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

Paolo Pegolo,1 Federico Grasselli,1 and Stefano Baroni1,2

1SISSA – Scuola Internazionale Superiore di Studi Avanzati, Trieste, Italy
2CNR – Istituto Officina dei Materiali, SISSA, 34136 Trieste

(Dated: July 1, 2020)

Abstract

Thouless’ quantization of adiabatic particle transport permits to associate an integer topological charge with each atom of an electronically gapped material. When these charges are additive and independent of atomic positions, they provide a rigorous definition of atomic oxidation states and atoms can be identified as integer-charge carriers in ionic conductors. If these conditions are met, charge transport is necessarily convective, i.e. it cannot occur without substantial ionic flow. We study the topological requirements that allow these conditions to be broken and charge to flow without any ionic convection, even in electronic insulators, a transport regime that we call anomalous. We first identify the topological features of the electronic ground state of a system that make anomalous transport possible. These features can induce a quantized charge-pump mechanism and lead to a non-vanishing charge transport with no net ionic displacement, yet retaining the insulating character of the ground state, which allows the system to be treated in the adiabatic approximation, from where all of our theoretical results derive. These results are then demonstrated with simple molecular models where adiabatic anomalous transport occurs. We finally examine the impact of our findings on the transport properties of non-stoichiometric alkali-halide melts, where most of the total charge current results to be uncorrelated from the ionic ones.

PACS numbers: 66.10.-x 61.20.Ja

Keywords: Oxidation states, Topological quantum numbers, Thouless’ charge pump, Adiabatic dynamics

I. INTRODUCTION

Atomic oxidation states (OS) are ubiquitous in chemistry and widely used to describe redox reactions, electrolysis, and many electro-chemical processes. In spite of their fundamental nature, OSs have long eluded a proper quantum-mechanical interpretation. As a matter of fact, the commonly accepted definition provided by IUPAC (OS of an atom is the charge of this atom after ionic approximation of its heteronuclear bonds [1]) can hardly be given a rigorous quantitative meaning. As one sees, this statement stands on approximating a real number that expresses a static property (the atomic charge, which is not even well-defined quantum-mechanically) to the closest integer, a procedure that is intrinsically ill-defined and potentially misleading in some cases [2, 3]. This predicament has been reversed by a recent paper [4] where, building on previous work [5] based on the modern theory of polarization [6, 7], it was shown that OSs can indeed be defined as topological quantum numbers [8] describing the charge dynamically displaced by individual atoms along closed paths in atomic configuration space, under periodic boundary conditions. By leveraging a recently established gauge invariance principle of transport [9, 10], it was also shown that, whenever topological charges are both additive and independent of atomic positions, atoms can be identified as integer carriers in adiabatic charge transport and the latter is purely convective, i.e. it can only occur along with the displacement of the atomic charge carriers. We call this transport regime normal. Of course, chemically relevant situations occur where different atoms of a same species feature different OSs, depending on the local chemical environment. Although the occurrence of such cases is indeed compatible with a comprehensive topological definition of OSs [5], breaking the additivity and position-independence of atomic OSs has important consequences on transport properties, the most perspicuous of which is the possibility that charge may be displaced without any associated atomic convection, a transport regime that we dub anomalous.

In this work we address the topological conditions to be met in order to break the additivity and position independence of topological charges, and discuss the impact of their occurrence on anomalous transport in the paradigmatic case of non-stoichiometric molten salts. To this end, we first introduce a toy model, the positive hydrogen trimer ion, $\text{H}_3^+$, displaying lack of topological-charge additivity; we then move to the KCl neutral complex, where different K atoms display different and non-additive topological charges, thus determining a Thouless’ pump mechanism whereby a (quantized) charge transport may occur without a net atomic displacement; building on these findings, we finally address anomalous transport in non-stoichiometric K$_x$(KCl)$_{1-x}$ melts, which display an insulator-to-metal transition for increasing alkali-metal concentration, $x$. For small enough $x$, the ionic melt features a finite electronic gap and the topology of the ground state is such that the total charge current mainly results from lone pairs of solvated electrons whose motion is largely uncorrelated from the ionic ones. Non-stoichiometric molten salts are paradigmatic cases of
systems featuring solvated electrons, other notable examples including non-stoichiometric electrolytes and metal solutions in a ionic solvent, to which we believe that the bulk of our analysis also applies [11–13].

II. THEORY

Charge transport in ionic conductors occurs through the rearrangement of charge inhomogeneities along with the motion of atomic nuclei in space. Ionic conductors are electronic insulators—a necessary condition for charge inhomogeneities to persist unscreened—so that their dynamics is accurately described in the adiabatic approximation, whereby electrons stay in their quantum ground state, while classical nuclei wander around in space. In the adiabatic approximation, the charge density depends on time through the dependence of the electronic Hamiltonian, \( \hat{H} \), and its ground state, \( \Psi_0 \), on nuclear coordinates: \( \hat{H}(\mathbf{R}(t))\Psi_0(t) = E_0(t)\Psi_0(t) \), where \( \mathbf{R} = \{r_1, \ldots, r_N\} \) is the set of positions of the \( N \) atoms in the system. We call the space of all possible atomic configurations the atomic configuration space (ACS) and its subspace whose configurations have a finite gap its adiabatic (sub-) space. We describe macroscopic bodies using periodic boundary conditions (PBC) with period \( L \) along each Cartesian direction, as they are the only ones able to sustain a steady-state current in finite systems [14]. When PBC are adopted, the ACS is isomorphic to a 3N-dimensional torus and any path in ACS linking two periodic images of the same configuration is isomorphic to a closed path on the torus. Paths in the adiabatic sub-space (be they closed or open) will be referred to as adiabatic paths. On a torus, a closed path, \( \mathcal{C} \), can be classified topologically by the number of windings it makes along each direction of the ACS \( \{n_{ia}[\mathcal{C}]\} \), the winding numbers: any such direction is identified by an atomic label, \( i \), and by the Cartesian direction, \( \alpha \), along which the atom moves. In the case depicted in Fig. 1 for instance, the horizontal green segment has winding numbers \((1,0)\), the vertical one \((0,1)\), and the blue path \((1,1)\). A path with all-zero winding numbers can be shrunk to a point on the torus and is called a trivial path.

The topological properties of the adiabatic sub-space will be key in our subsequent discussions, in view of which we introduce the concepts of adiabatic connectedness and strong adiabaticity (SA). The adiabatic sub-space is connected if any pair of points belonging to it can be joined by an (open) path entirely belonging to it; otherwise, it is the non-connected union of connected domains (in short: adiabatic domains). An adiabatic domain is said to be strongly adiabatic if any closed path belonging to it which is trivial on the torus is also trivial on it, \( i.e. \) it can be continuously shrunk to a point without ever closing the gap. In mathematical terms, SA amounts to saying that the fundamental group of the adiabatic domain is a subgroup of the fundamental group of the torus.

Closed adiabatic paths can be parametrized by a fictitious time, thus resulting in a time-periodic Hamiltonian, \( \hat{H}(t + T) = \hat{H}(t) \), featuring a finite gap at all times. In his seminal paper on quantization of particle transport [8], Thouless showed that, in the adiabatic approximation, the dipole displaced during a time period \( (or, equivalently, along a closed adiabatic path \( \mathcal{C} \)), \( \Delta \mu(T) = \Delta \mu[\mathcal{C}] \), is quantized in the large-\( L \) limit:

\[
\Delta \mu[\mathcal{C}] = \oint_{\mathcal{C}} d\mu_i = eLQ_\alpha[\mathcal{C}],
\]

where \( d\mu_i = \frac{\partial \mu_i(\mathbf{R})}{\partial \mathbf{R}} \cdot d\mathbf{R} \) is the electric dipole displaced along an infinitesimal segment of the path and \( Q_\alpha[\mathcal{C}] \) is an integer-valued functional of the path, which is therefore constant for any continuous deformation of its argument within an adiabatic domain.

The properties of the charge \( Q_\alpha[\mathcal{C}] \) strongly depend on the topology of the adiabatic domain to which \( \mathcal{C} \) belongs. Since the charges associated to any pair of adiabatic paths that can be deformed into one another coincide, if this domain is strongly adiabatic we conclude that \( Q_\alpha \) can only depend on the winding numbers of its argument: \( Q_\alpha[\mathcal{C}] = Q_\alpha(n_1, n_2, \cdots, n_N) \), where \( n_i = (n_{1i}, n_{2i}, \ldots, n_{Ni}) \) is the integer-valued 3-vector of the winding numbers of atom \( i \). Furthermore, it must be additive and isotropic. Additivity means that \( Q_\alpha \) is an integer-valued linear function of its integer arguments: \( Q_\alpha(\{n\}) = \sum \delta_{\alpha\beta} q_{\alpha\beta} n_{\beta} \); isotropy means that the \( q \) coefficients are integer multiples of the identity: \( q_{\alpha\beta} = q_{\delta\delta} \). Additivity is illustrated in Fig. 1. The concatenation of the two green paths with the reversed blue one is a trivial path: if SA holds, the total charge transported along it must be zero, so that the charge transported along the blue path must equal that transported along the green ones. Isotropy follows from a slight generalization of this argument. The combination of additivity and isotropy...
allows one to identify the $q_i$ charge with the oxidation number of the $i$-th atom \[i\]. When $N_S$ atoms of the same species $S$ are present, the ACS is the union of $N_S!$ disjoint domains that transform into each other under permutations. If these domains are strongly adiabatic and connected among themselves, one can swap two different atoms of the $S$ species without closing the electronic gap, implying that all the atoms of that species have the same OS. When two permutational domains are not connected, but still strongly adiabatic, an OS can still be assigned to each atom within a same domain, but atoms of the same chemical species belonging to different domains may feature different OSs: this is the case, e.g., of ferrous-ferric water solutions. When SA does not hold, instead, charge transport can no longer be characterized in terms of winding numbers on the torus, and the very concept of OS looses much of its topological meaning, with far reaching consequences on the transport mechanisms. In particular, SA breaking allows charge to flow in the absence of any ionic convection, even in electronic insulators, as illustrated in the following.

III. ANOMALOUS TRANSPORT

The simplest system displaying anomalous transport is probably the (linear) tri-hydrogen cation, $\text{H}_3^+$: three protons are aligned and the ground state of the two electrons is a singlet, therefore non-degenerate, resulting in a theoretical equilibrium interatomic distance $\Delta = 0.826$ Å. We treat the molecule using PBC with period $L = 10.6$ Å $\gg \Delta$ along the three Cartesian directions, thus amounting to enclose the molecule in a cubic supercell of side $L$. Further computational details are given in Appendix A. We now consider a closed path in ACS, consisting of the following three steps (see Fig. 2):
1. The B and C protons are first rigidly translated towards the end of the supercell until the distance between C and the periodic image of A (located at $x_A = L$) is $\Delta$ (red arrows, ending at configuration II);
2. The B proton, now located at $x_B = L - 2\Delta$, is moved back to its original position (green arrows, ending at configuration II);
3. Finally, the C proton is moved back from $x_C = L - \Delta$ to its original position (blue arrows, ending at config-
FIG. 3. A planar configuration of the K$_3$Cl system undergoing a loop in atomic configuration space. (a) Initial and final configurations. K and Cl atoms are indicated by pink and blue circles, respectively. The colored curved arrows indicate the 1D trajectories of the two K atoms participating in the loop. The color encodes the fictitious time parametrizing the loop (red → blue). (b) Closed path in the 2D projection of the atomic configuration space relative to the atoms that participate in the loop; the yellowish areas indicate regions where the ground state is degenerate. (c) Dipole displaced along the closed path. (d) Closed path in the 3D projection of the ACS where also the $x$ coordinate of atom A is shown. An animation illustrating the trajectory of the atoms participating in the loop can be found in the file Fig3_animated.mp4 in Ancillary Files. The green dots indicate the positions of the Wannier centers of the electrons in the system.

This path is periodic ($i.e.$ it is isomorphic to a trivial path on the torus), the last configuration being equal to the first. The ionization potential of H$_2$ is larger than that of H; therefore, along the path the pair of protons that is displaced or left behind stays neutral, and the electronic gap is always larger than that of H$_2$. If strong adiabaticity holds, the charge transported along the path must vanish and its transport be normal. In order to check if any anomalous transport occurs, we have computed the total dipole displaced along each segment of the path, $\Delta \mu$, according to the modern theory of the polarization in the Wannier representation [7],

$$\Delta \mu_{FP} = e \int_{FP} \left( \sum_{i=1}^{N} Z_i \, d\mathbf{r}_i - 2 \sum_{j=1}^{M} d\mathbf{w}_j \right),$$

where $Z_i$ is the positive core charge of atom $i$ ($Z_i = 1$, in the present case), $\mathbf{w}_j$ the position of the Wannier Center (WC) associated to the $j$-th occupied electronic band of the system, $M$ is the number of occupied states ($M = 1$, in the present case), and the factor 2 in front of the second sum accounts for the double occupancy of each molecular orbital. Our results, displayed in Fig. 2(c), indicate that a net charge, $Q = -2e$ is displaced along the path, thus revealing the existence of non-adiabatic domains in the ACS that the path loops around. Indeed, when the distance between any pair of protons is much larger than the molecular bond length, the ground state consists of two neutral atoms and one proton, and it is degenerate, because it does not matter which atoms are neutral and which one is ionized. The regions where this condition occurs is highlighted with yellowish triangles in Fig. 2(b), revealing that it is in fact encircled by the closed path. When the full 9-dimensional ACS is considered, the plane depicted in Fig. 2(b) is the locus where all the coordinates vanish but $x_B$ and $x_C$, and the triangles are the bi-dimensional sections over this plane of hyperprisms that pierce the entire ACS so that the loop cannot be shrunk to a point without closing the gap even when embedded in the full 9-dimensional space ($i.e.$ the loop is non trivial in the adiabatic subspace), as illustrated in Fig. 2(d).

Note that, while the total dipole is ill defined (both because it is intrinsically so when computed in PBC [10], and because the system is charged), dipole differences are perfectly well defined also in this case. Our previous considerations on the relative magnitude of the
ionization potentials of atomic and molecular hydrogen imply that WCs move (almost) rigidly with the proton pair being displaced, as illustrated in the animation Fig2_animated.mp4 to be found in the Ancillary Files. This implies that, when displaced individually, protons carry a unit charge, and one would be tempted to attribute an OS $q_H = 1$ to each of them. However, when they move in pairs, they carry a zero charge, a manifest breakdown of charge additivity, due to the breakdown of strong adiabaticity. The overall effect of the different charges transported by H atoms according to whether they are displaced individually or in pairs is that the total charge transported along the closed path of Fig. 2 does not vanish, while the net mass does.

The existence of adiabatic transport anomalies entails the occurrence of two partially conflicting requirements: a high degree of ionicity and the presence of loosely bound localized electronic states that can wander through the system without ever closing the gap. Non-stoichiometric molten salts seem therefore ideal candidates to display anomalous transport [17]. In order to prepare the study of such systems, we examine now the simplest molecular system possibly displaying their essential electronic features: the neutral K$_3$Cl complex. Computational details can be found in Appendix A. In Fig. 3 we show a planar configuration of this system, along with a closed path in ACS displaying charge transport without any net mass displacement. The dipole displaced by moving each of the atoms to their periodic images in the neighboring cell along the $x$ direction is, in units of $\epsilon L$, equal to $+1$ for A and C, equal to $-1$ for B and D. Conversely, moving any of the atoms to its periodic image in a direction perpendicular to the $x$ axis would break the bond of such atom with the rest of the system, resulting in a degenerate ground state. Moreover, as we verified that it is possible to swap atoms B and C without closing the gap, there is no way to uniquely associate an integer charge to each atom, whose OS would thus be topologically ill-defined. Based on our previous arguments, we conclude therefore that SA is violated here again.

In these systems for small enough concentrations. The numerical values of these energies are affected by DFT errors that lead to an underestimate of the electronic gaps. Notwithstanding, the system stays electronically insulating all along the AIMD trajectory, thus confirming the adequacy of an adiabatic treatment of transport in these systems for small enough concentrations. The average HOMO−1/LUMO gap would coincide with the average stoichiometric HOMO/LUMO gap for the stoichiometric K$_{32}$Cl$_{32}$ system.

FIG. 4. Time series of the HOMO/LUMO (blue) and HOMO−1/LUMO (orange) energy gaps. The horizontal red line indicates the thermal energy, $k_B T$. The horizontal green line is the average HOMO/LUMO gap for the stoichiometric K$_{32}$Cl$_{32}$ system.
confirms that the lone pair diffuses much faster than the cell, \( L \) covered a distance comparable to the size of the super-trajectory. One sees that, by the time the lone pair has arrived, all the atoms have traveled only a small fraction of this length. This suggests that charge transport in these systems may be strongly affected by the dynamics of the localized lone pairs, whose very existence we have seen to be closely related to the topological properties of the electronic ground state. The animation contained in the file K-KCl-trj.mp4, to be found in the Ancillary Files, confirms that the lone pair diffuses much faster than the ions. Its motion, while being uniquely determined by the ionic adiabatic dynamics, is largely uncorrelated from the electronic motion, and is thus expected to give rise to transport anomalies (the color code in the animation is the same as in Fig. 5). On the one hand, this indicates that non-stoichiometric molten salts can sustain an electric current that is not (or is very weakly) correlated with the ionic one; on the other hand, this lack of correlation is a manifestation of transport anomalies related to the breaking of SA. As discussed above, this suggests that different cations can carry different topological charges when making a non trivial loop, according to whether or not they drag along a lone pair in their displacement. This effect is substantiated by computing the dipole displaced along two distinct non-trivial loops in the K\(_{33}\)Cl\(_{31}\) ACS, beginning and ending at the same configuration, and differing by the identity of one K atom that is moved from its initial position to one of its periodic images, as depicted in Fig. 6. Even though in a physical trajectory no loops in ACS are expected to occur, nor the lone-pair to stay bound to a specific atom for much longer than the atomic diffusion time, the values of the dipoles displaced by the two K atoms prove the existence of an adiabatic domain in ACS where different topological charges can be associated to distinct atoms of the same species, which can be exchanged without closing the gap.

In order to evaluate the impact of anomalous transport on the electrical conductivity of our system, we computed it using the Helfand-Einstein relation \[ 4 2 2 \]

\[
\sigma = \frac{1}{3L^3k_B}\lim_{t\to\infty} \langle |\Delta \mu(t)|^2 \rangle, \quad (3)
\]

where \( \Delta \mu(t) \) is the electric dipole displaced along the AIMD trajectory in a time \( t \). \( \Delta \mu(t) \) has been alternatively computed from Eq. (2) and from:

\[
\Delta \mu_{1,F}^* = e \int_t^F \left( \sum_i q_i \, d\mathbf{r}_i - 2dw_{lp} \right) \quad (4)
\]

where \( w_{lp} \) is the position of the lone-pair WC, \( q_i = +1 \) for K atoms, \(-1\) for Cl atoms, and the factor \( q_{lp} = -2 \) reflects the occupancy of the loosely bound HOMO. The definition of \( \Delta \mu_{1,F}^* \) differs from that of \( \Delta \mu_{IF} \), Eq. (4), in that in Eq. (4) a fixed oxidation state is associated with all the atoms of a same species in the spirit of Ref. 4—and as it would be in a stoichiometric mixture—while the lone pair occupying the localized and loosely bound HOMO is treated as an independent charge carrier. Our results, illustrated in Fig. 7, yield the values \( 16.2 \pm 0.8 \) S/cm and \( 15.9 \pm 0.8 \) S/cm for the conductivities computed from definitions (2) and (1), respectively. All the numerical values of the transport coefficients reported here have been evaluated using the cepstral analysis method \[ 2 3 2 4 \], as briefly explained in Appendix B. We see that the two values coincide within statistical errors, giving substance to our topological analysis of transport anomalies in these systems. Maybe fortuitously, these values compare well with the experimental data at such concentration of K atoms \[ 2 5 \].
FIG. 6. (a) and (c): Different non-trivial closed paths in the \( K_{33}Cl_{31} \) atomic configuration space, whose initial and final configurations are the same snapshot from our AIMD trajectory. All K atoms but one are depicted in pink and feature zero winding numbers. One K atom, depicted in red, is moved from its initial position to its periodic image along the \( x \) direction, thus featuring a winding number \( n_{ix} = +1 \). Cl atoms are depicted in blue. (b) and (d): Dipoles displaced along the closed paths depicted on their left. One sees that the charge displaced along the two paths differ, in spite of the fact that the two atoms with the same winding numbers are of the same chemical species and can be swapped without closing the gap. This indicates that no oxidation state can be univocally associated with these atoms and transport anomalies have to be expected.

The conductivity is much larger than the value obtained from the ionic contribution in Eq. (4) (3.6 ± 0.3 S/cm, the green line in Fig. 7): this indicates that the conductivity is almost entirely determined by the diffusion of the solvated lone pair, and is in fact much larger than it typically is in stoichiometric molten salts (\( i.e., 3.2 \pm 0.2 \) S/cm [21]). Furthermore, we observe that the total conductivity coincides with the sum of the ionic and lone-pair contributions, implying that the cross correlation resulting from the product of the first and second terms on the right-hand side of Eq. (4) is negligible, as confirmed by the vanishing slope of the red curve in Fig. 7. We computed the diffusivity \( D_i \) of each species \( i = K, Cl, lp \) according to the Einstein formula:

\[
D_i = \lim_{t \to \infty} \frac{\langle |\Delta r_i(t)|^2 \rangle}{6t}.
\]

The mobilities, \( \mu_i = q_i e D_i / (k_B T) \), are then estimated to be 1.23 ± 0.02, 1.14 ± 0.07, and 102 ± 5 (10^{-3} \) cm$^2$ V$^{-1}$ s$^{-1}$) for K, Cl, and the lone solvated pair, respectively. The lone-pair mobility is two orders of magnitudes larger than the ionic ones, in agreement with experimental evidence [29] and with the observed predominance of the lone-pair contribution to the total conductivity.
FIG. 7. Adiabatic charge transport in molten K$_{0.06}$/(KCl)$_{0.94}$. Time series of the mean-square displaced dipole from definitions $\mathcal{E}$ (blue) and $\mathcal{I}$ (orange). The contribution due to the ionic cores and the tightly bound electrons is shown in green. The cross-correlation term is depicted in red. According to Eq. (1), the slope of the straight lines is a measure of the electric conductivity, whose actual value is estimated from cepstral analysis, as explained in Appendix B.

IV. CONCLUSIONS

Conducting materials are usually classified into two broad families: metals and ionic conductors. The charge carriers of metals are electrons, whose equilibrium and dynamical properties are strictly quantum mechanical and whose excitation spectrum is distinctly gapless. As a consequence, the charge current is largely uncorrelated from ionic currents and charge transport occurs without any significant mass displacement. The electronic spectrum of ionic conductors, instead, features an energy gap that constrains the electrons to remain in their instantaneous ground state at all times and their charge density and current to follow adiabatically the classical ionic motion. As a consequence, charge and mass currents are intrinsically entangled and charge transport cannot occur without mass convection.

Non-stoichiometric ionic conductors are somewhat intermediate between these two extrema. As the concentration of one the chemical species that make for the ionic components of the material is increased, it may happen that, not being compensated by ions of opposite charge, the chemical species in excess dissociates into a ionic moiety plus an unbound solvated electron. As the concentration of the excess species increases, the solvated electrons form an energy band that eventually merges into the unoccupied states of the stoichiometric system, thus turning the ionic conductor into a metal. Such a transition has been recently evinced by photo-electron spectroscopic measurements on alkali-metal solutions in liquid ammonia \cite{21}. Before this critical concentration is reached, the excess electrons may coalesce into localized pairs that diffuse through the ionic matrix largely uncorrelated from the ionic motion, thus determining a transport regime where most of the charge is transported without appreciable mass displacement, while the system remains non-metallic.

In this paper we have revealed and analysed the topological conditions that make this anomalous transport regime possible. Our results open the way to a number of interesting fundamental and applicative perspectives. On a more fundamental side, the question is open on how a unified theoretical framework can be devised to describe quantum metallic and classical ionic conduction on a same footing and encompassing the intermediate anomalous adiabatic regime. The impact of anomalous charge transport on heat transport is also of great interest. In particular, anomalous charge transport may determine a high electric conductivity in electrolytes, not accompanied by a large heat conductivity, which is of potential interest for thermoelectric applications.

ACKNOWLEDGMENTS

This work was partially funded by the EU through the MAX Centre of Excellence for supercomputing applications (Project No. 824143). We thank Luca Grisanti for insightful suggestions and a critical reading of the manuscript. FG thanks Stefano de Gironcoli and Luigi Grasselli for fruitful discussions.

Appendix A: Computational details

Electronic structure calculations and AIMD simulations are carried out within DFT using the plane-wave pseudopotential method with the pw.x and cp.x codes of the QUANTUM ESPRESSO package \cite{30, 31}. The transformation to the Wannier representation is performed, when needed, using the WANNIER90 code \cite{32, 33}.

For the H$_3^+$ system, the PBE0 hybrid functional \cite{34} is used in order to minimize self-interaction artifacts. A norm-conserving pseudopotential for H atoms has been generated to be consistent with the hybrid functional. The plane-wave kinetic-energy cutoff is set to 80 Ry for wavefunctions and to 320 Ry for both the charge density and non-local exchange operator.

For K$_3$Cl, DFT calculations are performed at the GGA level in the PBE flavor \cite{35}. Norm-conserving pseudopotentials from the SG15 data set \cite{36, 37} are used for K and Cl. The kinetic energy cutoff is set to 55 and 220 Ry for wave-functions and charge densities, respectively. Brillouin-zone (BZ) sampling is performed using a 6×6×6 Monkhorst-Pack set of k-points \cite{38}.

The computational parameters for K$_{33}$Cl$_{31}$ are the same as for K$_3$Cl but for the BZ sampling, which is restricted to the Γ point. The dynamics is carried out according to the Car-Parrinello Lagrangian scheme \cite{18} using a fictitious electronic mass $\mu = 400 m_e$, $m_e$ being
allows one to express the conductivity as

where $S(\omega)$ is the power spectral density (PSD) of the electric current. The electric current, $J(t) = \frac{d\mu(t)}{dt}$, where $\mu$ is any Cartesian component of the displaced dipole defined in Eqs. [2] or [4], is an extensive quantity whose density has correlations that are usually short-ranged. Therefore, according to the central limit theorem, $J(t)$ is a Gaussian process whose Fourier transform, $\hat{J}(\omega)$, is normally distributed and such that $\hat{J}(\omega)$ is uncorrelated from $J(\omega')$ for $\omega \neq \omega'$ in the large-time limit.

For any discrete realization of the continuous current process, $\hat{J}_n = J(n\epsilon)$, with $n = 1, \ldots, N$, we define its discrete Fourier transform, $\hat{\hat{J}}_k = \sum_n J_n e^{i2\pi \frac{kn}{N}}$ and the periodogram as the random variate

$$\hat{S}_k = \frac{\epsilon}{N} |\hat{\hat{J}}_k|^2. \quad (B2)$$

Due to the Gaussian nature of $\hat{J}_n$, $\hat{S}_k$ is proportional to a $\chi^2$ random variate, and its expected value is the PSD in Eq. (B1). The application of a low-pass filter to the logarithm of this quantity, $\hat{L}_k$, yields a consistent estimator of the logarithm of the conductivity; the low-pass filter consists in the retention of a number $P^* \ll N/2$ of (inverse) Fourier components of $\hat{L}_k$, whose value is chosen according to the Akaike Information Criterion (AIC) [40] of model selection. In order to limit the analysis to an appropriate low-frequency portion of the entire PSD, it is expedient to re-sample the electric current time-series with a rate corresponding to an effective Nyqvist frequency, $f^*$. In Fig. 8 we show the filtered PSDs for the electric currents computed both with Eq. (2) and (4). The cepstral analysis was performed with the Thermocepstrum code [41, 42]. For both currents, the value chosen by the AIC is $P^* = 8$. The estimated conductivities depend very little on the resampling frequency, which has been set to $f^* = 10$ THz.

FIG. 8. Low-frequency portion of the PSD of the displaced dipole computed according to Eq. (2) (blue) and Eq. (4) (orange). The noisy lines are the window-filtered PSDs (with a window of 0.1 THz), while the smooth lines are the cepstral estimates.
Ilya A Shkrob, “Ammoniated electron as a solvent stabilized multimer radical anion,” J. Phys. Chem A 110, 3967–3976 (2006).

Eva Pavarini, Erik Koch, Richard Scalettar, and Richard M Martin, The physics of correlated insulators, metals, and superconductors, Tech. Rep. (Theoretische NanoElektronik, 2017).

The fundamental group of a topological space is the set of its homotopy classes of loops equipped with an associative composition, the concatenation, at a given base point. The identity is given by the class of (trivial) paths homotopic to the base point; the inverse is defined for each class by travelling its paths backwards. See J. Munkres, Topology, (Prentice Hall, 2000). Rowland T. and Weistein E. W., Fundamental group, MathWorld-A Wolfram Web Resource http://mathworld.wolfram.com/FundamentalGroup.html (2020).

Richard M. Martin, “Comment on calculations of electric polarization in crystals,” Phys. Rev. B 9, 1998–1999 (1974).

Annabella Selloni, P Carnevali, Roberto Car, and M Parrinello, “Localization, hopping, and diffusion of electrons in molten salts,” Phys. Rev. Lett. 59, 823 (1987); E. S. Fois, A. Selloni, M. Parrinello, and R. Car, “Bipolarons in metal-metal halide solutions,” J. Phys. Chem. 92, 3268–3273 (1988).

R Car and M Parrinello, “Unified Approach for Molecular Dynamics and Density-Functional Theory,” Phys. Rev. Lett. 55, 2471–2474 (1985).

WW Warren, “Metal-metal salt solutions,” in Molten Salt Chemistry (Springer, 1987) pp. 237–257.

Pier Luigi Silvestrelli, Ali Alavi, Michele Parrinello, and Daan Frenkel, “Nonmetal-metal transition in metal–molen-salt solutions,” Phys. Rev. B 53, 12750–12760 (1996).

Tillmann Buttersack, Philip E Mason, Ryan S McMullen, H Christian Schewe, Tomas Martinez, Krystof Brezina, Martin Crhan, Axel Gomez, Dennis Hein, Garlef Wartner, et al., “Photoelectron spectra of alkali metal–ammonia microjets: From blue electrolyte to bronze metal,” Science 368, 1086–1091 (2020).

E Helfand, “Transport Coefficients from Dissipation in a Canonical Ensemble,” Phys. Rev. 119, 1–9 (1960).

These values are obtained via a more sophisticated, cepstral, analysis 24 25. See Appendix B for further information.

Loris Ercole, Aris Marcologo, and Stefano Baroni, “Accurate thermal conductivities from optimally short molecular dynamics simulations,” Sci. Rep. 7, 1–11 (2017).

Riccardo Bertossa, Federico Grasselli, Loris Ercole, and Stefano Baroni, “Theory and numerical simulation of heat transport in multicomponent systems,” Phys. Rev. Lett. 122, 255901 (2019).

In our case the concentration of K⁺(KCl)₁₋ₓ is x = 0.06. Experimentally, the mixture is below the metallic transition 27; thus, the conductivity measured in 28 is devoid of any conduction electron contribution, i.e. due to the adiabatic diffusion of ions and electrons.

D Natl Andrew, Harald Heyer, and W Freyland, “Metal-nonmetal transition in liquid alkali metal-alkalihalide melts: Electrical conductivity and optical reflectivity study,” Z. Phys. Chem. 149, 1–15 (1986).

HR Bronstein and MA Bredig, “The electrical conductivity of solutions of alkali metals in their molten halides,” J. Am. Chem. Soc. 80, 2077–2081 (1958).

William W Warren Jr, BF Campbell, and GF Brennert, “Picosecond recombination dynamics of electrons in ionic liquids,” Phys. Rev. Lett. 58, 941 (1987).

Paolo Giannozzi, Stefano Baroni, Nicola Bonini, Matteo Calandra, Roberto Car, Carlo Cavazzoni, Davide Ceresoli, Guido L Chiarotti, Matteo Cococcioni, Ismaila Dabo, et al., “Quantum espresso: a modular and open-source software project for quantum simulations of materials,” J. Phys. Condens. Matter 21, 395502 (2009).

Paolo Giannozzi, Oliviero Andreussi, Thomas Brumme, Oana Buna, M Buongiorno Nardelli, Matteo Calandra, Roberto Car, Carlo Cavazzoni, Davide Ceresoli, Matteo Cococcioni, et al., “Advanced capabilities for materials modelling with quantum espresso,” J. Phys. Condens. Matter 29, 465901 (2017).

Arash A Mostofi, Jonathan R Yates, Young-Su Lee, Ivo Souza, David Vanderbilt, and Nicola Marzari, “wannier90: A tool for obtaining maximally-localised wannier functions,” Comput. Phys. Commun. 178, 685–699 (2008).

Arash A Mostofi, Jonathan R Yates, Giovanni Pizzi, Young-Su Lee, Ivo Souza, David Vanderbilt, and Nicola Marzari, “An updated version of wannier90: A tool for obtaining maximally-localised wannier functions,” Comput. Phys. Commun. 185, 2309–2310 (2014).

Carlo Adamo and Vincenzo Barone, “Toward reliable density functional methods without adjustable parameters: The pbe0 model,” J. Chem. Phys. 110, 6158–6170 (1999).

John P. Perdew, Kieron Burke, and Matthias Ernzerhof, “Generalized gradient approximation made simple,” Phys. Rev. Lett. 77, 3865–3868 (1996).

D. R. Hamann, “Optimized norm-conserving vanderbilt pseudopotentials,” Phys. Rev. B 88, 085117 (2013).

M Schlipf and F Gygi, “Optimization algorithm for the generation of oncv pseudopotentials.” Comput. Phys. Commun. 196, 36 – 44 (2015) with pseudopotentials downloaded from http://www.quantum-simulation.org/potentials/sg15_oncv/upf/

James D. Pack and Hendrik J. Monkhorst, “Special points for Brillouin-zone integrations—a reply,” Phys. Rev. B 16, 1748–1749 (1977).

David C Champeney, A handbook of Fourier theorems (Cambridge University Press, 1989).

Hirotugu Akaike, “A new look at the statistical model identification,” IEEE transactions on automatic control 19, 716–723 (1974).

Loris Ercole, Riccardo Bertossa, and Sebastiano Biscachi, “ThermoCepstrum: a code to estimate transport coefficients from the cepstral analysis of a multi-variate current stationary time series,” https://github.com/lorisercole/thermocepstrum (2017–2020).

Stefano Baroni, Riccardo Bertossa, Loris Ercole, Federico Grasselli, and Aris Marcologo, “Heat transport in insulators from ab initio green-kubo theory,” in Handbook of Materials Modeling: Applications: Current and Emerging Materials edited by Wanda Andreoni and Sidney Yip (Springer International Publishing, Cham, 2018) pp. 1–36, 2nd ed., arXiv:1802.08006 [cond-mat.stat-mech].