# *the computer is a tool for clean thinking*

## *from unthinkable simulations to a deeper insight into heat transport*

Stefano Baroni
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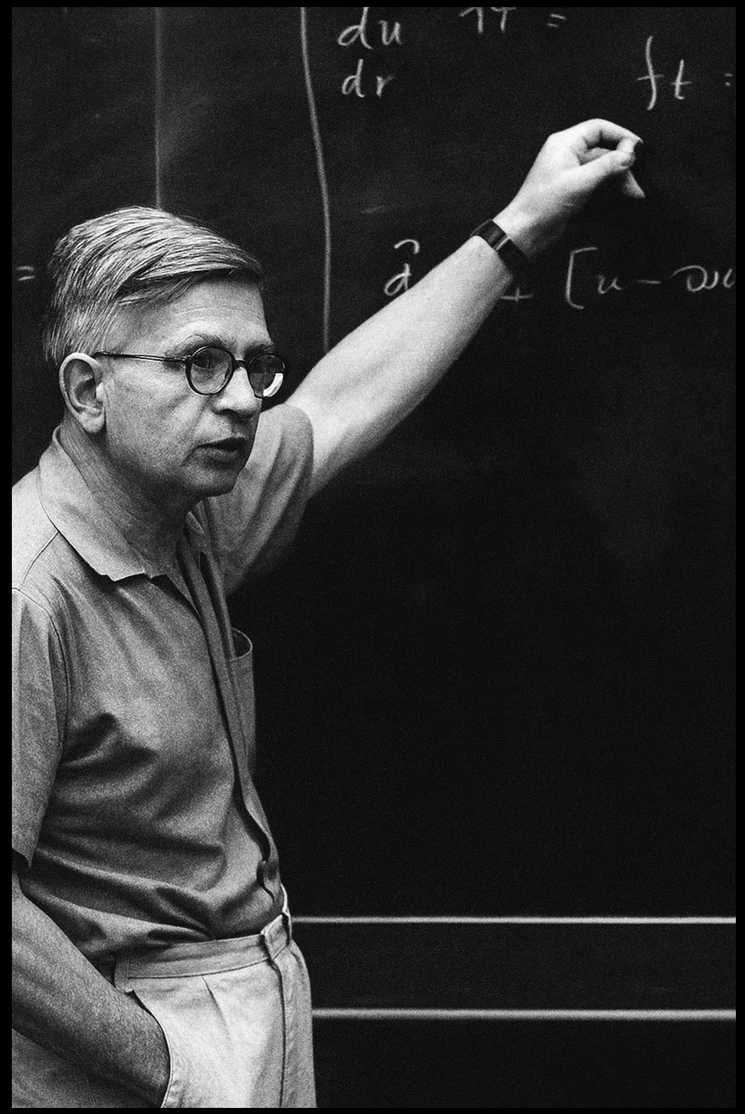
Trieste — Italy

talk given at the *APS Global Physics Summit*, Denver, March 18, 2026



A deeper insight is needed, because ...

*It seems there is no problem in modern physics for which there are on record as many false starts, and as many theories which overlook some essential feature, as in the problem of the thermal conductivity of non-conducting [materials].*

Rudolph E. Peierls [ca. 1960]

*how it all started*

# *hurdles toward an ab initio Green-Kubo theory*

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

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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†
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*Department of Computer Science, Louisiana State University, Baton Rouge, Louisiana 70803, USA*
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# how come?

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How is it that DFT, an exact theory of the electronic ground state, cannot account for all adiabatic properties, including heat transport?


# the culprit is *not* DFT

# *the linear-response theory of transport*

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$$J = -\kappa \nabla T$$

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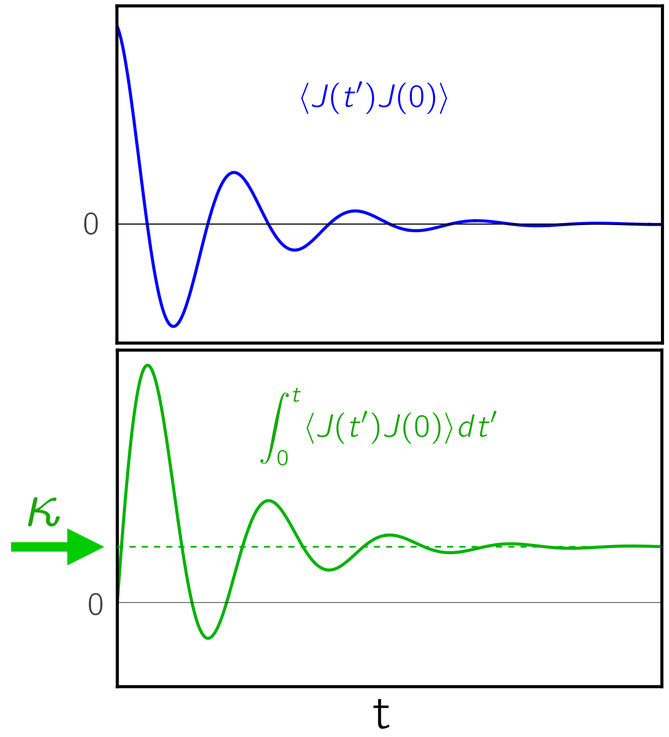

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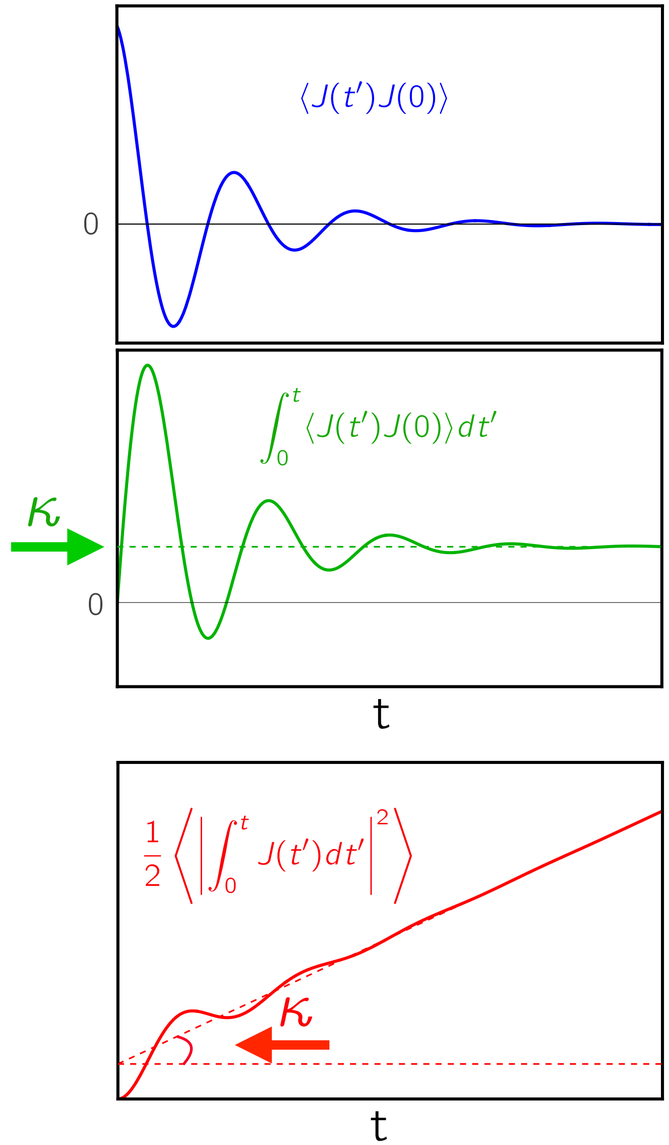

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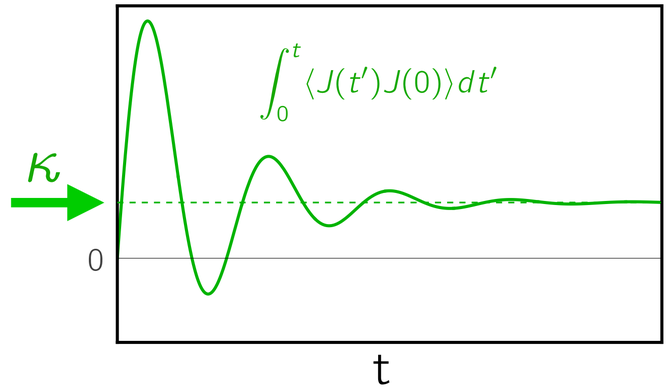


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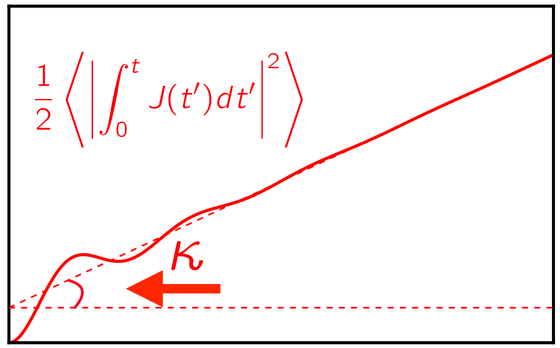
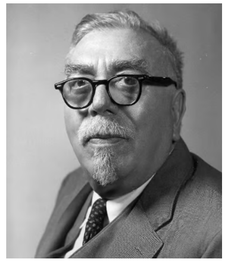
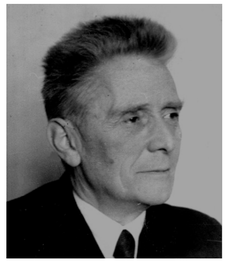
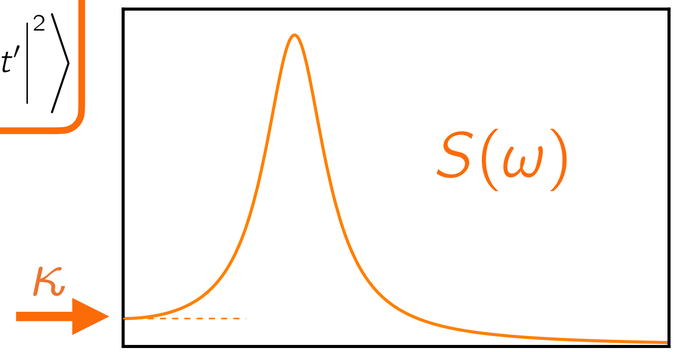



## Wiener-Khinchin

$$\kappa = \frac{\Omega}{k_B T} S(0)$$

$$S(\omega) = \begin{cases} \int_0^\infty \langle J(t)J(0)\rangle \cos(\omega t) dt \\ \lim_{t\to 0} \frac{1}{2t} \left\langle \left| \int_0^t J(t') \cos(\omega t') dt' \right|^2 \right\rangle \end{cases}$$



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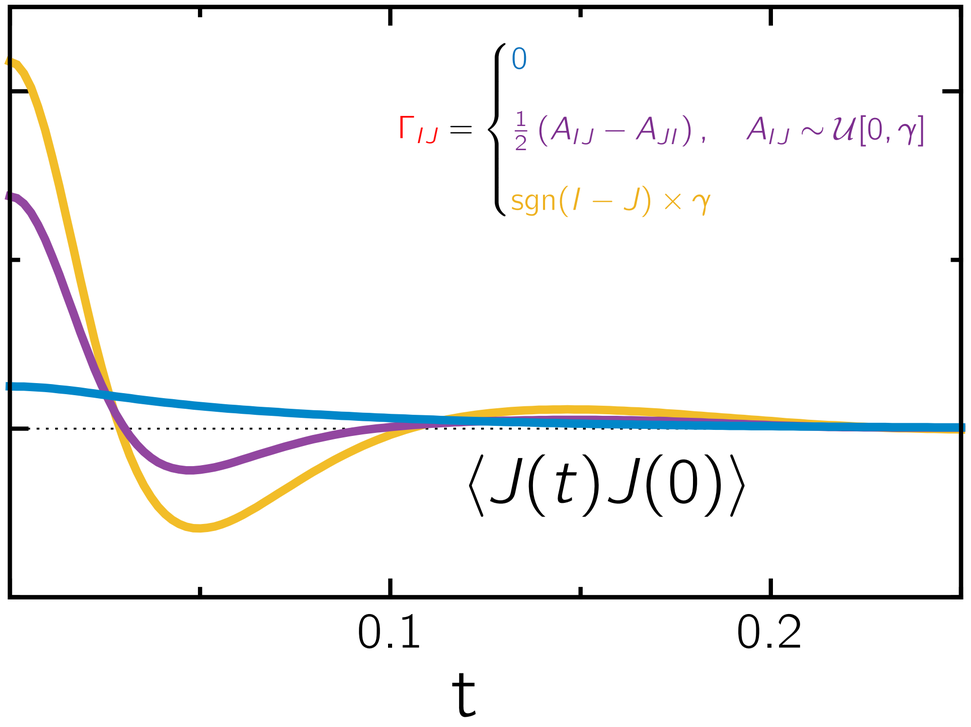

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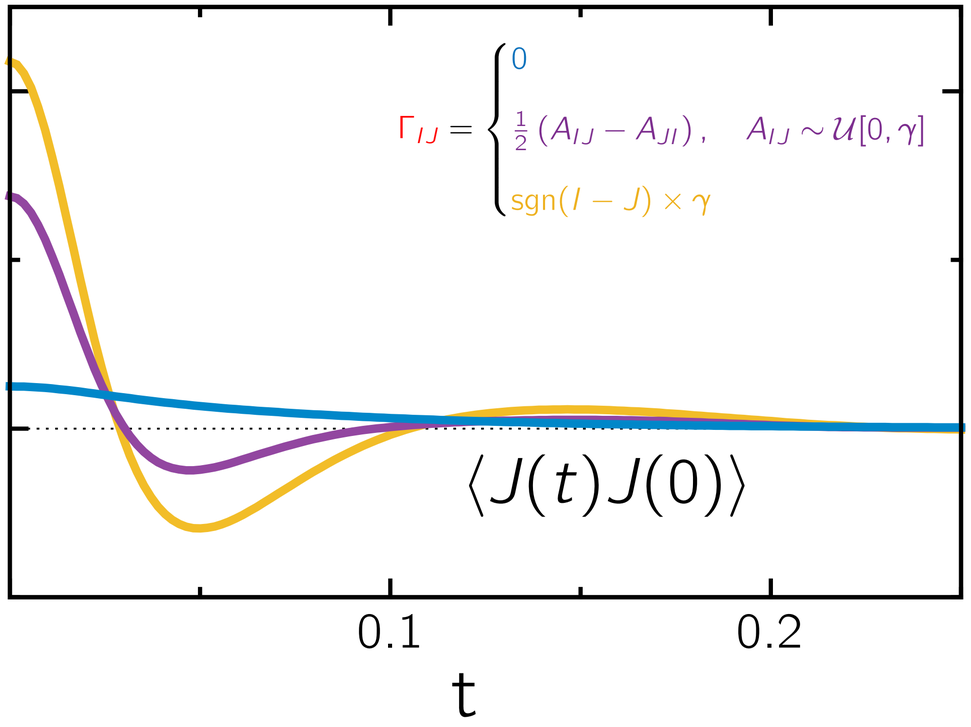


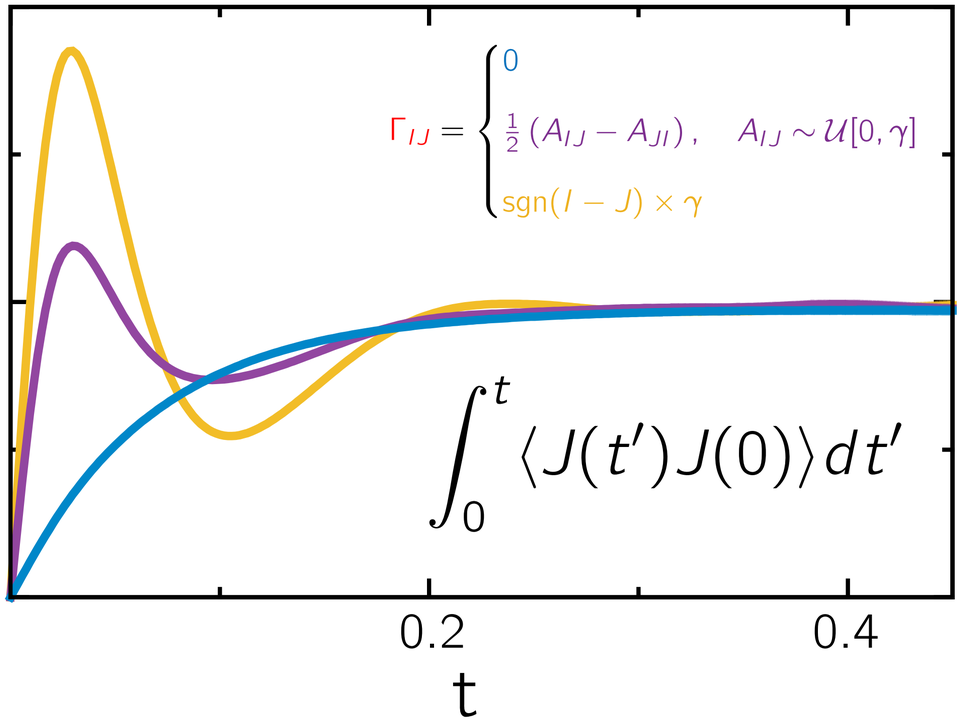

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$$= \mathbf{J} + \dot{\mathbf{P}}$$

$$\dot{\mathbf{P}} = \frac{\mathrm{d}}{\mathrm{dt}}\frac{1}{4}\sum_{I\neq J}\Gamma_{IJ}\; v(|\mathbf{R}_I - \mathbf{R}_J|)(\mathbf{R}_I - \mathbf{R}_I)$$

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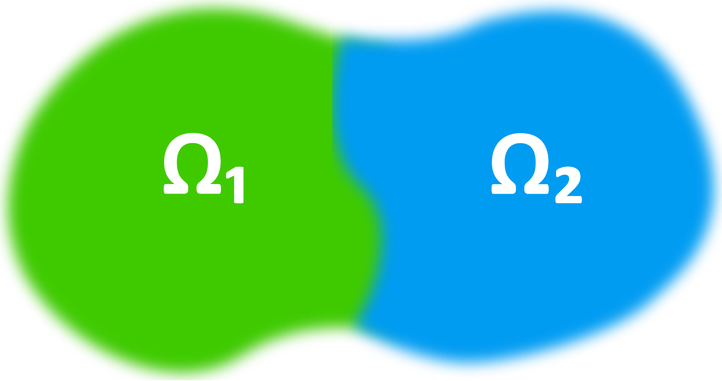


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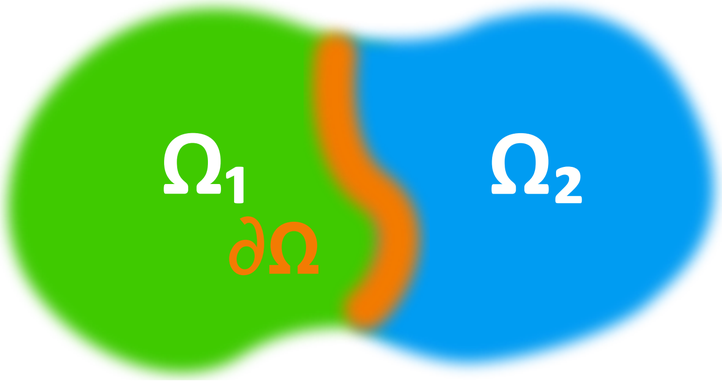


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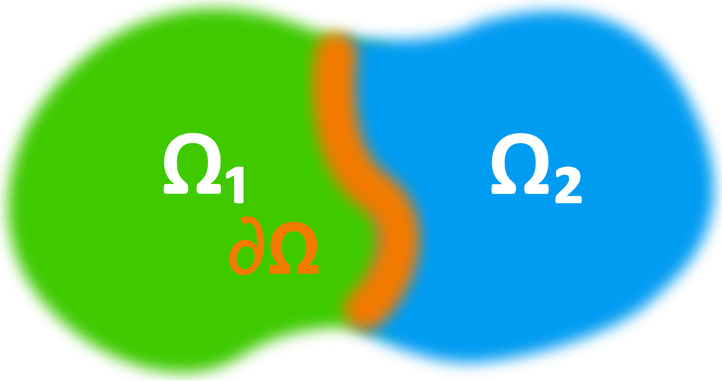


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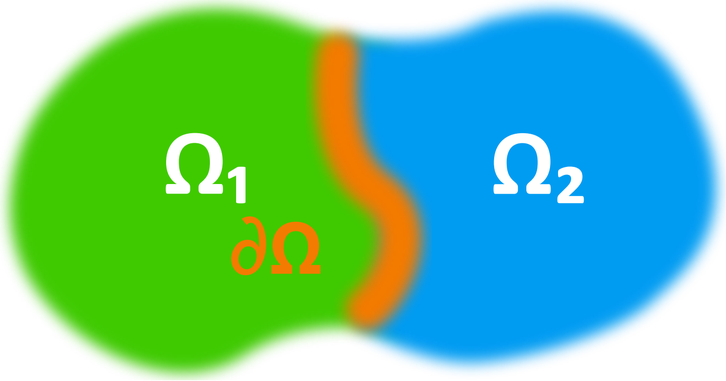


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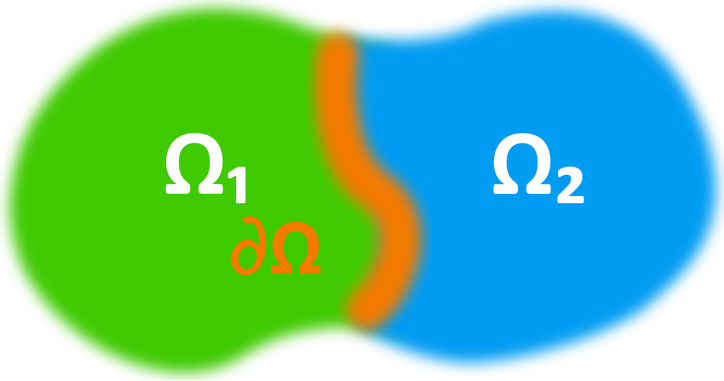


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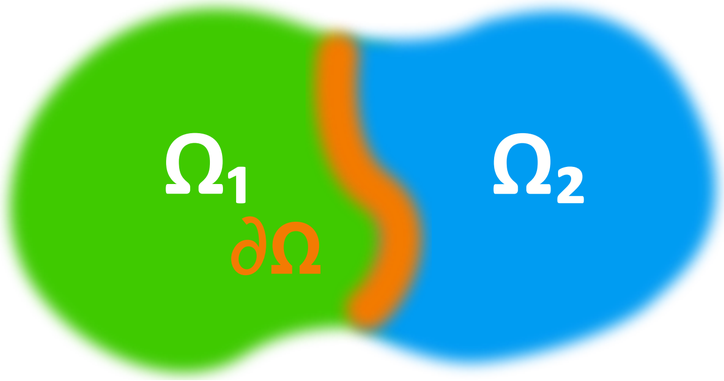


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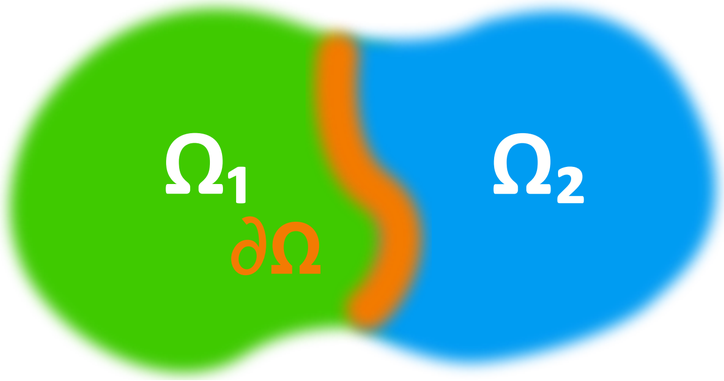


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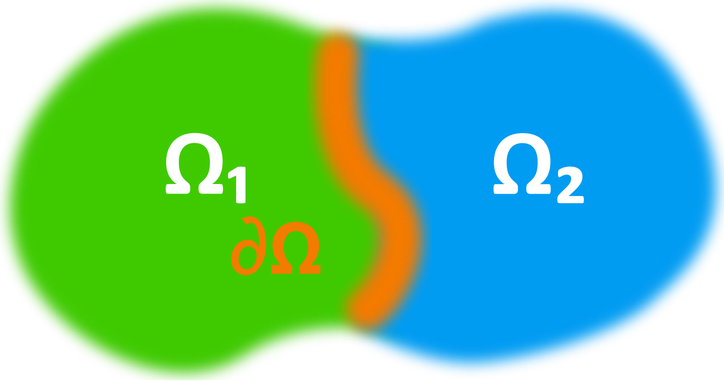


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$$\mathbf{P}(t) = \frac{1}{\Omega} \int \mathbf{p}(\mathbf{r}, t) d\mathbf{r}$$

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

# *gauge invariance of heat transport*

**Any two conserved densities differing by the divergence of a bounded vector field are physically equivalent:**

**their associated fluxes differ by a total time derivative, and the corresponding transport coefficients coincide.**

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**Microscopic theory and quantum simulation of atomic heat transport**

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

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**Microscopic theory and quantum simulation of atomic heat transport**

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

**solution:**

choose *any* local representation of the energy that integrates to the correct value — the conductivity computed from the resulting current will be *independent* of the chosen representation.

# ~~hurdles~~ toward an ab initio Green-Kubo theory

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*

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*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.

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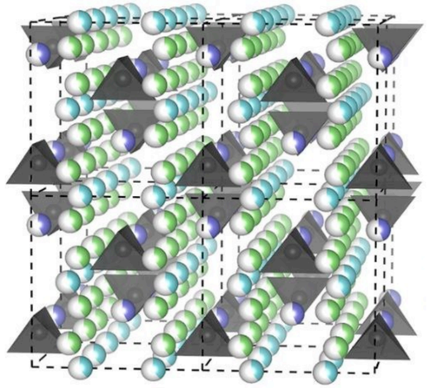
# *impact on ML MD simulations*



α-$Li_3PS_4$

$$E = \sum_I e_I(\mathbf{R})$$

PHYSICAL REVIEW MATERIALS **8**, 065403 (2024)

**Thermal conductivity of $Li_3PS_4$ solid electrolytes with *ab initio* accuracy**

Davide Tisi, Federico Grasselli, Lorenzo Gigli, and Michele Ceriotti*

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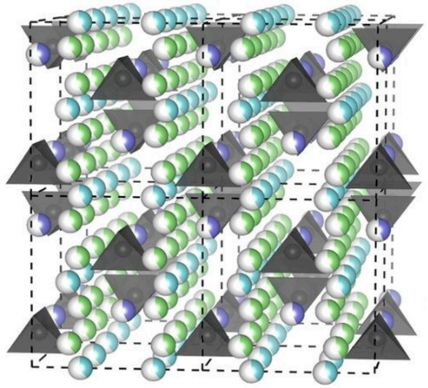

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ML model A
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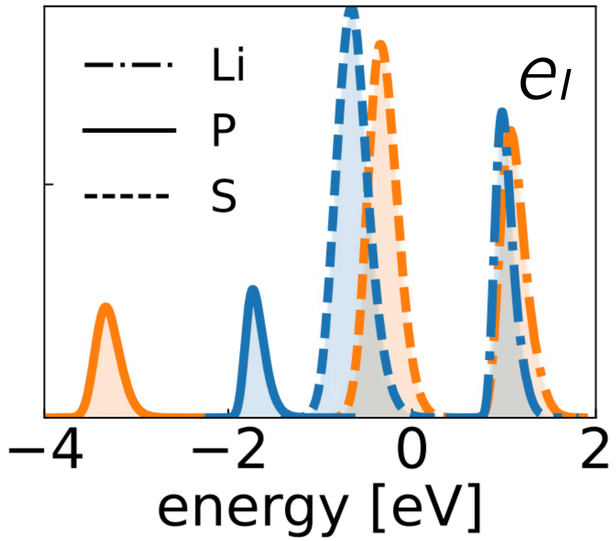


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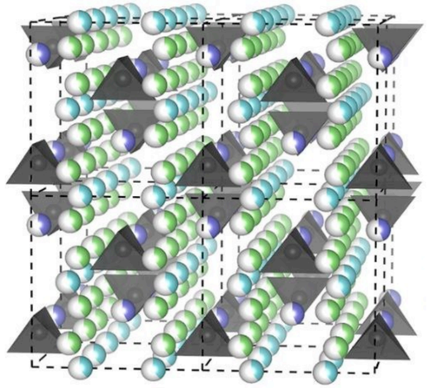

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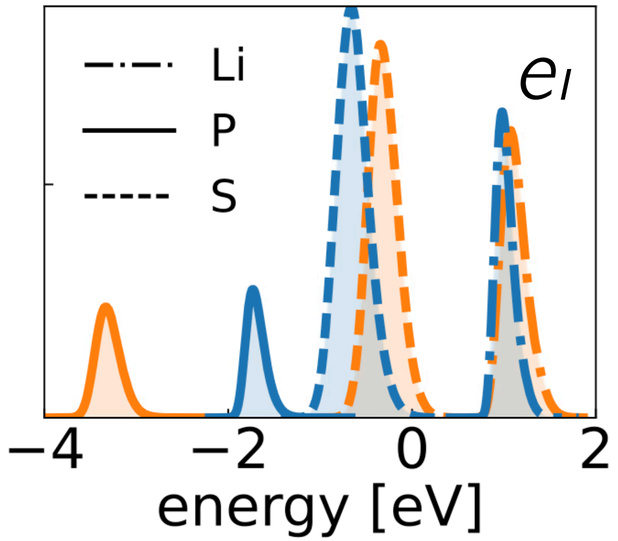


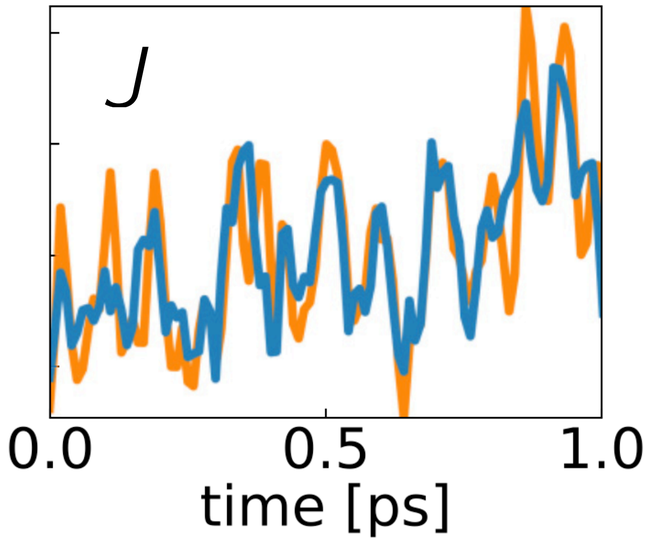


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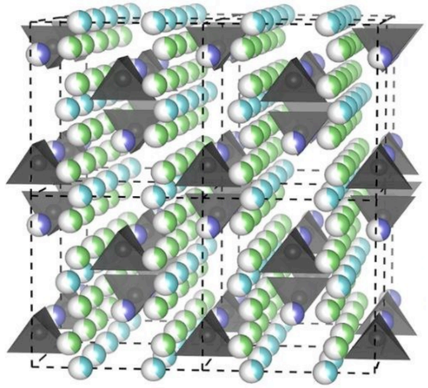

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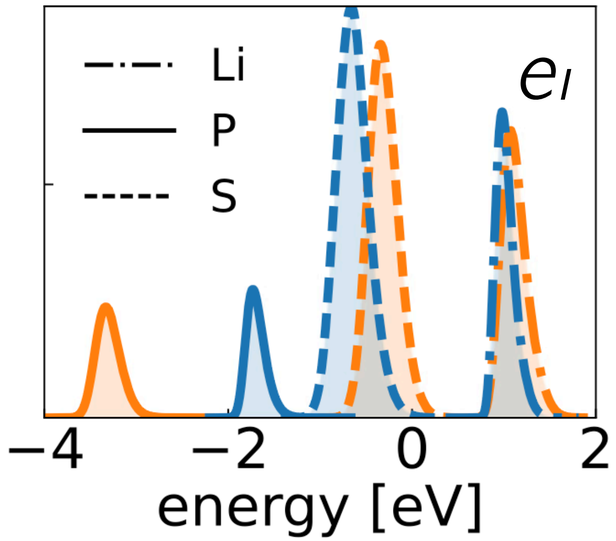


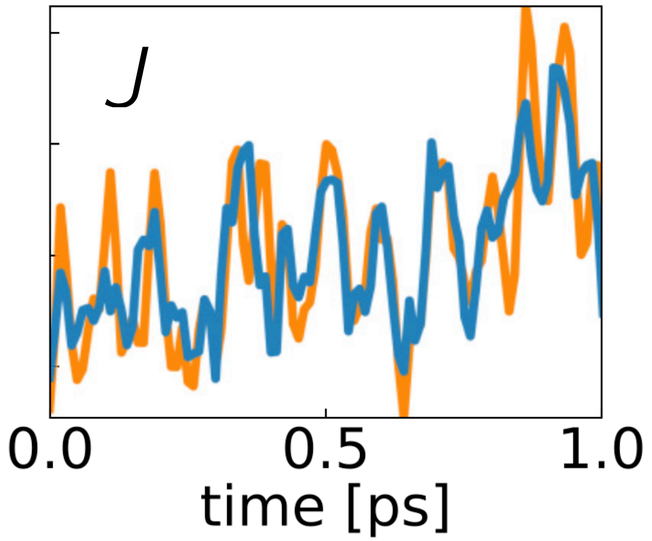


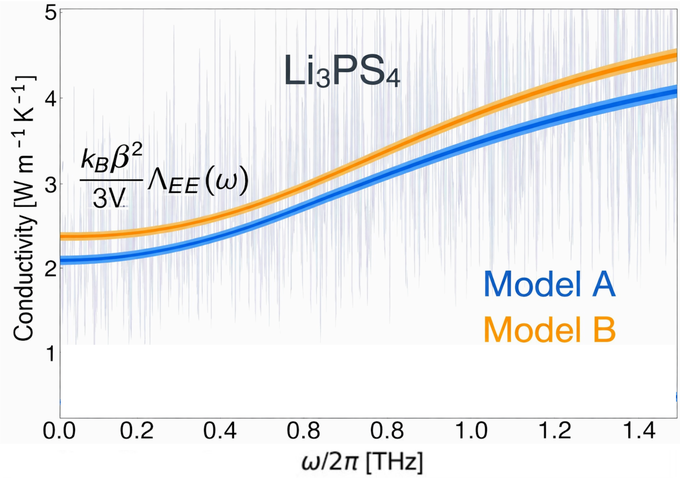


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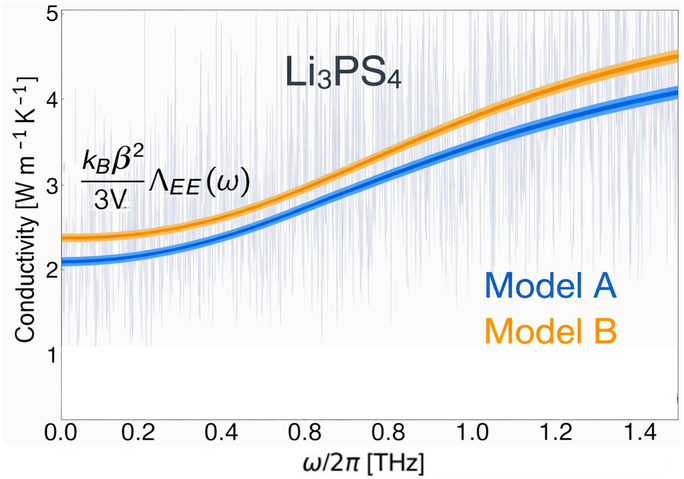


conserved quantities:

- ☑ energy
- ☑ Li mass

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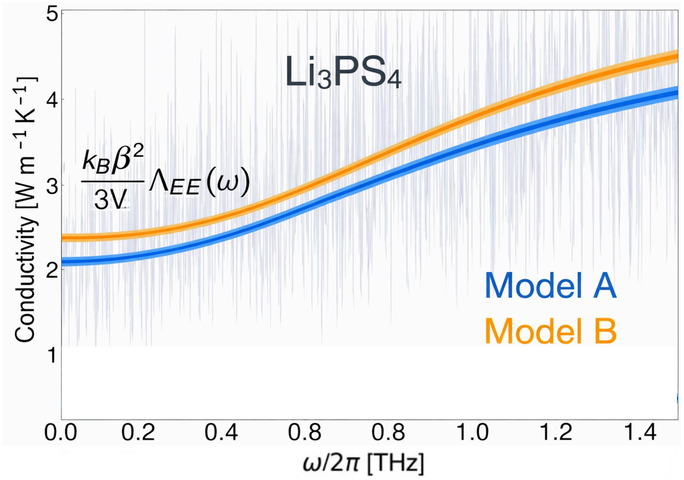


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conserved densities are adiabatically decoupled from the myriad fast atomic modes, but they interact with each other

$$J_E = \Lambda_{EE}\nabla\left(\frac{1}{T}\right) - \Lambda_{ELi}\nabla\left(\frac{\mu}{T}\right)$$

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*Onsager matrix*

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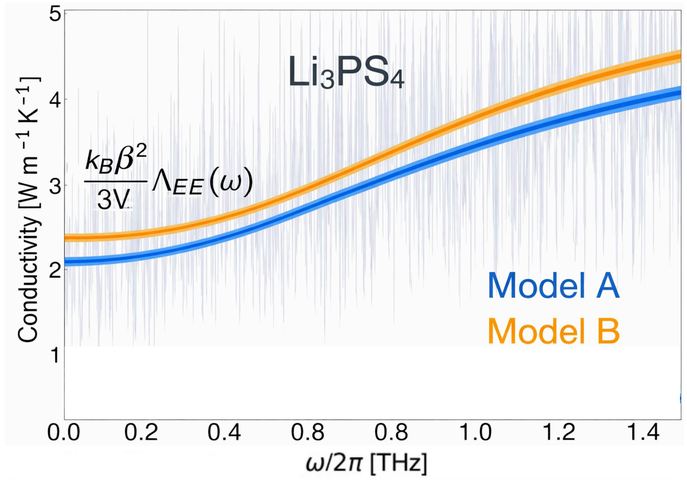


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$$J_{Li} = 0 \rightarrow \kappa = \frac{1}{T^2}\left(\Lambda_{EE} - \frac{\Lambda_{LiE}^2}{\Lambda_{LiLi}}\right) = 1/\left(\Lambda_{EE}\right)^{-1}$$

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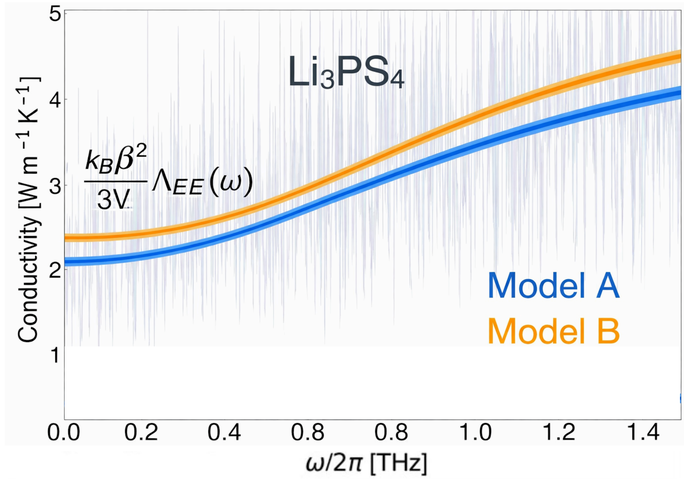


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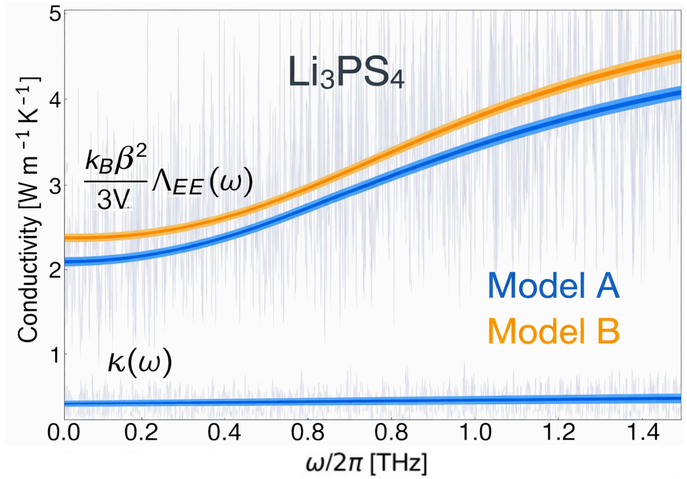


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PHYSICAL REVIEW LETTERS **122,** 255901 (2019)

**Theory and Numerical Simulation of Heat Transport in Multicomponent Systems**

Riccardo Bertossa,[1] Federico Grasselli,[1] Loris Ercole,[1,*] and Stefano Baroni[1,2,†]
[1]*SISSA—Scuola Internazionale Superiore di Studi Avanzati, Via Bonomea 265, 34136 Trieste, Italy*
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**convective invariance**

heat conductivity is invariant under the addition of any linear combination of convective currents to the energy current

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$$\nabla \cdot \boldsymbol{j}(\boldsymbol{r}, t) + \dot{\epsilon}(\boldsymbol{r}, t) = 0 \qquad \Rightarrow \qquad \boldsymbol{J}' = \int \dot{\epsilon}'(\boldsymbol{r})\boldsymbol{r}d\boldsymbol{r}$$

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$$\begin{aligned}
\boldsymbol{J}' &= \int \dot{\epsilon}'(\boldsymbol{r})\boldsymbol{r}d\boldsymbol{r} \\
&= \sum_I \left( \int \boldsymbol{r} \otimes \overbrace{\frac{\partial \epsilon'(\boldsymbol{r}|R)}{\partial \boldsymbol{r}_I}}^{\boldsymbol{\varphi}'_I(\boldsymbol{r}|R)} d\boldsymbol{r} \right) \cdot \boldsymbol{v}_I \\
&= \sum_I \boldsymbol{\mathcal{D}}'_I(R) \cdot \boldsymbol{v}_I
\end{aligned}$$

$$\epsilon' = \epsilon_2 - \epsilon_1$$

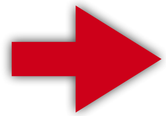
$$R = \{\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots \boldsymbol{r}_N\}$$

# *the nuts and bolts of gauge invariance*

$$J' = \int \dot{\epsilon}'(r) r dr$$
$$= \sum_I \mathcal{D}'_I(R) \cdot v_I$$

$f_2 = f_1$ $\quad \int \varphi'_I(r|R) dr = 0$

short sightedness $\quad \varphi'_I(r|R) = 0 \quad$ for $\quad |r - r_I| > R_c$



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$$\int_0^T J'(t) dt = \int_{R^0}^{R^T} \sum_I \mathcal{D}'_I(R) \cdot dr_I = G'(R^0, R^T)$$

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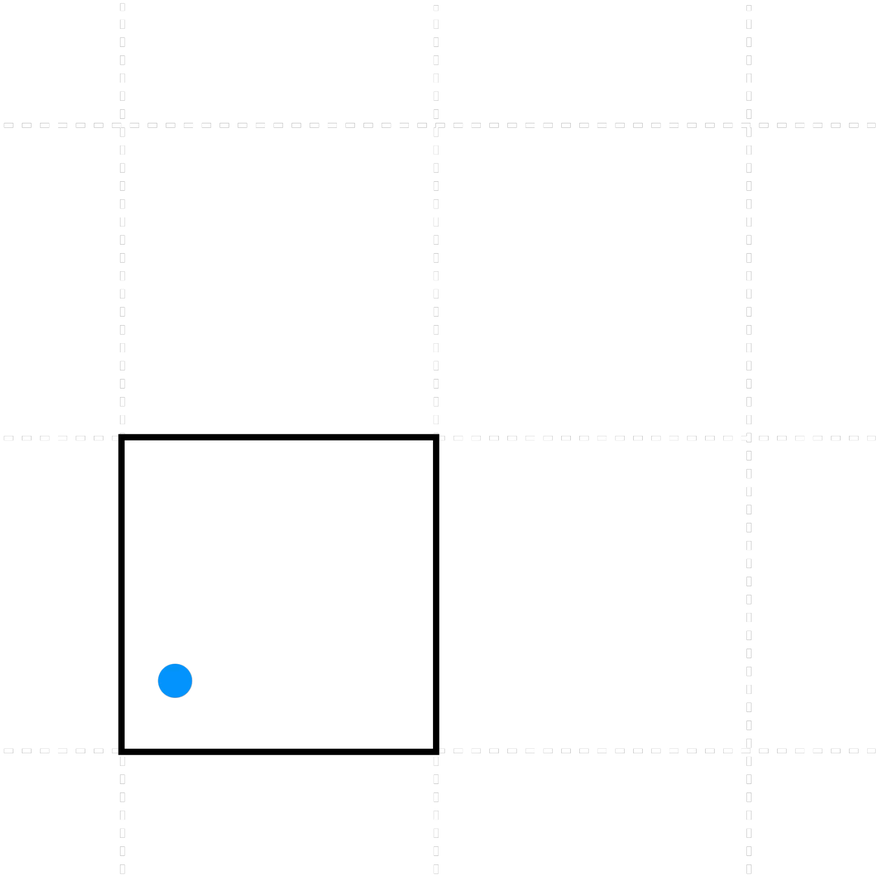

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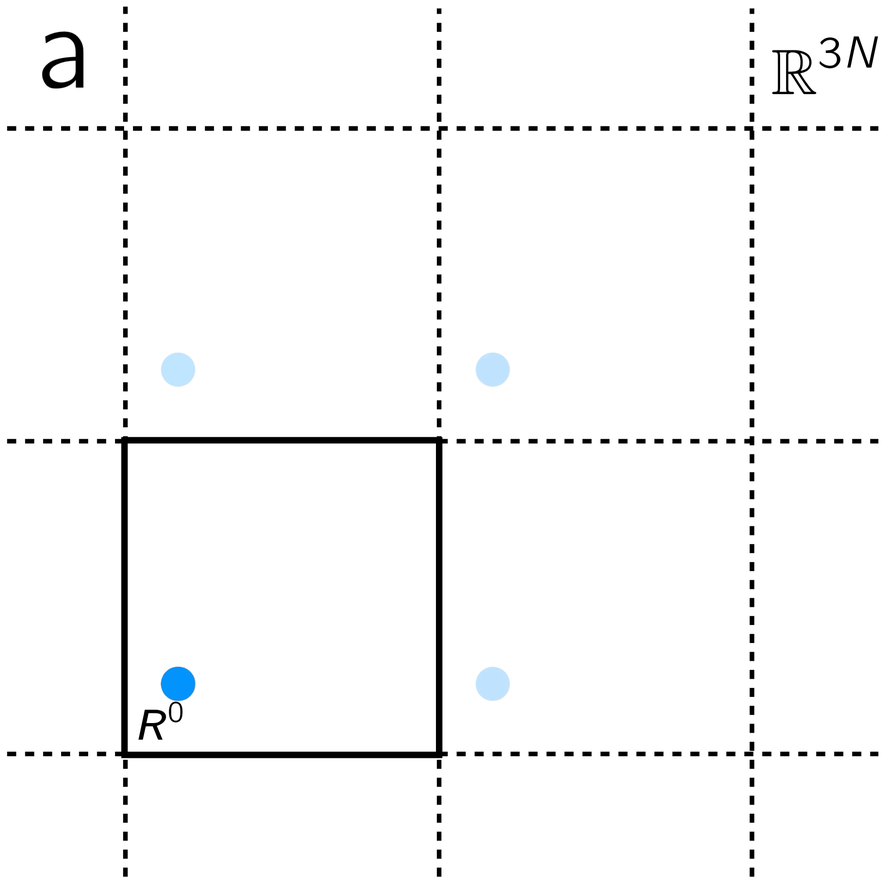

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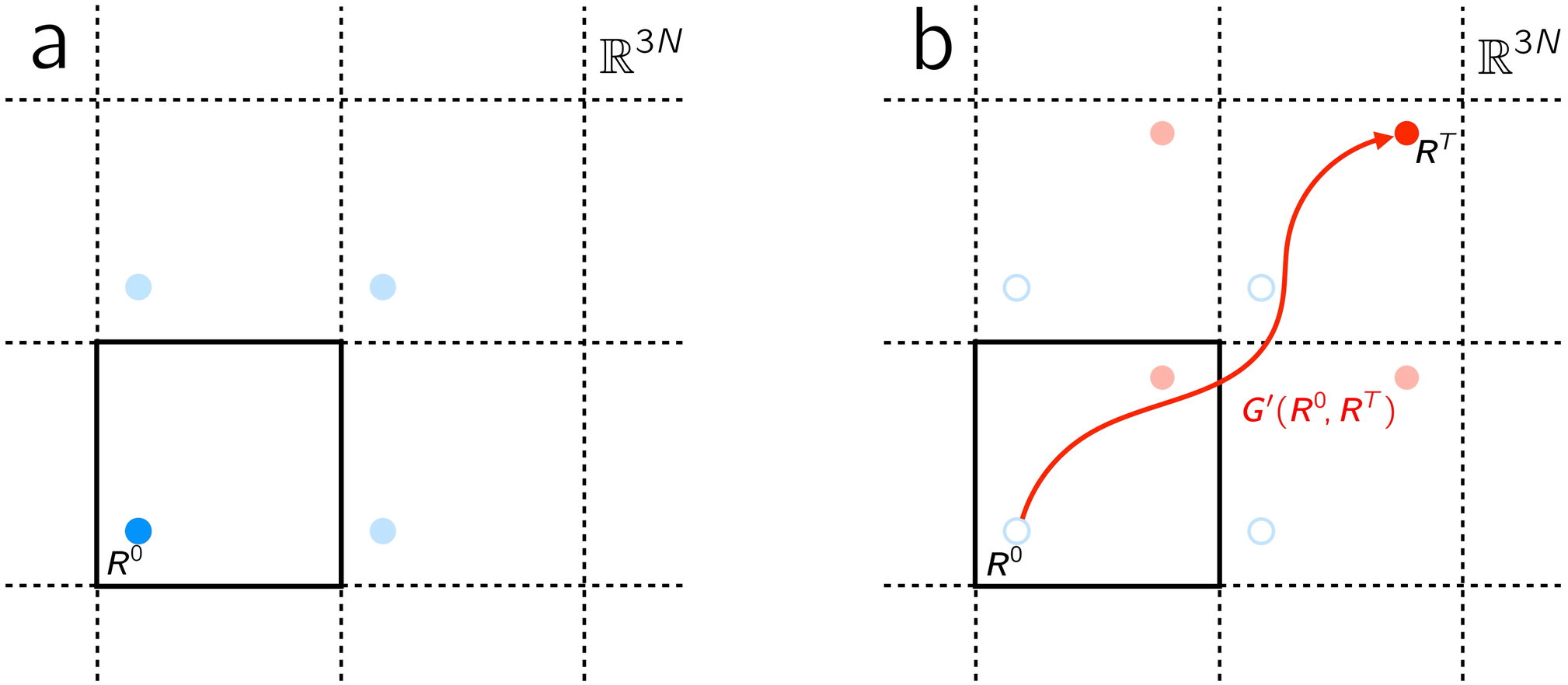

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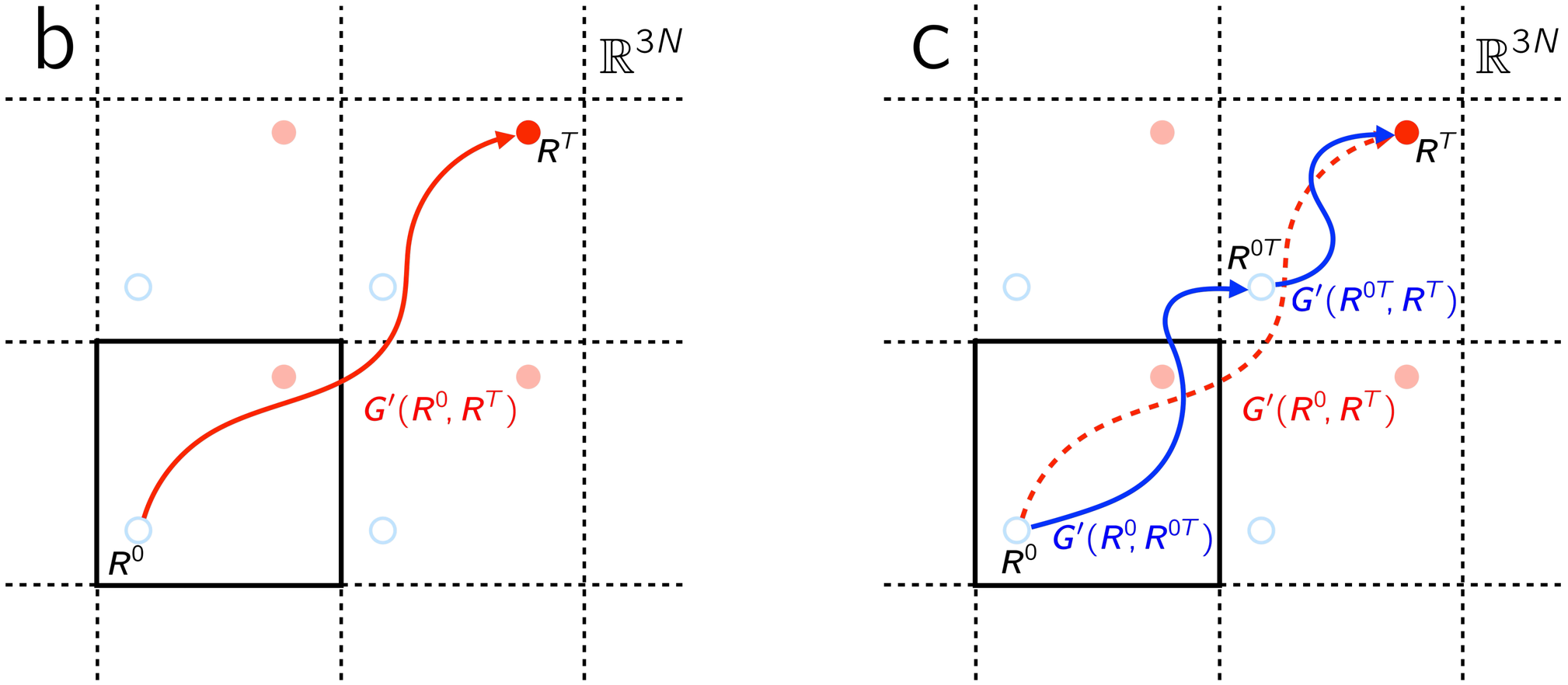


$$G'(R^0, R^T) = G'(R^0, R^{0T}) + G'(R^{0T}, R^T)$$

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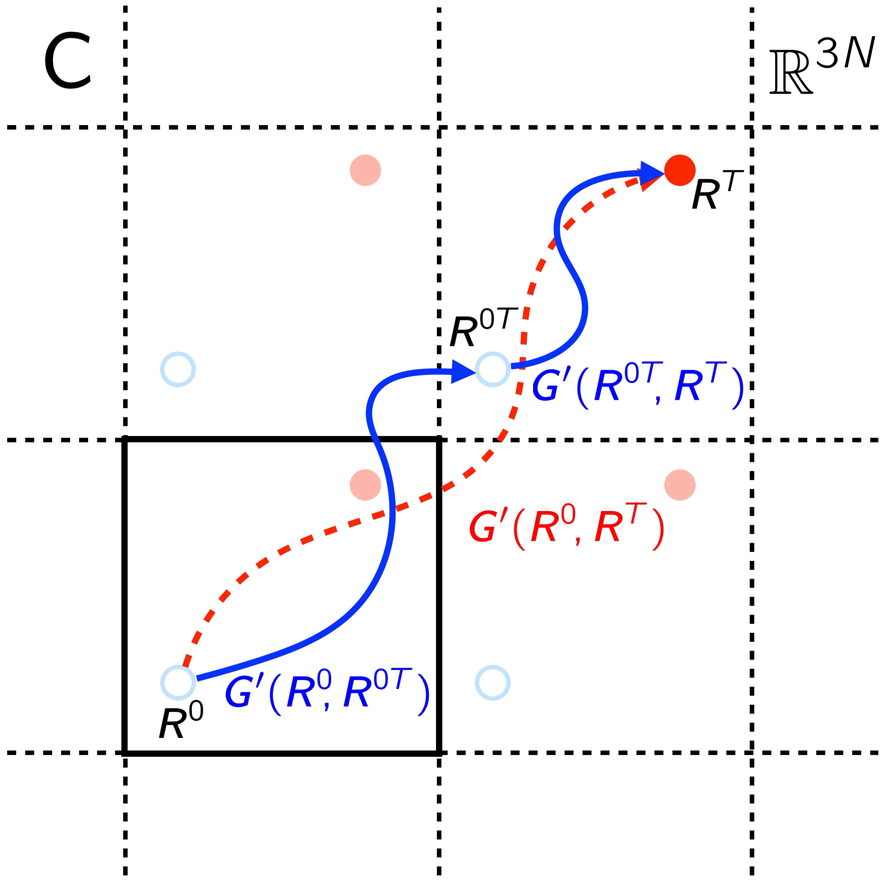


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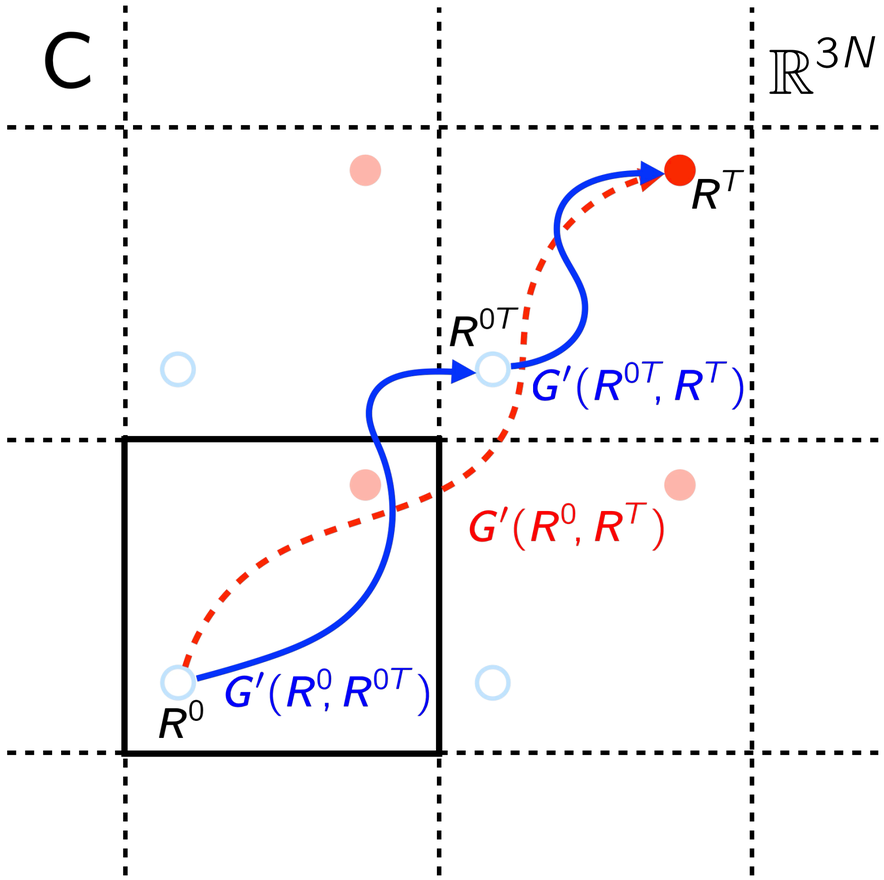


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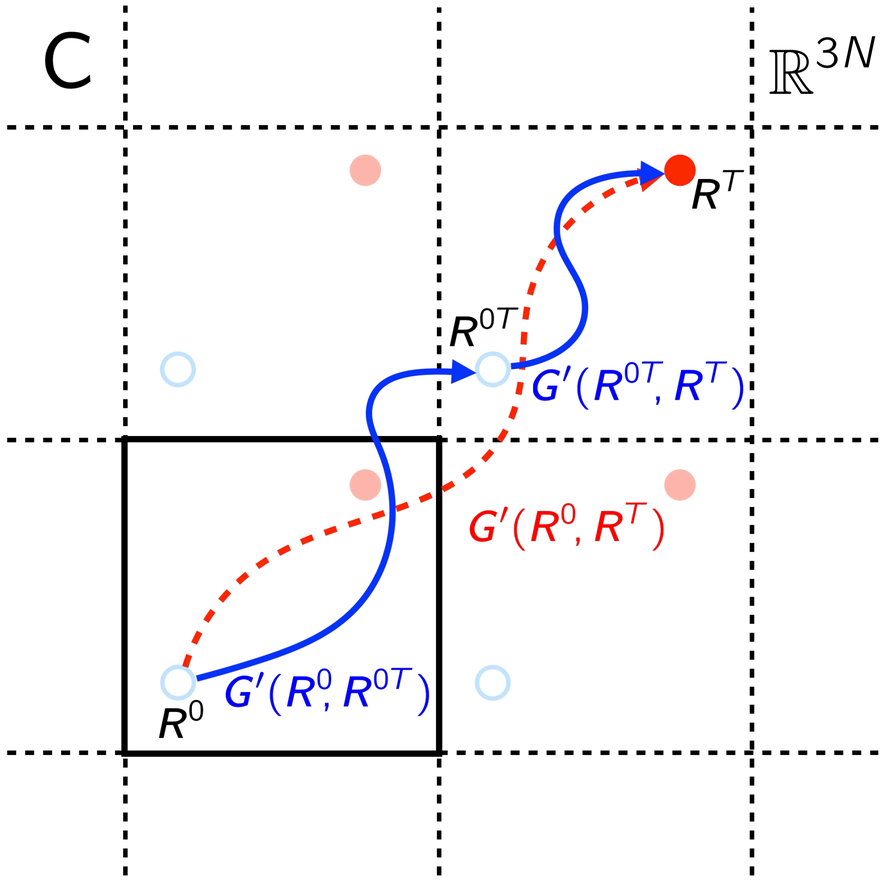


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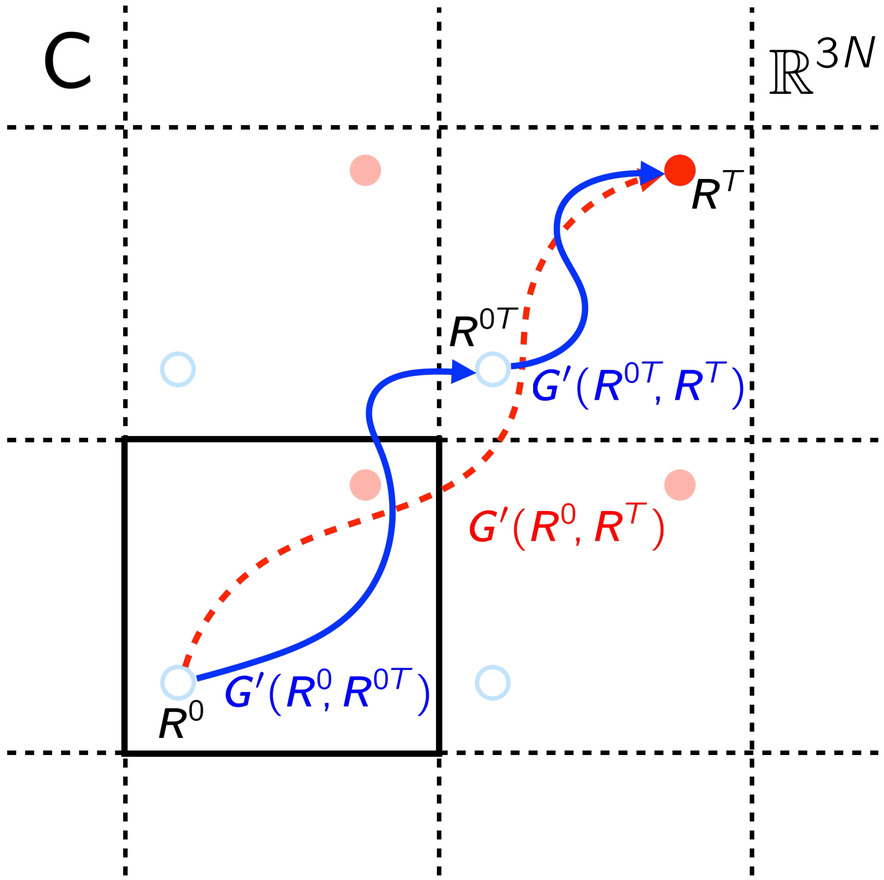


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$$\begin{aligned} G'(R^0, R^T) &= \sum_I q_I (r_I^T - r_I^0) + \sum_I q_I (r_I^{0T} - r_I^T) + G'(R^{0T}, R^T) \\ &= \sum_I q_I \int_0^T \boldsymbol{v}_I(t)dt + \mathcal{O}(1) \end{aligned}$$

# *the nuts and bolts of gauge invariance*

$$\int_0^T \boldsymbol{J}'(t)dt = \sum_I q_I \int_0^T \boldsymbol{v}_I(t)dt + \mathcal{O}(1)$$

Two short-sighted energy gauges yielding identical atomic forces generate energy fluxes that differ only by a convective term, and hence result in the same heat conductivity


The Journal of Chemical Physics ARTICLE pubs.aip.org/aip/jcp

The nuts and bolts of gauge invariance of heat transport

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# *conclusions*

- different local, short-sighted, representations of a system's potential energy that yield the same atomic forces give rise to the same heat conductivity

- the resulting energy-energy diagonal elements of the Onsager matrix, though, may differ

- the correct multi-component formula for the heat conductivity must always be used when computing the thermal conductivity of a system with diffusing mass currents

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- **the effort to compute properties that defy proper implementation sometimes yields insight worth having, because ...**

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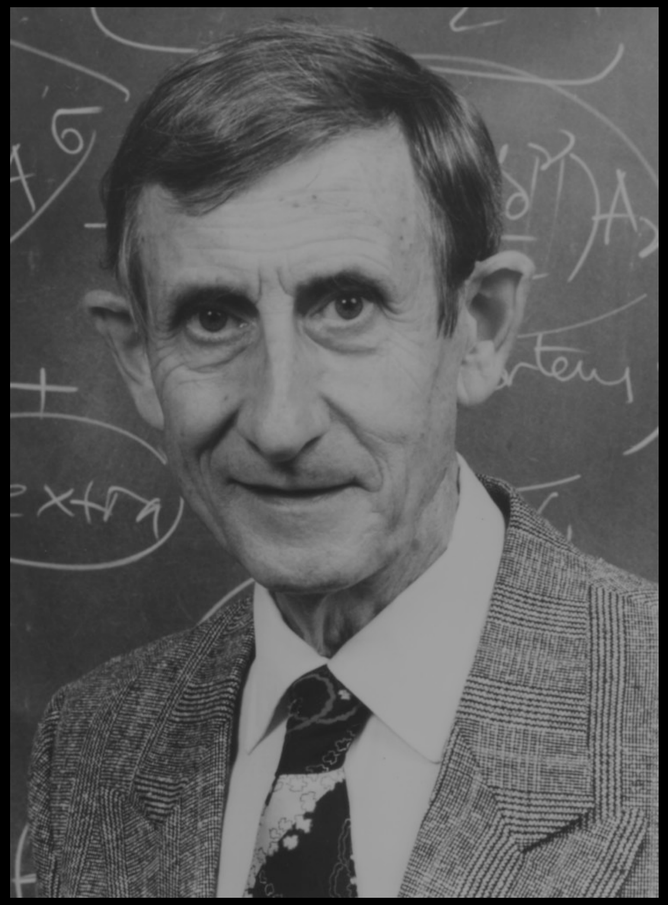


*the computer is a tool for clean thinking*

Freeman J. Dyson,
*Imagined Worlds*,
Harvard University Press (1997)

*For seminal contributions to the development of first-principles methods to investigate the electronic and thermal properties of condensed systems, and for the development and dissemination of open-source software for electronic structure calculations that has been widely adopted.*

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this talk


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Loris Ercole


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*For seminal contributions to the **development of first-principles methods to investigate the electronic** and thermal **properties of condensed systems**, and for the development and dissemination of open-source software for electronic structure calculations that has been widely adopted.*

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# density-functional perturbation theory

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**Green's-Function Approach to Linear Response in Solids**

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**Phonons and related crystal properties from density-functional perturbation theory**

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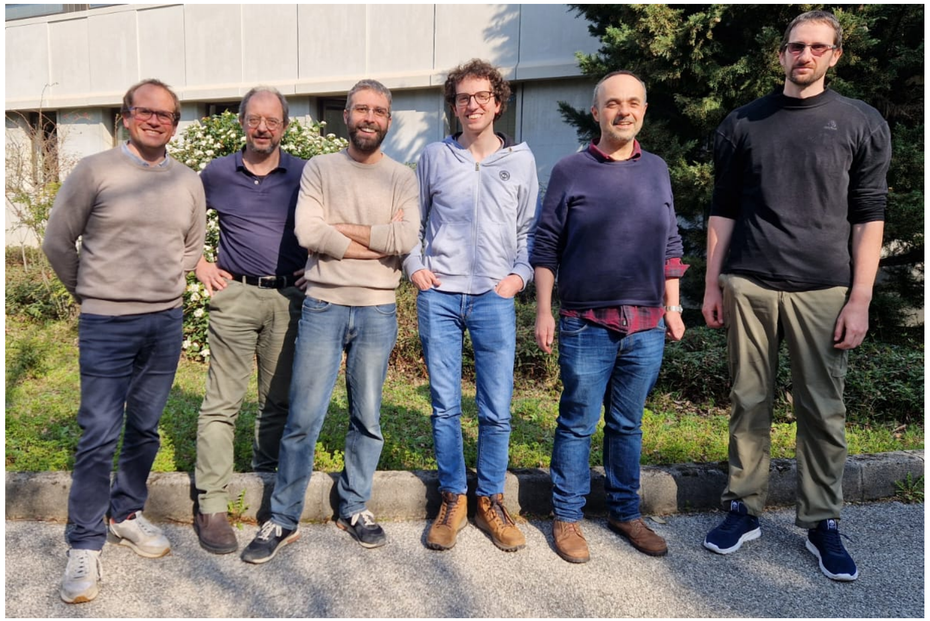

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