Microscopic theory and quantum simulation of atomic heat transport

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Quantum simulation methods based on electronic-structure theory are deemed unfit to cope with atomic heat transport within the Green–Kubo formalism, because quantum-mechanical energy densities and currents are inherently ill-defined at the atomic scale. We show that, although this difficulty would also affect classical simulations, thermal conductivity is indeed insensitive to such ill-definedness by virtue of a kind of gauge invariance resulting from energy extensivity and conservation. On the basis of these findings, we derive an expression for the adiabatic energy flux from density-functional theory, which allows heat transport to be simulated using ab initio equilibrium molecular dynamics. Our methodology is demonstrated by comparing its predictions to those of classical equilibrium and ab initio non-equilibrium (Müller–Plathe) simulations for a liquid-argon model, and by applying it to heavy water at ambient conditions.

Understanding heat transport is key in many fields of science and technology, such as materials and planetary sciences, energy saving, heat dissipation and shielding, or thermoelectric conversion, to name but a few. Heat transport in insulators is determined by the dynamics of atoms, the electrons following adiabatically in their ground state. Simulating atomic heat transport usually relies on Boltzmann’s kinetic approach1, or on molecular dynamics (MD), both in its equilibrium (Green–Kubo, GK; refs 2–5) and non-equilibrium6–8 flavours. The Boltzmann equation applies only to crystalline solids well below melting, whereas classical MD (CMD) bears on those materials and conditions that can be modelled by interatomic potentials. Equilibrium ab initio (AI) MD (refs 7,8) is set to overcome these limitations, but it is still surprisingly thought to be unfit to cope with thermal transport ‘because in first-principles calculations it is impossible to uniquely decompose the total energy into individual contributions from each atom’ (excerpted from ref. 9). Such a unique decomposition is not possible in classical mechanics either, because the potential energy of a system of interacting atoms can be partitioned into local contributions in an infinite number of equivalent ways. The quantum-mechanical energy density is also affected by a similar indeterminacy. Notwithstanding, the expression for the heat conductivity derived from any sensible energy partitioning or density should obviously be well defined, as any measurable quantity must.

In this work we first demonstrate that the thermal conductivity resulting from the GK relation is unaffected by the indeterminacy of the microscopic energy density; we then introduce a form of energy density, and a corresponding adiabatic energy flux, from which heat-transport coefficients can be computed within the GK formalism, using density-functional theory9,10 (DFT). Our approach is validated by comparing the results of equilibrium AIMD to those of non-equilibrium (Müller–Plathe, MP; ref. 6) AIMD and equilibrium CMD simulations for a liquid-argon model, for which accurate interatomic potentials are derived by matching the forces generated by them with quantum-mechanical forces computed along the AIMD trajectories. The case of molecular fluids is finally addressed, and illustrated in the case of water at ambient conditions.

Theory

According to the GK theory2–4, the atomic thermal conductivity of an isotropic system is given by:

\[ \kappa = \frac{1}{3 k_B T^2} \int_0^\infty \langle J_e(t) \cdot J_e(0) \rangle \, dt \] (1)

where brackets \( \langle \cdot \rangle \) indicate canonical averages, \( k_B \) is the Boltzmann constant, \( V \) and \( T \) are the system volume and temperature. \( J_e(t) = \int (j_e(r,t) + \langle \rho_e(r,t) \rangle \mathbf{v}(r,t)) \, dr \) is the macroscopic heat flux, with \( j_e \), \( v \), \( \rho_e \), and \( \langle \cdot \rangle \) being the energy-current density, local velocity field, and equilibrium values of pressure and energy density, respectively12,13. For further reference, we define as diffusive a flux that results in an non-vanishing GK conductivity, according to equation (1). The integral of the velocity field is non-diffusive in solids and can be assumed to vanish in one-component fluids, because of momentum conservation. In these cases, as well as in molecular fluids, as we will see, we can therefore assume that heat and energy fluxes coincide.

Energy is extensive: it can thus be expressed as the integral of a density, which is defined up to the divergence of a bounded vector field: two densities that differ by such a divergence, \( e(r) \) and \( e(r) = e(r) + \partial \cdot \mathbf{p}(r) \), are indeed equivalent, in that their integrals over any finite domain differ by a boundary term, which is irrelevant in the thermodynamic limit, and can thus be thought of as different gauges of the same scalar field. Energy is also conserved: therefore, for any given gauge of its density, \( e \), a corresponding current density, \( j_e \), can be defined so as to satisfy the continuity equation:

\[ \partial \cdot \mathbf{j}_e(r,t) = 0 \] (2)

According to equation (2) the macroscopic fluxes in two different energy gauges differ by a total time derivative, which is non-diffusive: \( \mathbf{j}_1(t) = \mathbf{j}_1(t) + \mathbf{P}(t) \), where \( \mathbf{P}(t) = \int \mathbf{p}(r,t) \, dr \) is the equality of the corresponding heat conductivities results from the following Lemma. Let \( \mathbf{j}_1 \) and \( \mathbf{j}_2 \) be two macroscopic fluxes defined for the same system, and let \( \mathbf{j}_1 = \mathbf{j}_1(t) \) be their sum. The corresponding GK conductivities, \( \kappa_1 \), \( \kappa_1 \), and \( \kappa_2 \), satisfy the relation:

\[ |\kappa_{12} - \kappa_1 - \kappa_2| \leq 2 \sqrt{\kappa_1 \kappa_2} \]
Proof. Let the energy displacement associated with the flux \( J_i(t) \) be defined as: \( D_i(t) = 1/\sqrt{6\pi^2 t} \int J_i(t') dt' \). The standard Einstein relation\(^{11}\) states that: \( \kappa_i = \lim_{t \rightarrow \infty} (\langle D_i(t)^2 \rangle / t) \); it follows that: \( \kappa_{12} = \kappa_1 + \kappa_2 + \lim_{t \rightarrow \infty} 2 \langle D_i(t) \cdot D_j(t) \rangle / t \). Canonical averages of products of phase-space functions can be seen as scalar products; the lemma then follows from the Cauchy–Schwarz inequality, as applied to the last relation.

The application of the GK methodology to multi-component fluids requires some generalizations because the presence of multiple atomic species and the existence of additional hydrodynamical modes (one conserved number per atomic species) do not permit one to identify the velocity field with the mass-current density, its integral with the total momentum, and the heat flux with the energy flux. In molecular fluids, however, this identification can still be done because the integral of the velocity field, although not a constant, is a non-diffusive flux, thus not contributing to the heat conductivity. To demonstrate this statement, we first define the fluxes \( J_{SL} = n_A \nu_A - n_B \nu_B \), where \( A \) and \( B \) indicate any two atomic species, \( n_A / n_B \) is their stoichiometric ratio, and \( \nu_A = \sum_{\alpha a} \nu_a \) is the sum of the velocities of all the atoms of the same species \( S \). The integral \( \int J_{SL}(t') dt' \) is equal to the sum of the variations of all the AB relative positions in the same molecule, which is bound by the sum of the variations of all the AB distances. \( J_{SL} \) is therefore a non-diffusive flux. We have \( N(N - 1)/2 \) non-diffusive fluxes, with \( N \) being the number of species, of which only \( N - 1 \) are linearly independent; furthermore, the flux \( J_{SL} = \sum_{i} M_i \nu_i \) (\( M_i \) is the mass of the \( i \)th atomic species) is the total momentum, and is thus non-diffusive. We have therefore \( N \) independent linear combinations of the \( \nu_i \) fluxes that are non-diffusive. We conclude that all of them, as well as their sum, \( \mathbf{V}(t) = \sum \nu_i(t) = 1/V \int \mathbf{v}(\mathbf{r}, t) d\mathbf{r} \), are also non-diffusive.

To derive an expression for the macroscopic energy flux appearing in the GK formula, equation (1), we first multiply the continuity equation, equation (2), by \( \mathbf{r} \) and integrate by parts, to obtain the first moment of the time derivative of the energy density:

\[
J_i(t) = \int \hat{c}_i(\mathbf{r}, t) d\mathbf{r}
\]

In periodic boundary conditions (PBCs) equation (3) is ill-defined for the very same reason why macroscopic polarization in dielectrics is so\(^{15}\). In CMD the usual expression for the energy flux in terms of atomic energies and forces\(^{2}\) is recovered from equation (3) by the somewhat arbitrary definition: \( e(\mathbf{r}, t) = \sum_i \epsilon_i(\mathbf{R}, \mathbf{V}) \delta(\mathbf{r} - \mathbf{R}_i) \), where \( \epsilon_i = (1/2)M_i \nu_i^2 + 1/2 \sum_{\alpha a} \nu_a \) (\( \mathbf{R}_i = \{ \mathbf{R}_i \} \) and \( \mathbf{V}_i = \{ \mathbf{V}_i \} \) are the atomic energies, positions and velocities, and by reducing the resulting expression to a boundary-insensitive form. In DFT an energy density can be defined, which is however inherently ill-determined because of the non-uniqueness of the quantum-mechanical kinetic and classical electrostatic energy densities\(^{16,17}\). Our previous analysis demonstrates that, in spite of previous worries to the contrary, the transport coefficients derived from a DFT energy density through the GK formula, equation (1), are well defined, provided a macroscopic energy flux can be computed from equation (3) in PBCs. To this end, among many equivalent gauges, we choose to represent the DFT total energy as the integral of the density:

\[
e_{\text{DFT}}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{R}_i) \epsilon_i + \sum_v \psi^*_v(\mathbf{r}) \left( \hat{H}_{KS} \psi_v(\mathbf{r}) \right) - \frac{1}{2} \rho(\mathbf{r}) v_{\mathbf{r}}(\mathbf{r}) + \left( \epsilon_{\text{XC}}(\mathbf{r}) - v_{\mathbf{r}}(\mathbf{r}) \right) \rho(\mathbf{r})
\]

where \( \epsilon_i = (1/2)M_i \nu_i^2 + w_i \) are bare ionic energies; with \( M_i, Z_i \), and \( w_i = 1/2 \sum_{\alpha a} (\mathbf{Z}_a Z_a / |\mathbf{R}_i - \mathbf{R}_a|) \) being ionic masses, charges and electrostatic energies, respectively; the electron charge is assumed to be one; \( \hat{H}_{KS} \) is the instantaneous Kohn–Sham (KS) Hamiltonian, \( \varphi_v \) are its occupied eigenfunctions, and \( \rho(\mathbf{r}) = \sum_v |\varphi_v(\mathbf{r})|^2 \) is the ground-state electron-density distribution; \( v_{\mathbf{r}} \) and \( v_{\text{XC}} \) are Hartree and exchange-correlation (XC) potentials, and \( \epsilon_{\text{XC}} \) is a local XC energy per particle, defined by the relation:

\[
E_{\text{xc}} = \int v_{\text{xc}}(\rho)(\rho) \rho(\rho) \rho(\rho) \epsilon_{\text{XC}}(\rho) \text{d}\rho(\rho) \text{d}\rho(\rho) \text{d}\rho(\rho)
\]

The five fluxes in equation (5) are defined as:

\[
J_i = J_{KS} + J_B + J_0 + J_I + J_{xc}
\]

Equation (6) can be derived from equations (3)–(4) with some tedious but straightforward algebra (see Methods). The last four terms on its right-hand side, equations (7)–(10), are manifestly boundary-insensitive, whilst the first, equation (6), is not, because the position operator appearing therein is ill-defined in PBCs. Within the adiabatic time evolution that is assumed in AIMD, however, the time derivative of a KS orbital, and its product with the KS Hamiltonian, are orthogonal to the orbital itself in the ‘parallel transport’ gauge where KS orbitals are real\(^2\) and \( |\varphi_v(\mathbf{r})|^2 \) is vanishing. The concept of gauge for the quantum-mechanical representation of molecular orbitals should not be confused with that introduced in this paper for the energy density). Therefore, to evaluate equation (6), one needs only the projection of \( |\varphi_v(\mathbf{r})|^2 \) onto the manifold orthogonal to \( \varphi_v \), which is well defined in PBCs. Actually, by expanding \( \varphi_v \) in the basis of the eigenstates of the instantaneous KS Hamiltonian, one sees that only the projection of \( |\varphi_v(\mathbf{r})|^2 \) onto the empty-state manifold, \( |\varphi_v(\mathbf{r})|^2 = \hat{P}_v \chi^\ast(\mathbf{r}) \varphi_v \) contributes to \( J_{KS} \), where \( \hat{P}_v = 1 - \sum_v |\varphi_v(\mathbf{r})|^2 \) and \( \chi^\ast \) is the \( \delta \)th Cartesian component of \( \mathbf{r} \) (ref. 21). Using the standard prescription adopted in density-functional perturbation theory, such a projection can be computed by solving the linear equation\(^{2\dagger}\):

\[
(\hat{H}_{KS} - \mathbf{e}_v)|\varphi_v(\mathbf{r})\rangle = \hat{P}_v \left[ \hat{H}_{KS} \chi^\ast \right]|\varphi_v(\mathbf{r})\rangle
\]
whose DFT BO energy surface can be accurately mimicked by pair potentials. Not aiming at a realistic description of any specific system, but rather at the ease and accuracy of the classical representation of the DFT BO surface, we choose liquid argon and use the LDA XC functional, in spite of the well-known inability of the latter to capture dispersion forces. This reference system will be dubbed 'LDA-Ar'. KS orbitals are treated within the plane-wave (PW) pseudo-potential (PP) method. PP datasets from the Quantum ESPRESSO public repository (http://pseudopotentials.quantum-espresso.org) have been used throughout. In the present case, the Ar.pz-rrkj.UPF data set was adopted with a PW kinetic-energy cutoff of 24 Ry. Our model consists of 108 atoms in a periodically repeated cubic supercell with an edge of 33 a.u., corresponding to a density of 1.34 g cm\(^{-3}\). AIMD trajectories were generated using the CP dynamics\(^2\) for 100 ps, with a time step of 0.242 fs and a fictitious electronic mass of 1,000 electronic masses, at two different temperatures, \(T = 250\) and 400 K. The fictitious electronic temperature was monitored and checked not to be subject to any significant drift. The BO energy surface was modelled with a sum of classical pair potentials of the form \(V(r) = P_2(r)e^{-|r|}\), where \(P_2\) is a second-order polynomial, whose parameters were determined independently for each temperature by a least-square fit of the classical versus quantum-mechanical forces computed along the AIMD trajectory. Self-diffusion coefficients of (10.8 ± 0.1) and (15.6 ± 0.2) \(\times 10^{-3}\) cm\(^2\) s\(^{-1}\) were estimated along the two AIMD trajectories, in close agreement with the CMD values (10.3 ± 0.1) and (15.8 ± 0.2) \(\times 10^{-3}\) cm\(^2\) s\(^{-1}\), thus confirming the quality of the classical model. Radial distribution functions computed from AIMD and CMD trajectories were also found to be very similar.

In Fig. 1a we compare the time correlation functions of the energy flux in LDA Ar, as computed from AIMD and CMD at \(T = 250\) K. The CMD and AIMD correlation functions differ not as much because they correspond to different systems—which are actually close enough as to show similar equilibrium and diffusion properties—as because the AIMD and CMD fluxes derive from a different unpacking of the total energy into local contributions. In Fig. 1b we show the integrals \(\kappa(t) = \int_0^\infty 1/(3\sqrt{k_B T})\langle J_\alpha(t)\cdot J_\beta(0)\rangle dt\); the AIMD and CMD heat conductivities, \(\kappa = -\lim_{t\to\infty}\kappa(t)\), coincide within statistical errors with each other and with the CMD value evaluated from a 1-ns-long simulation: 103 ± 5, 100 ± 6 and 104 ± 2 (mW K\(^{-1}\) m\(^{-1}\)), respectively. A similar level of agreement is obtained for the other temperature, \(T = 400\) K 118 ± 8, 112 ± 7 and 110 ± 2 (mW K\(^{-1}\) m\(^{-1}\)).

To further validate these results, we have recomputed the thermal conductivities of our LDA-argon model, using non-equilibrium (MP) AIMD (ref. 6). A detailed comparison of GK versus MP AIMD for heat-transport simulations is outside the scope of the present paper, and we have limited ourselves to two MP simulations, aimed at mimicking the physical conditions of the GK simulations reported above, and performed using minimal simulation settings: we used \(2 \times 2 \times 5\) supercells, where the notation indicates multiples of a 4-atom cubic unit cell, thus resulting in 80-atom tetragonal supercells whose size was chosen so as to result in the same mass density of 1.34 g cm\(^{-3}\) as used before. MP simulations were performed by subdividing the supercell into eight equally spaced layers stacked along the \(c\) axis and by swapping the velocities of the hottest atom in the cool region and the coolest atom in the hot region every picosecond. Rather long simulations (\(\geq 360\) ps) were necessary to achieve an acceptable statistical accuracy, resulting in estimated thermal conductivities of 94 ± 13 and 109 ± 11 (mW K\(^{-1}\) m\(^{-1}\)) at the temperatures of 287 and 423 K, respectively. Our GK and MP AIMD results are compared in Fig. 2, witnessing to a convincing validation of our approach based on the GK formalism.

We have applied our newly developed method to compute the heat conductivity of heavy water at ambient conditions. We
have generated a 90-ps-long AIMD trajectory for a system of 64 heavy-water molecules in a cubic supercell with an edge of 23.46 a.u., corresponding to the experimental density of 1.11 g cm\(^{-3}\), and at an estimated temperature \(T = 385\) K, using the Perdew–Burke–Ernzerhof (PBE) XC energy functional\(^\text{14}\). In this case we used the H.pbe-vbc.UPF and O.pbe-hgh.UPF PP datasets from the Quantum ESPRESSO public repository (http://pseudopotentials.quantum-espresso.org) and a PW kinetic-energy cutoff of 80 Ry. A time step of 0.0726 fs and a fictitious electronic mass of 340 electron masses were used in this case. The resulting self-diffusion coefficient was estimated to \((2.6 \pm 0.2) \times 10^{-6}\) cm\(^2\)s\(^{-1}\), to be compared with an experimental value of \(2.0 \times 10^{-6}\) cm\(^2\)s\(^{-1}\) at \(T = 298\) K, following the common practice of comparing experimental data for water at ambient conditions to AIMD-PBE simulations performed at \(\sim 400\) K (ref. 24). The power spectrum of the computed energy flux is characterized by three relatively narrow peaks in correspondence to the intramolecular vibrational modes\(^\text{25}\), resulting in long-lived high-frequency oscillations in the integrand of equation (1), that plague the evaluation of the integral as a function of the upper limit of integration well beyond the time where the noise of the integrand becomes larger than the amplitude of its oscillations. As the computation of transport coefficients from the Einstein relation\(^\text{14}\) is less affected by the high-frequency components of the power spectrum\(^\text{26}\), this ailment is alleviated by evaluating the heat conductivity as the slope of the energy squared displacement, \(D^2(t) = 1/(6VnBT^2)(\int_0^t \langle J(t')^2 \rangle dt'^2)\), as a function of \(t\) in the large-time limit. A direct application of this technique is however not possible as the long-time behaviour of the energy squared displacement does not allow us to extrapolate a straight line before it becomes too noisy to analyse. This state of affairs indicates the existence of a slowly decaying mode in the energy-flux correlation function, possibly associated with a non-diffusive flux. As we have seen, the total velocity \(V\) is such a non-diffusive flux. The value of the corresponding GK conductivity, equation (1), however, goes to zero very slowly as a function of the upper limit of integration. This suggests that the slow convergence of the heat conductivity of water as estimated from the slope of the energy squared displacement as a function of time is possibly due to large correlations existing between the energy flux and the total velocity. We have therefore decided to analyse, instead of \(J_0\), the modified flux \(J^*_0 = J_0 + \lambda t V\), where \(\lambda t\) has been fixed in such a way as to minimize the correlations between \(J^*_0\) and \(V\). Figure 3 shows the squared energy displacement computed from \(J^*_0\) as a function of time and demonstrates that a constant slope can indeed be identified in the long-time limit, giving a value for the heat conductivity of heavy water of \(740 \pm 120\) mW m\(^{-1}\) K\(^{-1}\), to be compared with an experimental value of \(606\) mW m\(^{-1}\) K\(^{-1}\) and \(595\) mW m\(^{-1}\) K\(^{-1}\) for light and heavy water respectively at ambient conditions\(^\text{27}\). The inset shows the behaviour of \(\kappa(t)\) (see caption to Fig. 1) as a function of the upper limit of integration in the GK formula, indicating that a direct use of equation (1) would be extremely difficult in this case. A more detailed error analysis and a systematic extension of this study to different isotopic compositions and other conditions of temperature and pressure is in the works.

Conclusions

We believe that the discussion presented in this work will clarify the scope of a number of assumptions that, although routinely made in the classical simulation of heat transport, have never been fully understood, thus hampering their generalization to quantum simulations. We are confident that the resulting new methodology will have an impact on important problems where other methods may fail, such as, for example, liquids and glasses, particularly at extreme conditions of temperature and pressure.

Methods

Methods and any associated references are available in the online version of the paper.

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**Author contributions**

All authors contributed to all aspects of this work.

**Additional information**

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**Competing financial interests**

The authors declare no competing financial interests.
Methods

To derive equations (5)–(10), we start from equation (4), which we rewrite as:
\[ e_{\text{KS}}(r) = e_{\text{el}}(r) + e_{\text{v}}(r) + e_{\text{xc}}(r) \] (13)

where
\[ e_{\text{ks}}(r) = \text{Re} \sum_i \psi_i^*(r) (\hat{H}_{\text{KS}} \psi_i)(r) \] (14)
\[ e_{\text{v}}(r) = \sum_i \delta(\mathbf{r} - \mathbf{R}_i) \left( \frac{1}{2} M_i \mathbf{V}_i^2 + w_i \right) \] (15)
\[ e_{\text{xc}}(r) = -\frac{1}{2} \rho(\mathbf{r}) V_{\text{xc}}(\mathbf{r}) \quad \text{and} \]
\[ e_{\text{xc}}(r) = (e_{\text{xc}}(r) - \nu_{\text{xc}}(r)) \rho(\mathbf{r}) \] (17)
\[ \epsilon_{\text{xc}} \] is a local XC energy per particle, defined by the relation
\[ E_{\text{xc}} = \int e_{\text{xc}}(\rho)(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \] (18)
and the XC potential \( \nu_{\text{xc}} \) is
\[ \nu_{\text{xc}}(\mathbf{r}) = \frac{\partial \epsilon_{\text{xc}}(\rho)(\mathbf{r})}{\partial \rho(\mathbf{r})} \]
\[ = e_{\text{xc}}(\mathbf{r}) + \int \frac{\partial \epsilon_{\text{xc}}(\mathbf{r}')}{\partial \rho(\mathbf{r}')}(\mathbf{r}') d\mathbf{r}' \] (19)

In the LDA, \( \epsilon_{\text{xc}} \) is a function of the local density, whereas in the GGA it is a function of the local density and density gradients:
\[ \epsilon_{\text{xc}}^{\text{LDA}}(\rho)(\mathbf{r}) = e_{\text{xc}}^{\text{LDA}}(\rho(\mathbf{r})) \]
\[ \epsilon_{\text{xc}}^{\text{GGA}}(\rho)(\mathbf{r}) = e_{\text{xc}}^{\text{GGA}}(\rho(\mathbf{r}), \nabla \rho(\mathbf{r})) \] (20)

We now proceed to computing the first moments of the time derivatives of the above four densities, according to equation (3). To simplify the notation, the time dependence of the various quantities will be omitted. Let us start with the Kohn–Sham energy density, equation (14).
\[ \dot{e}_{\text{ks}}(\mathbf{r}) = \sum_i (\dot{\psi}_i^*(\mathbf{r}) \hat{H}_{\text{KS}} \psi_i(\mathbf{r}) + \dot{\psi}_i^*(\mathbf{r}) \hat{H}_{\text{KS}} \psi_i(\mathbf{r}) + \dot{\psi}_i^*(\mathbf{r}) \hat{H}_{\text{KS}} \psi_i(\mathbf{r})) \]
\[ = \dot{e}_{\text{ks}}(\mathbf{r}) + \dot{e}_{\text{v}}(\mathbf{r}) + \dot{e}_{\text{el}}(\mathbf{r}) + \dot{e}_{\text{xc}}(\mathbf{r}) \] (23)

where
\[ \dot{\epsilon}_{\text{ks}}(\mathbf{r}) = \sum_i (e_{\text{ks}}^*(\mathbf{r}) \dot{\psi}_i(\mathbf{r}) + e_{\text{ks}}^*(\mathbf{r}) \dot{\psi}_i(\mathbf{r}) + e_{\text{ks}}^*(\mathbf{r}) \dot{\psi}_i(\mathbf{r})) \] (24)
\[ \dot{e}_{\text{v}}(\mathbf{r}) = \sum_i \dot{\psi}_i^*(\mathbf{r}) \dot{\psi}_i(\mathbf{r}) \] (25)
\[ \dot{e}_{\text{el}}(\mathbf{r}) = \dot{\nu}_{\text{el}}(\mathbf{r}) \rho(\mathbf{r}) \quad \text{and} \]
\[ \dot{e}_{\text{xc}}(\mathbf{r}) = \dot{\nu}_{\text{xc}}(\mathbf{r}) \rho(\mathbf{r}) \] (26)

The macroscopic flux deriving from \( \dot{\epsilon}_{\text{ks}} \), equation (24), is the ‘Kohn–Sham’ flux of equation (6):
\[ \int \dot{\epsilon}_{\text{ks}}(\mathbf{r}) d\mathbf{r} = J_{\text{ks}} \] (28)

The other three terms, equations (25)–(27), result from the external-, Hartree- and XC-potential contributions to the time derivative of the KS Hamiltonian (third term in equation (22)). The corresponding fluxes combine with the fluxes originating from the energy densities of equations (15)–(17), as explained below.

The first moment of the ‘ionic potential’ energy-density derivative, equation (25), reads:
\[ \int \dot{\epsilon}_{\text{v}}(\mathbf{r}) d\mathbf{r} = \sum_e \langle \psi_e | \hat{\mathbf{r}} | \psi_e \rangle \]
\[ = \sum_{\mathbf{r}} \langle \psi_e | (\mathbf{r} - \mathbf{R}_\nu) | \psi_e \rangle \]
\[ = \sum_{\mathbf{r}} \langle \psi_e | (\mathbf{r} - \mathbf{R}_\nu) | \psi_e \rangle \]
\[ + \mathbf{R}_\nu \langle \psi_e | (\mathbf{r} - \mathbf{R}_\nu) | \psi_e \rangle \]
\[ = \mathbf{J}_\nu - \sum \mathbf{R}_\nu \langle \psi_e | \mathbf{F}_e \rangle \] (29)

where \( \mathbf{J}_\nu \) is the flux of equation (8), and \( \mathbf{F}_e \) is the electronic (Hellmann–Feynman) contribution to the force acting on the \( \nu \)th atom. The corresponding (second) term in the energy flux of equation (29) is ill-defined in PBCs but, as we will see shortly, it cancels with a similar term coming from the first moment of the ‘ionic’ energy density, equation (15).

The time derivative of the ‘ionic’ energy density, equation (15), reads:
\[ \dot{\epsilon}_{\text{el}}(\mathbf{r}) = \sum_i \left( \dot{e}_i^\nu \mathbf{V}_i + \dot{\nu}_i \mathbf{V}_i \right) \]
\[ + \sum_{\mathbf{r}} \left( \mathbf{R}_\nu (\mathbf{r}) \right) \]
\[ \times \left( M_i \mathbf{V}_i + \sum_j \mathbf{V}_j \mathbf{V}_j \right) \] (30)

We now use Newton's equations of motion (\( M_i \dot{\mathbf{V}}_i = \mathbf{F}_i \), where \( \mathbf{F}_i \) is the force acting on the \( i \)th atom), and split \( \mathbf{F}_i \) into an electronic (Hellmann–Feynman) contribution, plus a sum of pair-wise electrostatic terms, \( \mathbf{F}_e = \mathbf{F}_e + \sum_{\mathbf{r}_j} \mathbf{V}_j \mathbf{V}_j \), to obtain:
\[ \int \dot{\epsilon}_{\text{el}}(\mathbf{r}) d\mathbf{r} = \sum_i \left( \dot{e}_i^\nu \mathbf{V}_i + \dot{\nu}_i \mathbf{V}_i \right) \]
\[ + \sum_{\mathbf{r}} \left( \mathbf{R}_\nu (\mathbf{r}) \right) \]
\[ \times \left( M_i \mathbf{V}_i + \sum_j \mathbf{V}_j \mathbf{V}_j \right) \] (31)

where \( \mathbf{J}_\nu \) is the energy flux of equation (9) and the third step follows from the second by interchanging the dummy indices of one of the two sums over \( i \) and \( j \). As anticipated before, the second term on the right-hand side of equation (31), which is ill-defined in PBCs, cancels a similar term in equation (29), leaving all of the surviving terms well defined. We summarize equations (29) and (31) as:
\[ \int \dot{\epsilon}_{\text{v}}(\mathbf{r}) + \dot{\epsilon}_{\text{el}}(\mathbf{r}) d\mathbf{r} = \mathbf{J}_\nu + \mathbf{J}_\nu \] (32)

where \( \mathbf{J}_\nu \) and \( \mathbf{J}_\nu \) are the energy fluxes of equations (8) and (9), respectively.

We then combine the time derivative of the ‘Hartree’ energy density, equation (16), with the ‘Hartree-potential’ energy-density derivative, equation (26):
\[ \dot{\epsilon}_{\text{xc}}(\mathbf{r}) = \dot{\epsilon}_{\text{el}}(\mathbf{r}) + \dot{\epsilon}_{\text{v}}(\mathbf{r}) \]
\[ = \frac{1}{2} \left( \dot{\nu}_{\text{el}}(\mathbf{r}) \rho(\mathbf{r}) - \dot{\rho}(\mathbf{r}) \nu_{\text{el}}(\mathbf{r}) \right) \]
\[ = \frac{1}{8 \pi} \mathbf{V} \cdot \mathbf{V}_{\text{el}}(\mathbf{r}) - \dot{\nu}_{\text{el}}(\mathbf{r}) \mathbf{V}_{\text{el}}(\mathbf{r}) \]
\[ + \frac{1}{8 \pi} \mathbf{V} \cdot \mathbf{V}_{\text{el}}(\mathbf{r}) \mathbf{V}_{\text{el}}(\mathbf{r}) - \dot{\nu}_{\text{el}}(\mathbf{r}) \mathbf{V}_{\text{el}}(\mathbf{r}) \] (33)
Multiplying equation (33) by \( r \) and integrating by parts, one obtains:

\[
J_H = \int r \dot{\mathcal{E}}_H(r) \, dr
= \frac{1}{4\pi} \int \dot{v}_H(r) \nabla v_H(r) \, dr
\]

which is equation (7).

We finally address the first moments of the time derivative of the 'XC' energy density, equation (17), and of the 'XC-potential' energy-density derivative, equation (27). We define:

\[
\dot{\mathcal{E}}_{XC}(r) = \dot{\mathcal{E}}_{XC}(r) + \dot{\mathcal{E}}_{XC}'(r)
= \rho(r) \int \frac{\delta \mathcal{E}_{XC}(r)}{\delta \rho(r')} \, \rho(r') \, dr' - \rho(r) \int \frac{\delta \mathcal{E}_{XC}(r)}{\delta \rho(r')} \, \rho(r') \, dr'
\]

which derives from the definition of the XC potential, equation (19), and from the chain rule as applied to the time derivative of \( \mathcal{E}_{XC} \):

\[
\dot{\mathcal{E}}_{XC}(r) = \int \frac{\delta \mathcal{E}_{XC}(r)}{\delta \rho(r')} \, \rho(r') \, dr'
\]

The first moment of equation (35) reads:

\[
J_{XC} = \int r \dot{\mathcal{E}}_{XC}(r) \, dr
= \int (r - r') \rho(r) \dot{\rho}(r') \frac{\delta \mathcal{E}_{XC}(r)}{\delta \rho(r')} \, dr'\, dr
\]

In the LDA, because of the local dependence of \( \mathcal{E}_{XC} \) on the electron density, the functional derivative in equation (37) is proportional to \( \delta(r - r') \), thus making the integral vanish. In the GGA equation (21) gives:

\[
\frac{\delta \mathcal{E}_{GGA}^{XC}(r)}{\delta \rho(r')} = \mathcal{E}_{GGA}'(r) \delta(r - r') + \sum_a \partial_a \mathcal{E}_{GGA}^{XC}(r) \nabla_a \delta(r - r')
\]

where \( \mathcal{E}_{GGA}'(r) = \partial \mathcal{E}_{GGA}(\rho, \nabla \rho)/\partial \rho \big|_{\rho = \rho(r)}, \) and \( \partial_a \mathcal{E}_{GGA}^{XC}(r) = \partial \mathcal{E}_{GGA}(\rho, \nabla \rho)/\partial \nabla_a \rho \big|_{\rho = \rho(r)}. \) The first term on the right-hand side of equation (38) does not contribute to the XC energy flux as in the LDA. By inserting the second term into equation (37), one finally arrives at the expression for the XC energy flux of equation (10), thus completing the derivation of equations (6)–(10).