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A pure state decomposition approach of the mixed dynamic form factor for mapping atomic orbitals

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ABSTRACT

We demonstrate how the mixed dynamic form factor (MDFF) can be interpreted as a quadratic form. This makes it possible to use matrix diagonalization methods to reduce the number of terms that need to be taken into account when calculating the inelastic scattering of electrons in a crystal. It also leads in a natural way to a new basis that helps elucidate the underlying physics. The new method is applied to several cases to show its versatility. In particular, predictions are made for directly imaging atomic orbitals in crystals.

1. Introduction

Nowadays, simulations are indispensable both for planning and for interpreting experiments in the transmission electron microscope (TEM), in particular when working with electron energy loss spectrometry (EELS). The key quantity for simulating inelastic electron scattering is the mixed dynamic form factor (MDFF) [1–4]. In many cases, this complex quantity is simplified by several approximations, like, for instance, the dipole approximation. Recently, it has been shown, however, that this can lead to quite severe errors [5]. Furthermore, with recent advances of aberration corrected microscopes, more accurate calculations of the MDFF will become essential for future experiments.

In this work, we will give a brief repetition of the mixed dynamic form factor. It has been well known for a long time that in dipole approximation, the MDFF can be written in the form $a\boldsymbol{q}\cdot\boldsymbol{q}'$ ($+\boldsymbol{q}\times\boldsymbol{q}'$ in the case of magnetism; see, e.g., [6,7]). Our work goes beyond this approximation by showing that all multipole orders can be written as a quadratic form. This is followed by an analysis of how a basis transformation can bring it into a simpler, diagonal form that is much easier to handle numerically. Furthermore, the physical significance of this procedure will be outlined. The general concept of factorizing and diagonalizing density matrices (i.e., writing the corresponding density operator as an incoherent sum of pure states) is well known [8,9] and is also applied in other fields (e.g., [10]). However, to the best of our knowledge, it was not yet applied in the way presented here to simplify the MDFF.

In the last part, the new formalism will be applied to both existing and new measurement setups to study its applicability and versatility.

2. The mixed dynamic form factor and its pure state decomposition

In the most general approach, the quantum mechanical system consisting of both the probe electron and the sample can best be described by a density operator $\hat{\rho}$ or its matrix elements, the so-called density matrix ρ [8]. Adopting the density matrix formalism instead of the simpler wave function approach is greatly beneficial as one cannot observe the target's final state directly. This ignorance of a part of the system after an inelastic interaction gives rise to a mixed state which can be described very effectively using the density matrix [3,4,8].

Before the interaction, the probe and the target systems can be considered independent. For the sake of simplicity, we will furthermore assume that both systems are initially in a pure state, i.e., each can be described by a single wave function. Then, the density operator of the whole system before the interaction is given by

$$\hat{\rho}_{\mathrm{tot},0} = |i\rangle\langle i|\otimes|I\rangle\langle I| = |I\rangle|i\rangle\langle i|\langle I|, \tag{1}$$

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where $\otimes$ denotes the direct product. Throughout this paper, we use small letters when referring to the probe beam and capital letters when referring to the target.

In first order Born approximation, the density operator after the inelastic interaction mediated by an interaction potential $\hat{V}$ is given by

$$\hat{\rho}_{\mathrm{tot}} = \hat{V}|I\rangle|i\rangle\langle i|\langle I|\hat{V}^{\dagger}\delta(E+E_I-E_F), \tag{2}$$

where E is the "energy loss" of the probe beam (i.e., the energy transferred from the probe beam to the target electron), and E_I, E_F are the initial and final state energies of the target. Since the target system is not observed directly, one has to construct the reduced density operator for the probe beam by summing incoherently over all possible final states of the target. This reduced density operator is given by

$$\hat{\rho} = \sum_F \langle F|\hat{V}|I\rangle|i\rangle\langle i|\langle I|\hat{V}^{\dagger}|F\rangle\delta(E+E_I-E_F), \tag{3}$$

which can then be propagated elastically through the crystal and be used to predict the outcome of measurements in different geometries. It must be emphasized that the ordering of the terms is vital here, since $\hat{V}$ in general acts on both the probe and the target states, which results in an entanglement of the two.

In EELS experiments, the interaction operator $\hat{V}$ is the Coulomb interaction operator. Its two most common basis representations are in configuration space,

$$\begin{aligned}\hat{V}(\boldsymbol{r},\boldsymbol{r}') &= \langle \boldsymbol{r}|\hat{V}|\boldsymbol{r}'\rangle = \frac{e^2}{4\pi\epsilon_0}\frac{\delta(\hat{\boldsymbol{R}}-\hat{\boldsymbol{R}}')}{|\boldsymbol{r}-\hat{\boldsymbol{R}}|}\delta(\boldsymbol{r}-\boldsymbol{r}')\\ &=:\hat{V}(\boldsymbol{r})\delta(\boldsymbol{r}-\boldsymbol{r}'),\end{aligned} \tag{4}$$

and in reciprocal space,

$$\begin{aligned}\hat{V}(\boldsymbol{k},\boldsymbol{k}') &= \langle \boldsymbol{k}|\hat{V}|\boldsymbol{k}'\rangle = \frac{e^2}{4\pi\epsilon_0}\frac{\mathrm{e}^{\mathrm{i}(\boldsymbol{k}'-\boldsymbol{k})\cdot\hat{\boldsymbol{R}}}}{|\boldsymbol{k}'-\boldsymbol{k}|^2}\delta(\hat{\boldsymbol{R}}-\hat{\boldsymbol{R}}')\\ &=:\frac{e^2}{4\pi\epsilon_0}\frac{\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\hat{\boldsymbol{R}}}}{|\boldsymbol{q}|^2}\delta(\hat{\boldsymbol{R}}-\hat{\boldsymbol{R}}')\\ &=:\hat{V}(\boldsymbol{q}).\end{aligned} \tag{5}$$

Here, e is the elementary charge and ϵ_0 is the permittivity of vacuum.

In these two representations, the reduced density matrix reads

$$\begin{aligned}\boldsymbol{\rho}(\boldsymbol{r},\boldsymbol{r}') &= -4\pi^2\sum_F\int \mathrm{d}\tilde{\boldsymbol{r}}\langle F|\langle \boldsymbol{r}|\hat{V}|\tilde{\boldsymbol{r}}\rangle|I\rangle\langle\tilde{\boldsymbol{r}}|i\rangle\\ &\quad\int \mathrm{d}\tilde{\boldsymbol{r}}'\langle i|\tilde{\boldsymbol{r}}'\rangle\langle I|\langle\tilde{\boldsymbol{r}}'|\hat{V}^{\dagger}|\boldsymbol{r}'\rangle|F\rangle\delta(E+E_I-E_F)\\ &= -4\pi^2\sum_F\langle F|\hat{V}(\boldsymbol{r})|I\rangle\langle I|\hat{V}^{\dagger}(\boldsymbol{r}')|F\rangle\\ &\quad\langle\boldsymbol{r}|i\rangle\langle i|\boldsymbol{r}'\rangle\delta(E+E_I-E_F)\\ &= S(\boldsymbol{r},\boldsymbol{r}')\langle\boldsymbol{r}|i\rangle\langle i|\boldsymbol{r}'\rangle\end{aligned}$$

$$\begin{aligned}\boldsymbol{\rho}(\boldsymbol{k},\boldsymbol{k}') &= -4\pi^2\sum_F\int \mathrm{d}\tilde{\boldsymbol{k}}\langle F|\langle \boldsymbol{k}|\hat{V}|\tilde{\boldsymbol{k}}\rangle|I\rangle\langle\tilde{\boldsymbol{k}}|i\rangle\\ &\quad\int \mathrm{d}\tilde{\boldsymbol{k}}'\langle i|\tilde{\boldsymbol{k}}'\rangle\langle I|\langle\tilde{\boldsymbol{k}}'|\hat{V}^{\dagger}|\boldsymbol{k}'\rangle|F\rangle\delta(E+E_I-E_F)\\ &= -4\pi^2\sum_F\iint \mathrm{d}\boldsymbol{q}\,\mathrm{d}\boldsymbol{q}'\langle F|\hat{V}(\boldsymbol{q})|I\rangle\langle I|\hat{V}^{\dagger}(\boldsymbol{q}')|F\rangle\\ &\quad\langle\boldsymbol{k}+\boldsymbol{q}|i\rangle\langle i|\boldsymbol{k}'+\boldsymbol{q}'\rangle\delta(E+E_I-E_F)\\ &= \iint \mathrm{d}\boldsymbol{q}\,\mathrm{d}\boldsymbol{q}' S(\boldsymbol{q},\boldsymbol{q}')\langle\boldsymbol{k}+\boldsymbol{q}|i\rangle\langle i|\boldsymbol{k}'+\boldsymbol{q}'\rangle.\end{aligned} \tag{6}$$

Here, the MDFF $S(\boldsymbol{q},\boldsymbol{q}')$ and the real-space MDFF (rMDFF) $S(\boldsymbol{r},\boldsymbol{r}')$ were introduced which are related by a Fourier transformation.[1]

It is noteworthy that — due to the particular properties of the Coulomb operator — the rMDFF can be multiplied on the initial probe wave functions, whereas the MDFF has to be convolved with them.

In order to perform calculations, one not only has to specify a basis for the probe states, but also for the target states. Usually, one chooses a spherical harmonics basis which is particularly useful for describing the tightly bound initial states that give rise to EELS core losses. Hence, the initial state is written as $|l\tfrac{1}{2}jj_z\rangle$,[2] while the final states are expanded in terms of $|LM\tfrac{1}{2}S\rangle$. In the following, we will also sum incoherently over j_z since that quantum number of the initial state is typically unknown. In the Kohn–Sham approximation, the MDFF is then given by [11–13]

$$\begin{aligned}S(\boldsymbol{q},\boldsymbol{q}') &= -4\pi^2\sum_{\bar{j}_z}\sum_{LMSL'M'S'}\left\langle F|LM\frac{1}{2}S\right\rangle\left\langle LM\frac{1}{2}S|\hat{V}(\boldsymbol{q})|l\frac{1}{2}jj_z\right\rangle\\ &\quad\left\langle l\frac{1}{2}jj_z|\hat{V}^{\dagger}(\boldsymbol{q}')|L'M'\frac{1}{2}S'\right\rangle\left\langle L'M'\frac{1}{2}S'|F\right\rangle\delta(E+E_I-E_F)\\ &= -\frac{\pi e^4}{\epsilon_0^2 q^2 q'^2}(2l+1)(2j+1)\sum_{mm'}\sum_{LMSL'M'S'}\sum_{\lambda\mu\lambda'\mu'}\\ &\quad \mathrm{i}^{\lambda-\lambda'}\sqrt{(2\lambda+1)(2\lambda'+1)(2L+1)(2L'+1)}\\ &\quad Y_{\lambda}^{\mu}(\boldsymbol{q}/q)^*\langle j_{\lambda}(q)\rangle_{ELSj}Y_{\lambda'}^{\mu'}(\boldsymbol{q}'/q')\langle j_{\lambda'}(q')\rangle_{EL'S'j}\\ &\quad \begin{pmatrix} l & \lambda & L\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l & \lambda' & L'\\ 0 & 0 & 0\end{pmatrix}\\ &\quad \begin{pmatrix} l & \lambda & L\\ -m & \mu & M\end{pmatrix}\begin{pmatrix} l & \lambda' & L'\\ -m' & \mu' & M'\end{pmatrix}\\ &\quad \sum_{j_z}(-1)^{m+m'}\begin{pmatrix} l & \frac{1}{2} & j\\ m & S & -j_z\end{pmatrix}\begin{pmatrix} l & \frac{1}{2} & j\\ m' & S' & -j_z\end{pmatrix}\\ &\quad \sum_{\boldsymbol{kn}}D_{LMS}^{\boldsymbol{kn}}(D_{L'M'S'}^{\boldsymbol{kn}})^*\delta(E+E_{nlj}-E_{\boldsymbol{kn}}).\end{aligned} \tag{7}$$

Here,

$$\langle j_{\lambda}(q)\rangle_{ELSj} = \int u_{LS}(r)j_{\lambda}(qr)R_{lj}(r)r^2\,\mathrm{d}r \tag{8}$$

is the weighted radial wave function overlap [11,14] with the initial state's radial wave function $R_j(r)$, the final state's radial wave function $u_{LS}(r)$[3] and the spherical Bessel function j_{λ}. The $\sum_{\boldsymbol{kn}}D_{LMS}^{\boldsymbol{kn}}(D_{L'M'S'}^{\boldsymbol{kn}})^*$ (over a shell of constant energy) is the cross-density of states (XDOS) and the $\begin{pmatrix}:&:&:\end{pmatrix}$ are Wigner 3j symbols.

While this choice of basis is very convenient as a starting point (as it is used, e.g., in WIEN2k [15]), it is by no means the only or the optimal choice. This can be seen by collecting terms depending on $\boldsymbol{q}$ and terms depending on $\boldsymbol{q}'$. With the abbreviations

$$\alpha = (\lambda,\mu,L,S)$$

$$\alpha' = (\lambda',\mu',L',S')$$

$$g_{\alpha}(\boldsymbol{q}) = \frac{1}{q^2}Y_{\lambda}^{\mu}(\boldsymbol{q})\langle j_{\lambda}(q)\rangle_{ELSj}$$

$$\begin{aligned}\Xi_{\alpha\alpha'} &= -\frac{\pi e^4}{\epsilon_0^2}(2l+1)(2j+1)\sum_{mm'}\sum_{MM'}\\ &\quad \mathrm{i}^{\lambda-\lambda'}\sqrt{(2\lambda+1)(2\lambda'+1)(2L+1)(2L'+1)}\\ &\quad \begin{pmatrix} l & \lambda & L\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l & \lambda' & L'\\ 0 & 0 & 0\end{pmatrix}\\ &\quad \begin{pmatrix} l & \lambda & L\\ -m & \mu & M\end{pmatrix}\begin{pmatrix} l & \lambda' & L'\\ -m' & \mu' & M'\end{pmatrix}\end{aligned}$$

[1] Contrary to the convention adopted in previous works, we include the $1/q^2q'^2$ term in the definition of the MDFF as it makes the definition more concise and easy to use.

[2] This takes into account the spin-orbit coupling of the tightly bound core states [11].

[3] This is to be understood as the radial wave function of the projection of the (delocalized) final Bloch state onto an LS state at the scattering center, e.g., a muffin-tin state.