The Magic Angle “Mystery” in Electron Energy Loss Spectra: Relativistic and Dielectric Corrections

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Recently it has been demonstrated that a careful treatment of both longitudinal and transverse matrix elements in electron energy loss spectroscopy (EELS) can explain the mystery of relativistic effects on the magic angle. Here we show that there is an additional correction of order \((Z\alpha)^2\) where \(Z\) is the atomic number and \(\alpha\) the fine structure constant, which is not necessarily small for heavy elements. Moreover, we suggest that macroscopic electrodynamic effects can give further corrections which can break the sample-independence of the magic angle.

I. INTRODUCTION

The title of this article is in reference to a recent work by Jouffrey et al with the title “The Magic Angle: A Solved Mystery.” The magic angle in electron energy loss spectroscopy (EELS) is a special value of the microscope collection-angle \(\theta_c\) at which the measured spectrum “magically” becomes independent of the angle between the incoming beam and the sample “c-axis.” The mystery, in the context of 200 keV electron microscopy, is that standard semi-relativistic quantum theory yields a ratio of the magic angle \(\theta_M\) to “characteristic angle” \(\theta_E\) of more than twice the observed value. Unfortunately, time and again the theoretical justification of the factor of two turned out to be an errant factor of two elsewhere in the calculation. A key contribution of Jouffrey et al. was the observation that relativistic “transverse” effects, when properly included in the theory, naturally give a factor of two correction to the non-relativistic magic angle. Here we show that there are yet additional corrections to the theory which can even break the sample independence of the magic angle.

As in Ref. [1], we consider here the problem of a relativistic probe electron scattering off of a macroscopic condensed matter sample. Similar problems have been solved long ago using both semi-classical and fully quantum-mechanical approaches. Indeed, the fully quantum-mechanical, relativistic case of scattering two plane-wave electrons has long been a textbook problem. This classic problem was revived recently in the works of Jouffrey et al. and of Schattschneider et al., in which a “flaw” in the standard theory is pointed out. The flaw is the approximation that the so-called “longitudinal” and “transverse” matrix elements for the scattering process may be summed incoherently, as argued by Fano in a seminal paper. In fact, this approximation is only valid when the sample under consideration possesses certain symmetries. In a later review article, Fano states this condition explicitly; namely that his original formula for the cross-section is only applicable to systems of cubic symmetry. However, this caveat, seems to have been generally ignored, and hence turns out to be the source of the magic angle “mystery.” Jouffrey et al., and later Schattschneider et al., showed that if one correctly sums and squares the transition matrix elements then, in the dipole approximation, one finds the magic angle corrected by a factor of two.

Our aim here is to examine the theory in more detail in order to derive both relativistic and material-dependent corrections to the magic angle. In Section II we consider relativistic electron scattering within the formalism of quantum electrodynamics (QED). Working the Coulomb gauge, we show that one can almost reproduce the results of Jouffrey et al. and the theory of Schattschneider et al., apart from a simple correction term of order \(\hbar\omega/mc^2\), which is not always negligible. Here \(\hbar\omega\) is the energy lost by the probe and \(mc^2\) is the rest energy of an electron. In Section III we suggest the possibility of incorporating macroscopic electrodynamic effects into the theory, which can break the symmetry of sample independence of the magic angle.

II. COULOMB GAUGE CALCULATION

An appealing aspect of the formalism of Schattschneider et al. is its simplicity. Their approach is similar to the semi-classical approach of Møller but with the added simplification of working with a probe and sample described by the Schrödinger equation, rather than the Dirac equation. They also find that the theory is simplified by choosing to work in the Lorentz gauge. Unfortunately, however, the theory of Møller is somewhat ad hoc in that a classical calculation in the Lorentz gauge is modified by replacing the product of two classical charge densities by the product of four different wavefunctions in order to obtain the transition matrix element. For the Møller case this procedure is justified a posteriori by the fact that it reproduces the correct result, but is only rigorously justified by appealing to the method of second quantization. Møller’s procedure is physically reasonable a priori, because Møller was interested in the...
scattering of electrons in vacuum. However, the theory of Schattschneider et al., which largely mimics Møller’s theory, is less physically reasonable a priori, since the electrons are not scattering in vacuum, but are inside a solid which can screen the electrons. Nevertheless, since the discrepancy is small, the Schattschneider et al., theory is justified a posteriori to a lesser extent by experiment 2. We thus refer to the theory of Schattschneider et al. as a “vacuum-relativistic theory.” Consequently, in an effort to account for the discrepancy with experiment, we feel it is useful to rederive the results of Jouffrey et al. from a more fundamental starting point.

It is easy to see that the theory of Schattschneider et al. is not formally exact, though for many materials the error in the vacuum relativistic limit is negligible. In fact, the discrepancy can be easily explained via single-particle quantum mechanics: although Schattschneider et al. work explicitly in the Lorentz gauge, they also make the assumption that the momentum and the vector potential commute,

\[ p \cdot A(r) = A(r) \cdot p. \tag{1} \]

Of course, this commutation relation is only exact in the Coulomb gauge. In the end, however, the error in this approximation only effects the final results (e.g., matrix elements) by a correction of order \( \hbar \omega / mc^2 \) compared to unity, where \( \hbar \omega \) is the energy lost by the probe. Since \( \hbar \omega / mc^2 \) is at most \((Z\alpha)^2\) for deep-core energy loss, the effect is usually negligible, except of course, for very heavy atoms. To see how corrections such as the above enter into the theory, and further to determine whether or not such corrections are meaningful or simply artifacts of the various approximations used in the theory of Schattschneider et al., we find it useful to present a fully quantum-mechanical, relativistic many-body treatment along the lines of Fano 3 but without any assumption of symmetry of the sample. Our treatment is at least as general as that of Schattschneider et al. as far as the symmetry of the sample is concerned. Thus going beyond the formulations of Schattschneider et al. and Møller, we take as our starting point the many-particle QED Hamiltonian. We then show that in a single-particle approximation the theory yields the result of Schattschneider et al. together with the correction mentioned above.

Our starting point therefore is the Hamiltonian in Coulomb gauge 2,

\[ H = H_{\text{el}} + H_{\text{int}} + H_{\text{rad}}, \tag{2} \]

where the unperturbed electron has been split into three parts: i) the unperturbed (transverse) radiation part

\[ H_{\text{rad}} = \sum_{k} \sum_{i=1}^{2} a_{k,i}^\dagger a_{k,i} \hbar \omega_k, \tag{4} \]

where \( a_{k,i} \) destroys a photon of momentum \( k \), polarization \( \epsilon_{k,i} \), and energy \( \hbar \omega_k \); and

ii) the unperturbed (transverse) radiation part

\[ H_{\text{int}} = + e \int d^3 x \psi^\dagger(x) [\alpha \cdot A(x) \psi(x), \]

\[ + \frac{e^2}{2} \int d^3 x d^3 y \frac{\psi^\dagger(x) \psi^\dagger(y) \psi(y) \psi(x)}{|x-y|}, \tag{5} \]

where

\[ A(x) = \sum_{k,i} \sqrt{\frac{2\pi \hbar c^2}{\hbar \omega_k}} \left( a_{k,i} \epsilon_{k,i} e^{ik \cdot x} + a_{k,i}^\dagger \epsilon_{k,i}^* e^{-ik \cdot x} \right), \tag{6} \]

\( e = |e| \) is the charge of the proton, and \( V \) is the system volume.

Let us next specialize to the case of a fixed number \((N+1)\) of electrons where the \((N+1)\)-th electron is singled out as the “fast probe” traveling with velocity \( v_0 \), and the remaining \( N \) electrons make up the sample. We also introduce a lattice or cluster of ion-cores (below we consider only elemental solids of atomic number \( Z \) but the generalization to more complex systems is obvious) which is treated classically, and which gives rise to a potential \( v_{\text{core}}(x) = \sum_{i=1}^{N/2} (-Ze^2)/|x-R_i| \) as seen by the electrons. In this case our Hamiltonian becomes:

\[ H = \left[ e\alpha \cdot (p + \frac{e}{c} A(r)) + \beta mc^2 \right] + v_{\text{core}}(r) \]

\[ + \sum_{i=1}^{N} \left[ e \psi^\dagger(r(i)) \left( p + \frac{e}{c} A(r(i)) \right) + \beta(r(i)) mc^2 \right] \]

\[ + \frac{e^2}{2} \sum_{i=1}^{N} \frac{1}{|r - r(i)|} + \frac{e^2}{2} \sum_{1 \leq i \neq j \leq N} \frac{1}{|r(i) - r(j)|} \]

\[ + \sum_{i=1}^{N} v_{\text{core}}(r(i)) + v_{\text{core}} + H_{\text{rad}}, \tag{7} \]

where the coordinates which are not labelled by an index refer to the probe electron. The interaction \( v_{\text{core-core}} \) between ion cores is a constant and is henceforth dropped.

To proceed to a single-particle approximation for the sample, the interaction of the sample electrons among themselves and with the potential of the ion cores may be taken into account by introducing a single-particle self-consistent potential \( v(x) \) which includes both \( v_{\text{core}}(x) \) and exchange-correlation effects. The interaction of the probe electron with the effective single electron of the sample will be considered explicitly. The difference between this interaction and the actual interaction between the probe and sample can be accounted for by introducing another potential \( v'(x) \) which is not necessarily the
same as $v(x)$; $v'(x)$ is, in theory, “closer” to the pure $v_{\text{core}}(x)$ potential than $v(x)$ though, in practice, this difference may not be of interest (see the Appendix for further explanation of this point). The potential $v'(x)$ leads to diffraction of the probe electron, which will not be considered in this paper in order to make contact with the theory of Schattschneider et al. It is also for this reason that we have introduced a single-particle picture of the sample, along with the fact that we want to apply this theory to real condensed matter systems in a practical way. The extension to the many-body case, in which the only single-body potential seen by the probe is due to the ion-cores, is given in the Appendix. Thus using the single-particle approximation for the sample,

$$
H = \left[ c \alpha \cdot \mathbf{p} + \frac{e}{c} A(r) \right] + \beta mc^2 \\
+ \left[ c \alpha_s \cdot \mathbf{p}_s + \frac{e}{c} A(r_s) \right] + \beta_s mc^2 \\
+ v'(r) + \frac{1}{|r - r_s|} + v(r_s) + H_{\text{rad}}, \tag{8}
$$

where the quantities labeled by the letter $s$ refer to the sample electron and the unlabeled quantities refer to the probe electron. In the remainder of this paper we set $v' \to 0$, though the generalization of the theory to include diffraction is not expected to be difficult.

As it turns out, we may start from an effective Schrödinger treatment of both the sample and the probe rather than a Dirac treatment. The treatment of the probe by a “relativistically corrected” Schrödinger equation is standard practice in much of EELS theory, and is appropriate for modern microscope energies of interest here (e.g., a few hundred keV). The relativistic correction to the Schrödinger equation of the probe consists in simply replacing the mass of the probe $m$ by the relativistic mass $m' = m \gamma$ where $\gamma = 1/\sqrt{1 - v^2/c^2}$. Moreover working with a Schrödinger equation treatment facilitates contact with the “vacuum-relativistic” magic-angle theory of Schattschneider et al. We will indicate later how the results change if we retain a full Dirac treatment of the electrons. Thus we may start with the Hamiltonian

$$
H = \frac{\left[ \mathbf{p} + (e/c) A(r) \right]^2}{2m'} + \frac{\left[ \mathbf{p}_s + (e/c) A(r_s) \right]^2}{2m} \\
+ v(r_s) + \frac{e^2}{|r_s - r|} + H_{\text{rad}} \\
= H_0 + \frac{e}{mc} \mathbf{p} \cdot A(r) + \frac{e}{mc} \mathbf{p}_s \cdot A(r_s) \\
+ \frac{e^2}{|r_s - r_p|} + O(A^2). \tag{9}
$$

In this theory the unperturbed states are then direct products of unperturbed sample electron states (which in calculations can be described, for example, by the computer code FEFF8) unperturbed probe electron states (plane-waves, ignoring diffraction), and the free (transverse) photon states. Also, from now on we ignore the interaction terms which are $O(A^2)$. Thus our perturbation is

$$
U = \frac{e^2}{|r - r_s|} + \frac{e}{mc} \mathbf{p} \cdot A(r) + \frac{e}{mc} \mathbf{p}_s \cdot A(r_s), \tag{10}
$$

and we are interested in matrix elements of

$$
U + U G_0 U + \ldots \tag{11}
$$

where the one-particle Green’s function is

$$
G_0(E) = \frac{1}{E - H_0 + i\eta} \tag{12}
$$

and $\eta$ is a positive infinitesimal. The matrix elements are taken between initial and final states (ordered as: probe, sample, photon)

$$
|I\rangle = |k_f\rangle |i\rangle \quad \text{and} \quad |F\rangle = |k_F\rangle |f\rangle |0\rangle. \tag{13}
$$

To lowest order ($e^2$) there will be a “longitudinal” (instantaneous Coulomb) contribution to the matrix element, and a “transverse” (photon mediated) contribution, as illustrated in Fig. 1.

Instead of elaborating the details from standard perturbation theory, we simply write down the result for the matrix element

$$
M = \frac{4\pi e^2}{V} \left[ \frac{1}{q^2} \langle f | e^{i\mathbf{q} \cdot \mathbf{r}_s} | i \rangle \\
+ \frac{1}{\omega^2 - c^2 q^2/m'} \langle f | \frac{\mathbf{p}_j^l}{m} e^{i\mathbf{q} \cdot \mathbf{r}_s} | i \rangle \right], \tag{14}
$$

where $k_T$ (see Fig. 2) is the part of the initial (or final) momentum which is perpendicular to the momentum transfer $\hbar \mathbf{q}$. In the remainder of this paper we will choose our units such that $\hbar = 1$.

$$
k_T = \left( \delta_{ij} - \frac{q_i q_j}{q^2} \right) k_F^l = \left( \delta_{ij} - \frac{q_i q_j}{q^2} \right) k_F^l. \tag{15}
$$

The result of Eq. (14) is easy to understand diagramatically. For example, to each wiggly line of momentum $\mathbf{q}$ and energy $\omega$ we may assign a value

$$
\frac{1}{\omega - c|\mathbf{q}|} \left( \delta_{ij} - \frac{q_i q_j}{q^2} \right) \frac{2\pi e}{\sqrt{|\mathbf{q}|}}. \tag{16}
$$

At this point we note that the relativistic many-body version of Eq. (14) can be obtained by making intuitively reasonable replacements such as $\mathbf{p}/m \rightarrow c \alpha x$, $e^{i\mathbf{q} \cdot \mathbf{r}_s} \rightarrow \sum_i e^{i\mathbf{q} \cdot \mathbf{r}_s^{(i)}}$. See the Appendix for further details.

Eq. (14) is equivalent to the matrix elements given by Fano in Eq. (12) of Ref. [8]. The cross-section given by Fano in Eq. (16) of Ref. [8], in which the matrix elements have been summed incoherently, is not generally correct and is the source of the magic angle “mystery” [11].
Before continuing to the dipole approximation it is useful to rewrite Eq. (14) using the definition

\[ k_T = k_I - \frac{q \cdot k_I}{q^2} \]  

(17)

to eliminate \( k_T \) in favor of \( k_I \) (or equivalently \( v_0 = \frac{k_I}{m'} \)). Making this replacement we obtain

\[
M = \frac{4\pi e^2}{V} \left[ \frac{1}{q^2} \langle f | e^{iq \cdot r} | i \rangle - \frac{q \cdot v_0}{mq^2} \frac{\langle f | q \cdot pe^{iq \cdot r} | i \rangle}{\omega^2 - c^2q^2} \right. \\
+ \frac{\langle f | v_0 \cdot (p/m)e^{iq \cdot r} | i \rangle}{\omega^2 - c^2q^2} \left. \right],
\]

(18)

which can be rewritten as:

\[
M = \frac{4\pi e^2}{V} \frac{1}{q^2 - (\omega^2/c^2)} \langle f | e^{iq \cdot r} \times \left[ 1 - \frac{v_0 \cdot p}{mc^2} - \frac{\omega^2}{q^2c^2}(1 - \frac{q \cdot p}{m\omega}) \right] | i \rangle,
\]

(19)

where we have made use of \( q \cdot v_0 = \omega \) in order to cancel certain terms which appear after commuting the exponential through to the far left. Also, we have removed the label \( s \) from the position and momentum of the sample electron. This change in notation will be used throughout the remainder of this paper.

Eq. (19) is the same as Eq. (6) of Schattschneider et al., except for an “extra” term

\[
\langle f | e^{iq \cdot r} \left( 1 - \frac{q \cdot p}{m\omega} \right) | i \rangle.
\]

(20)

Fortunately, this term may be simplified by considering the commutator

\[
[e^{iq \cdot r}, H_0] = [e^{iq \cdot r}, \frac{p^2}{2m}] = e^{iq \cdot r} \left( -\frac{p \cdot q}{m} - \frac{q^2}{2m} \right),
\]

(21)

where the first equals sign follows from the fact that \( e^{iq \cdot r} \) commutes with everything in \( H_0 \) except for the kinetic term of the sample electron (by its definition \( H_0 \) explicitly contains only local potentials). Then, using the fact that for any operator \( O \),

\[
\langle f | [O, H_0] | i \rangle = \langle f | O | i \rangle (E_i - E_f) = \langle f | O | i \rangle (-\omega)
\]

(22)

we have

\[
\langle f | e^{iq \cdot r} | i \rangle (-\omega) = \langle f | e^{iq \cdot r} \left( \frac{p \cdot q}{m} + \frac{q^2}{2m} \right) | i \rangle
\]

(23)
and thus
\[ \langle f \rangle e^{i\mathbf{q} \cdot \mathbf{r}}(1 - \frac{\mathbf{p} \cdot \mathbf{q}}{m \omega}) |i\rangle = \langle f \rangle e^{i\mathbf{q} \cdot r} \frac{q^2}{2m \omega} |i\rangle . \] (24)

Making the above replacement in Eq. (19) we find
\[ M = \frac{4\pi e^2}{V} \frac{1}{q^2 - \omega^2/c^2} \langle f \rangle e^{i\mathbf{q} \cdot \mathbf{r}} \left(1 - \frac{\mathbf{v}_0 \cdot \mathbf{p}}{mc^2} - \frac{\omega}{q^2 c^2} \frac{q^2}{2m \omega} \right) |i\rangle \]
where the above integral, with the potentials considered
and magnitude of the “extra” term.

Thus we see that the “extra” term only changes the result by order \( \omega/mc^2 \) where \( mc^2 \) is the rest energy of an electron and \( \omega \) is the energy lost;
\[ M = \frac{4\pi e^2}{V} \frac{1}{q^2 - \omega^2/c^2} \langle f \rangle e^{i\mathbf{q} \cdot \mathbf{r}} \left(1 - \frac{\mathbf{v}_0 \cdot \mathbf{p}}{mc^2} - \frac{\omega^2}{q^2 c^2} \frac{q^2}{2m \omega} \right) |i\rangle \]
and where the “extra” term only changes the result by order \( \omega/mc^2 \) where \( mc^2 \) is the rest energy of an electron and \( \omega \) is the energy lost;
\[ M = \frac{4\pi e^2}{V} \frac{1}{q^2 - \omega^2/c^2} \langle f \rangle e^{i\mathbf{q} \cdot \mathbf{r}} \left(1 - \frac{\mathbf{v}_0 \cdot \mathbf{p}}{mc^2} - \frac{\omega^2}{q^2 c^2} \frac{q^2}{2m \omega} \right) |i\rangle \]
and where the “extra” term only changes the result by order \( \omega/mc^2 \) where \( mc^2 \) is the rest energy of an electron and \( \omega \) is the energy lost;
\[ M = \frac{4\pi e^2}{V} \frac{1}{q^2 - \omega^2/c^2} \langle f \rangle e^{i\mathbf{q} \cdot \mathbf{r}} \left(1 - \frac{\mathbf{v}_0 \cdot \mathbf{p}}{mc^2} - \frac{\omega^2}{q^2 c^2} \frac{q^2}{2m \omega} \right) |i\rangle \]
and where the “extra” term only changes the result by order \( \omega/mc^2 \) where \( mc^2 \) is the rest energy of an electron and \( \omega \) is the energy lost;
\[ M = \frac{4\pi e^2}{V} \frac{1}{q^2 - \omega^2/c^2} \langle f \rangle e^{i\mathbf{q} \cdot \mathbf{r}} \left(1 - \frac{\mathbf{v}_0 \cdot \mathbf{p}}{mc^2} - \frac{\omega^2}{q^2 c^2} \frac{q^2}{2m \omega} \right) |i\rangle \]
and where the “extra” term only changes the result by order \( \omega/mc^2 \) where \( mc^2 \) is the rest energy of an electron and \( \omega \) is the energy lost;
\[ M = \frac{4\pi e^2}{V} \frac{1}{q^2 - \omega^2/c^2} \langle f \rangle e^{i\mathbf{q} \cdot \mathbf{r}} \left(1 - \frac{\mathbf{v}_0 \cdot \mathbf{p}}{mc^2} - \frac{\omega^2}{q^2 c^2} \frac{q^2}{2m \omega} \right) |i\rangle \]
and where the “extra” term only changes the result by order \( \omega/mc^2 \) where \( mc^2 \) is the rest energy of an electron and \( \omega \) is the energy lost;
\[ M = \frac{4\pi e^2}{V} \frac{1}{q^2 - \omega^2/c^2} \langle f \rangle e^{i\mathbf{q} \cdot \mathbf{r}} \left(1 - \frac{\mathbf{v}_0 \cdot \mathbf{p}}{mc^2} - \frac{\omega^2}{q^2 c^2} \frac{q^2}{2m \omega} \right) |i\rangle \]
and where the “extra” term only changes the result by order \( \omega/mc^2 \) where \( mc^2 \) is the rest energy of an electron and \( \omega \) is the energy lost;
III. MACROSCOPIC ELECTRODYNAMIC EFFECTS

As discussed above, the result of Schattschneider et al. is nearly in agreement with that obtained in Section II of this paper in the vacuum relativistic limit. However, because of the residual discrepancy between these results and experiment we now consider how macroscopic electrodynamic effects can be incorporated into the quantum mechanical single-particle formalism. We find that the corrections to the magic angle which result can be quite substantial at low energy-loss. However, we are unaware of any experimental data in this regime with which to compare the theory. Nevertheless, the inclusion of dielectric response introduces a sample dependence of the theoretical magic angle which is consistent with the sign of the observed discrepancy.

Certain condensed matter effects are already present in the existing formalism via the behavior of the initial and final single-particle states in the sample, and in many-electron effects which are neglected in the independent electron theory. However, the macroscopic response of the sample can be taken into account straightforwardly within a dielectric formalism. This procedure is similar to the well-known “matching” procedure between atomic calculations and macroscopic-dielectric calculations of the stopping power.16,17,18 That is, the fast probe may interact with many atoms at once, as long as the condition \( v_0 >> \omega_0 a \) (where \( \omega_0 \) is a typical electronic frequency and \( a \) a typical length scale) is fulfilled. Under these conditions the sample can be treated using the electrodynamics of continuous media.16

Effects due to the macroscopic response of the system can be included within a formalism that parallels that of Schattschneider et al. simply by choosing the “generalized Lorentz gauge”19 for a given dielectric function \( \epsilon(\omega) \), instead of the Lorentz gauge of the vacuum-relativistic theory. In the generalized Lorentz gauge, most of the formal manipulations of Schattschneider et al. carry through in the same way, except that instead of Eq. (19) we end up with

\[
M = \frac{4\pi \epsilon^2}{\epsilon(\omega) V} \frac{1}{q^2 - \epsilon(\omega) \omega^2/c^2} \times \langle f | e^{iq \cdot r} \left[ 1 - \frac{\epsilon(\omega) \nu_0}{mc^2} \cdot (p + q/2) \right] | i \rangle . \tag{35}
\]

The factors of \( \epsilon \) in Eq. (35) can be understood physically as due to the fact that \( c = c/\sqrt{\epsilon} \) in the medium, and also to the fact that the sample responds to the electric field \( E \) rather than the electric displacement \( D \). Eq. (35) is derived in the following subsection.

A. Generalized Lorentz Gauge calculation

We consider a probe electron which passes through a continuous medium characterized by a macroscopic frequency-dependent dielectric constant \( \epsilon(\omega) \) and magnetic permeability \( \mu = 1 \). It is appropriate to ignore the spatial dispersion of the dielectric constant at this level of approximation. Then Maxwell’s equations are

\[
\nabla \cdot D = 4\pi \rho_{\text{ext}}, \tag{36}
\]

with \( D = \epsilon E \). And

\[
\nabla \times B = \frac{4\pi j_{\text{ext}}}{c} + \frac{1}{c} \frac{\partial D}{\partial t}, \tag{37}
\]

where the charge/current densities \( \rho_{\text{ext}} \) and \( j_{\text{ext}} \) refer only to the “external” charge and current for a probe electron shooting through the material at velocity \( v_0 \). The other two Maxwell equations refer only to \( E \) and \( B \), and can be satisfied exactly using the definitions

\[
E = -\nabla \phi - \frac{1}{c} \frac{\partial A}{\partial t}, \tag{38}
\]

and

\[
B = \nabla \times A . \tag{39}
\]

We next insert Eqs. (38) and (39) into Eqs. (36) and (37) and choose the generalized Lorentz gauge19

\[
\nabla \cdot A + \frac{1}{c} \frac{\partial}{\partial t} \int dt' \epsilon(t-t')\phi(t') = 0 . \tag{40}
\]

This gauge choice leads to the momentum space (\( q, \omega \)) equations

\[
-q^2 + \epsilon(\omega) \frac{\omega^2}{c^2} \phi(q, \omega) = 4\pi \frac{\rho_{\text{ext}}(q, \omega)}{\epsilon(\omega)}, \tag{41}
\]

and

\[
-q^2 + \epsilon(\omega) \frac{\omega^2}{c^2} A(q, \omega) = 4\pi \frac{j_{\text{ext}}(q, \omega)}{c} . \tag{42}
\]

We now write \( \rho_{\text{ext}}(q, \omega) = -(2\pi \epsilon) \delta(\omega - q \cdot v_0) \) and \( j_{\text{ext}} = v_0 \rho_{\text{ext}} \) to find explicit expressions for \( \phi \) and \( A \):

\[
\epsilon(\omega) \phi(q, \omega) = \frac{4\pi (-2\pi \epsilon) \delta(\omega - q \cdot v_0)}{[\epsilon(\omega) \omega^2/c^2] - q^2}, \tag{43}
\]

and

\[
A(q, \omega) = \frac{v_0}{c} \epsilon(\omega) \phi(q, \omega) . \tag{44}
\]

Then, proceeding roughly in analogy with Schattschneider et al., we have

\[
H = H_0 + \frac{\epsilon}{2mc} (p \cdot A + A \cdot p) - e\phi + O(A^2)
\]

\[
= H_0 + \frac{\epsilon}{2mc} (2A \cdot p - i\nabla \cdot A) - e\phi + O(A^2) . \tag{45}
\]

Next, evaluating the perturbation \( U \equiv H - H_0 \) with \( A = (v_0/c)\epsilon(\omega)\phi \), we find

\[
U = \frac{\epsilon}{mc} \left( \phi \frac{\epsilon(\omega) v_0 \cdot p - i\frac{v_0}{2c} \nabla \phi}{c} \right) - e\phi . \tag{46}
\]
In calculating the matrix element of $U$ it is appropriate to replace $\nabla \phi$ by $i q \phi$ for the case when the final states are on the left in the matrix element. Thus

$$M \equiv \langle f \mid k_f \rangle U \mid k_i \rangle = -e \phi(q, \omega) \times \langle f \mid e^{i q \cdot r} \left[ 1 - \frac{\epsilon(\omega)}{mc^2} \vec{v}_0 \cdot (\vec{p} + q/2) \right] \mid i \rangle . \quad (47)$$

Alternatively, since

$$\phi(q, \omega) = \frac{-4\pi e}{\epsilon(\omega) (q^2 - \omega^2 \epsilon(\omega)/c)} , \quad (48)$$

we have

$$M = \frac{4\pi e^2}{\epsilon(\omega)(q^2 - \epsilon(\omega)\omega^2/c^2)} \langle f \mid e^{i q \cdot r} \times \left[ 1 - \frac{\epsilon(\omega)}{mc^2} \vec{v}_0 \cdot (\vec{p} + q/2) \right] \mid i \rangle . \quad (49)$$

In the dipole approximation Eq. (49) reduces to

$$\frac{4\pi e^2}{\epsilon(\omega) \bar{V} q^2 - \epsilon(\omega)\omega^2/c^2} \langle f \mid \left[ q - \epsilon(\omega) \frac{\vec{v}_0 \cdot (\vec{v} \cdot \vec{v})}{c^2} \right] \cdot \vec{r} \mid i \rangle , \quad (50)$$

where $\epsilon(\omega)$ is the generally complex valued macroscopic dielectric constant as which can be calculated, for example, by the FEFFOP code. Consequently we find that instead of the longitudinal $q$-vector replacement

$$q_z \rightarrow q_z (1 - \beta^2) \quad (51)$$

found by Jouffrey et al. and Schattschneider et al., we obtain the replacement

$$q_z \rightarrow q_z [1 - \epsilon(\omega) \beta^2], \quad (52)$$

which is appropriate for an electron traversing a continuous dielectric medium. In the same way that Eq. (52) can be understood classically as being due to a charge in uniform motion in vacuum Eq. (52) can be understood as due to a charge is in uniform motion in a medium. Because the motion is uniform, the time dependence can be eliminated in favor of a spacial derivative opposite to the direction of motion and multiplied by the speed of the particle. For motion in the $z$-direction

$$\frac{\partial}{\partial t} \rightarrow -v_0 \frac{\partial}{\partial z} \quad (53)$$

Therefore, if we consider the electric field

$$\vec{E} = -\nabla \phi - \frac{\partial \vec{A}}{c \partial t} \rightarrow -\nabla \phi + \frac{v_0}{c} \frac{\partial \vec{A}}{\partial z} . \quad (54)$$

Eq. (51) follows from the substitution $A_z = (v_0/c) \phi$, whereas Eq. (52) follows by making the correct substitution in the presence of a medium

$$A_z = \frac{v_0}{c} \epsilon \phi , \quad (55)$$

which in Fourier space gives

$$\vec{E}(q, \omega) = \left[ -i q + \frac{\epsilon(\omega) \vec{v}_0^2}{c^2} q_z \right] \phi(q, \omega) , \quad (56)$$

which is equivalent to Eq. (52).

Because Eq. (52) depends on the macroscopic dielectric function the ratio $\theta_M/\theta_E$, which formerly was a function only of $v_0$, will now show material dependence. This is seen from the generalization of Eqs. (55) and (54), the equality of which gives the magic angle. Instead of Eq. (53) for $F(\alpha_c)$ we now have

$$F(\alpha_c) \equiv \int_0^{\alpha_c} d\theta \theta \frac{1}{\theta^2 + \theta^2_E} , \quad (57)$$

and, instead of Eq. (54) we now have

$$G(\alpha_c) \equiv 2\theta^2_E |g|^2 \int_0^{\alpha_c} d\theta \frac{1}{\theta^2 + \theta^2_E} , \quad (58)$$

where

$$g = 1 - \epsilon(\omega) \nu_0^2/c^2 \quad (59)$$

is a complex number which replaces $1/\gamma^2$ in the vacuum relativistic theory.

If one can calculate the macroscopic dielectric function of the sample by some means the then material dependent magic angle can be determined theoretically and compared to experiment. Furthermore, the correction to the magic angle given by the introduction of the macroscopic dielectric constant relative to the relativistic macroscopic “vacuum value” of Jouffrey et al. is seen to be typically positive (since Re$[\epsilon]$ ∼ 1 and 0 ≤ Im$[\epsilon]$), in rough agreement with observation. In fact, it turns out that the correction is always positive for the materials we consider and is substantial only for low energy-loss where the dielectric function differs substantially from its vacuum value. For modern EELS experiments which use relativistic microscope energies and examine low energy-loss regions, the effect of the dielectric correction on the magic angle should be large.

Example calculations using our relativistic dielectric theory compared to both the relativistic vacuum theory of Schattschneider et al. and to the non-relativistic vacuum theory are shown in Fig. 1 for the materials boron nitride and graphite. The data of Daniels et al. is also shown in the figures. We have not attempted to estimate the true error bars for the data; the error bars in the figure indicate only the error resulting from the unspecified finite convergence angle.

**IV. CONCLUSIONS**

We have developed a fully relativistic theory of the magic angle in electron energy loss spectra starting from the QED Hamiltonian of the many body system. As
FIG. 3: The magic angle to characteristic angle ratio $\theta_M/\theta_E$ is compared for three differing theories and one experiment. The materials considered in the figure are boron nitride (top figure) and graphite (bottom). The microscope voltage is fixed at 195 keV. Both the non-relativistic and relativistic vacuum theories show no dependence on the energy-loss and no dependence on the material. The relativistic dielectric theory shows that the magic angle should deviate from the vacuum value by a significant amount in regions where the macroscopic dielectric response is substantial.

Several other factors may be important for correctly describing the energy loss dependence of the magic angle in anisotropic materials. In particular, we believe that further study of the many body effects (beyond a simple macroscopic dielectric model) via explicit calculations of the microscopic dielectric function and including time-dependant density functional/Bethe-Salpeter theory TDDFT/BSE are an important next step in the description of all EELS phenomena, including the magic angle.

V. ACKNOWLEDGMENTS

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between eigenstates of the unperturbed Hamiltonian. We are interested in matrix elements of the perturbation \( M \) on the sample Hamiltonian which includes not only the single-particle (the e-core) potential but also the Coulomb interactions between all the sample electrons. Consequently, working with a unit volume and proceeding exactly as in the single-particle case, we find a “longitudinal” contribution to the matrix element
\[
M_L = \frac{4\pi e^2}{q^2} u^\dagger(k_f) u(k_i) \langle \Psi_f \mid \sum_{i=1}^N e^{i\mathbf{q} \cdot \mathbf{r}_i} \mid \Psi_i \rangle, \tag{A.5}
\]
and a “transverse” contribution
\[
M_T = \frac{4\pi e^2}{\omega^2/c^2 - q^2} u^\dagger(k_f) \alpha_T u(k_i) \langle \Psi_f \mid \sum_{i=1}^N \alpha^{(i)} e^{i\mathbf{q} \cdot \mathbf{r}_i} \mid \Psi_i \rangle, \tag{A.6}
\]
where
\[
\alpha_T = \alpha - q \cdot \alpha \frac{q^2}{q^2} , \tag{A.7}
\]
and where the \( u(p) \) are the usual free-particle Dirac spinors, normalized such that
\[
u^\dagger(p) u(p) = 1. \tag{A.8}
\]

The two matrix elements \( M_L \) and \( M_T \) are to be summed and then squared, but before proceeding with this plan we make the following useful definitions: The transverse Kronecker delta function (transverse to momentum-transfer)
\[
\delta_T^{ij} = \delta^{ij} - \frac{q^i q^j}{q^2}; \tag{A.9}
\]
the (Fourier transformed) density operator
\[
n(q) = \sum_{i=1}^N e^{-i\mathbf{q} \cdot \mathbf{r}^{(i)}}; \tag{A.10}
\]
and the (Fourier transformed) current operator
\[
j(q) = \sum_{i=1}^N c \alpha^{(i)} e^{-i\mathbf{q} \cdot \mathbf{r}^{(i)}}. \tag{A.11}
\]

Next, we recall some properties of the Dirac spinors \( u(p) \) and of Dirac matrices which we will presently find useful: i) There are four independent spinors \( \{ u^{(1)}, u^{(2)}, u^{(3)}, u^{(4)} \} \), the first two of which will refer to positive energy solutions, and the second two of which will refer to negative energy solutions (and are not used in this calculation); ii) the positive energy spinors satisfy a “spin sum”
\[
\sum_{s=1}^2 u^{(s)}(p) u^{(s)\dagger}(p) = \frac{1}{2E(p)} \left(E(p) + c \alpha \cdot p + \beta mc^2\right) \tag{A.12}
\]
where \( E(p) = \sqrt{p^2 c^2 + m^2 c^4} \); iii) the Dirac matrices satisfy the trace identities
\[
\text{Tr}(\alpha_i \alpha_j) = 4 \delta_{ij} , \tag{A.13}
\]
\[
\text{Tr}(\alpha_i \alpha_j \beta \alpha_k) = 4 \left( \delta_{ij} \delta_{kl} - \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk} \right) , \tag{A.14}
\]
\[
\text{Tr}(\alpha^\dagger_i \alpha^\dagger_j \alpha_i \alpha_j) = 4 \delta_T^{ij} , \tag{A.15}
\]
\[
\text{Tr}(\alpha^\dagger_i \alpha^\dagger_j \alpha^k \alpha^l) = 4 \left( \delta_T^{ij} \delta^{kl} - \delta_T^{ik} \delta_T^{jl} + \delta_T^{il} \delta_T^{jk} \right) . \tag{A.16}
\]

iv) Finally, we note that in this calculation there are many simplifications due to the fact that \( \omega << mc^2 < E(k_i) \approx E(k_F) \). For example,
\[
\frac{1}{2E_i E_j} \left(E_i E_j + m^2 c^4 + c^2 \mathbf{k}_i \cdot \mathbf{k}_j\right) = \frac{1}{2} \left[ \frac{\omega^2}{E(k_i)} + O\left(\frac{\omega^4}{E(k_i)^2}\right) \right] \approx 1; \tag{A.17}
\]

APPENDIX: RELATIVISTIC EFFECTS

Starting from Eq. (7) we write (the notation \( H_0 \) in the Appendix differs from that in the main body of the text):
\[
H_0 = c \alpha \cdot \mathbf{p} + \beta mc^2 + \nu_{\text{e-core}}(\mathbf{r}) + \sum_{i=1}^N \left[ c \alpha^{(i)} \cdot \mathbf{p}^{(i)} + \beta^{(i)} mc^2 + \nu_{\text{e-core}}(\mathbf{r}^{(i)}) \right] + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \frac{e^2}{|\mathbf{r}^{(i)} - \mathbf{r}^{(j)}|^2} + H_{\text{rad}}, \tag{A.1}
\]
and
\[
U = c \alpha \cdot \mathbf{A}(\mathbf{r}) + \sum_{i=1}^N \frac{e^2}{|\mathbf{r} - \mathbf{r}^{(i)}|^2} + \sum_{i=1}^N c \alpha^{(i)} \cdot \mathbf{A}(\mathbf{r}^{(i)}). \tag{A.2}
\]
We are interested in matrix elements of the perturbation
\[
U + U G_0 U + \ldots \tag{A.3}
\]
between eigenstates of the unperturbed Hamiltonian
\[
|I\rangle = |k_i\rangle \langle \Psi_i| 0\rangle \quad \text{and} \quad |F\rangle = |k_f\rangle \langle \Psi_f| 0\rangle. \tag{A.4}
\]
The difference between the many-body case and the single-particle theory of the sample is that the wavefunction of the sample now depends on \( N \) electron coordinates, instead of one effective coordinate. Also we see that the only potential “seen” by the probe (i.e., included in the unperturbed probe Hamiltonian) is the \( \nu_{\text{e-core}} \) potential. This is to be contrasted with the “perturbed” sample Hamiltonian which includes not only the \( \nu_{\text{e-core}} \) but also the Coulomb interactions between all the sample electrons.

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throughout the calculation we ignore terms of order $\omega/E(p_I)$ Using these identities it is easy to see that

$$\frac{1}{2} \sum_{s_i = 1}^{2} \sum_{s_f = 1}^{2} |M_{L_T}|^2 = \left( \frac{4\pi e^2}{q^2} \right)^2 \frac{1}{q^2(\omega^2/c^2 - q^2)} \frac{}{b}$$

which has the same form as in the non-relativistic case (up to order $\omega/E_i$); the squared matrix element is much simplified by the sum over probe-spins and average over initial probe-spin. Of course, the matrix element itself is completely general in terms of probe-spin, but many simplification arise from ignoring the probe-spin and exploiting the spin-sums.

Continuing on to the transverse matrix element—and including a few more of the details ($a$, $b$, $c$, and $d$ are Dirac indices)—we find

$$\frac{1}{2} \sum_{s_i = 1}^{2} \sum_{s_f = 1}^{2} |M_{T}|^2 = \left( \frac{4\pi e^2}{\omega^2/c^2 - q^2} \right)^2 \times u(k_f)_a^{(s_f)} \alpha_T^{mb} u(k_i)_b^{(s_i)} u(k_i)_c^{(s_i)} \alpha_T^{cd} u(k_f)_d^{(s_f)} \times \langle \Psi_F | j_m(q) | \Psi_I \rangle \langle \Psi_I | j_n(q) | \Psi_F \rangle$$

$$= \left( \frac{4\pi e^2}{\omega^2/c^2 - q^2} \right)^2 \langle \Psi_F | j_m(q) | \Psi_I \rangle \langle \Psi_I | j_n(q) | \Psi_F \rangle \times \text{Tr} \left( (E(k_f) + h_D(k_f)) \alpha_T^{mp} (E(k_i) + h_D(k_i)) \alpha_T^{np} \right)$$

$$= \left( \frac{4\pi e^2}{\omega^2/c^2 - q^2} \right)^2 \langle \Psi_I | \nu_T \cdot j(q) | \Psi_F \rangle ^2.$$

For the cross term we find

$$\frac{1}{2} \sum_{s_i = 1}^{2} \sum_{s_f = 1}^{2} M_L M_T = \left( \frac{4\pi e^2}{q^2(\omega^2/c^2 - q^2)} \right) \times \langle \Psi_F | n^1(q) | \Psi_I \rangle \langle \Psi_I | j(q) \cdot \nu_T | \Psi_F \rangle.$$  

Thus we have finally derived an expression for the relativistic many-body summed-then-squared matrix elements summed and averaged over spins,

$$\frac{1}{2} \sum_{s_i} \sum_{s_f} |M_L + M_T|^2 = \left( \frac{4\pi e^2}{V} \right)^2$$

$$\times \frac{\langle \Psi_I | n(q) | \Psi_F \rangle}{q^2} + \frac{\langle \Psi_I | \nu_T \cdot j(q) | \Psi_F \rangle}{\omega^2 - q^2 c^2}$$

$$= \left[ \frac{4\pi e^2}{V(\omega^2/c^2 - q^2)} \right]^2 \langle \Psi_I | n(q) - \frac{v_0 \cdot j(q)}{c^2} | \Psi_F \rangle.$$  

The last equality follows from

$$q \cdot \langle \Psi_I | j(q) | \Psi_F \rangle = \omega \langle \Psi_I | n(q) | \Psi_F \rangle,$$  

which itself follows by considering the commutator analogous to that of Eq. (21).

The final line of Eq. (A.20) is quite pleasing since we have found that if we can “ignore” the spin of the probe particle, we may as well have started by taking matrix elements between electronic states only of the much simpler interaction Hamiltonian

$$U' = \int d^3x \left[ n(x) \phi_\omega(x - x_p) - \frac{j(q) \cdot A_\omega(x - x_p)}{c^2} \right],$$  

where the fields $\{ \phi_\omega, A_\omega \}$ are just the $e^{-i\omega t}$ components of the classical field of a point charge of velocity $v_0$ in the Lorentz gauge, and where

$$n(x) = \sum_i^N \delta(x - x^{(i)}),$$  

and

$$j(x) = \sum_i^N c \alpha^{(i)} \delta(x - x^{(i)}).$$  

That is, if we take Eq. (A.22) as our starting point and proceed in the usual way, we will find that our squared matrix elements are exactly the same as what we know to be correct from Eq. (A.21). The photons have dropped out entirely!