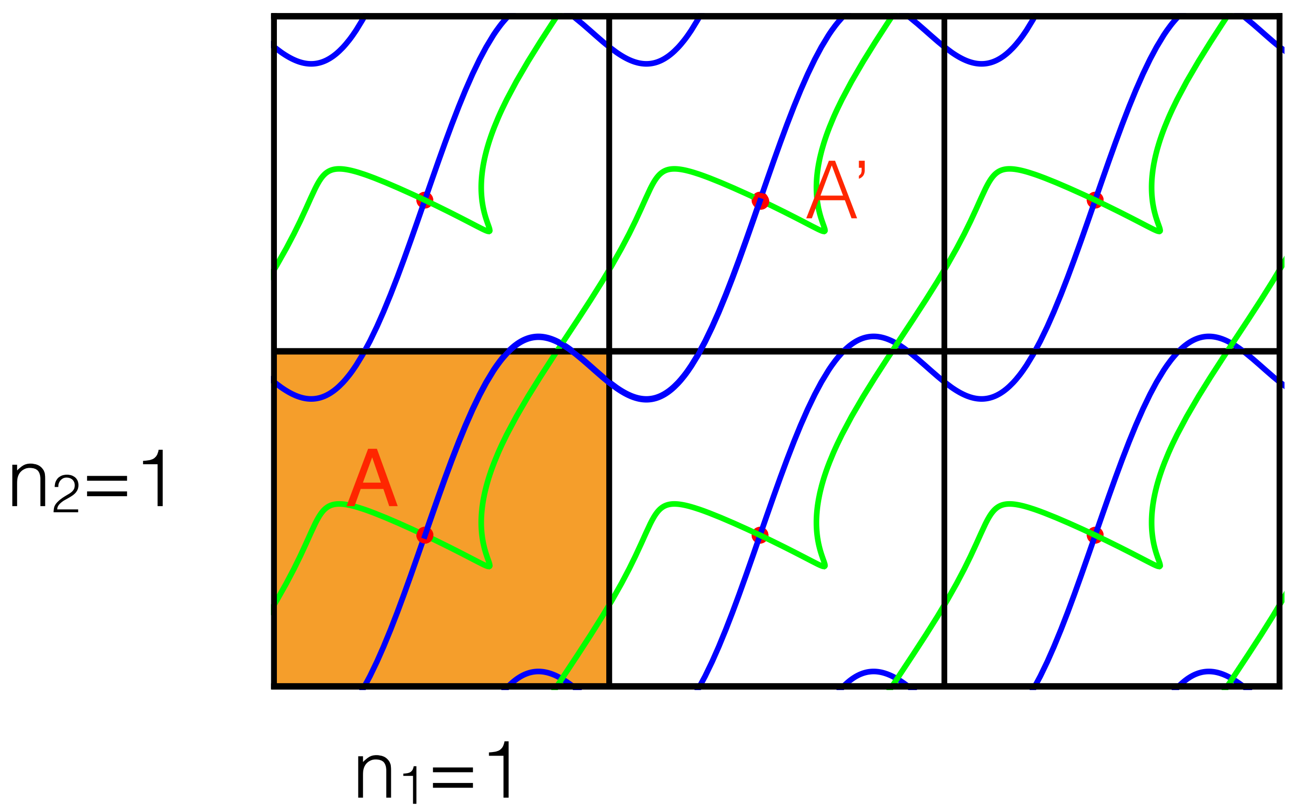


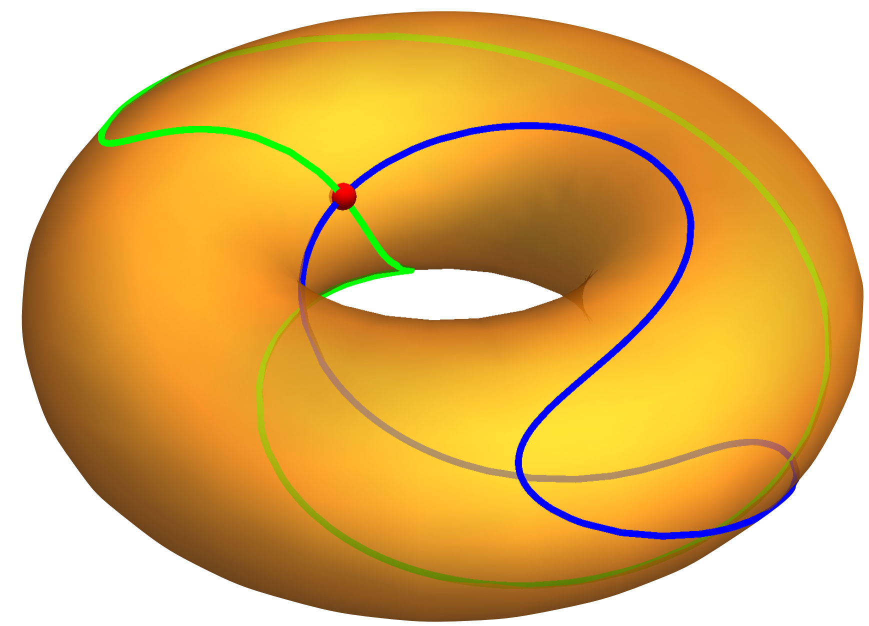
what are oxidation states, in the first place?



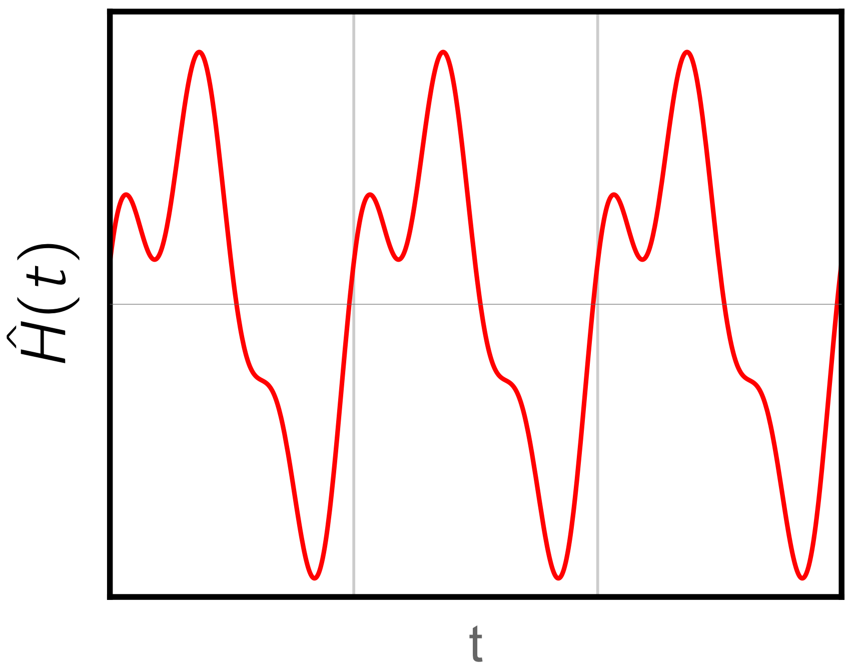


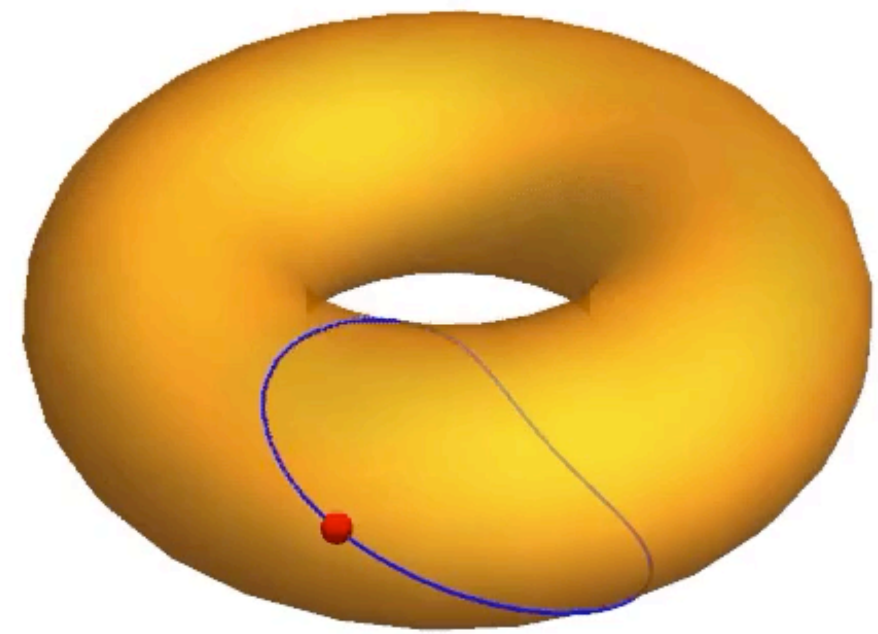
what are oxidation states, in the first place?





what are oxidation states, in the first place?





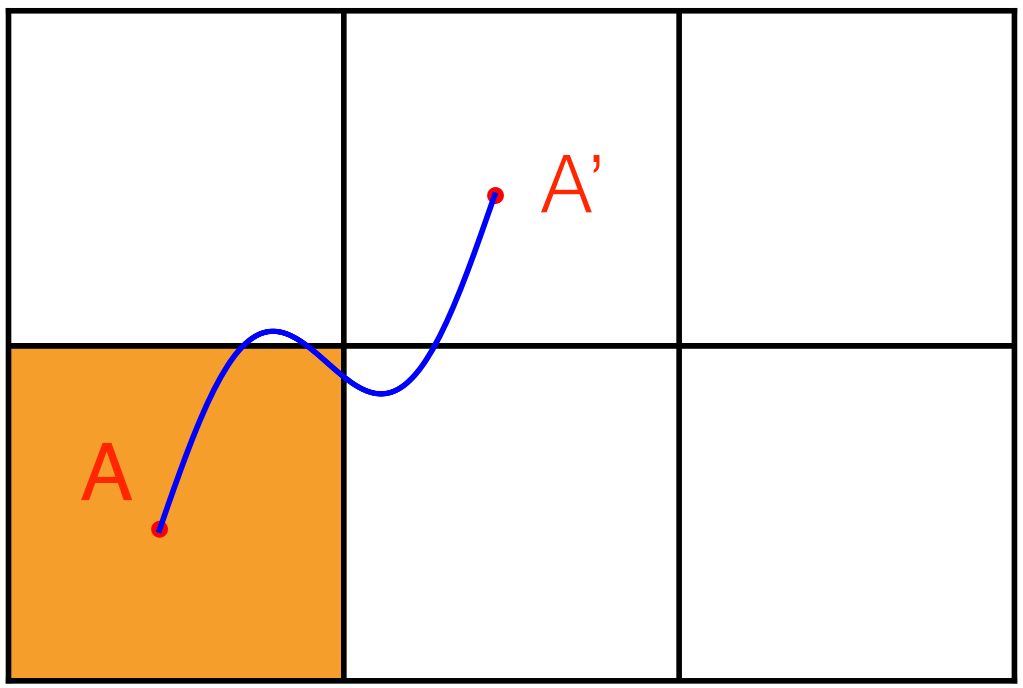
$$\hat{H}(t+T) = \hat{H}(t)$$

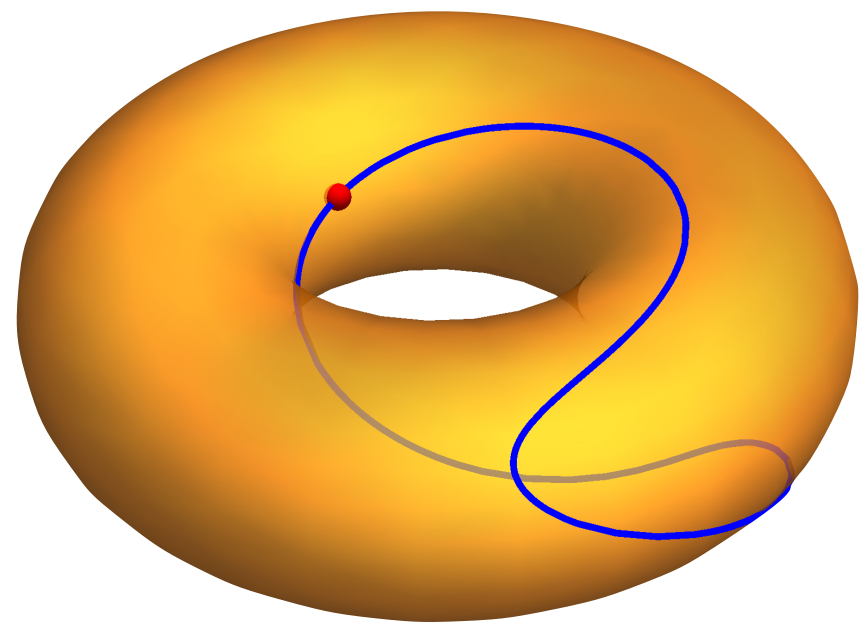
$$\frac{L^{d-1}}{e}\int_0^T J_\alpha(t)dt = n \in \mathbb{Z}$$

D.J. Thouless, *Quantization of particle transport*, Phys. Rev. B **27**, 2083 (1983)

what are oxidation states, in the first place?

$$\frac{L^{d-1}}{e}\int_0^T J_\alpha(t)dt = n \in \mathbb{Z}$$





$$\int_A^{A'} d\mu_\alpha = \frac{e}{L}\sum_i q_{S(i)} n_{i\alpha}$$

adiabatic heat transport

$$\mathbf{J}_{\mathcal{E}} = \sum_I e_I \mathbf{V}_I + \frac{1}{2}\sum_{I\neq J} (\mathbf{V}_I \cdot \mathbf{F}_{IJ})(\mathbf{R}_I - \mathbf{R}_J)$$

$$-\frac{\partial e_I}{\partial \mathbf{R}_J}$$

$$\sigma = \frac{\Omega}{3k_B T^2}\int_0^\infty \langle \mathbf{J}_{\mathcal{E}}(t)\cdot\mathbf{J}_{\mathcal{E}}(0)\rangle dt$$

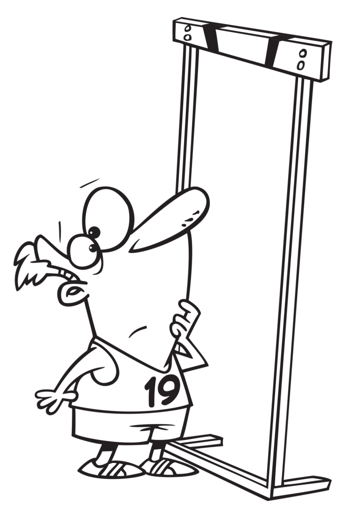
PRL **104,** 208501 (2010) PHYSICAL REVIEW LETTERS week ending 21 MAY 2010

Thermal Conductivity of Periclase (MgO) from First Principles

Stephen Stackhouse*
Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan, 48109-1005, USA

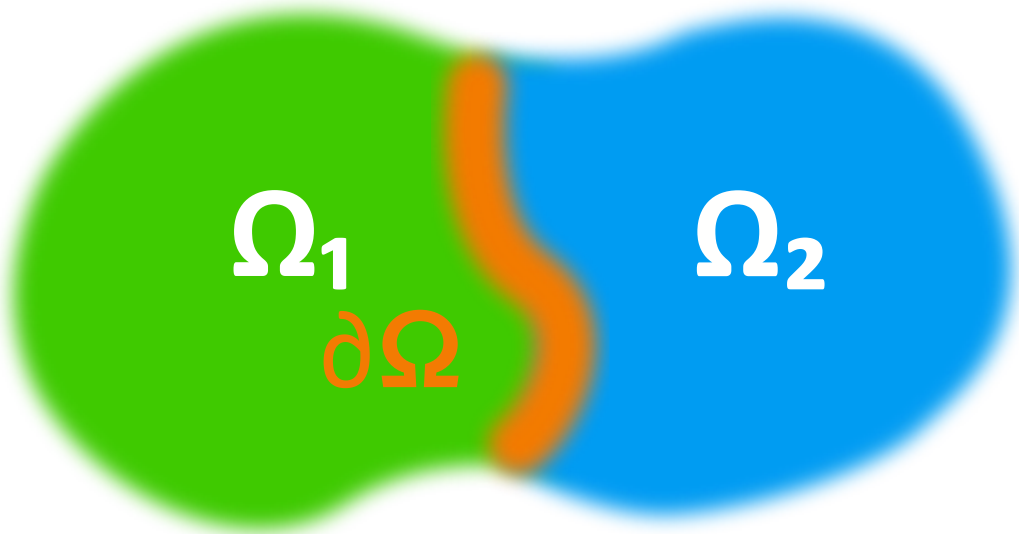
Lars Stixrude†
Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, United Kingdom

Bijaya B. Karki‡
Department of Computer Science, Louisiana State University, Baton Rouge, Louisiana 70803, USA and Department of Geology and Geophysics, Louisiana State University, Baton Rouge, Louisiana 70803, USA



sensitive to the form of the potential. The widely used Green-Kubo relation [14] does not serve our purposes, because in first-principles calculations it is impossible to uniquely decompose the total energy into individual contributions from each atom.

gauge invariance of transport coefficients



$$E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2]$$

extensiveness $$\mathcal{E}[\Omega] = \int_\Omega e(\mathbf{r})\, d\mathbf{r}$$

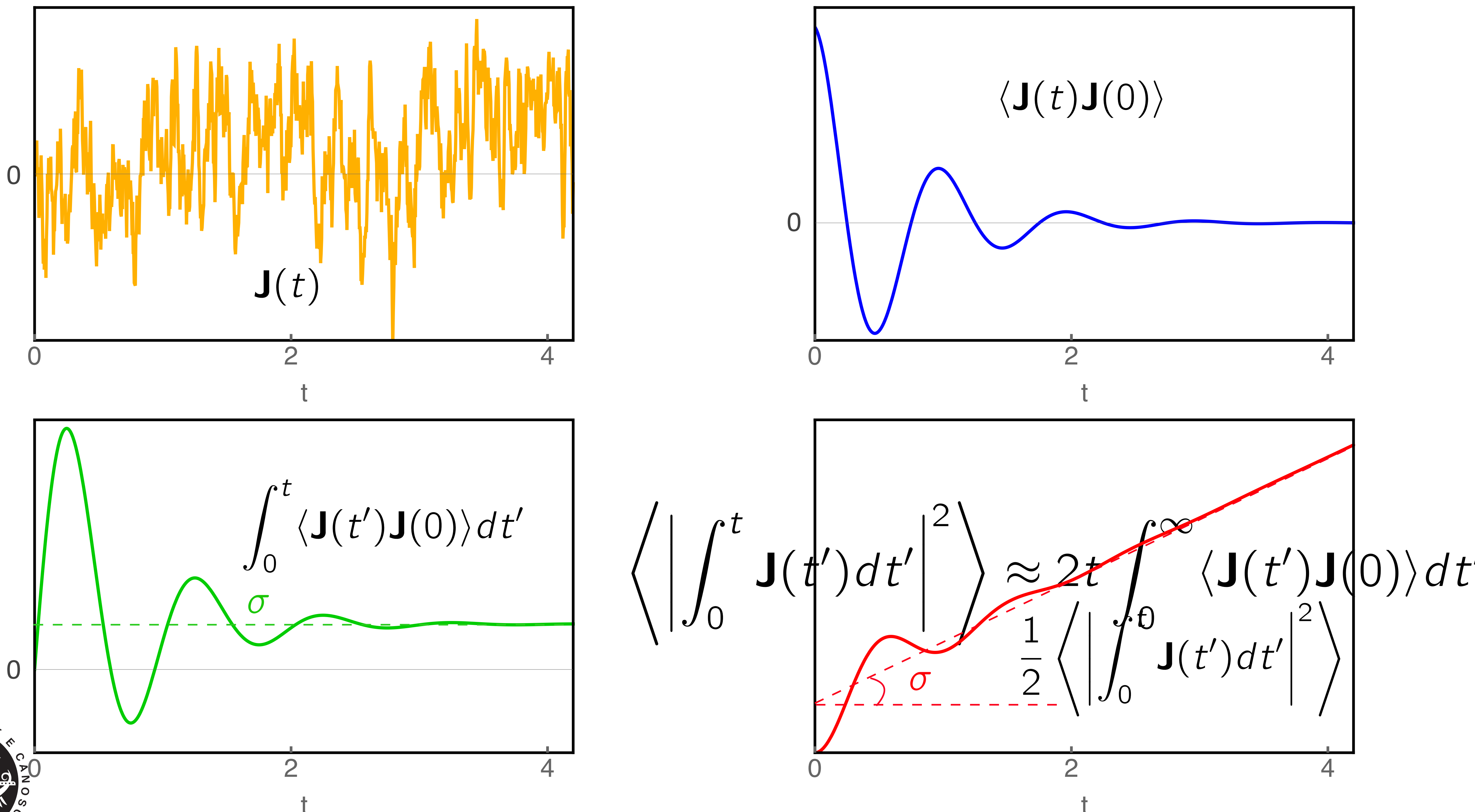
conservation $$\dot{e}(\mathbf{r}, t) = -\nabla \cdot \mathbf{j}(\mathbf{r}, t)$$

$$\mathbf{J}'(t) = \mathbf{J}(t) + \dot{\mathbf{P}}(t)$$

gauge invariance $$\mathcal{E}'[\Omega] = \mathcal{E}[\Omega] + \mathcal{O}[\partial\Omega]$$

the Einstein-Helfand relations

$$\sigma = \frac{\Omega}{3k_B T} \int_0^\infty \langle \mathbf{J}(t) \cdot \mathbf{J}(0) \rangle dt$$



$$\left\langle \left| \int_0^t \mathbf{J}(t')dt' \right|^2 \right\rangle \approx 2t \int_0^\infty \langle \mathbf{J}(t')\mathbf{J}(0) \rangle dt'$$

gauge invariance of transport coefficients

$$J' = J + \dot{P}$$

$$\lambda \sim \frac{1}{2t} \mathrm{v}ar\left[D(t)\right] \qquad D(t) = \int_0^t J(t')dt'$$

$$D'(t) = D(t) + P(t) - P(0)$$

$$\mathrm{var}\left[D'(t)\right] = \mathrm{var}\left[D(t)\right] + \cancel{\mathrm{var}\left[\Delta P(t)\right]} + \cancel{2\mathrm{cov}\left[D(t) \cdot \Delta P(t)\right]}$$

gauge invariance of transport coefficients

$$J' = J + \dot{P}$$

$$\lambda \sim \frac{1}{2t} var[D(t)] \qquad D(t) = \int_0^t J(t')dt'$$

$$D'(t) = D(t) + P(t) - P(0)$$

$$\lambda' = \lambda$$

$$var[D'(t)] = \underbrace{var[D(t)]}_{\mathcal{O}(t)} + \underbrace{var[\Delta P(t)] + 2cov[D(t) \cdot \Delta P(t)]}_{\mathcal{O}(t^{\frac{1}{2}})}$$

gauge invariance of transport coefficients

$$J' = J + \dot{P}$$

any two conserved densities that differ by the divergence of a (bounded) vector field are physically equivalent

$$\lambda \sim \frac{1}{2t}\mathrm{var}\left[D(t)\right], \quad D(t) = \int_0^t J(t')\,dt'$$

the corresponding conserved fluxes differ by a total time derivative, and the transport coefficients coincide

$$D'(t) = D(t) + P(t) - P(0)$$

$$\lambda' = \lambda$$

$$\mathrm{var}\left[D'(t)\right] = \underbrace{\mathrm{var}\left[D(t)\right]}_{\mathcal{O}(t)} + \underbrace{\mathrm{var}\left[\Delta P(t)\right] + 2\mathrm{cov}\left[D(t)\cdot\Delta P(t)\right]}_{\mathcal{O}(t^{\frac{1}{2}})}$$

gauge invariance of heat transport

PRL **104,** 208501 (2010) PHYSICAL REVIEW LETTERS week ending 21 MAY 2010

Thermal Conductivity of Periclase (MgO) from First Principles

Stephen Stackhouse*
Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan, 48109-1005, USA

Lars Stixrude†
Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, United Kingdom

Bijaya B. Karki‡
Department of Computer Science, Louisiana State University, Baton Rouge, Louisiana 70803, USA
and Department of Geology and Geophysics, Louisiana State University, Baton Rouge, Louisiana 70803, USA

sensitive to the form of the potential. The widely used Green-Kubo relation [14] does not serve our purposes, because in first-principles calculations it is impossible to uniquely decompose the total energy into individual contributions from each atom.

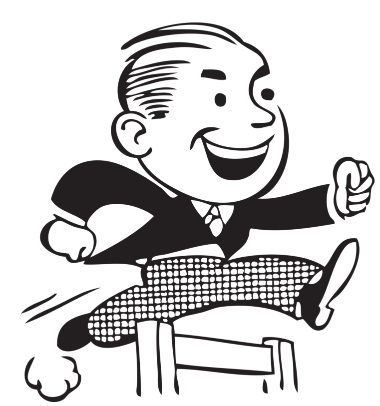
solution:

choose *any* local representation of the energy that integrates to the correct value and whose correlations decay at large distance — the conductivity computed from the resulting current will be *independent* of the representation.

nature physics ARTICLES
PUBLISHED ONLINE: 19 OCTOBER 2015 | DOI: 10.1038/NPHYS3509

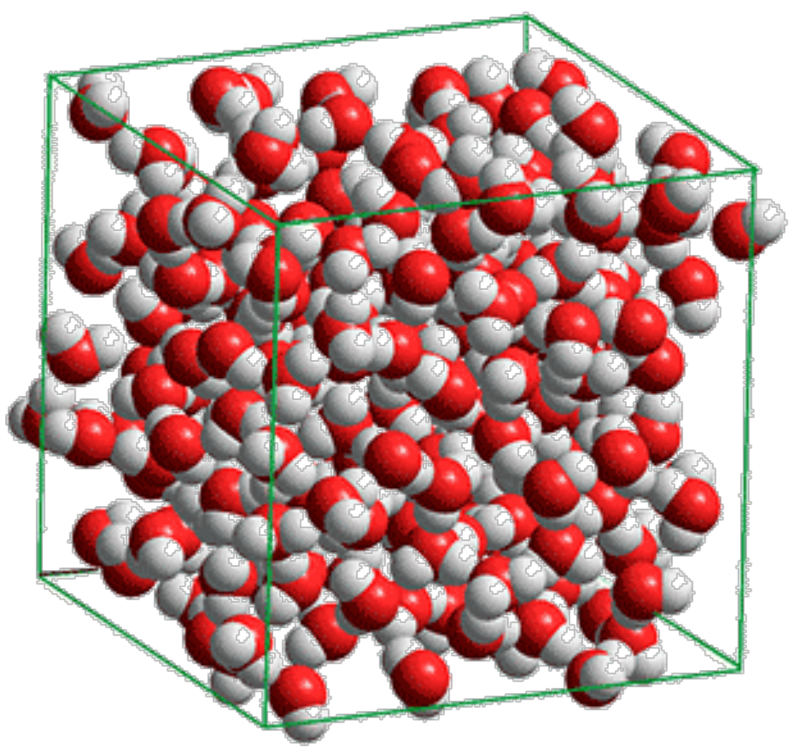
Microscopic theory and quantum simulation of atomic heat transport

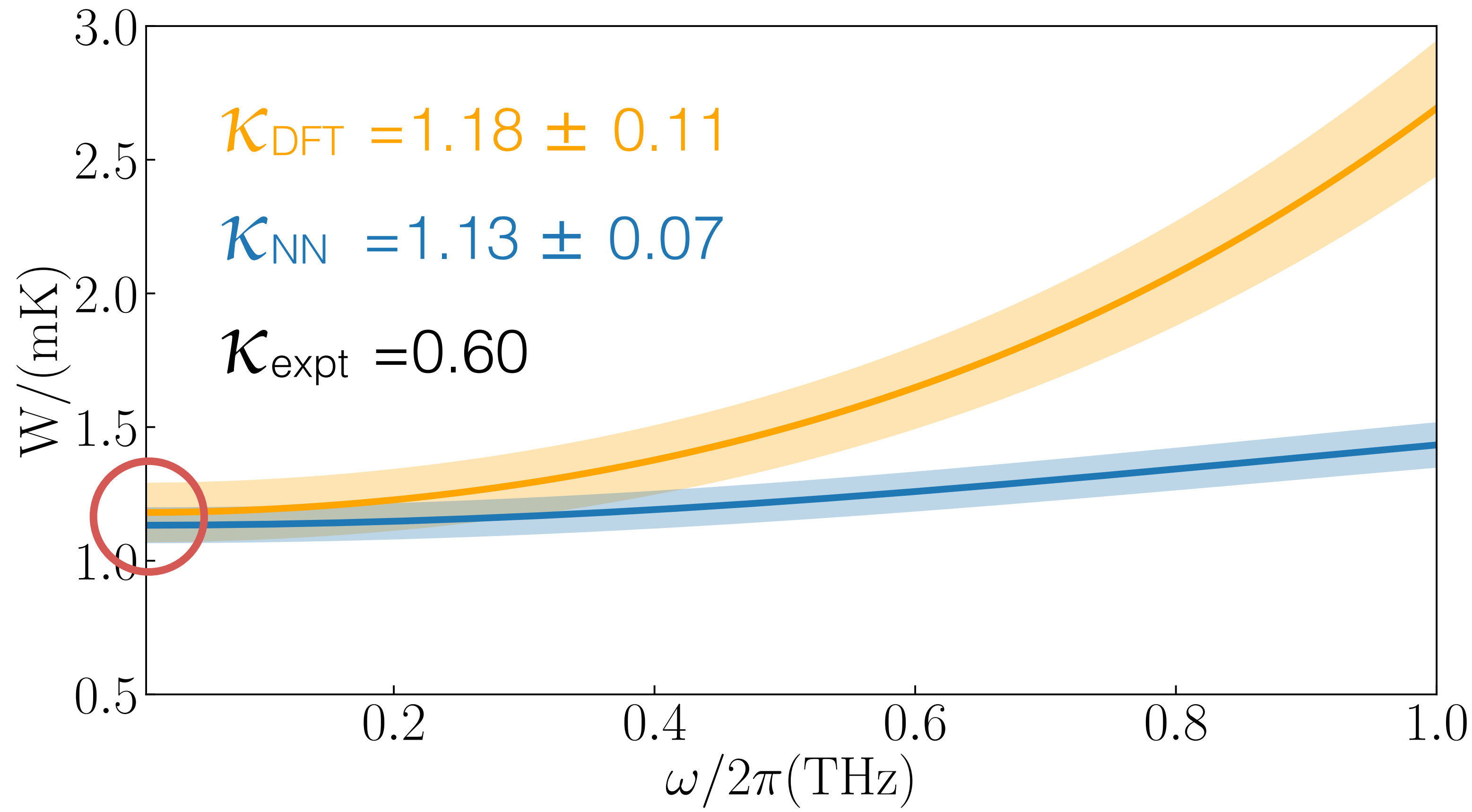
Aris Marcolongo[1], Paolo Umari[2] and Stefano Baroni[1]*



thermal conductivity of liquid water from DFT

H_2O

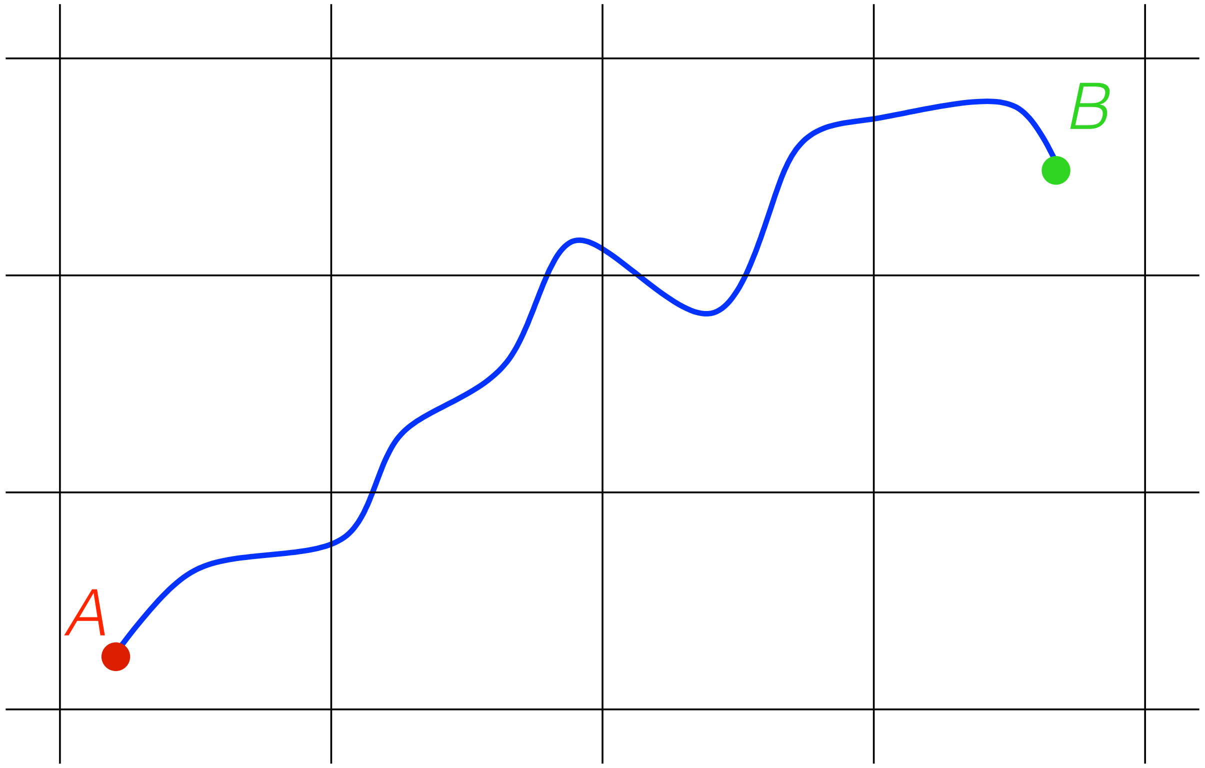




back to our business

electric conductivities can be computed from oxidation states, instead of from effective charges

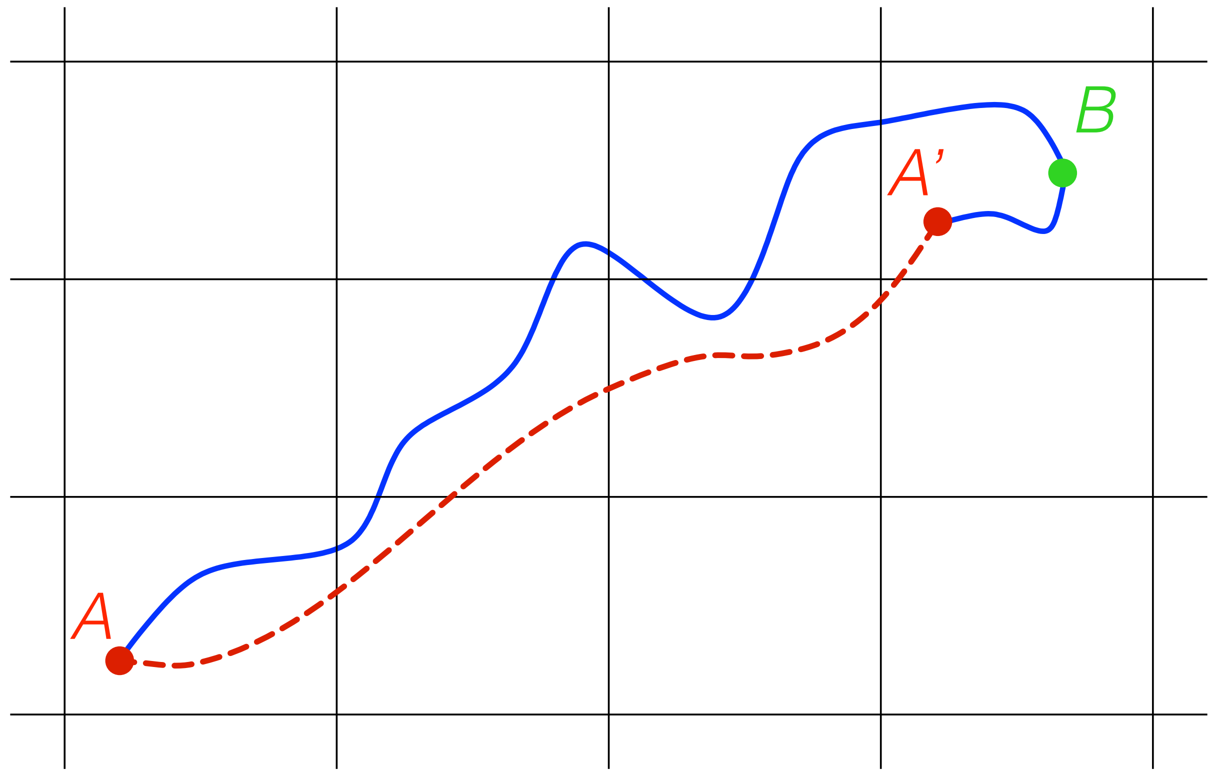
gauge invariance of charge transport



$$\sigma \propto \lim_{t\to\infty} \frac{1}{2t} \left\langle |\mu_{AB}|^2 \right\rangle$$

$$\mu_{AB} = \int_0^t J(t')dt'$$

gauge invariance of charge transport



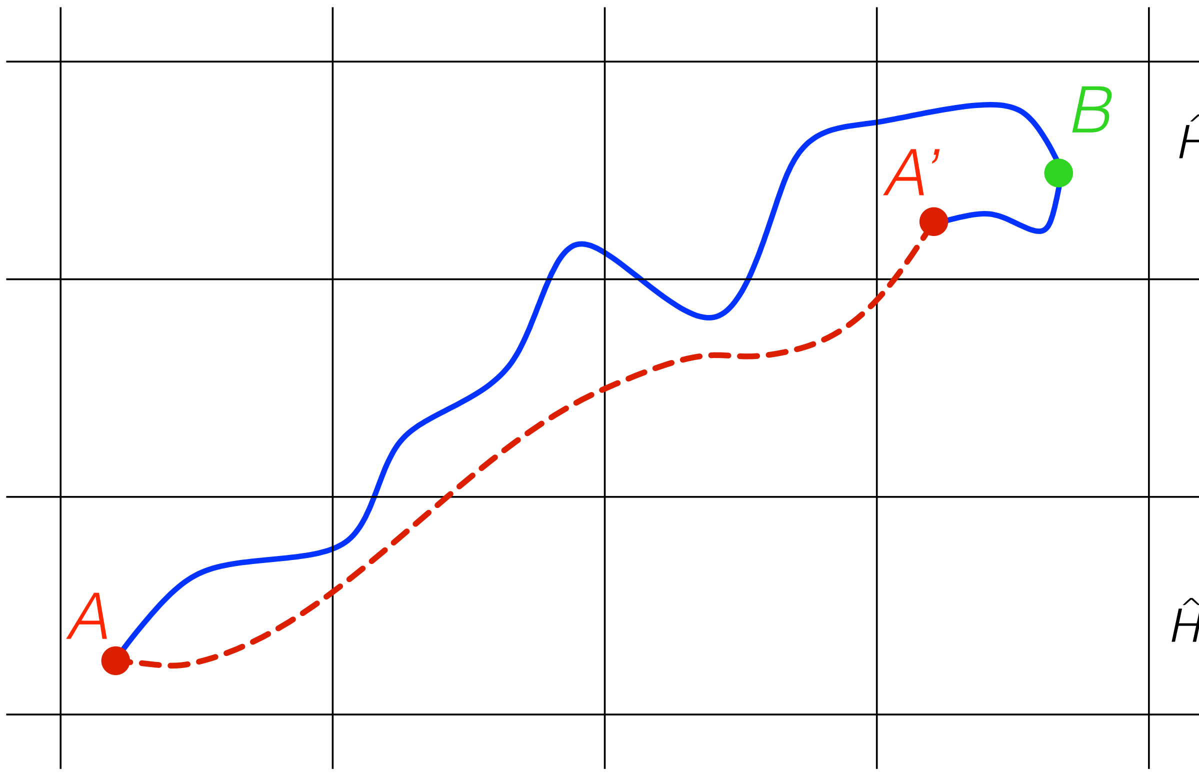
$$\sigma \propto \lim_{t\to\infty} \frac{1}{2t} \langle |\mu_{AB}|^2 \rangle$$

$$\mu_{AB} = \int_0^t J(t')dt'$$
$$= \mu_{AA'} + \mu_{A'B}$$

$$\mathrm{var}\left[\mu_{AB}\right] = \mathrm{var}\left[\mu_{AA'}\right] + \underbrace{\mathrm{var}\left[\mu_{A'B}\right]}_{bounded} + 2\,\underbrace{\mathrm{cov}\left[\mu_{AA'}\cdot\mu_{A'B}\right]}_{\mathcal{O}\left(\mathrm{var}\left[\mu_{AA'}\right]^{\frac{1}{2}}\right)}$$

$$\sigma \propto \lim_{t\to\infty} \frac{1}{2t} \langle |\mu_{AA'}|^2 \rangle$$

gauge invariance of charge transport



$\hat{H}(B) \neq \hat{H}(A)$

$$\sigma \propto \lim_{t\to\infty} \frac{1}{2t} \left\langle |\mu_{AB}|^2 \right\rangle$$

$$\mu_{AB} = \int_0^t J(t')dt'$$

$$\mu_{AB} = \int_0^t \sum_i Z_i^*(t') v_i(t') dt'$$

$J(t')$

$\hat{H}(A') = \hat{H}(A)$

$$\sigma \propto \lim_{t\to\infty} \frac{1}{2t} \left\langle |\mu_{AA'}|^2 \right\rangle$$

$$\mu_{AA'} = \frac{e}{L} \sum_i q_{S(i)} n_i = \frac{e}{L^2} \sum_i q_{S(i)} \Delta R_i$$

$$= \frac{e}{L^2} \sum_i q_{S(i)} \left(\int_0^t v_i(t')dt' + \Delta x_i \right)$$

$$= \underbrace{\int_0^t \tilde{J}(t')dt'}_{\mathcal{O}(t^{\frac{1}{2}})} + \mathcal{O}(1)$$

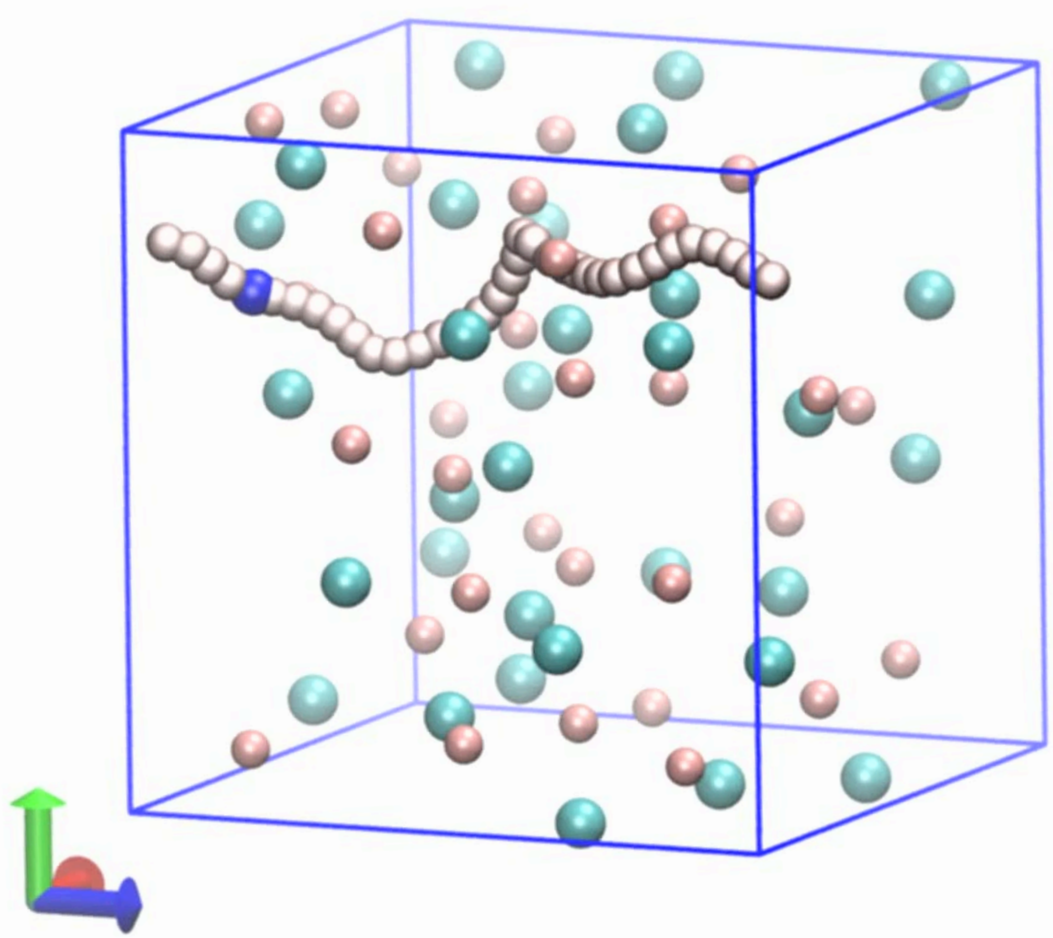
gauge invariance of charge transport

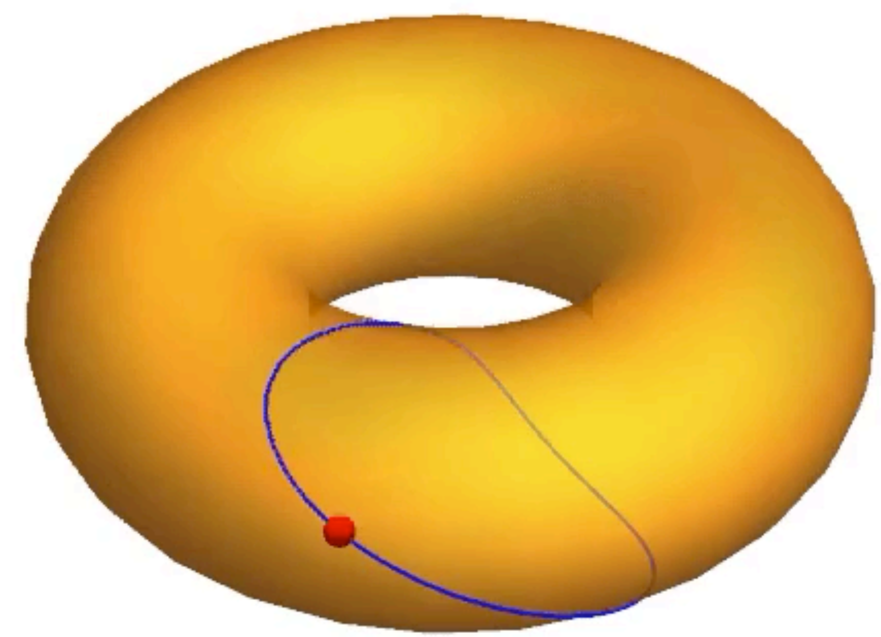
$$\lim_{t\to\infty}\frac{1}{t}\left\langle\left|\int_0^t J(t')dt'\right|^2\right\rangle = \lim_{t\to\infty}\frac{1}{t}\left\langle\left|\int_0^t \tilde{J}(t')dt'\right|^2\right\rangle$$

$$J_\alpha(t) = \sum_{i\beta} Z^*_{i\alpha\beta}(t)v_{i\beta}(t) \qquad \tilde{J}_\alpha(t) = \sum_i q_{S(i)}v_{i\alpha}(t)$$

adiabatic electric conductivities can be calculated from the Green-Kubo theory of linear response in terms of integer, scalar, and time-independent topological atomic oxidation states, instead of from real, tensor, and time-dependent Born effective charges

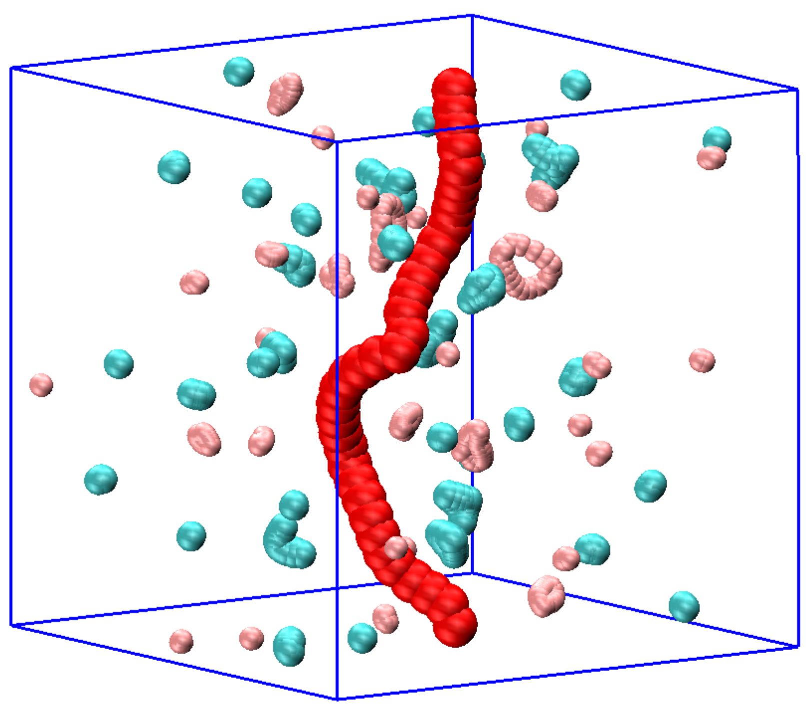
a numerical experiment on molten KCl

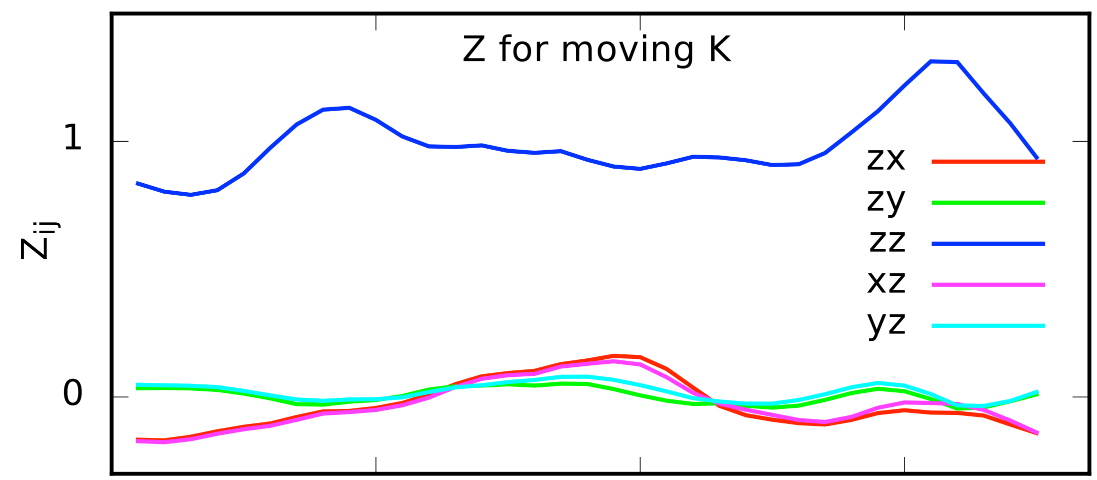


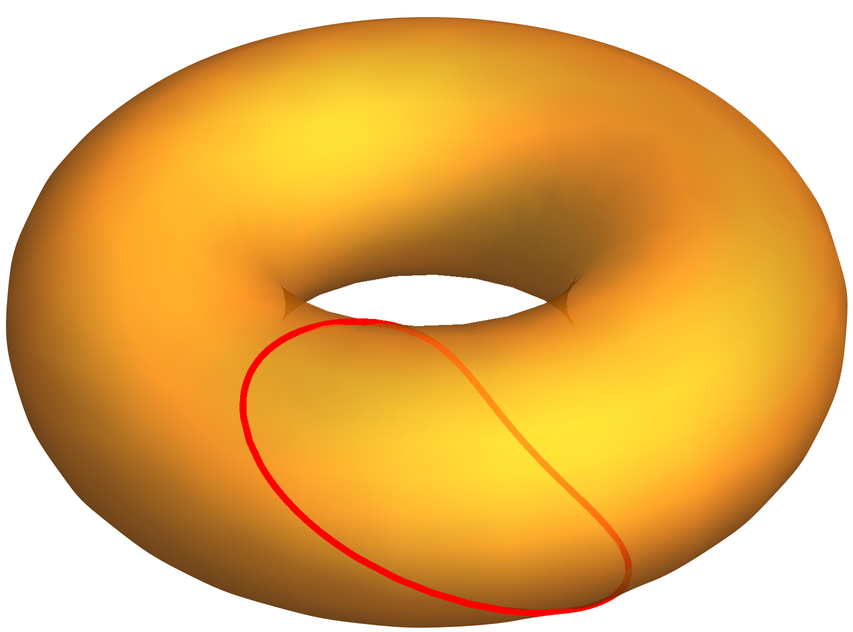


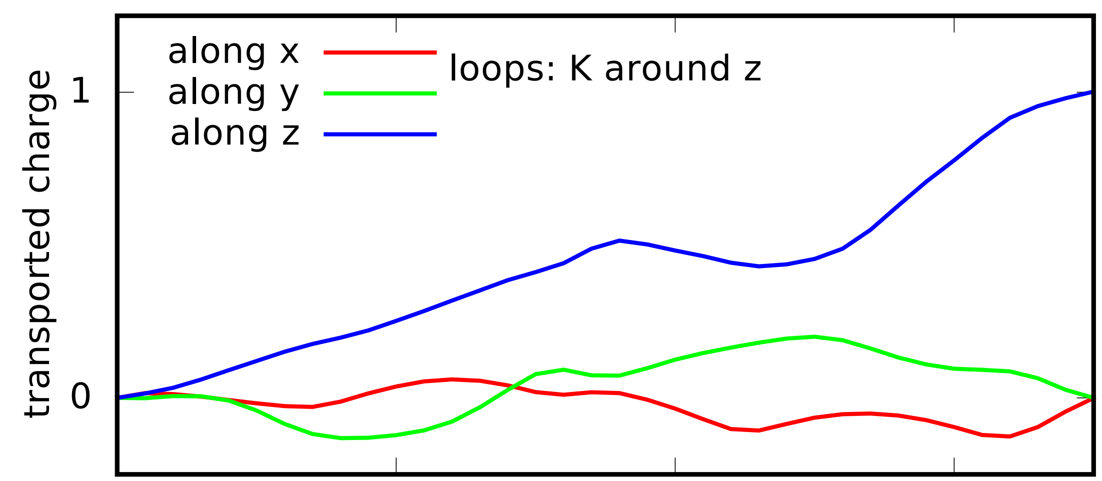
a topologically non-trivial minimum-energy path
connecting two identical configurations of a ionic fluid

a numerical experiment on molten KCl



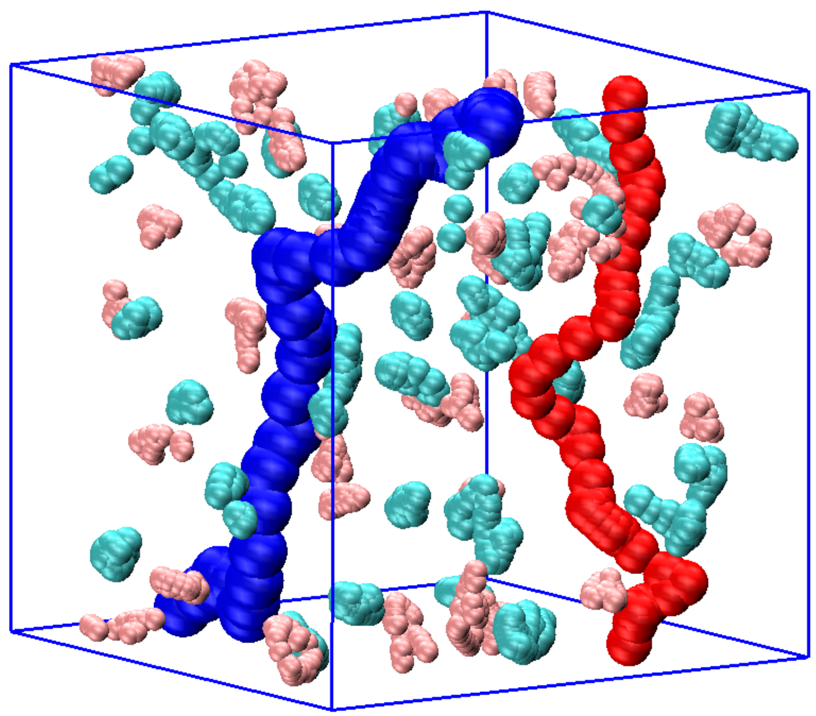






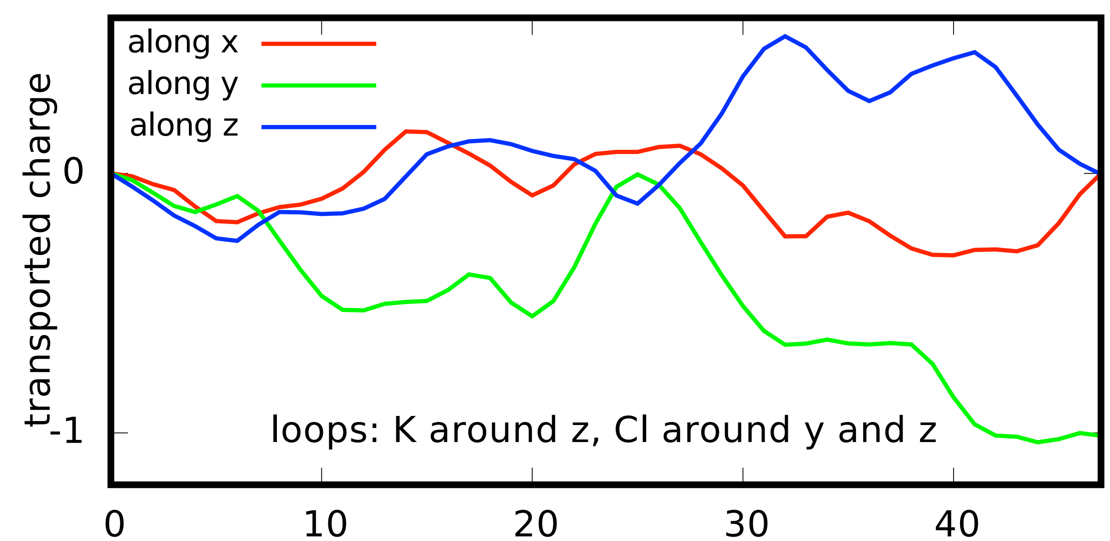
qx = =-0.000(6);   qy = 0.000(2);   qz = 1.00(18)

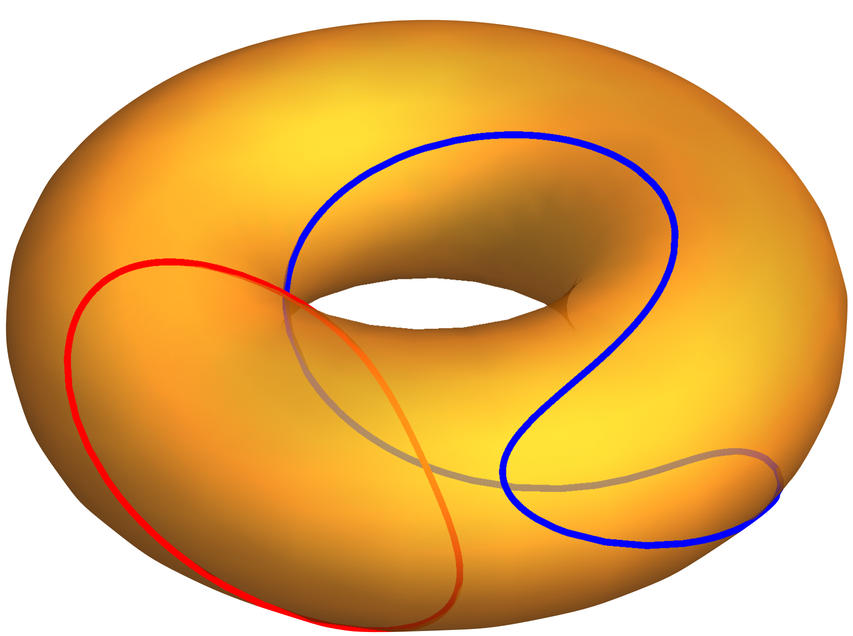
a numerical experiment on molten KCl



$Q_z[Cl]=-1$ $Q_y[Cl]=-1$

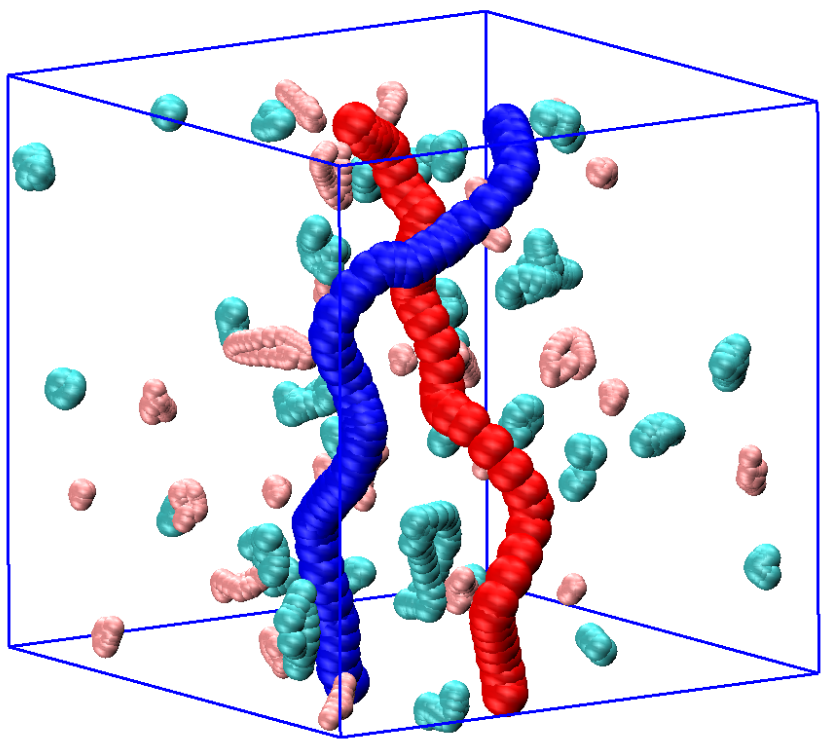
$Q_z[K] = 1$ $Q_z[K] = 0$

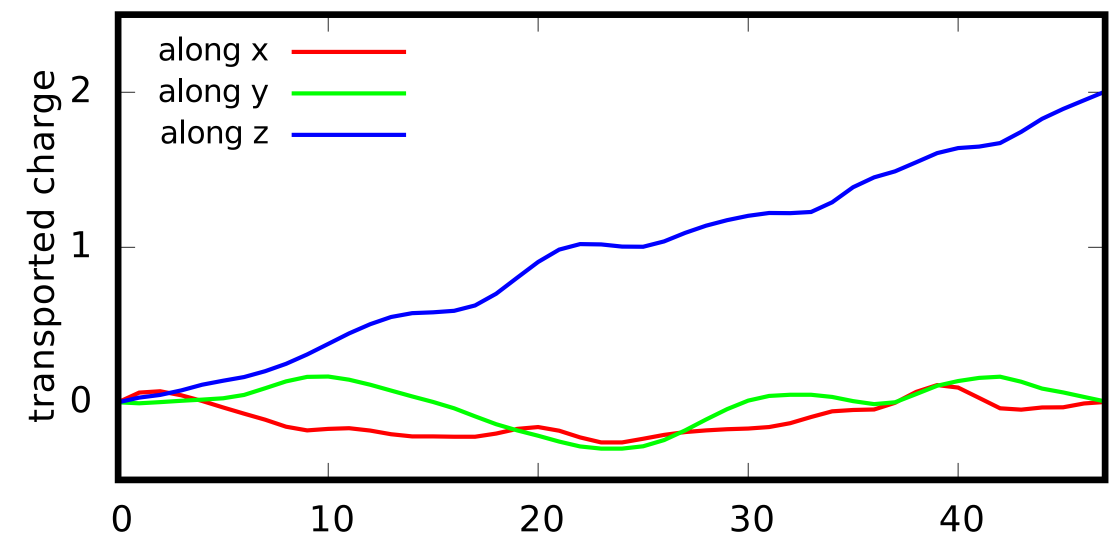


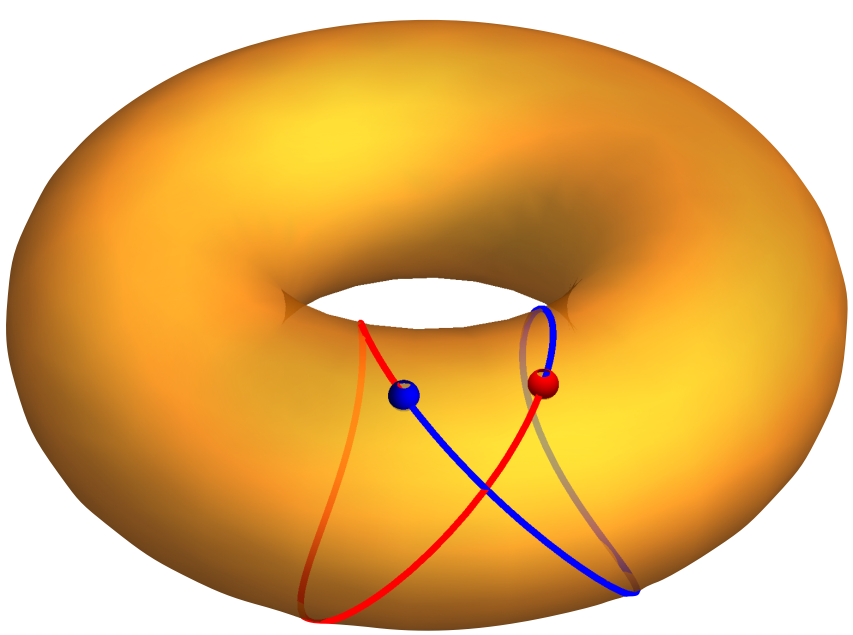


the charges transported by K and Cl around z cancel exactly

a numerical experiment on molten KCl





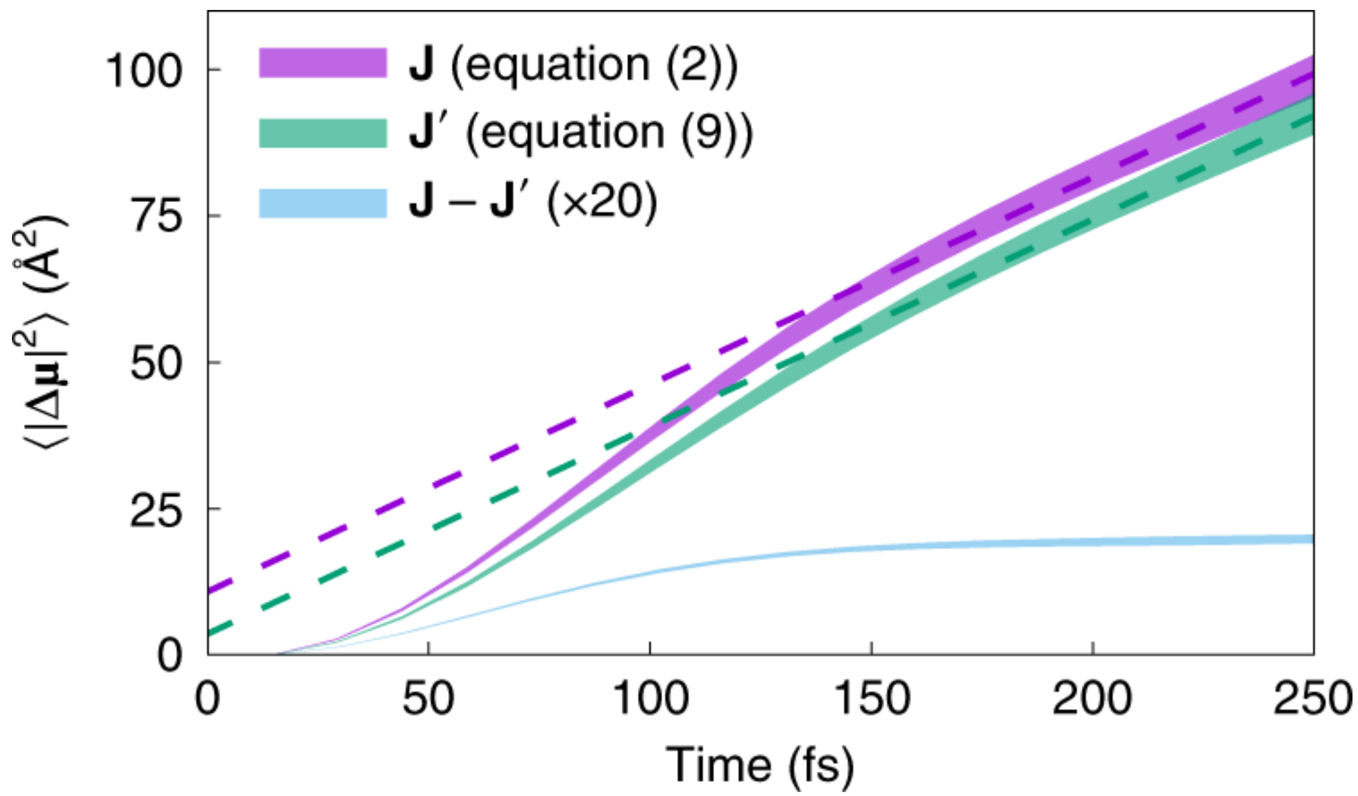


the exchange of two cations
transports a net charge equal to +2

strongly adiabatic transport

$$J_\alpha = \sum_{i\beta} Z^*_{i\alpha\beta} v_{i\beta} \qquad (2)$$

$$J'_\alpha = \sum_{i} q_{S(i)} v_{i\alpha} \qquad (9)$$



$$\left\langle \left| \int_0^t \mathbf{J}(t')dt' \right|^2 \right\rangle$$

nature physics

ARTICLES

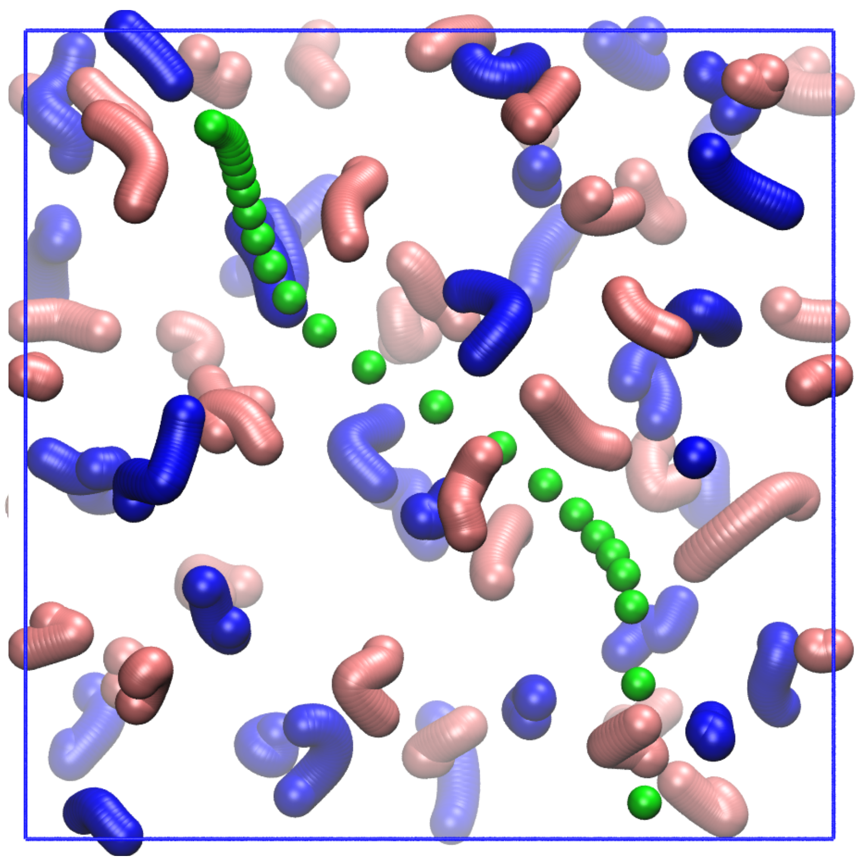
https://doi.org/10.1038/s41567-019-0562-0

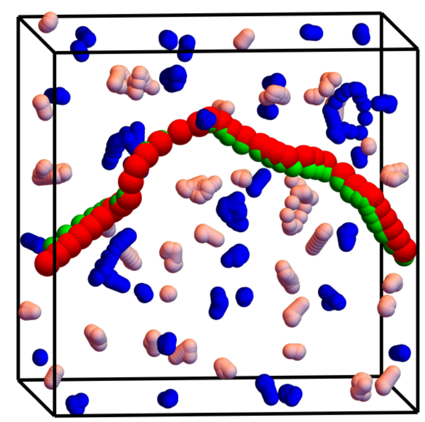
Topological quantization and gauge invariance of charge transport in liquid insulators

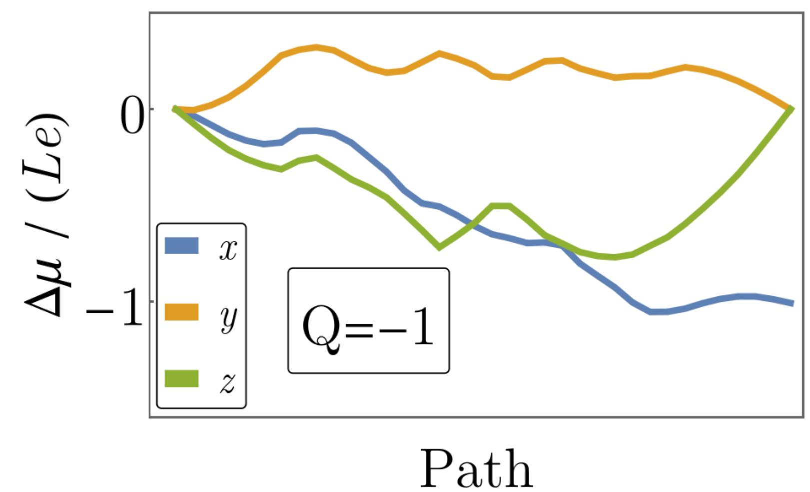
Federico Grasselli[1] and Stefano Baroni[1,2*]

non-stoichiometric melts

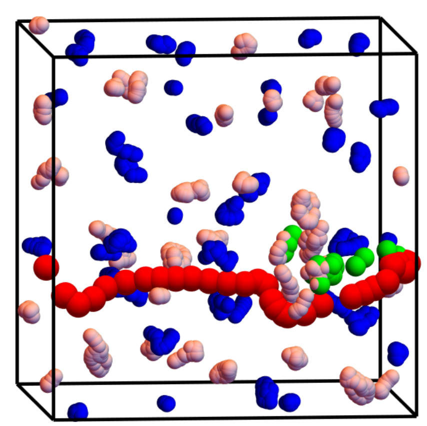
$K_x(KCl)_{1-x}$

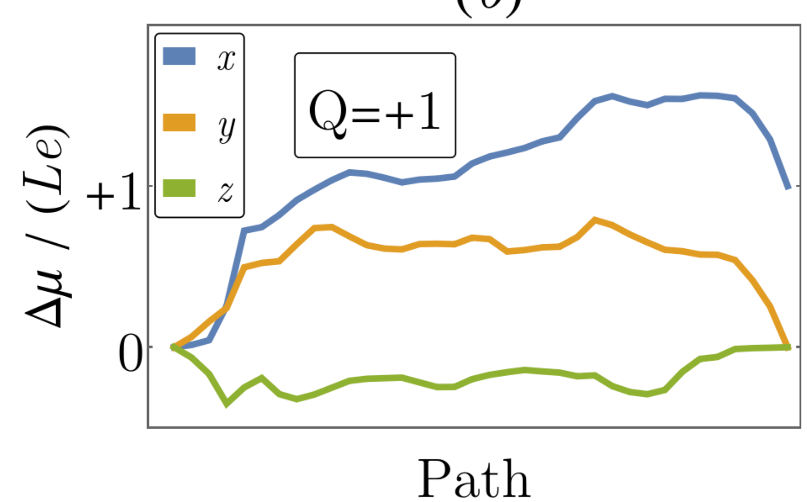






(b)

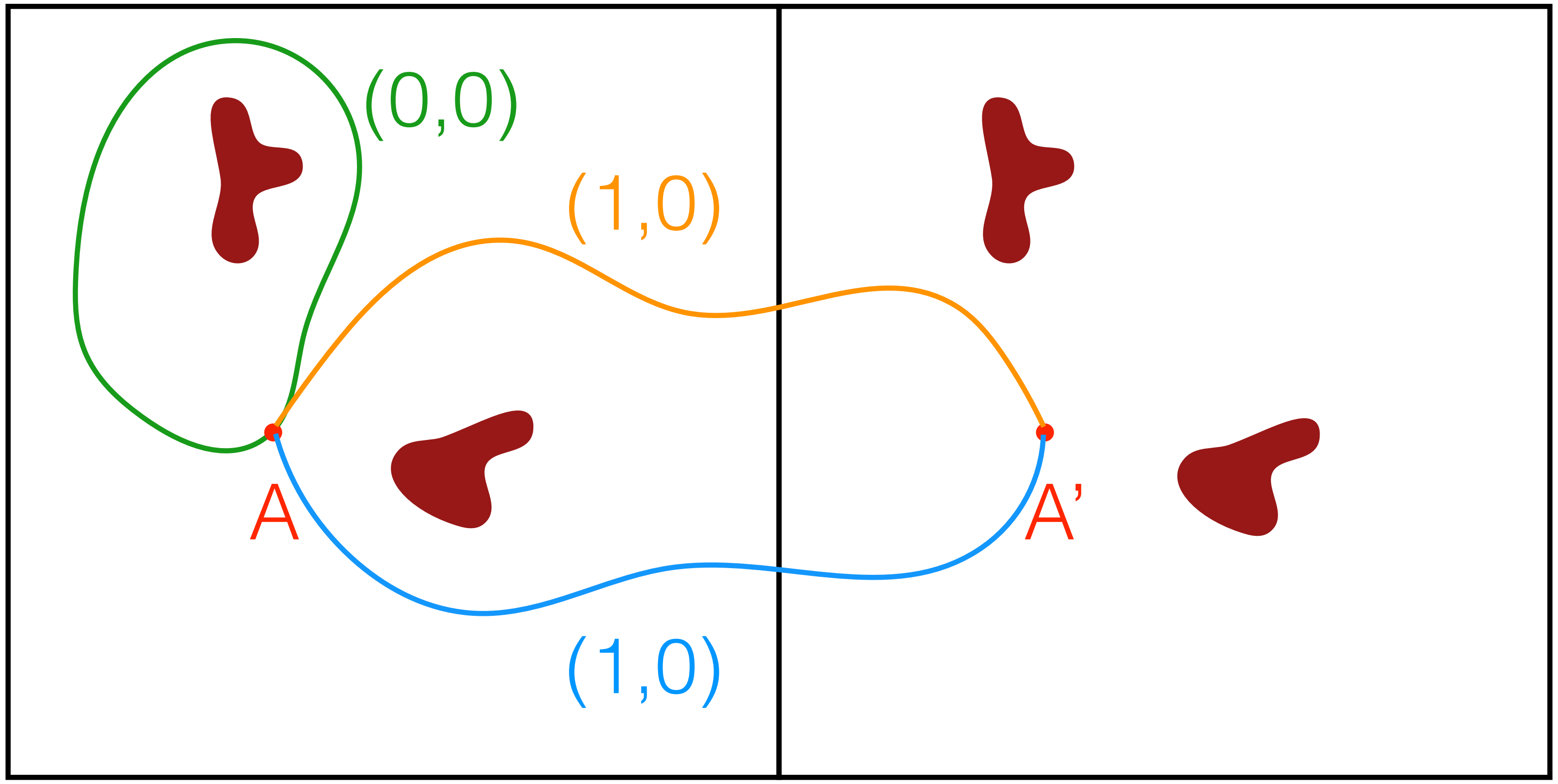




$K_{33}Cl_{31}$

$x \approx 0.06$

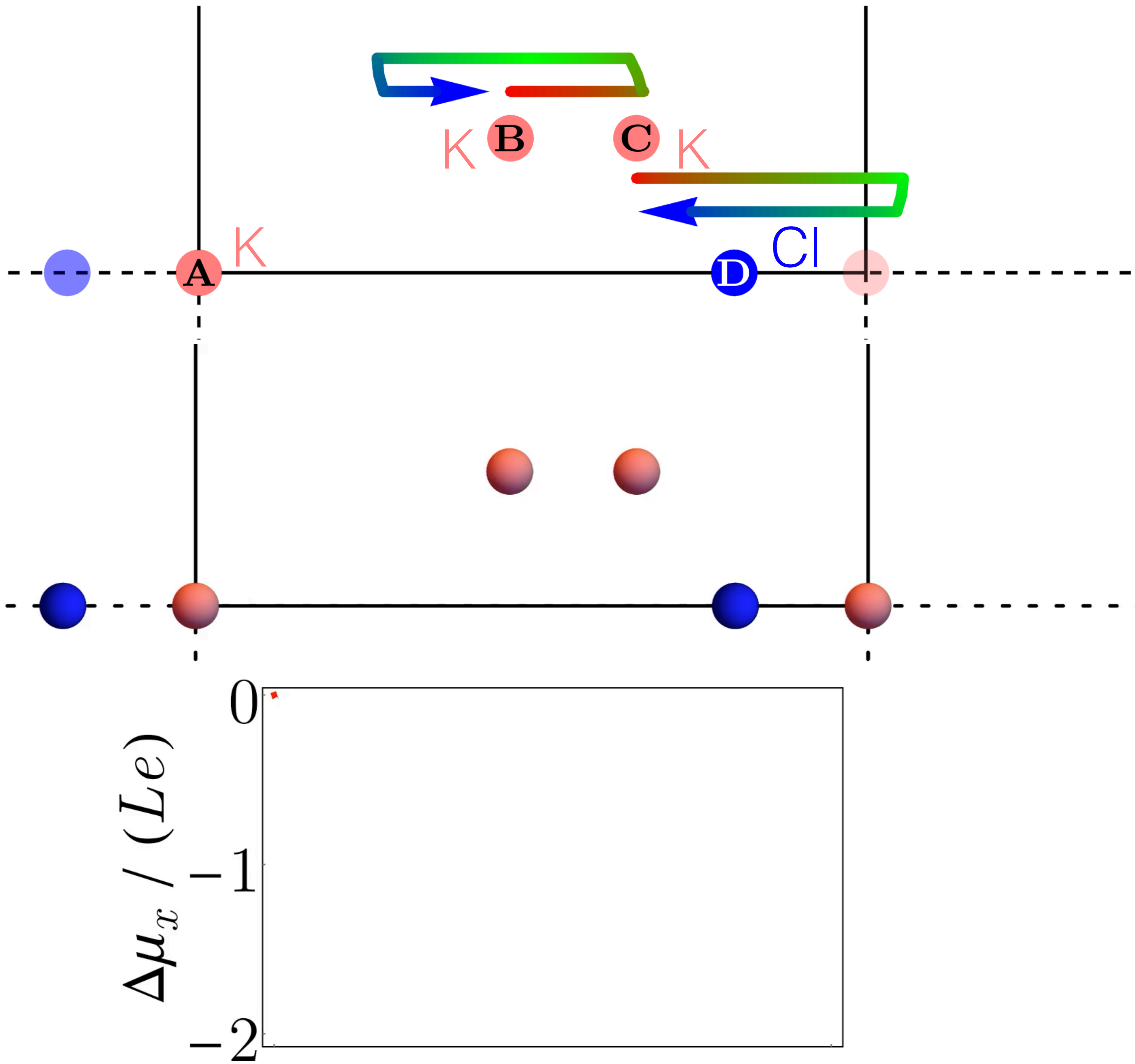
breach of strong adiabaticity



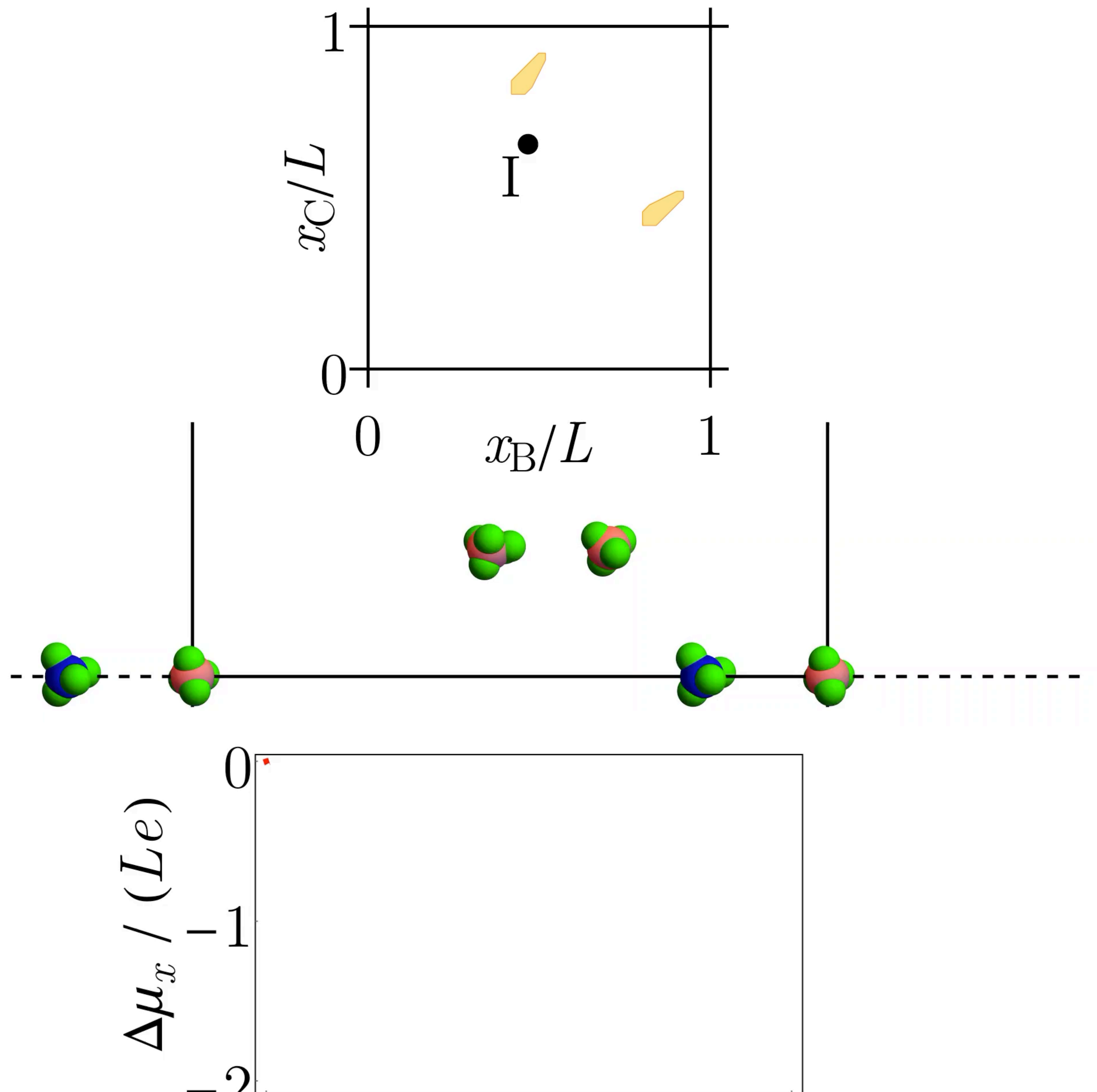
$$\mu \neq \mu^*$$

$$\mu \neq 0$$

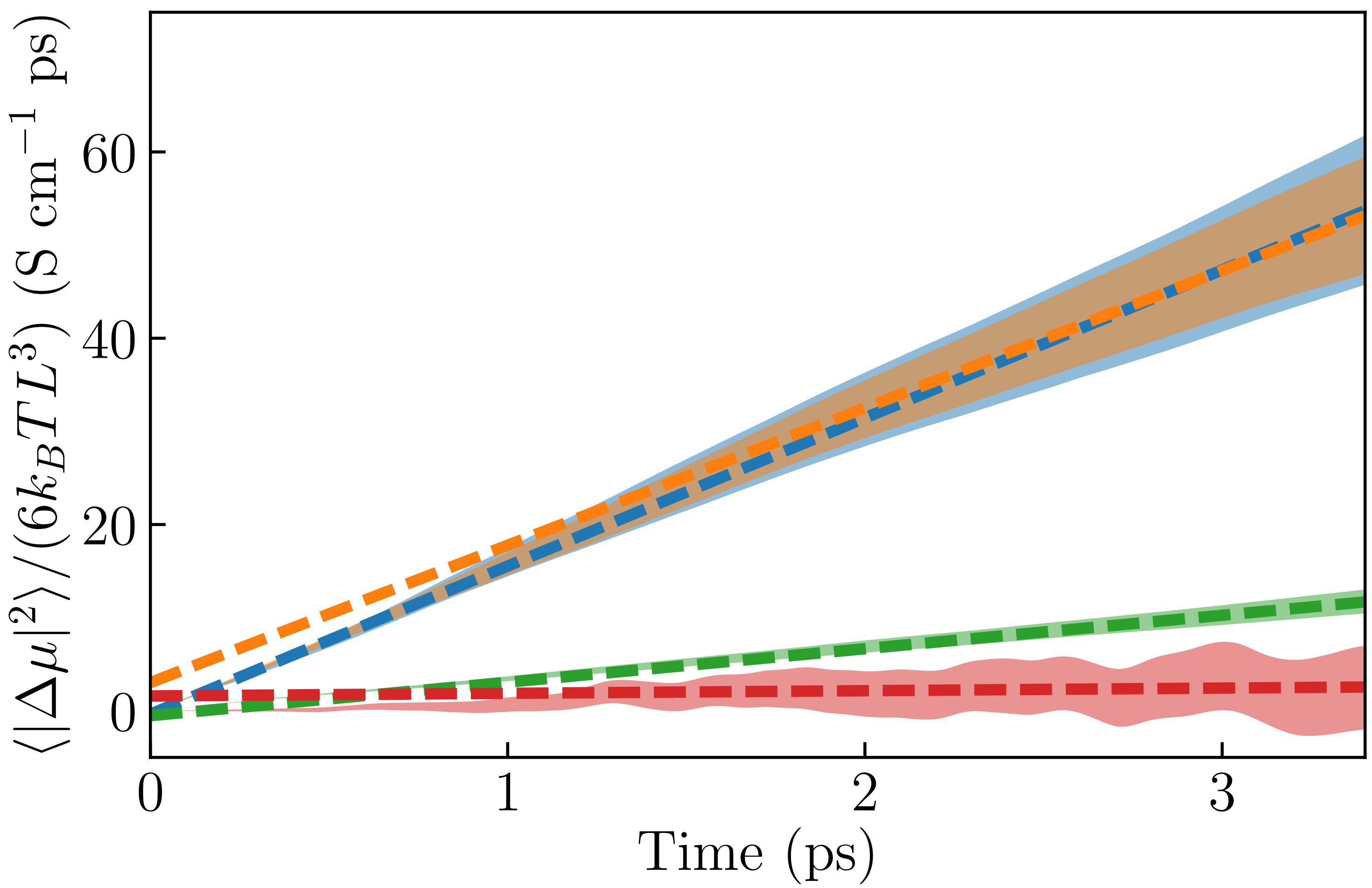
non-trivial particle transport



non-trivial particle transport



weakly adiabatic transport



$$\Delta\boldsymbol{\mu} = e\int_0^t \mathbf{J}(t')dt'$$

$$J_\alpha(t) = \sum_{i\beta} Z^*_{i\alpha\beta}(t)v_{i\beta}(t)$$

$$J_\alpha(t) = \sum_i q_{S(i)}v_{i\alpha}(t) - 2v^{lp}_\alpha(t)$$

cross term

Cornell University arXiv:2006.16749

arXiv.org > cond-mat > arXiv:2006.16749

Condensed Matter > Materials Science

[Submitted on 30 Jun 2020]

Oxidation states, Thouless' pumps, and anomalous transport in non-stoichiometric ionic conductors

Paolo Pegolo, Federico Grasselli, Stefano Baroni

conclusions

- transport coefficients are to a large extent independent of the specific microscopic representation of the conserved densities and currents;
- this *gauge invariance* of transport coefficients makes it possible to compute thermal conductivities from DFT using equilibrium AIMD and the Green-Kubo formalism;
- *topological quantisation* of charge transport allows one to give a rigorous definition of the atomic oxidation states;
- *gauge invariance* and *topological quantisation* of charge transport make the electric conductivity of (stoichiometric) ionic conductors depend on the formal oxidation numbers of the ionic species, via the Green-Kubo formula;
- non-stoichiometric solutions may breach strong adiabaticity, thus determining an adiabatic transport regime where charge can flow without any concomitant mass flow.

QUANTUM ESPRESSO

QUANTUM ESPRESSO FOUNDATION

MAX

Federico Grasselli
SISSA, now @EPFL

Paolo Pegolo
SISSA