Thermal Expansion of Solids from Ab initio Simulations and its Effect on the Electron Momentum Density

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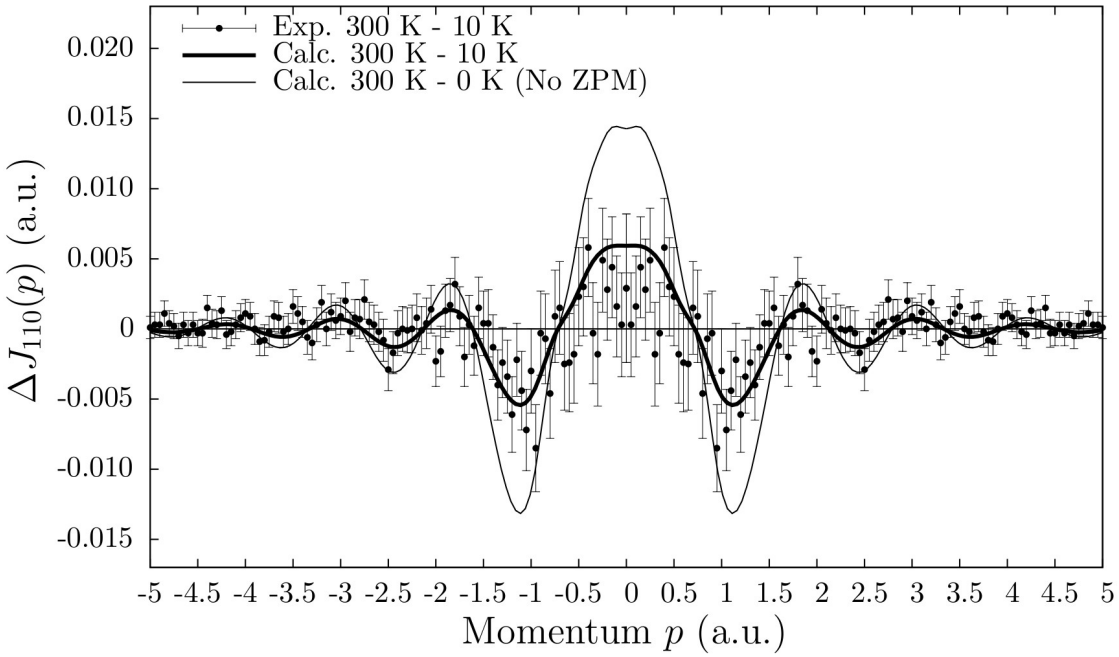
Temperature affects the electron distribution quite differently in position and momentum spaces. As electrons do follow the respective nuclei almost instantaneously, thermal disorder has necessarily to be taken into account if the electron charge density is considered, even at room temperature. Thermal effects on the electron momentum density, on the contrary, are much subtler, have been systematically neglected in most theoretical models (with few exceptions [1]) and, more generally, have been overlooked for a long time. In recent years, however, the enhanced resolution of modern synchrotron radiation-based Compton scattering measurements has allowed for unambiguously detecting such fine effects [2]. From a theoretical point of view, as thermal effects on the electron momentum density (EMD) of solids are tiny, rather sophisticated computational approaches combined with a high numerical accuracy are required in order to reveal them with general *ab initio* methods.

In this contribution, we apply a recently developed automated scheme for the *ab initio* evaluation of the lattice thermal expansion of solids [3,4] to the investigation of thermal effects on the EMD of crystalline LiF. High-resolution directional Compton profiles are measured at 10 K and 300 K, using synchrotron radiation, with a high momentum resolution of 0.11 a.u. The sole thermal expansion of the lattice accounts for the whole thermal response of the system, within the experimental accuracy, which clearly manifests as regular oscillations up to p = 4 a.u. The effect of zero-point motion (ZPM) is quantified and shown to be rather large.



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