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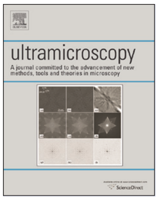

The role of symmetry in the theory of inelastic high-energy electron scattering and its application to atomic-resolution core-loss imaging

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ABSTRACT

The inelastic scattering of a high-energy electron in a solid constitutes a bipartite quantum system with an intrinsically large number of excitations, posing a considerable challenge for theorists. It is demonstrated how and why the utilization of symmetries, or approximate symmetries, can lead to significant improvements in both the description of the scattering physics and the efficiency of numerical computations. These ideas are explored thoroughly for the case of core-loss excitations, where it is shown that the coupled angular momentum basis leads to dramatic improvements over the bases employed in previous work. The resulting gains in efficiency are demonstrated explicitly for *K*-, *L*- and *M*-shell excitations, including such excitations in the context of atomic-resolution imaging in the scanning transmission electron microscope. The utilization of other symmetries is also discussed.

1. Introduction

Notwithstanding the fact that electron scattering calculations greatly facilitate technique development and data interpretation in transmission electron microscopy (TEM), such calculations can, in some cases, require computation times so long that the benefits become outweighed by the time that must be invested. This is particularly the case for techniques that specifically utilize inelastic scattering, where calculations lasting hours, days, or even weeks are not uncommon. The long computation times for inelastic scattering are the result of the large number of outgoing scattering channels that must be considered, which in turn corresponds to the many possible excitations of a typical TEM sample.

In the case of core-level excitations, which form the foundation of unambiguous chemical analysis techniques in the TEM, the number of outgoing channels is dictated firstly by the number of atoms of the species of interest, and secondly by the number of excited states of each such atom that must be considered. Even for the thin samples studied in the TEM, the number of atoms can easily exceed several thousand, and while the number of excited states per atom is dependent on many parameters, it is typically between 4 and 10 for any given energy loss within about 50 eV of a core-level excitation threshold. Hence many thousands of outgoing channels is not uncommon, and in some cases this number reaches into the millions. When an attempt is made to include dynamical elastic scattering in the calculation, as is often required for accuracy, the mutual incoherence of the outgoing channels must be maintained, which essentially implies a separate elastic scattering calculation for each outgoing channel – a challenging and time-consuming task. This is exacerbated in the case of scanning TEM (STEM), where the calculations must, in some way, be performed for each position of the STEM probe. Hence maximizing the efficiency of such calculations is highly desirable, since this not only relieves some of the burden of long computations, but also has practical benefit of enabling faster feedback on experiments.

The subject of theoretical and computational efficiency in electron-induced core-level excitations has some history in the field of TEM. The theory of atomic inner-shell excitations by high-energy charged particles goes back to Bethe [1]. Notable early works, specifically in the context of TEM, are those of Kainuma [2] and Yoshioka [3], who laid the groundwork by formulating a general and detailed theory of inelastic high-energy electron diffraction, and Humphreys and Whelan [4], who specifically considered single-electron excitations in the context of dynamical scattering. The first works that correctly considered the relevant phases of the inelastic partial waves from inner-shell ionization were those of Maslen and Rossouw [5,6] and Rossouw and Maslen [7]. Those authors used a hydrogenic model for the atomic states and employed a description whereby the final states are labeled by the ejected atomic electron's asymptotic linear momentum κ. Rossouw and Maslen [7] used their theory to great effect in

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calculating oxygen and magnesium *K*-loss diffraction patterns of MgO. However, it was subsequently pointed out by Saldin and Rez [8] that, for electron energy-loss spectroscopy (EELS), κ "is not a good quantum number", and the latter authors advocated that the excited states should be described in terms of the ejected electron's angular momentum, "as is appropriate for an atom." Later it was shown by Weickenmeier and Kohl [9] that the efficiency of Saldin and Rez's treatment of dynamical scattering could also be further improved. It should also be pointed out that if the ejected atomic electron is observed, as in (e, $2e$) experiments, then κ is actually a good quantum number.

The relatively recent ability to perform core-level EELS at atomic spatial resolution has sparked a resurgence in theoretical considerations. Especially notable in this regard is the early work of Kohl and Rose [10], who pioneered the consideration of atomic-resolution core-loss images in TEM and STEM approximately two decades before it was experimentally feasible. Another notable work on the spatial resolution of inelastic scattering in STEM is that of Muller and Silcox [11]. Later theoretical works on atomic-resolution core-loss STEM also incorporated the dynamical elastic scattering, which, as mentioned above, turns out to be important for accurate results. In this regard, the description of Rossouw and Maslen was utilized and extended by Oxley et al. [12,13], while the description of Saldin and Rez was implemented as a multislice theory and generalized to include relativistic effects by Dwyer et al. [14–16]. The latter approach has also been adopted by Allen and coworkers [17–19]. The effects of dynamical elastic scattering are also important in the context of atomic-resolution energy-filtered TEM, as considered explicitly by Verbeeck et al. [20] and others [18,21,22].

Returning to the question of efficiency, the statements of Saldin and Rez reproduced above are particularly relevant to the present work. However, their statements do not tell the full story. As demonstrated below, it is actually most appropriate to describe the excited atomic states in terms of the *coupled* angular momentum of the ejected electron and the inner-shell hole, since such a description makes full use of the available symmetry. As it turns out, the mathematical manipulations used by Saldin and Rez [8], which followed the earlier work of Manson [23], yielded a simplified expression for the mixed-dynamic form factor (MDFF) that is actually identical to that obtained using the coupled angular momentum basis. However, the reason for the simplification, namely full use of the atom's symmetry, was not pointed out explicitly by any of those authors.

In the present work, we consider the theoretical and computational efficiency of inelastic high-energy electron scattering. We demonstrate explicitly how the use of symmetry leads to simplification of the theory, which ultimately leads to greater efficiency in computation. These considerations are applied to the case of atomic-resolution core-loss imaging, where the relevant symmetries are those of the atom being excited. We also describe how other symmetries can be incorporated, such as those relevant to the explicit consideration of core-loss scattering as a function of energy loss, as well as the symmetry relevant to the solid-state effects that give rise to a core-loss near-edge structure. We show how the resulting gains in efficiency can be quantified in terms of the degree of entanglement. In so doing, we outline a general principle regarding the use of symmetry, entanglement and information in inelastic high-energy electron scattering.

2. General theory

We first briefly review the theory used for calculations that incorporate both inelastic scattering and dynamical elastic scattering of high-energy electrons.

For definiteness, we consider the case of a thin solid illuminated by a beam of high-energy electrons, as in EELS in the TEM/STEM. The sample and the high-energy electron can be viewed as a bipartite quantum system. This system is assumed to be isolated from the rest of the world so that it has a definite energy. (While this precludes thermal fluctuations of the sample and therefore a correct description of thermal diffuse scattering at non-zero temperature, such scattering can be re-introduced at a later stage using a frozen phonon algorithm, for example.) Since the system has a definite energy E, its wave function satisfies a time-independent Schrödinger equation

$$\left(H_S + \frac{\hat{p}^2}{2m} + V\right)\Psi = E\Psi, \tag{1}$$

where H_S is the hamiltonian for the sample only, $\hat{p}^2/2m$ represents the high-energy electron's kinetic energy, and V represents the electron–sample interaction. Without approximation, we can write the system's wave function Ψ as a sum of products of sample wave functions and electron wave functions [24]

$$\Psi(x_1, x_2, \dots; x_e) = \sum_\alpha \phi_\alpha(x_1, x_2, \dots)\psi_\alpha(x_e). \tag{2}$$

Here the ϕ_α's are energy eigenstates of the sample

$$H_S\phi_\alpha = E_\alpha\phi_\alpha, \tag{3}$$

and the single index α is used to denote the set of quantum numbers needed to label the sample states.

The ψ_α's in Eq. (2) are *partial electron waves*, one for each state of the sample. For simplicity, the sample is assumed to be initially in its ground state, labeled by $\alpha = 0$, so that ψ_0 is referred to as the *elastic wave*. Inelastic scattering leaves the sample in an excited state $\alpha \neq 0$, so that $\psi_{\alpha\neq0}$ is an *inelastic wave*.

In EELS, the quantity of interest is the flux of outgoing electrons that have lost a certain amount of energy by exciting a specific set of states of the sample. Hence this flux can be regarded as being composed of the partial electron waves corresponding to the specific set of excited states. Assuming that the sample states ϕ_α are orthonormal (and, in fact, they can essentially always be chosen to be so), and assuming that we do not observe the particles in the sample directly (which is essentially always the case in TEM), it can be shown that the partial waves ψ_α are mutually incoherent [25], that is, they do not exhibit quantum interference with one another and they therefore represent mutually exclusive outcomes of the experiment. In the present example of core-loss EELS, the excited states correspond to the excitation of the inner-shell of a particular atomic species. For a given atom, there are mutually incoherent partial waves associated with each of the relevant excited states of that atom. To good approximation, we can regard as mutually incoherent the partial waves that arise from the excitation of different atoms (this point is discussed by Maslen [26] and supported by the agreement between theory and experiment obtained by Xin et al. [27] and Zhu and Dwyer [28]).

Adopting a paraxial approximation to Yoshioka's equations [3] for elastic and inelastic scattering of high-energy electrons, and assuming that the single inelastic scattering approximation holds (which it typically does for core-level excitations in the TEM because the sample is usually much thinner than the relevant mean-free path), a partial wave at the exit surface of a sample of