Scattering of carriers by impurities is one of the fundamental mechanisms of resistivity in solids [1]. Within the single-particle theory, this problem can be efficiently addressed with the use of well-established techniques of potential scattering theory. Electron-electron interactions can be included, at this level, within the ground-state density-functional theory [2, 3] as electrostatic and exchange-correlation effective static potential which scatters the electrons as single particles [4, 5]. However, the single-particle approach fails to account for the dynamical exchange and correlation effects which cannot be forced into the mold of a static mean field theory.

A powerful theoretical tool has been devised to account, in principle exactly, for dynamical electron-electron interaction effects in inhomogeneous systems. This is known as the time-dependent density functional theory (TDDFT) [6]. Historically, TDDFT was developed to improve the calculation of atomic scattering cross-sections and excitation energies in both bounded [7] and extended systems [8, 9]. However, in recent years this theory has often been applied to the treatment of static phenomena (e.g., the polarizability of polymer chains [10, 11]), and steady-state transport phenomena (e.g., the stopping power of metals for slow ions [12, 13], and the conductance of quantum point contacts [14, 15]). In these applications one needs to take the zero-frequency limit of a time-dependent process, which can be properly described by TDDFT or its current generalization – the time-dependent current density functional theory (TD-CDFT) [16, 20].

Moving in the same direction, in this Letter we present the first complete TDDFT formulation for the impurity resistivity of metals. We derive an exact formula for the frequency-dependent resistivity in terms of quantities that can be calculated entirely within density functional theory. While the standard Kubo formula gives a formally exact expression for the conductivity, our formula gives an exact expression for the resistivity, and furthermore does not require that we calculate explicitly the current distribution. A major advantage of working with the resistivity rather than with the conductivity is that physically distinct dissipative processes enter the resistivity as additive contributions (Matthiessen’s rule [21]). In particular, we find that our expression for the resistivity naturally separates into a single-particle contribution and a dynamical many-body contribution. The former is shown to reduce to the classical potential-scattering formula for the resistivity; the latter takes into account the viscosity of the electron liquid [22].

Our formula appears to be a promising tool for a systematic improvement on the existing calculations of the resistivity of metals. We demonstrate this in a concrete application, namely the model calculation of the residual resistivity of aluminum as a function of the atomic number of the impurities. We show that the inclusion of many-body corrections considerably improves the agreement between theory and experiment.

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volume $V$ as [? ]
\[ j_i(\omega) = \frac{ie}{\omega V} \int d\mathbf{v} d\mathbf{v}' \tilde{\chi}_{ij}(\mathbf{v}, \mathbf{v}', \omega) E_{\text{ext},j}, \]
(2)

where $\tilde{\chi}_{ij}(\mathbf{v}, \mathbf{v}', \omega)$ is the current-density response function of the inhomogeneous electron gas with impurities. A summation over the repeated Cartesian index $j$ is implied. We transform Eq. (2) with the help of the sum-rule [?]

\[ c(\omega^2 - \omega_p^2) \int \tilde{\chi}_{ij}(\mathbf{v}, \mathbf{v}', \omega) d\mathbf{v}' = \frac{c}{m} \times \int \tilde{\chi}_{ik}(\mathbf{v}, \mathbf{v}', \omega) \nabla_k \nabla_j V_0(\mathbf{v}') d\mathbf{v}' + \frac{e \omega^2}{m} n_0(\mathbf{v}) \delta_{ij}, \]
(3)

where
\[ V_0(\mathbf{v}) = \sum_k v_0(\mathbf{v} - \mathbf{R}_k), \]
(4)

$v_0(\mathbf{v})$ is the bare potential of one impurity centered at origin, $n_0(\mathbf{v})$ is the ground-state electron density, $\omega_p = \sqrt{4\pi e^2 n_0/m}$ is plasma frequency of the homogeneous electron gas without impurities, and $c$ and $m$ are the speed of light in vacuum and the mass of electron, respectively. Applying Eq. (3) twice with respect to the speed of light in vacuum and the mass of electron, re-

without we find that the resistivity can be written as [\[ \]

\[ \chi(\mathbf{v}, \mathbf{v}', \omega) = -\frac{e \omega^2}{\hbar^2} \nabla_i \cdot \tilde{\chi}_{ij}(\mathbf{v}, \mathbf{v}', \omega) \cdot \nabla_j, \]

(5)

we eventually write the current-density as
\[ j_i(\omega) = \frac{ie}{\omega V} \left\{ \bar{n}_0 E_{\text{ext},j} + \frac{1}{m(\omega^2 - \omega_p^2)V} \int d\mathbf{v} \int d\mathbf{v}' \times [\nabla_j V_0(\mathbf{v})][\chi(\mathbf{v}, \mathbf{v}', \omega) - \chi(\mathbf{v}, \mathbf{v}', 0)][\nabla_j V_0(\mathbf{v}')] E_{\text{ext},j} \right\}. \]
(6)

Independently of the foregoing considerations, just from Maxwell’s equations for the electromagnetic field, we can see that the resistivity can be written as [? ]

\[ \rho(\omega) = \frac{E_i(\omega)}{j_i(\omega)} = \frac{1}{\omega} \left( \frac{4\pi \hbar e + \omega E_{\text{ext}}^2}{j_i E_{\text{ext},i}} \right). \]
(7)

From Eq. (5) we conclude that the expression in the parentheses of Eq. (7) is zero at $\omega = 0$. Taking the limit $\omega \to 0$ in Eq. (7) by L’Hôpital’s rule and using Eq. (6) again, we arrive at
\[ \rho = -\frac{1}{en_0 V} \int \left[ \nabla V_0(\mathbf{r}) \cdot \mathbf{E}_{\text{ext}} \right][\nabla' V_0(\mathbf{r}')] \cdot \mathbf{E}_{\text{ext}} \]
\[ \times \frac{\partial \text{Im} \chi(\mathbf{r}, \mathbf{r}', \omega)}{\partial \omega} \bigg|_{\omega=0} d\mathbf{r} d\mathbf{r}', \]
(8)

where $\mathbf{E}_{\text{ext}}$ is the unit vector parallel to $\mathbf{E}_{\text{ext}}$.

Equation (8) is the formal solution to the problem of expressing the resistivity in terms of the density-density response function $\chi$ of the interacting inhomogeneous electron gas with impurities. Using the relation [6]

\[ \chi^{-1}(\mathbf{r}, \mathbf{r}', \omega) = \chi_{KS}^{-1}(\mathbf{r}, \mathbf{r}', \omega) - f_{xc}(\mathbf{r}, \mathbf{r}', \omega) - \frac{1}{|\mathbf{r} - \mathbf{r}'|}. \]
(9)

we can conveniently rewrite Eq. (8) in terms of the Kohn-Sham (KS) density-density response function $\chi_{KS}$ of non-interacting electrons and the dynamical exchange and correlation kernel $f_{xc}$ [? ]

\[ \rho = \rho_1 + \rho_2, \]
(10)

\[ \rho_1 = -\frac{1}{en_0^2 V} \int \left[ \nabla V_{KS}(\mathbf{r}) \cdot \mathbf{E}_{\text{ext}} \right][\nabla' V_{KS}(\mathbf{r}')] \cdot \mathbf{E}_{\text{ext}} \]
\[ \times \frac{\partial \text{Im} \chi_{KS}(\mathbf{r}, \mathbf{r}', \omega)}{\partial \omega} \bigg|_{\omega=0} d\mathbf{r} d\mathbf{r}', \]
(11)

\[ \rho_2 = -\frac{1}{en_0^2 V} \int \left[ \nabla n_0(\mathbf{r}) \cdot \mathbf{E}_{\text{ext}} \right][\nabla' n_0(\mathbf{r}')] \cdot \mathbf{E}_{\text{ext}} \]
\[ \times \frac{\partial \text{Im} f_{xc}(\mathbf{r}, \mathbf{r}', \omega)}{\partial \omega} \bigg|_{\omega=0} d\mathbf{r} d\mathbf{r}'. \]
(12)

The first equation (11) is the single-particle (KS) contribution to the resistivity. The second (12) is the dynamical exchange-correlations contribution. If the frequency dependence of $f_{xc}$ is neglected – as one does, for example, in the adiabatic approximation to TDDFT – then Eq. (12) yields $\rho_2 = 0$.

To establish the connection between $\rho_1$ and the classical potential-scattering result of Eq. (9), we must neglect in Eq. (11) the coherent scattering from multiple impurities. To do this we replace the full KS potential $V_{KS}(\mathbf{r})$ by the KS potential associated with a single impurity in the electron gas, and we interpret the KS response function $\chi_{KS}(\mathbf{r}, \mathbf{r}', \omega)$ accordingly. The normalization volume is taken to be equal to the volume per impurity, i.e., $V = 1/n_i$. It can be rigourously proved [? ] that Eq. (11), thus modified, is equivalent to Eq. (11).

This result, combined with the discussion of the previous paragraph, leads to the important conclusion that the adiabatic approximation to TDDFT is equivalent to the classical potential-scattering (T-matrix) approach as far as the calculation of the resistivity is concerned.

The single-particle contribution to the resistivity is conventionally obtained from Eq. (11) [? ], using the T-matrix (phase-shift) technique to calculate the scattering cross-section from the static KS potential [13]. To find the many-body contribution to the resistivity from Eq. (12), we need a good approximation to the dynamical exchange and correlation kernel $f_{xc}$. It is known [24] that $f_{xc}(\mathbf{r}, \mathbf{r}')$ is strongly non-local (i.e. a long-ranged...
function of $|\mathbf{r} - \mathbf{r}'|$) and this non-locality is crucial to a proper description of many-body effects in transport phenomena, even on a qualitative level [13]. This immediately poses the problem of constructing a reasonably accurate non-local approximation for $f_{xc}$. In a recent paper [13] we have shown how this can be done starting from an exact representation of the scalar $f_{xc}$ kernel in terms of the tensorial exchange and correlation kernel $f_{xc}$ of time-dependent current density functional theory. This representation reads

$$f_{xc} = -\frac{e^2}{c} \nabla^2 \cdot \left( \hat{f}_{xc} \left( \chi_{KS}^{-1} - \hat{f}_{xc} \right) \left[ \hat{\mathcal{T}} \left( \chi_{KS}^{-1} - \hat{f}_{xc} \right) \hat{\mathcal{T}} \right]^{-1} \times \left( \chi_{KS}^{-1} - \hat{f}_{xc} \right) \left( \hat{\mathcal{T}} \chi_{KS}^{-1} \hat{\mathcal{T}} \right)^{-1} \hat{\mathcal{T}} \chi_{KS}^{-1} \cdot \nabla \nabla^{-2} \right), \quad (13)$$

where $\chi_{KS}$ is the KS current-density response function and $\hat{T}$ is the projector operator onto the subspace of transverse vector fields (i.e. divergence-free fields) [?]. By making use of the local density approximation (LDA) for the tensorial $\hat{f}_{xc}$ in the right-hand side of Eq. (13), we obtain a non-local approximation for the scalar $f_{xc}$ which satisfies the zero-force sum-rule requirements [2,13], and can, therefore, be considered a promisingly accurate approximation for transport problems.

In Refs. [20, 26], the LDA to the exchange and correlation kernel $f_{xc}$ of the TDCDFT has been worked out within the framework of the hydrodynamics of inhomogeneous viscous electron liquid. We, therefore, use Eq. (12) with $f_{xc}$ given by Eq. (13) and $f_{xc}$ as expressed in Ref. [26] through the viscoelastic constants of electron liquid. In Fig. 1 we present results for resistivity for substitutional impurities of atomic number $Z$ from 11 through 32 in an aluminum host. The latter is modeled as a jellium with Wigner-Seitz radius $r_s = 2.07$. In this calculation we have neglected the coherent scattering from multiple impurities, focusing instead on the many-body dynamical exchange and correlations effects. The values of the viscoelastic constants were taken from Ref. [23]. Our purpose is not to take into account all the effects that could possibly contribute to the resistivity in a real solid aluminum, but rather to show that the many-body viscosity corrections are sizeable and indeed of the right order of magnitude to account for the observed discrepancy between available theoretical calculations and experimental data.

The single-particle contribution $\rho_1$ calculated from Eq. (11) and represented by the chained curve with squares (black online) is found to be in agreement with earlier calculations [4,5]. The total resistivity, including dynamical exchange and correlation contributions, is represented by the chained curve with circles (red online). An improved agreement between theory and experiment can be clearly seen from the figure. The effects left out by our calculation that could possibly contribute to the remaining disagreement between the theory and experiment are (i) the band structure and lattice distortion effects, (ii) the possible spin-polarization, and (iii) the coherent scattering by the impurities at different sites. Another potentially important source of error can be in the values of the visco-elastic constants of the electron liquid.

Finally we note that Eq. (15) allows us to establish a general relation between the impurity resistivity and the friction coefficient [? ] of the same host for the same type of impurity atom. The latter can be written as [12]

$$Q = -\int \left[ \nabla V_0(r) \cdot \hat{\mathbf{v}} \right] \left[ \nabla' V_0(r') \cdot \hat{\mathbf{v}}' \right] \times \frac{\partial \text{Im} \chi(r, r', \omega)}{\partial \omega} \bigg|_{\omega=0} \, d\mathbf{r} \, d\mathbf{r}', \quad (14)$$

where $\mathbf{v}$ is the velocity of the atom, and, comparing with Eq. (8), we can write

$$\rho = n_i Q/(e \tilde{n}_0^2). \quad (15)$$

We point out that the relation (15) quite generally holds within the many-body theory and is a stronger statement than $\rho_1 = n_i Q_1/(e \tilde{n}_0^2)$, which is a simple consequence of Eq. (11) and the corresponding single-particle result for the friction coefficient $Q_1 = \tilde{n}_0 k_F \sigma_{tr}(k_F)$ [27].

In conclusion, we have developed the non-adiabatic time-dependent density functional formalism for a systematic calculation of the dc residual resistivity of metals with impurities. The contribution to the resistivity arising from the many-body interactions has been expressed through the dynamical exchange and correlation kernel $f_{xc}$. We have shown that all the dynamical effects of the electron-electron interaction are contained in the
frequency dependence of $f_{xc}$. The adiabatic approximation, which neglects this frequency dependence, is exactly equivalent to the conventional single-particle potential-scattering theory of the resistivity, provided the coherent scattering from multiple impurities is neglected as well. Our calculations of the residual resistivity of Al with various impurity atoms of different nuclear charge show that the inclusion of dynamical exchange and correlation considerably improves the agreement between theory and experiment.

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