Exchange corrections for inelastic electron scattering rates in condensed matter

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A method is presented for quantifying quantum-mechanical exchange effects within the dielectric theory of electron scattering, the prevailing model for electron energy losses in condensed-matter systems. The approach utilizes a uniquely symmetric view of direct and exchange scattering events along with a generalized interference phase to account physically for the reduced scattering rates required by the Pauli exclusion of final-state fermions with corresponding spin, energy, and momentum. It is found that existing implementations either neglect or substantially overestimate the impact of exchange interference for condensed materials with broad optical loss spectra due to mathematical approximations or physical assumptions which are largely avoidable. The results suggest that the impact of exchange may alter inelastic scattering cross sections by between 10% and 20% for incident energies below 200 eV, a critical energy range for current investigations in electron and photoelectron spectroscopies.

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I. INTRODUCTION

Inelastic scattering rates for electrons in a solid are a fundamental material property of critical importance to an immense range of physical, chemical, and spectroscopic studies and, increasingly, for modern imaging and metrology [1]. Their computation is a longstanding problem harking back to the early days of quantum theory [2], with significant developments in the field still being made even in the last few years. This is particularly true with respect to the behavior of slow-moving electrons, where energies fall well below 1 keV, whose quantitative properties are needed for developments of the latest technologies in electron microscopy and nanoelectronics.

Following recent improvements in measurement techniques for low-energy electron inelastic mean free paths (IMFPs) [3,4], a large number of theoretical investigations have been made to critically examine the many potential deficiencies in the prevailing theory of inelastic scattering for slow electrons in condensed matter [5–10]. A principal problem is that while there is a sound quantum-mechanical basis for most of the existing calculations, first-principles results for solids are extremely difficult to obtain and tend to be highly limited in scope [11].

It is therefore most common to calculate electron scattering rates in condensed matter via a dielectric theory following either the Quinn-Penn formalisms [12,13] or the Lundqvist model for self-energy [14,15]. These models, implemented usually within the Born approximation, tend to be quite accurate for fast-moving electrons but also tend to break down below 100 eV [16]. In the absence of a tractable many-body theory describing all scattering mechanisms within a well-defined band structure beyond a few tens of eV, we thus require improved methods to apply the lessons of the fundamental quantum theory to our dielectric models to ensure accuracy down to these critical energies.

In this spirit, this work presents an implementation of the effects of electron exchange interference within a dielectric model. It utilizes as its basis the coupled-plasmon model (CPM) of Bourke and Chantler [8], which is an extension of the full Penn algorithm [17] and thus aligned with the most common usage of the Quinn-Penn theory. A recent review of the CPM, including its origins from the random-phase approximation [18] and subsequent extensions, can be found in [19].

II. INELASTIC CROSS SECTIONS

We begin with consideration of the electron IMFP λ, which quantifies the mean distance traveled by an electron between successive inelastic collisions. It is standard to define it in terms of the double-differential cross section (DDCS) as

$$\lambda^{-1} = \int_0^{\omega_{\max}} \int_{q_-}^{q_+} N \frac{d^2\sigma}{d\omega dq} dq d\omega, \tag{1}$$

where N is the number density of atoms, ω is the energy transferred by an inelastic scattering event, and q is the transferred momentum in atomic units. The integration limits are conventionally determined by kinematic constraints on the incident electron and are given by

$$\omega_{\max} = T' - E_F, \tag{2a}$$

$$q\pm = \sqrt{2T'} \pm \sqrt{2(T' - \omega)}, \tag{2b}$$

where $T' = T + E_F$ and T is the energy of the incident electron relative to the Fermi energy E_F of the scattering material. The DDCS is then related to the imaginary part of the electron self-energy and, secondarily, to the complex dielectric function via the theory of Quinn and Ferrell [12].

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The nonrelativistic formulation of this theory is described by Tanuma *et al.* [20] and yields

$$\frac{d^2\sigma(\omega)}{d\omega dq} = \frac{1}{N}\frac{1}{\pi T'}\frac{1}{q}\mathrm{Im}\left[\frac{-1}{\epsilon(q,\omega)}\right]. \tag{3}$$

This theory and its affiliates have had great success in tabulating accurate IMFPs for a wide range of elemental and molecular systems [20,21]. Recent work has also extended its applicability to the low-energy regime with improvements in the self-consistent derivation of the energy loss function (ELF), given by $\mathrm{Im}[\frac{-1}{\epsilon(q,\omega)}]$ [8].

This standard formulation, however, lacks a physical implementation of the electron exchange interaction. The exchange interaction takes different forms depending on the electron states being discussed. For example, the state of the scattering material should ideally be affected by electron exchange, such as via an exchange hole [22], and this would alter the dielectric function and hence $\mathrm{Im}[\frac{-1}{\epsilon(q,\omega)}]$ [23]. In this work we are concerned with the exchange interaction between the two final-state electrons that propagate after a scattering event, and thus we are interested in the direct correspondence between the ELF and the DDCS given by Eq. (3).

III. EXISTING EXCHANGE MODELS

There exist in the literature few models that attempt to account for exchange in the relationship between the cross section and the ELF, but it is useful to recount two of them explicitly not only as a comparison to the model presented here but also as an effective explanation for the physical nature of the effect. As with the current approach, they both rely on an extension of the electron-electron scattering formula given by Mott in the absence of spin polarization [2,24]:

$$\sigma = \frac{k_1 k_2}{k_0}\iint |f(k_1,k_2)|^2 + |g(k_1,k_2)|^2 - \mathrm{Re}[f(k_1,k_2)g^*(k_1,k_2)]. \tag{4}$$

Here k_0 is the initial momentum of the system, while f and g are transition amplitudes with final-state electron momenta of k_1 and k_2. f is conventionally denoted as the direct scattering amplitude, while g is the exchange scattering where the final electron states are switched. We therefore have a symmetry constraint [25]:

$$f(k_1,k_2) = g(k_2,k_1), \tag{5}$$

which is necessary for the final term in Eq. (4) to be reduced to its real component. The most direct interpretation of Mott's formula in terms of the electron ELF is given by Emfietzoglou *et al.* [26]:

$$\frac{d\sigma_{\mathrm{XI}}}{d\omega} = \frac{d\sigma(\omega)}{d\omega} + \frac{d\sigma(T'-E_F-\omega)}{d\omega} - \left[\frac{d\sigma(\omega)}{d\omega}\frac{d\sigma(T'-E_F-\omega)}{d\omega}\right]^{\frac{1}{2}}, \tag{6}$$

where σ_{XI} is the cross section inclusive of an exchange-interference correction and we make the inference that, for example,

$$\frac{d\sigma(T'-E_F-\omega)}{d\omega} = \frac{1}{N}\frac{1}{\pi T'}\int_{q_-}^{q_+}\frac{1}{q}\mathrm{Im}\left[\frac{-1}{\epsilon(q,T'-E_F-\omega)}\right]. \tag{7}$$

This provides a good intuitive view of the scattering contributions. From the right-hand side of Eq. (6), the first term relates the direct scattering, conventionally where the incoming electron loses less than half of its initial energy, the second term is the exchange analog where the incoming electron finishes with less than half its initial energy, and the third term is the interference caused by Pauli's exclusion principle. In the case of the final states being equivalent, the interference reduces the differential cross section (DCS) by half due to the 50% probability of the spins being aligned. The total cross section is then obtained by integrating $\frac{d\sigma}{d\omega}$ from 0 to $\frac{\omega_{\max}}{2}$.

Physically, it is important that the direct and exchange scatterings be treated equivalently (even if they are not equal) because the convention dictating the definition of each is arbitrary. This is the essence of the symmetry condition of Eq. (5). Equation (6) satisfies this requirement in terms of the energy integral—it does not matter whether the integration range runs from 0 to $\frac{\omega_{\max}}{2}$ or from $\frac{\omega_{\max}}{2}$ to $\omega_{\max}$—but it breaks the symmetry condition with respect to the momentum integration because $q\pm$ is dependent on the energy transfer. This problem is not significant in terms of the actual cross sections calculated using this approach; however, we point it out here because it is increasingly important for extensions of the model.

An issue that is significant numerically, however, is the way that Eq. (6) treats the exchange interference. Because the ELF is being treated as a substitute for the transition amplitude, the interference term loses the phase factors intrinsic to f and g. Thus the final-state electrons are modeled as being in phase regardless of their respective momenta, leading to a substantial overestimation of their interference and a corresponding underestimation of the total cross section. For large energies of the incident electron, the interference becomes negligible due to the dominance of the direct scattering contribution, but at energies below a few hundred eV this error becomes too large for this model to be useful.

Accordingly, it is more common to see calculations performed using an alternative approximation inspired by Ochkur [27]. Ochkur found that, to within a first-order application of the Born-Oppenheimer model, the direct and exchange transition amplitudes for an atomic ionization event can be simply related via

$$g(k_1,k_2) \approx \left(\frac{q}{k_0}\right)^2 f(k_1,k_2). \tag{8}$$

This would notionally remove the need for a phase factor as the entire calculation could be carried out in terms of the direct scattering amplitude. It leads to the following form for the cross section, used by [28,29], among others:

$$\sigma = N\frac{1}{\pi T'}\int_0^{\frac{\omega_{\max}}{2}}\int_{q_-}^{q_+}\frac{1}{q}[1+f_{\mathrm{ex}}]\mathrm{Im}\left[\frac{-1}{\epsilon(q,\omega)}\right]dqd\omega, \tag{9}$$

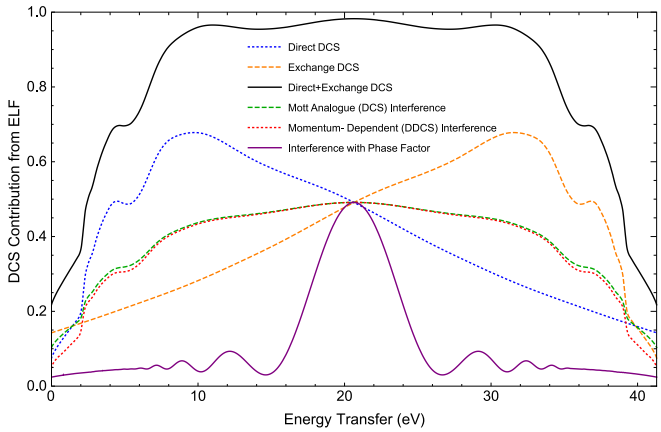

FIG. 1. Contributions to the differential cross section $\frac{d\sigma}{d\omega}$ for copper for a primary electron energy of 50 eV. Plotted are the direct scattering (blue dotted line), exchange scattering (orange dashed line), total scattering (solid black line), and interference terms using different models. The current model, in purple, correctly and uniquely possesses a magnitude of half the sum of the direct and exchange scattering terms only when the final-state excitations are energetically similar.

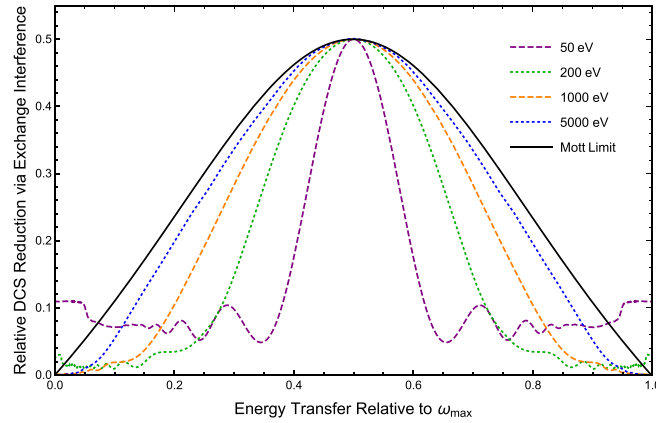

FIG. 2. The contribution of exchange interference to the total DCS, scaled by the sum of the direct and exchange scattering amplitudes. The high-energy behavior resembles that of an ideal Mott scattering between two free particles.

where

$$f_{ex} = \left(\frac{q}{k_0}\right)^4 - \left(\frac{q}{k_0}\right)^2. \tag{10}$$

The Ochkur approximation tends to yield far more realistic cross sections than the direct Mott analog [30,31], particularly at energies between roughly 100 eV and 1 keV [26]; however, this is somewhat due to canceling of errors. Although the form of Eq. (9) has no obvious problems with symmetry, the underlying premise that the exchange scattering can be represented by a scaling of the direct scattering is strictly true only for a very limiting case. Specifically, Eq. (8) may be derived within the dielectric theory only by using a single-pole model with approximately zero plasma frequency (corresponding to a zero-density free-electron gas) and in the limit of extremely high incident electron energy. This limit is workable for the atomic ionizations Ochkur was tackling, but in the case of a solid where a broad spectrum of electron and quasiparticle resonances exist or in a region of relatively low incident electron energy, the model breaks down entirely.

The simplest illustration of said breakdown comes when we consider the component of the integral when $k_1 = k_2$. In this case Eq. (8) clearly does not satisfy the symmetry condition of Eq. (5), so if the contribution to the cross section is significant in this region, the result from Ochkur's approximation will be aberrant. The later example of copper shown in Figs. 1 and 3 demonstrates that this is very much so for projectile energies at or below ∼50 eV. Hybrid models favoring aspects of the Ochkur approximation and aspects of the direct Mott analog for different limiting cases have been proposed [31]; however, this is also likely to be more of an exercise in error compensation rather than the basis of a meaningful model.

As such, we require two corrections to existing models to obtain a satisfactory exchange-interference contribution for the total inelastic cross section: A formalism in which the symmetry of the exchange interaction is rigorously maintained and one in which the relative phase of the final-state excitations is properly implemented.

IV. EXCHANGE SYMMETRY

The difficulty in treating the direct and exchange terms equivalently is primarily due to the kinematic model that gives us our momentum integration limits $q\pm$. These limits impose a free-electron-like final-state dispersion relation on the incident electron, so that we have, in atomic units, $E_1 = k_1^2/2$, where E_1 is the final energy of the incident electron ($E_1 = T' - \omega$ in the direct scattering case). For most scattering events this is a sensible approximation, and it provides us with a range of possible momenta for the scattered electron (or bulk excitation) based on conservation of both momentum and energy.

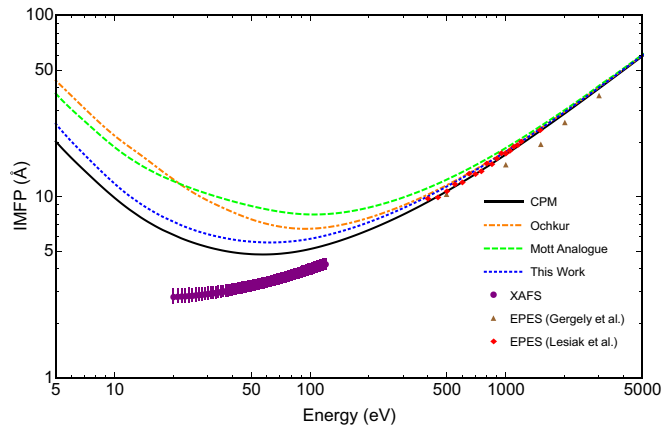

FIG. 3. IMFPs calculated for copper using different exchange-interference models. The CPM curve uses the existing coupled-plasmon model without an interference correction. The Ochkur curve uses the exchange-interference correction from Eq. (9), while the Mott analog uses the correction from Eq. (6). This work, in blue, uses the model from Eq. (24). Comparisons to experimental data from the XAFS [3] and EPES [32,33] techniques are also shown.

The above kinematic model creates a problem, however, in that it constrains our model to treat any final state that does not exhibit free-electron dispersion as certainly being the "excited" particle and not the scattered one. Although we cannot discard this approach entirely without altering the overall range of integration, which is known to be valid at high energies, we can adjust our formalism in order to treat the final states equivalently so that even though one of them must adhere to a free-particle dispersion, it does not matter which one it is.

We do this by transforming our expression for the DCS to treat the problem in terms of the relative scattering angle θ between the two final-state particles. θ is related to the final-state momenta of the incident and scattered electrons by

$$\theta = \cos^{-1}\left(\frac{k_0^2 - (k_1^2 + k_2^2)}{2k_1k_2}\right), \tag{11}$$

which, importantly, does not depend upon the choice of particle labels. It is then possible to choose arbitrarily one momentum, in this case k_2, to define the relations needed for the change of variable:

$$k_2 = -k_1\cos\theta + \sqrt{k_0^2 - k_1^2\sin^2\theta}, \tag{12a}$$

$$\frac{dk_2}{d\theta} = k_1\sin\theta - \frac{k_1^2\cos\theta\sin\theta}{\sqrt{k_0^2 - k_1^2 sin^2\theta}}. \tag{12b}$$

We can then express the total cross section, in the absence of exchange interference, as

$$\sigma = \int_0^{\omega_{\max}}\int_0^{\pi} N\frac{1}{\pi T'}\frac{1}{-k_1\cos\theta + \sqrt{k_0^2 - k_1^2\sin^2\theta}} \times \mathrm{Im}\left[\frac{-1}{\epsilon(q,\omega)}\right]\left(k_1\sin\theta - \frac{k_1^2\cos\theta\sin\theta}{\sqrt{k_0^2 - k_1^2\sin^2\theta}}\right)d\theta d\omega, \tag{13}$$

where the integrand is the new DDCS, $\frac{d^2\sigma}{d\omega d\theta}$.

With this representation it is possible to revisit the Mott analog of Eq. (6), but instead using the DDCS so that the interference term can depend explicitly on the momentum transfer:

$$\frac{d^2\sigma_{\mathrm{XI}}}{d\omega d\theta} = \frac{d^2\sigma(\omega)}{d\omega d\theta} + \frac{d^2\sigma(T' - E_F - \omega)}{d\omega d\theta} - \mathrm{Re}\left\{\left[e^{i\tau(k_1,k_2)}\frac{d^2\sigma(\omega)}{d\omega d\theta}\frac{d^2\sigma(T' - E_F - \omega)}{d\omega d\theta}\right]^{\frac{1}{2}}\right\}, \tag{14}$$

where we have included a generalized phase term that will be discussed in the next section and have specified the real component by analogy with Eq. (4). This transformation affects only the interference term and is a surprisingly small correction when the phase term is neglected. The reason for this, however, is of physical interest. Transforming to an angular integral aligns scattering events which produce two free-electron-like final-state particles to states where $\theta = \pi/2$. This means, for example, that in a model absent of quasiparticle states or electrons modulated by a material potential, Eq. (14) would produce results identical to Eq. (6) because it aligns all excitations that lie along the Bethe ridge (i.e., all such excitations correspond to the same θ). It also produces results identical to Ochkur's approximation when the incident energy is sufficiently high because then the material behaves like a low-density free-electron gas in keeping with Ochkur's derivation. As such, differences in this approach from the existing models of exchange interference are significant only insofar as the material in question varies from an ideal low-density free-electron gas.

V. PHASE-DEPENDENT INTERFERENCE

Despite the minor impact of the transformation to an angular-dependent model, it is quite necessary to the theory because it facilitates a solution to the problem of the relative phase in the interference term. The phase factor is necessarily momentum dependent but must also be treated symmetrically with respect to the final state particles.

Without a first-principles calculation for the transition amplitudes f and g it is impossible to account for the phase term exactly; however, it is certainly possible to derive a meaningful approximation via established functional forms. For this purpose we take the transition form given by Rudge [30]:

$$f(k_1,k_2) = -(2\pi)^{-5/2}\exp\left[i\Delta(k_1,k_2)\right] \times \int \Psi(\mathscr{H} - E)\Phi dr_1 dr_2, \tag{15}$$

where Ψ is the total wave function, r_1, r_2 are the spatial indices of the interacting electrons, and Φ is a radial function constrained to ensure a normalized, asymptotic form over all space. This amplitude is designed to describe ionization in hydrogen but can be applied more generally to a central-potential scattering problem. The original derivation is given by Peterkop [34], while the specific form we have adopted was developed by Rudge and Seaton [35]. Although the details of both Ψ and Φ are certainly dependent not only on the nature of the scattering atom but also on the band structure of the material, for our purpose it is the phase term $\exp\left[i\Delta(k_1,k_2)\right]$ that is important, and this can be expressed directly in terms of the respective momenta:

$$\Delta(k_1,k_2) = 2\left[\frac{z_1}{k_1}\ln\left(\frac{k_1}{k_0}\right) + \frac{z_2}{k_2}\ln\left(\frac{k_2}{k_0}\right)\right], \tag{16}$$

where k_0, k_1, and k_2 are as previously defined and the z parameters are effective charge distributions which satisfy [30]

$$\frac{z_1}{k_1} + \frac{z_2}{k_2} = \frac{1}{k_1} + \frac{1}{k_2} - \frac{1}{|\mathbf{k}_1 - \mathbf{k}_2|}. \tag{17}$$

Given this phase factor, coupled with the symmetry condition, we can see that the interference term in Eq. (14) must be modulated by a factor of $\exp[i\tau(k_1,k_2)]$, where

$$\tau(k_1,k_2) = \Delta_d(k_1,k_2) - \Delta_e(k_2,k_1). \tag{18}$$

The above expression is modified from that of Peterkop [36] to include the subscripts d and e, corresponding to the direct and exchange contributions. We do this to clarify that, although the expressions are analogous, it is necessary to compute the k_1

and k_2 values separately for each case. This is because they are dependent on the energy transfer, which we denote ω for the direct scattering case and $T' - E_F - \omega$ for exchange, and thus cannot be interchanged freely except along the Bethe ridge or in the high-energy limit. Therefore the only difference mathematically in the direct and exchange contributions throughout our model is whether the initial electron loses more or less than half of its available energy.

The only ingredient then missing is a set of forms for z_1, z_2, which satisfy Eq. (17). Since the difference term $|\mathbf{k}_1 - \mathbf{k}_2|$ depends also on the relative angle of scattering, it is convenient to reparameterize the effective charges, without loss of generality, as

$$z_1 = 1 - \frac{k_1}{|\mathbf{k}_1 - \mathbf{k}_2|} G_1, \tag{19a}$$

$$z_2 = 1 - \frac{k_2}{|\mathbf{k}_1 - \mathbf{k}_2|} G_2. \tag{19b}$$

We can now rewrite our mathematical constraint as

$$G_1 + G_2 = 1, \tag{20}$$

where G_1 determines the transition from direct- to exchange-dominated scattering regimes and vice versa for G_2. This is analogous to Rudge's physicality conditions [30]:

$$\lim_{k_1 \to 0} z_1 = 1; z_2 = 0, \tag{21a}$$

$$\lim_{k_2 \to 0} z_1 = 0; z_2 = 1, \tag{21b}$$

which give us the exchange and direct boundary conditions, respectively, for G_1 in the high-energy limit,

$$\lim_{k_1 \to 0} G_1 = 0, \tag{22a}$$

$$\lim_{k_2 \to 0} G_1 = 1, \tag{22b}$$

and corresponding values for G_2 from Eq. (20). Rudge has demonstrated nonsymmetric forms for z_n that can reasonably be applied in the high-energy limit for direct scattering [30] or can even reproduce Ochkur's result [27]. It is also possible to derive trivial forms for G_1 and G_2 that exactly reproduce the exchange-interference phase obtained by Mott for isolated free electrons, thus showing Mott's formalism to be a special case of this model [37].

Our parametrization, however, allows us to go a step further. We already possess knowledge of the relative strengths of the two regimes in the form of their double-differential cross sections. Therefore we can meaningfully quantify our G functions, and thus the effective charge distribution, via

$$G_1 = \frac{d^2\sigma(\omega)}{d\omega\theta}\left[\frac{d^2\sigma(\omega)}{d\omega d\theta} + \frac{d^2\sigma(T' - E_F - \omega)}{d\omega d\theta}\right]^{-1}. \tag{23}$$

This not only gives us a physical constraint via the actual dielectric response of the material but also guarantees adherence to the boundary conditions [Eqs. (21) and (22)] in the high-energy limit. We can now express the cross section more generally as

$$\sigma_{\mathrm{XI}} = \int_0^{\frac{\omega_{\max}}{2}} \int_0^{\pi} \left\{ \frac{d^2\sigma(\omega)}{d\omega d\theta} + \frac{d^2\sigma(T' - E_F - \omega)}{d\omega d\theta} - \cos[\tau(k_1, k_2)] \left[\frac{d^2\sigma(\omega)}{d\omega d\theta} \frac{d^2\sigma(T' - E_F - \omega)}{d\omega d\theta} \right]^{\frac{1}{2}} \right\} d\theta d\omega, \tag{24}$$

where the double-differential terms correspond to the integrand of Eq. (13), the range of the energy integral is now halved, and the phase term becomes a cosine as the real part of a complex exponential. This generalized form allows us to incorporate a momentum- (or angle-) dependent phase term into our interference model, facilitating a far more physical account of the effects of exchange within the DDCS.

VI. RESULTS

The test case of elemental copper is utilized as it is widely studied through both experiment [3] and theory [38] and possesses a broad loss function which is likely to be sensitive to the details of the exchange model. It is instructive to consider the various components of the differential cross section $\frac{d\sigma}{d\omega}$, which are plotted in Fig. 1 for an incident electron energy of 50 eV.

Here the dotted blue curve is the "direct" scattering contribution, where the incident electron may lose up to $\omega_{\max} = (50 - E_F)$ eV but is more likely to lose something closer to the plasma energy around ∼10 eV. Integration of this curve over the whole energy range yields the total inelastic cross section, absent exchange interference. The dashed orange curve is the exchange contribution, where the final states are reversed, and the black curve is their sum. Integration of the black curve over half the range, or 0 to $\frac{\omega_{\max}}{2}$, will also yield the total inelastic cross section, absent interference, corresponding to the first two terms of the right-hand side of Eq. (6).

The final term of Eq. (6), corresponding to the interference within the direct Mott analog, is shown in green. Here we see clearly one of the most significant problems with this model. Although it correctly infers a maximum relative interference when the final-state energies are equal, it also does so whenever the direct and exchange DCS values coincide, as they do around 2 eV. At this energy, the interference term is half the sum of the direct and exchange terms, meaning that half of all possible excitations are lost even though the final states are not at all similar. This is somewhat alleviated by the transformation to a momentum-/angular-dependent model, shown in red, where interference is included at the DDCS level. This transform alone does not, however, prevent highly dissimilar states from interfering strongly.

It is only when the phase term is included, as in the solid purple curve, that the model becomes satisfactory. It then yields qualitatively correct behavior both when the fi-

nal states are similar to one another and when they more closely resemble their distinct initial states. The result is a total inelastic cross section which, at 50 eV, is reduced by around 15% due to exchange interference. If we were to use the direct Mott analog (dashed green curve), the reduction would instead be a massive 46%. Given that we are assuming no spin polarization, this is close to the maximum possible reduction of 50% which would be obtained if the final-state electrons were otherwise always in the same quantum state. Accordingly, it is clear that the current approach leads to far more physically plausible values.

The form of the exchange-interference correction is highly energy dependent for copper due to its broad loss function. Figure 2 shows the strength of the interference term relative to the total DCS for different incident electron energies between 50 and 5000 eV. We see that as the energy is increased, the primary interference peak widens to encompass almost the entire energy-transfer range.

This leads to a result which, in the high-energy limit, approaches the Mott limit that is derivable from Eq. (4) for two free electrons subject only to their Coulomb interaction. The residual difference between the correction at 5000 eV and the Mott limit comes from the complex form of the plasmon excitations, which remain relevant for transitions where one electron state finishes close to the Fermi energy. Although it may appear from Fig. 2 that the impact of exchange interference is greater at high energies, the opposite is true due to the fact that at high energies relatively few excitations occur in the central region of the plot where the final-state electrons are similar.

The absolute energy dependence of the effect is best illustrated by the variation in the electron IMFP, defined relative to the DDCS by Eq. (1). This is plotted for copper for incident electron energies up to 5000 eV relative to the Fermi energy, $E_F = 8.7$ eV, in Fig. 3.

We can see that all of the approaches converge for high energies, which is primarily due to the highly disparate values of the DCS at opposite ends of the spectrum. This means that the interference term becomes vanishingly small compared with the sum of the direct and exchange amplitudes, so we revert to the result which is commonly reported in "exchange-free" theories.

For lower energies the choice of model becomes very important. While the Mott analog gives somewhat aberrant results below around 500 eV, the Ochkur approximation appears to perform much better, despite not being symmetric mathematically or obtaining the correct behavior at the critical point where $k_1 = k_2$. The current model provides some insight into why this may occur. We predict that at sufficiently high energies, the contributions to the direct, exchange, and interference terms are all dominated by their values on the Bethe ridge where $k_1 \gg k_2$ or $k_1 \ll k_2$, regions which Ochkur approximates well without the need for a phase correction. As such, the Ochkur approximation manages to agree with the current result down to around 250 eV. At lower energies, however, the asymmetry of the Ochkur model means the exchange and interference terms become badly wrong, most obviously below 20 eV, where the IMFP is more than doubled, which is not a physically possible consequence of the interference effect.

VII. SIGNIFICANCE AND DISCUSSION

The impact of the exchange-interference model presented here is significantly weaker than previous approaches and is also far more consistent across energies up to a few hundred eV. At 5 eV it predicts an increase in the IMFP of 25%, while at 100 eV the increase is 14%. These increases will have significant consequences for the analysis of many experiments, including electron microscopy [39], low-energy electron diffraction, electron energy loss spectroscopy [40], and photoelectron spectroscopies. In particular, the introduction of exchange increases the discrepancy with IMFP measurements from x-ray absorption fine structure (XAFS) by more than two standard errors, as seen in Fig. 3 [3]. At energies above 500 eV, the calculated IMFPs remain relatively consistent with the elastic peak electron spectroscopy (EPES) measurements of Lesiak *et al.* [33].

This result presents further challenges in rectifying the low-energy scattering anomalies that have been observed in recent years via not only XAFS but various other experimental methods [41,42]. It is, however, important to address each aspect of the theory thoroughly if we are to resolve these observed discrepancies. This is especially true when we consider that some results, such as those of Emfietzoglou *et al.* [26,42], suggest that in certain cases our calculated IMFPs may, in fact, need to be increased further at low energies, rather than decreased.

Such inconsistencies are suggestive that there are still significant effects that need correcting and that they may be more or less dominant for different kinds of materials. In addition to the likelihood that there still exist some systematic and other errors hidden within the experimental data, potential theoretical issues include, but are not limited to, effective exchange-correlation potentials impacting the dielectric function [43], the vertex correction [44], and second-order corrections to Quinn's self-energy model [15]. Even within the model presented here, some error is expected at low energies in the absence of an explicit modeling of the initial bound states, an effect which will scale with the Fermi energy/momentum [45]. In particular, while the dominant impact of the interference term exists when the energy transfer is roughly half of T, the lower bound of the momentum transfer integral at that point can be evaluated as $q_- \approx \sqrt{T}(\sqrt{2}-1) \approx 0.3k_0$. So these results can be considered quantitatively robust only when T is several times larger than E_F, while at lower projectile energies the uncertainty of the initial bound-state energy is likely to introduce a decoherence effect which would lower the interference contribution.

In terms of the exchange-interference correction presented herein, it should be considered that this model likely represents an upper bound of the plausible increase to the IMFP. This is because the extent to which the standard Mott scattering picture should be applied to excitations involving quasiparticles, which in this case chiefly pertains to the prevalence of plasmon excitations, is not entirely clear. It seems, on the one hand, unwise to directly apply Pauli's exclusion to the case of a single electron interfering with a bulk excitation, even if they possess the same energy and momenta. However, it could be that some level of the effect persists depending on the plasmonic spin polarization. It is also probable that,

because this model aligns excitations that lie along the Bethe ridge, the majority of the interference we quantify is, in any event, arising from the interference of excited single-electron states. So while the current result may still be an overestimate of the effect, it is reasonable to expect that the residual errors should be relatively small.

We have thus developed an improved model for the calculation of exchange interference within the framework of a dielectric theory. The model permits a far more physical view of the scattering processes whereby the choice of direct and exchange channels is rendered inconsequential and where the interference of final-state excitations corresponds far more directly to their differences in energy and momentum. These advances should improve our quantification of the exchange-interference effect and aid the rigor of further expansions of the standard dielectric scattering theory.

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