topology, oxidation states, and charge transport in ionic conductors

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serious answers to four silly questions
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how come the electric conductivity of molecular non-ionic fluids vanishes, when the current fluctuations that determine it, do not?
serious answers to four silly questions

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how come the conductivity of (stoichiometric) electrolytes is correctly predicted when real-valued, time-dependent, tensor Born effective charges are replaced with integer-valued, time-independent, scalar atomic oxidation states?
serious answers to four silly questions

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what are oxidation states, in the first place?
serious answers to four silly questions

- how come the electric conductivity of molecular non-ionic fluids vanishes, when the current fluctuations that determine it, do not?

- how come the conductivity of (stoichiometric) electrolytes is correctly predicted when real-valued, time-dependent, tensor Born effective charges are replaced with integer-valued, time-independent, scalar atomic oxidation states?

- what are oxidation states, in the first place?

- to start with: how come the heat conductivity is well defined, when the energy current that determines it, is not?
linear-response theory of transport

\[ J = \lambda F \]
linear-response theory of transport

\[ J = \lambda F \]

charge transport

\[ J_Q = \sum q_i V_i \]
\[ F_Q = -\nabla \phi \]

\( \lambda = \text{electric conductivity} \)
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energy transport

\[ J_\varepsilon = \sum_i e_i V_i + \frac{1}{2} \sum_{i \neq J} (V_i \cdot F_{iJ})(R_i - R_J) \]
\[ F_\varepsilon = -\nabla T \]
\[ \lambda = \text{heat conductivity} \]
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\[ \lambda = \text{heat conductivity} \]

\[ \lambda \propto \int_0^\infty \langle J(t)J(0) \rangle dt \]
Green-Kubo
linear-response theory of transport

\[ J = \lambda F \]

Green-Kubo

\[ \lambda \propto \int_0^\infty \frac{\langle J(t)J(0) \rangle dt}{\langle J^2 \rangle_T} \]

\[ \int_0^t \langle J(t')J(0) \rangle dt' \]
linear-response theory of transport

\[ \mathbf{J} = \lambda \mathbf{F} \]

Green-Kubo

\[ \lambda \propto \int_0^\infty \frac{\langle \mathbf{J}(t) \mathbf{J}(0) \rangle}{\langle \mathbf{J}^2 \rangle_T} dt \]

Einstein-Helfand

\[ \lambda \propto \lim_{t \to \infty} \frac{1}{2t} \text{var} \left[ \int_0^t \mathbf{J}(t') dt' \right] \]
a prequel:
heat transport
classical and quantum adiabatic heat transport

\[ J_\mathcal{E} = \sum_l e_l V_l + \frac{1}{2} \sum_{l \neq J} (V_l \cdot F_{IJ})(R_l - R_J) \]

Thermal Conductivity of Periclase (MgO) from First Principles

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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.
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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.
how come?
how come?

how is it that a formally exact theory of the electronic ground state cannot predict all measurable adiabatic properties?
gauge invariance of transport coefficients

energy is extensive

\[ E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2] \]
gauge invariance of transport coefficients

energy is extensive

$E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2] + W[\partial \Omega]$
gauge invariance of transport coefficients

energy is extensive

\[ E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2] + W[\partial \Omega] \]
\[ \Rightarrow \mathcal{E}[\Omega_1] + \mathcal{E}[\Omega_2] \]

\[ \mathcal{E}[\Omega] = \int_\Omega e(r) dr \]
gauge invariance of transport coefficients

energy is extensive

\[ E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2] + W[\partial \Omega] \]

thermodynamic invariance

\[ \mathcal{E}[\Omega] = \int_{\Omega} e(r) dr \]

\[ \mathcal{E}'[\Omega] = \mathcal{E}[\Omega] + O[\partial \Omega] \]
gauge invariance of transport coefficients

energy is extensive

\[ E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2] + W[\partial \Omega] \]

\[ \equiv \varepsilon[\Omega_1] + \varepsilon[\Omega_2] \]

\[ \varepsilon[\Omega] = \int_{\Omega} e(r) dr \]

thermodynamic invariance

\[ \varepsilon'[\Omega] = \varepsilon[\Omega] + O[\partial \Omega] \]

gauge invariance

\[ e'(r) = e(r) - \nabla \cdot p(r) \]
gauge invariance of transport coefficients

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

gauge invariance

\[ e'(r) = e(r) - \nabla \cdot p(r) \]

energy is conserved

\[ \dot{e}(r, t) = -\nabla \cdot j(r, t) \]

energy is extensive
gauge invariance of transport coefficients

energy is extensive

\[ E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2] + W[\partial \Omega] \]

\[ \equiv \mathcal{E}[\Omega_1] + \mathcal{E}[\Omega_2] \]

\[ \mathcal{E}[\Omega] = \int_{\Omega} e(r) dr \]

thermodynamic invariance

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

gauge invariance

\[ e'(r) = e(r) - \nabla \cdot p(r) \]

\[ j'(r, t) = j(r, t) + p(r, t) \]

energy is conserved

\[ \dot{e}(r, t) = -\nabla \cdot j(r, t) \]
gauge invariance of transport coefficients

energy is extensive

\[ E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2] + W[\partial \Omega] \]

\[ \implies E[\Omega_1] + E[\Omega_2] \]

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

thermodynamic invariance

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

\[ \mathbf{J}(t) = \frac{1}{\Omega} \int \mathbf{j}(\mathbf{r}, t) d\mathbf{r} \]

\[ \mathbf{P}(t) = \frac{1}{\Omega} \int \mathbf{p}(\mathbf{r}, t) d\mathbf{r} \]

gauge invariance

\[ e'(\mathbf{r}) = e(\mathbf{r}) - \nabla \cdot \mathbf{p}(\mathbf{r}) \]

\[ \mathbf{j}'(\mathbf{r}, t) = \mathbf{j}(\mathbf{r}, t) + \dot{\mathbf{p}}(\mathbf{r}, t) \]

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

energy is conserved

\[ \dot{e}(\mathbf{r}, t) = -\nabla \cdot \mathbf{j}(\mathbf{r}, t) \]
gauge invariance of transport coefficients

\[ J' = J + \dot{P} \]
gauge invariance of transport coefficients

\[ J' = J + \dot{P} \]

\[ \lambda \sim \frac{1}{2t} \text{var}[D(t)] \quad D(t) = \int_0^t J(t')dt' \]
The document contains a mathematical discussion on gauge invariance of transport coefficients, with the following equations:

\[ J' = J + \dot{P} \]

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

\[ D'(t) = D(t) + P(t) - P(0) \]
gauge invariance of transport coefficients

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\[ \text{var}[D'(t)] = \text{var}[D(t)] + \text{var}[\Delta P(t)] + 2 \text{cov}[D(t) \cdot \Delta P(t)] \]
gauge invariance of transport coefficients

\[ J' = J + \dot{P} \]

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\[ D'(t) = D(t) + P(t) - P(0) \]

\[ \text{var}[D'(t)] = \text{var}[D(t)] + \Delta P(t) + 2\text{cov}[D(t), \Delta P(t)] \]

\[ \mathcal{O}(t) \quad \mathcal{O}(1) \quad \mathcal{O}(t^{\frac{1}{2}}) \]
any two conserved densities that differ by the divergence of a (bounded) vector field are physically equivalent

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

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

\[ J' = J + \dot{P} \]
gauge invariance of heat transport
ionic transport
$J = \sigma E$
\[ \mathbf{J} = \sigma \mathbf{E} \]

\[ \mathbf{J} = \frac{1}{\Omega} \mu \]

\[ = \frac{1}{\Omega} \sum_{i} \mathbf{Z}_{i}^{*} \cdot \mathbf{v}_{i} \]
\[ \mathbf{J} = \sigma \mathbf{E} \]

\[
\mathbf{J} = \frac{1}{\Omega} \dot{\mu} \\
= \frac{1}{\Omega} \sum_i \mathbf{Z}_i^* \cdot \mathbf{v}_i
\]

\[ Z_{i\alpha\beta}^* = \frac{\partial \mu_{\alpha}}{\partial u_{i\beta}} \]
\[ \mathbf{J} = \sigma \mathbf{E} \]

\[ \mathbf{J} = \frac{1}{\Omega} \dot{\mathbf{\mu}} = \frac{1}{\Omega} \sum_{i} \mathbf{Z}_{i}^{*} \cdot \mathbf{v}_{i} \]

\[ \sigma = \frac{\Omega}{3k_{B}T} \langle |\mathbf{J}|^2 \rangle \times \tau_{J} \]
the conundrum

molecular H$_2$O

\[ J(t) \]

\[ J = \frac{1}{\Omega} \sum_{i} Z_i^* \cdot v_i \]

\[ \langle J^2 \rangle_\tau = ??? \]
the conundrum

molecular H$_2$O

\[
\mathbf{J} = \frac{1}{\Omega} \sum_i \mathbf{Z}_i^* \cdot \mathbf{v}_i \\
\langle \mathbf{J}^2 \rangle_T = ???
\]

\[
\sigma = \frac{\Omega}{3 k_B T} \int_0^\infty \langle \mathbf{J}(t) \cdot \mathbf{J}(0) \rangle \, dt
\]
Dynamical Screening and Ionic Conductivity in Water from \textit{Ab Initio} Simulations

Martin French,\textsuperscript{1} Sebastien Hamel,\textsuperscript{2} and Ronald Redmer\textsuperscript{1}

the conundrum
Dynamical Screening and Ionic Conductivity in Water from Ab Initio Simulations

Martin French,¹ Sebastien Hamel,² and Ronald Redmer¹
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 $Z_O=-2$.
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 $Z_O=-2$.\[\int_0^t \langle J(t') J(0) \rangle \, dt'\]
how come?

and what are oxidation states, in the first place?
quantisation of adiabatic particle transport

classical PBC

\[ V(x + L) = V(x) \]
quantisation of adiabatic particle transport

\[ V(x + L) = V(x) \]

\[ \psi(x + L) = \psi(x) \]
quantisation of adiabatic particle transport

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time periodicity

\[ V(x, t + T) = V(x, t) \]
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time periodicity

\[ V(x, t + T) = V(x, t) \]

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

quantisation of adiabatic particle transport

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

\[ J_\alpha(t) = \frac{e}{L^3} \sum_s Q_s V_s \alpha(t) + \frac{e}{2\pi L^2} \frac{d}{dt} \text{Im} \log \langle \Psi(t) | e^{i2\pi X_\alpha/L} | \Psi(t) \rangle \]

quantisation of adiabatic particle transport

\[
\frac{L^{d-1}}{\epsilon} \int_0^T J_\alpha(t) \, dt = n \in \mathbb{Z}
\]

\[
J_\alpha(t) = \frac{e}{L^3} \sum_s Q_s V_{s\alpha}(t) + \frac{\gamma(t)}{\epsilon}
\]

\[
\frac{e}{2\pi L^2} \frac{d}{dt} \text{Im} \log \langle \Psi(t)|e^{i\frac{2\pi X_\alpha}{L}}|\Psi(t)\rangle
\]

what are oxidation states, in the first place?
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\[ [0, L]^{3N} \xrightarrow{\text{PBC}} \mathbb{T}^{3N} \]
what are oxidation states, in the first place?
what are oxidation states, in the first place?

A = A'}
what are oxidation states, in the first place?
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\[ n_1 = 1 \quad n_2 = 0 \]
what are oxidation states, in the first place?
what are oxidation states, in the first place?
what are oxidation states, in the first place?

\[ n_1 = 2 \quad n_2 = 0 \]
what are oxidation states, in the first place?
what are oxidation states, in the first place?
what are oxidation states, in the first place?

\[ n_1 = 1 \]

\[ n_2 = 1 \]
what are oxidation states, in the first place?
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\[ \hat{H}(t + T) = \hat{H}(t) \]
what are oxidation states, in the first place?

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\[ \frac{L^2}{e} \int_0^T J_\alpha(t) \, dt = \frac{1}{Le} \int d\mu_\alpha[X] = Q_\alpha \in \mathbb{Z} \]

what are oxidation states, in the first place?

\[
Q_\alpha(AA') = Q_\alpha(AA') = Q_\alpha[n_1 = 1, n_2 = 1]
\]
what are oxidation states, in the first place?

\[ Q_\alpha[C] = \frac{1}{\ell} \mu_\alpha[C] \]
what are oxidation states, in the first place?

\[ Q_\alpha[C] = \frac{1}{\ell} \mu_\alpha[C] \]

\[ = Q_\alpha(n_{1x}, n_{1y}, n_{1z}, \cdots n_{Nz}) \]
what are oxidation states, in the first place?

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\[ Q_\alpha[C_1 \circ C_2] = Q_\alpha[C_1] + Q_\alpha[C_2] \]
what are oxidation states, in the first place?

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Q_\alpha[C] = \frac{1}{\ell} \mu_\alpha[C] \\
= Q_\alpha(n_{1x}, n_{1y}, n_{1z}, \ldots n_{Nz})
\]

\[
Q_\alpha[C_1 \circ C_2] = Q_\alpha[C_1] + Q_\alpha[C_2]
\]

\[
Q_\alpha(n_{1x}, n_{1y}, n_{1z}, \ldots n_{Nz}) = \sum_{i\beta} q_{i\alpha\beta} n_{i\beta}
\]
what are oxidation states, in the first place?

\[ Q_\alpha[C] = \frac{1}{\ell} \mu_\alpha[C] \]
\[ = Q_\alpha(n_{1x}, n_{1y}, n_{1z}, \cdots n_{Nz}) \]
\[ Q_\alpha[C_1 \circ C_2] = Q_\alpha[C_1] + Q_\alpha[C_2] \]
\[ Q_\alpha(n_{1x}, n_{1y}, n_{1z}, \cdots n_{Nz}) = \sum_{i\beta} q_{i\alpha\beta} n_{i\beta} \]

• All loops can be shrunk to a point without closing the gap (strong adiabaticity);

• Any two like atoms can be swapped without closing the gap
what are oxidation states, in the first place?

\[ Q_\alpha[\mathcal{C}] = \frac{1}{\ell} \mu_\alpha[\mathcal{C}] \]
\[ = Q_\alpha(n_{1x}, n_{1y}, n_{1z}, \ldots n_{Nz}) \]

\[ Q_\alpha[\mathcal{C}_1 \circ \mathcal{C}_2] = Q_\alpha[\mathcal{C}_1] + Q_\alpha[\mathcal{C}_2] \]
\[ Q_\alpha(n_{1x}, n_{1y}, n_{1z}, \ldots n_{Nz}) = \sum_{i\beta} q_{i\alpha\beta} n_{i\beta} \]

• All loops can be shrunk to a point without closing the gap (strong adiabaticity);

• Any two like atoms can be swapped without closing the gap

\[ q_{i\alpha\beta} = q_{S(i)} \delta_{\alpha\beta} \]

atomic oxidation state

... they are topological invariants!
a numerical experiment on molten KCl

a topologically non-trivial minimum-energy path connecting two identical configurations of a ionic melt
a numerical experiment on molten KCl

a topologically non-trivial minimum-energy path connecting two identical configurations of a ionic melt
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a numerical experiment on molten KCl

$Q_x = -0.000(6); \quad Q_y = 0.000(2); \quad Q_z = 1.00(18)$
a numerical experiment on molten KCl

the charges transported by K and Cl around z cancel exactly

\[ Q_z[Cl] = -1 \quad Q_y[Cl] = -1 \]
\[ Q_z[K] = 1 \quad Q_z[K] = 0 \]
a numerical experiment on molten KCl

the charges transported by K and Cl around z cancel exactly
gauge invariance of charge transport

\[
\sigma \propto \lim_{t \to \infty} \frac{1}{2t} \text{var}[\mu_{AB}(t)]
\]

\[
\mu_{AB}(t) = \int_0^t J(t')dt'
\]
gauge invariance of charge transport

\[ \hat{H}(B) \neq \hat{H}(A) \]
\[ \hat{H}(A') = \hat{H}(A) \]

\[
\begin{align*}
\sigma & \propto \lim_{t \to \infty} \frac{1}{2t} \text{var} [\mu_{AB}(t)] \\
\mu_{AB}(t) & = \int_0^t J(t') dt'
\end{align*}
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\[ \mu_{AB}(t) = \int_{0}^{t} J(t')dt' \]
\[ = \mu_{AA'} + \mu_{A'B} \]
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\]

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\sigma \propto \lim_{t \to \infty} \left( \frac{1}{2t} \right) \text{var} [\mu_{AB}(t)]
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\[
= \mu_{AA'} + \mu_{A'B}
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gauche invariance of charge transport

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\[ J_\alpha = \sum_{i\beta} Z^*_{i\alpha\beta} v_{i\beta} \]
\[ J'_\alpha = \sum_i q_{S(i)} v_{i\alpha} \]

\[ \sigma \propto \lim_{t \to \infty} \frac{1}{2t} \var\left[ \mu_{AB}(t) \right] \]
\[ \mu_{AB}(t) = \int_0^t J(t') dt' \]
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gauge invariance of charge transport

\[ \hat{H}(B) \neq \hat{H}(A) \]
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\[ J_\alpha = \sum_{i\beta} Z^*_{i\alpha\beta} v_{i\beta} \]
\[ J'_\alpha = \sum_i q_{S(i)} v_{i\alpha} \]

\[ \mu_{AB}(t) = \mu_{AA'} + \mu_{AB} + O(1) \]
\[ \hat{H}(B) \neq \hat{H}(A) \]
\[ \hat{H}(A') = \hat{H}(A) \]

\[ J_\alpha = \sum_{i, \beta} Z^*_{i, \alpha \beta} v_{i \beta} \]
\[ J'_{\alpha} = \sum_{i} q_{S(i)} v_{i \alpha} \]

\[ \mu_{AB}(t) = \mu_{AA'} + O(1) \]
\[ \mu_{AB}(t) = \mu'_{AA'} + O(1) \quad \text{(Thouless)} \]
gauge invariance of charge transport

\[ \hat{H}(B) \neq \hat{H}(A) \]
\[ \hat{H}(A') = \hat{H}(A) \]

\[ \sigma \propto \lim_{t \to \infty} \frac{1}{2t} \text{var} [\mu_{AB}(t)] \]
\[ \mu_{AB}(t) = \int_0^t J(t') dt' \]
\[ = \mu_{AA'} + \mu_{AB} \]

\[ J_\alpha = \sum_{i} Z_{i \alpha \beta} v_{i \beta} \]
\[ J'_\alpha = \sum_{i} q_{S(i)} v_{i \alpha} \]

\[ \mu_{AB}(t) = \mu_{AA'} + O(1) \]
\[ = \mu_{AA'}' + O(1) \quad \text{(Thouless)} \]
\[ = \mu_{AB}' + O(1) \]
gauge invariance of charge transport

\[ \hat{H}(B) \neq \hat{H}(A) \]
\[ \hat{H}(A') = \hat{H}(A) \]

\[ J_\alpha = \sum_{i\beta} Z_{i\alpha\beta}^{*} v_{i\beta} \]
\[ J'_\alpha = \sum_{i} q_{S(i)} v_{i\alpha} \]

\[ \sigma \propto \lim_{t \to \infty} \frac{1}{2t} \text{var} \left[ \mu_{AB}(t) \right] \]
\[ \mu_{AB}(t) = \int_{0}^{t} J(t') dt' \]
\[ = \mu_{AA'} + \mu_{A'B} \]

\[ \mu_{AB}(t) = \mu_{AA'} + O(1) \]
\[ = \mu'_{AA'} + O(1) \quad \text{(Thouless)} \]
\[ = \mu'_{AB} + O(1) \]

\[ \sigma = \sigma' \]
currents from atomic oxidation numbers

\[ J_\alpha = \sum_{i \beta} Z_{i \alpha \beta} v_{i \beta} \]  \hspace{1cm} \text{(2)}

\[ J'_\alpha = \sum_i q_{S(i)} v_{i \alpha} \]  \hspace{1cm} \text{(9)}
non-stoichiometric melts

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

$K_{33}Cl_{31}$

$x \approx 0.06$
non-stoichiometric melts

\[ K_x(KCl)_{1-x} \]

\[ K_{33}Cl_{31} \]

\( x \approx 0.06 \)
non-stoichiometric melts

\[ K_x(KCl)_{1-x} \]

\[ K_{33}Cl_{31} \]

\[ x \approx 0.06 \]
non-stoichiometric melts

\[ K_x(KCl)_{1-x} \]

\[ K_{33}Cl_{31} \quad x \approx 0.06 \]
non-stoichiometric melts

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

$K_{33}Cl_{31}$

$x \approx 0.06$
non-trivial particle transport
non-trivial particle transport
non-trivial particle transport
breach of strong adiabaticity

\[ \mu = \mu^* \]
breach of strong adiabaticity

\[ \mu = \mu^* \]

\[ \mu = 0 \]
breach of strong adiabaticity

\[ \mu \neq \mu^* \]

\[ \mu \neq 0 \]
strongly adiabatic transport

$$\mu = \mu^*$$  
$$\mu = 0$$

weakly adiabatic transport

$$\mu \neq \mu^*$$  
$$\mu \neq 0$$
not trivial weakly adiabatic conductivity

\[ \Delta \mu = e \int_0^t J(t') dt' \]

\[ J_\alpha(t) = \sum_{i\beta} Z_{i\alpha\beta}^*(t) v_{i\beta}(t) \]

\[ J_\alpha(t) = \sum_i q_{S(i)} v_{i\alpha}(t) - 2 v_\alpha^{lp}(t) \]

cross term
conclusions
conclusions

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- gauge invariance and quantisation of charge transport make the electric conductivity of stoichiometry electrolytes depend on the formal oxidation numbers of the ionic species, via the Green-Kubo formula;
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- Gauge invariance and quantisation of charge transport make the electric conductivity of stoichiometry electrolytes depend on the formal oxidation numbers of the ionic species, via the Green-Kubo formula.

- Breach of strong adiabaticity in non-stoichiometric electrolytes triggers an anomalous transport regime, intermediate between metallic and ionic, whereby charge may be transported without any concurrent mass displacement.
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