On the breakdown of the electric dipole approximation for hard X-ray photoionization cross sections

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The concept of the electric dipole approximation (EDA) for the interaction of matter with electromagnetic radiation is fundamental to all branches of spectroscopy and is described in nearly all textbooks on quantum mechanics. The EDA assumes that the radiation field, i.e., the plane wave expanded in a Taylor series as $e^{i\mathbf{k}\cdot\mathbf{r}} = 1 + i\mathbf{k}\cdot\mathbf{r} - \frac{1}{2}(\mathbf{k}\cdot\mathbf{r})^2 + \cdots$, can be truncated to unity. In this situation, all higher order multiplet interactions, like electric quadrupole, magnetic dipole, etc., are neglected. In the IR, optical, UV, and VUV spectroscopies, the EDA is well justified for total cross sections by the following two realistic assumptions: (i) photoelectron velocities are extremely small compared to the speed of light which makes relativistic effects negligible, and (ii) the wavelength of the light is much larger than the orbitals from which electrons are ejected, eliminating contributions of higher terms in the Taylor expansion.

In the X-ray photoelectron spectroscopy, many extensive theoretical and experimental studies of the limits of the EDA have been reported (see, e.g., review [1]). In almost all studies, breakdowns of the EDA are manifested as deviations from dipolar angular distributions of photoelectrons [1]. The latter are known to be much more sensitive to the relative contributions from different photoelectron partial waves than the total cross sections. Therefore, relatively moderate contributions of higher multiplet interactions, which are nearly invisible in the total cross sections in soft X-ray range, become observable in the photoelectron angular distribution parameters. In hard X-ray limit, the EDA breaks down essentially completely, and nondipole contributions must also be visible in the total cross sections. Unfortunately, a low fluence of synchrotron radiation makes the direct observation of these effects in hard X-ray region rather unlikely, since photoionization cross sections usually decrease rapidly with the incident photon energy.

The situation becomes very promising by the advent of X-ray free electron lasers (XFELs). Nowadays, XFELs produce hard X-rays up to about 20 keV with peak brightness nearly ten orders of magnitude higher than the conventional synchrotron sources. XFELs enable single-shot femtosecond diffractive imaging [2] with the main application to biologically relevant molecules, which consist mainly of low and intermediate Z elements. What can be expected as an outcome of such experiments? Obviously, photons of high energy will mainly interact with deepest atomic shells, whose ionization potentials are below the photon energy. These deep atomic shells (e.g., K- and L- shells of intermediate Z elements from third or fourth row) are strongly localized compared to the 1s-orbital of hydrogen. An important physical question immediately arises, does the EDA breakdown vary for different low and intermediate Z elements? In particular, is the error introduced to the total ionization cross section by the EDA dependent on the atomic structure and charge, and for which elements this error can be neglected for a given hard X-ray photon energy?

Here, we investigate the breakdown of the EDA for K- and L- photoionization of H, He, Be, Ne, Ar, and Kr atoms by hard X-ray radiation, which is within the reach of present or planned XFELs. Numerical calculations [3], performed in the relativistic Pauli-Fock approximation, demonstrate that the computed *relative* contributions of the nondipole interactions to the cross sections grow as a function of the photoelectron kinetic energy almost equally for the 1s and 2s shells of all considered atoms. The same holds for the 2p shells of Ne, Ar, and Kr. We, thus, confirm analytical predictions of the Born approximation suggesting that in the considered energy range the *relative* error introduced to the ionization cross section of low and intermediate Z elements by the electric dipole approximation is almost independent of the spatial extent of the absorbing atomic orbital.

References

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