Comment on "Magnetic circular dichroism versus orbital magnetization"

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In a recent article [Resta, Phys. Rev. Research **2**, 023139 (2020)] it is argued, based on the dichroic sum rules derived from the modern theory of orbital magnetization, that the x-ray magnetic circular dichroism (XMCD) orbital magnetization sum rule is not providing an expectation value of the orbital angular momentum and of the orbital part of the magnetic moment, but a different quantity, also related to the breakdown of time-reversal invariance, but different. In this Comment, it is shown that this conclusion is incorrect, and that the XMCD sum rule, within its assumptions, delivers an essentially exact expectation value of the orbital angular momentum and of the orbital moment.

I. INTRODUCTION

In a recent publication [1], an interesting discussion is provided about the relationship between the orbital sum rule for XMCD (x-ray magnetic circular dichroism) [2,3], and the expression derived some years ago for the orbital magnetization of an independent-electron solid (the so-called modern theory of orbital magnetization) and some related sum rules [4]. This is highly relevant, as both results had considerable impact, well documented in the literature: the XMCD sum rule is very often applied to x-ray dichroic spectra of ferro- and paramagnetic systems, in order to extract element-specific orbital magnetic information, hardly obtainable by other means; and the modern theory of orbital magnetization is remarkable for its deep connections to geometrical and topological aspects of Bloch band theory.

It is, however, necessary, before proceeding to such discussion, to recall the very different assumptions underlying these two results, and the different nature of the sum rules.

The orbital XMCD sum rule is, apart from small corrections, precisely quantified below, essentially exact for atomic or ioniclike rotation invariant systems, in which the many-electron energy eigenstates are eigenstates of the total angular momentum and can be expanded as superpositions of Slater determinants of one-electron orbitals, characterized by l^2, l_z and corresponding spin quantum numbers. The spectral region to which the sum rule applies is limited to the region where dipole transitions from the full set of core levels with $l^2 = c(c + 1)$ to an incomplete d or f shell are allowed, and yields, as stated before, a result for the expectation value of

the orbital angular momentum of that final shell, accurate to the order of a small dimensionless parameter: the ratio of two energies, i.e., the overall spectral energy extent of the region described above, determined by a convolution of the core level spin-orbit splitting and the overall multiplet spectral extension, on the one hand, and the average x-ray transition photon energy (as an example, typically $\simeq 30$ eV for the numerator and $\simeq 700$–850 eV for the Fe, Co, and Ni $L_{2,3}$ edges), on the other. It is important to underline that all intra-atomic interactions (direct and exchange Coulomb integrals) are included in this description, and that therefore Hund's rules (which are extremely important for the origin of orbital moments) and atomic multiplet theory find full application. This is therefore a sum rule for the optical intensities of a specific and well delimited class of initial and final states, and belongs to a class of sum rules which have been used in atomic physics for some decades [5]. The character of these sum rules is exact and relies on results of angular momentum and spherical tensor theory; nonetheless, the single-ion approach for a periodic solid can of course appear as a crude approximation and can be invoked to explain discrepancies with solid-state experiments (see, however, arguments to the contrary in Ref. [6]). Within the single-ion limit, the expectation value of the magnetic moment **m** component along the quantization axis is related to the spin and orbital angular momenta by the well-known relation

$$\langle \mathbf{m} \rangle_z = -\mu_B (\langle \mathbf{L} \rangle_z + 2\langle \mathbf{S} \rangle_z), \tag{1}$$

where μ_B is the Bohr magneton, **L** and **S** are in units of $\hbar$, and the first addendum in parentheses corresponds to the orbital magnetic moment.

The modern theory of orbital magnetization, on the other hand, is by definition taking full account of the periodicity of the solid, and also provides, in principle, exact statements, but, in this case as well, only within a crucial assumption: that the electronic ground state of the solid is described by a single Slater determinant of Bloch functions, as for example produced by application of Kohn-Sham density functional theory. This is an assumption that is often extremely good

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to describe charge densities and bonding in solids, but that has serious consequences for the description of magnetically ordered phases; and in fact several attempts to reintroduce short-range electronic correlations to improve agreement of DFT calculations with experiments have taken place, based on *ad hoc* orbital polarization functionals [7,8], LDA + U, or DFT + DMFT calculations [9,10].

The single atom and the modern theory approaches are therefore approximate descriptions that are, in a sense, complementary; the marriage of localized correlations and of itinerant aspects of electronic structure being one of the major challenges of contemporary condensed matter physics. In the rest of this Comment, it is argued that the results of Ref. [1] have no bearing on the XMCD orbital sum rule, and, in particular, the claim that the XMCD orbital sum rule does not, even in principle, determine the orbital magnetization (or, more precisely the ground state expectation value of the orbital moment in an incomplete shell) is not valid. It is based on the unjustified assumption that the XMCD sum rule is an approximation to the dichroic sum rules, as given by Souza and Vanderbilt, obtained by restricting the range of integration to a finite interval, or by considering only the contribution of a single band. It does not take into account the special selection rules and ratios among matrix elements to different final states implied by the spherical symmetry, which are crucial in the proof of the XMCD orbital sum rule.

II. XMCD ORBITAL SUM RULE AND DICHROIC SUM RULES OF THE MODERN THEORY OF ORBITAL MAGNETIZATION

Since the 1920s a set of sum rules for the optical properties of electronic matter have been established, the best known of which is the *f-sum rule* of Thomas, Reiche, and Kuhn [11]. These sum rules are (a) very general, as they can be derived using the basic commutation relations between canonical observables, and the completeness of the eigenstates of self-adjoint operators; or, alternatively, using the Kramers-Kronig dispersion relations for the optical constants, based on the principle of causality; (b) they are formulated in terms of integrals over the whole range (from 0 to ∞) of frequencies, which, incidentally, makes their actual experimental application very difficult; we shall refer to them as "dispersion sum rules." A result of this kind is obtained within the modern theory of orbital magnetization (for independent electrons) by Souza and Vanderbilt [4]. The modern theory cleverly avoids divergent integrals and ill-defined quantities, and, within the independent electron approximation formulates the main results in the following way:

$$\int_0^\infty \sigma_{x,y}^{(2)}(\omega) d\omega = \gamma \sum_{i,\text{occ}} \sum_{j,\text{unocc}} (\langle i|\mathbf{r}|j\rangle \times \langle j|\mathbf{v}|i\rangle)_z, \quad (2)$$

where γ is a combination of the normalization volume and fundamental constants, $\mathbf{v}$ is the velocity operator, the summation over i is restricted to the one-electron wave functions occupied in the ground state, and that over j to unoccupied ones. The expectation value of the orbital angular momentum, on the other hand, is given by

$$\langle L_z \rangle = \gamma \sum_{i,\text{occ}} \sum_j (\langle i|\mathbf{r}|j\rangle \times \langle j|\mathbf{v}|i\rangle)_z, \quad (3)$$

where j runs over *all* states, whether occupied in the ground state or not.

So, if we consider this sum rule, one is perfectly correct in saying that the dispersion MCD sum rules do not add up to the expectation value of the orbital angular momentum (or the orbital moment), but to a different quantity; and that restricting the range of integration does not help to recover the orbital momentum, *in the general case*. But as we argue below, this does not rule out particular cases, and has nothing to say on the XMCD orbital sum rule and its validity (while indeed the expression "XMCD" and all reference to x rays is avoided in Ref. [1], statements in the introduction and in the conclusions of the paper point to strong implications for the XMCD sum rule).

To clarify this point, let us now turn to the "atomic" sum rules, such as the orbital XMCD sum rule, or, for example, the sum rule derived in the Appendix of Ref. [5]. A brief inspection of the statement and of the derivation of this different kind of sum rules shall explain why the conclusions drawn in Ref. [1] are not applicable. Starace's sum rule states that the sum of the square of the dipole matrix elements (averaged over polarization, as in a gas-phase experiment) for an ion in one of the initial states $|I\rangle$ of the configuration $[(n_i l_i)^{4l_i+2}(n_f l_f)^N]$ to all final states $|F\rangle$ of the configuration $[(n_i l_i)^{4l_i+1}(n_f l_f)^{N+1}]$ is given by

$$\text{Av}(q) \sum_F \left| \langle I| \sum_j r_j C_q^{(1)}(\Omega_j)|F\rangle \right|^2$$
$$= \frac{\langle n_i l_i|r|n_f l_f\rangle^2 (l_i\|C^{(1)}\|l_f)^2}{3(2l_f+1)}(4l_f+2-N). \quad (4)$$

Here, $\text{Av}(q)$ denotes the average over the polarization direction, the numerator of the fraction on the right-hand side contains the radial matrix element and the reduced matrix element (in the sense of the Wigner-Eckart theorem [12]) of the $l = 1$ spherical harmonics, and the other quantities are parameters of the incomplete shell.

Since the algebra leading to Eq. (4) can be checked as an exercise in angular momentum theory, it would not be correct to argue that the equation is invalid because it cannot be derived by considering the general form of the f-sum rule and restricting its range of summation or integration. It is absolutely crucial to use the spherical symmetry of the atomic Hamiltonian to define the eigenstates as angular momentum eigenfunctions, which is not the case in the most general expression of the f-sum rule. The same holds for the XMCD orbital sum rule, and in addition, following one simple derivation [3], it is important to underline that there is a normalization of the integrated dichroic spectrum by the integral of the isotropic polarization case absorption [essentially three times the right-hand side of Eq. (4)], in order to get rid of the radial matrix elements, so that the XMCD sum rule reads

$$\frac{I_1 - I_{-1}}{I_1 + I_0 + I_{-1}} = \frac{-\langle 0|L_z|0\rangle}{l_f(4l+2-N)}, \quad (5)$$

where I_q, with $q = -1, 0, 1$, denotes the oscillator strength sum over all dipole transitions from the initial core shell to the final shell $(n_f l_f)^N$ for polarization q. So the very structure of the sum rule (not a sum over oscillator strengths, but the ratio of two different sums) prevents one from considering it as a

component or as an approximation (on a reduced frequency interval) of a dispersion sum rule.

Therefore, one can perhaps argue that the atomic approximation is an inadequate approach for solids, but certainly not that the XMCD sum rule, as usually applied to analyze experimental x-ray data, produces a quantity that is different from the orbital angular momentum and the orbital moment.

[1] R. Resta, Phys. Rev. Research **2**, 023139 (2020).

[2] B. T. Thole, P. Carra, F. Sette, and G. van der Laan, Phys. Rev. Lett. **68**, 1943 (1992).

[3] M. Altarelli, Phys. Rev. B **47**, 597 (1993).

[4] I. Souza and D. Vanderbilt, Phys. Rev. B **77**, 054438 (2008). The results quoted in Eqs. (2) and (3) are for a finite volume crystallite.

[5] A. F. Starace, Phys. Rev. B **5**, 1773 (1972).

[6] Actually, though, it is argued by V. Yu. Irkhin and M. I. Katsnelson, Eur. J. Phys. B **45**, 1 (2005) that the one-electron orbitals that are eigenstates of angular momentum quantum numbers can be interpreted as a basis to represent Wannier functions for an arbitrary band structure, thus including itinerant effects. It is also interesting to note that the practical difficulties for the evaluation of XMCD sum rules for strongly correlated systems discussed in their paper only concern the spin sum rule, and not the orbital one, discussed here.

[7] O. Eriksson, M. S. S. Brooks, and B. Johansson, Phys. Rev. B **41**, 7311(R) (1990).

[8] O. Eriksson, B. Johansson, R. C. Albers, A. M. Boring, and M. S. S. Brooks, Phys. Rev. B **42**, 2707(R) (1990).

[9] S. Chadov, J. Minàr, M. I. Katsnelson, H. Ebert, D. Ködderitsch, and A. I. Lichtenstein, Europhys. Lett. **82**, 37001 (2008).

[10] L. Peters, I. Di Marco, O. Grånäs, E. Şaşıoğlu, A. Altun, S. Rossen, C. Friedrich, S. Blügel, M. I. Katsnelson, A. Kirilyuk, and O. Eriksson, Phys. Rev. B **93**, 224428 (2016).

[11] W. Thomas, Naturwissenschaften **13**, 627 (1925); W. Kuhn, Z. Phys. **33**, 408 (1925); F. Reiche and W. Thomas, *ibid.* **34**, 510 (1925).

[12] See, for example, A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, NJ, 1996).