Satellite lines in Manganese Kα X-ray spectra

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Physical sciences are forever in a process of modelling the natural world with mathematical abstraction. Quantum mechanics continues to be at the forefront of the beauty, and strangeness, of this paradigm. A rich source for work in this area is through studying characteristic X-ray radiation. Much work has been done in this area over the last decade that attempts to marry high accuracy experimental spectra to novel theoretical calculations.

The 3d transition metals offer insight into the multiconfigurational Dirac-Hartree-Fock approach to solving quantum systems. This is due to their electron configurations resulting in complex spin coupling states with open shells. Recent publications have calculated ab initio spectra for scandium [1] and copper [2]. In part, due to both recent high accuracy experiments to compare with [3,4] and each system having one unpaired electron in the ground state.

We have performed calculations of the manganese (Z = 25) Kα fluorescence spectra which ground state electron configuration is $[Ar]3d^5 4s^2$. The five 3d electrons provide us with the maximum number electron coupling states of the 3d transition metals. For example, there are 214 configuration states in the final state of the Mn Kα transition compared with 4 for copper or 12 for scandium. This issue compounds when considering shake-off events for satellite transitions and allowing electron excitations. These can often result in over one-million configuration state functions (CSFs) being required to build a basis set.

The computing power required to solve these systems of equations increases approximately with the square of CSFs. Therefore, we have had to employ several novel techniques to obtain answers to ab initio calculations for the Mn Kα spectrum.

These calculations have been married with recent experimental results from the Diamond Light Source Synchrotron (U.K.). The quality of data obtained allows us to test the theoretical approaches to this complex system at great accuracies.

We obtain results with a goodness-of-fit measure of $\chi^2_{reduced} \leq 1.6$ matching the current standards of theoretical calculations in X-ray fluorescence studies.

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[2] T. V. B. Nguyen, H. A. Melia, F. I. Janssens, C. T. Chantler, Theory of copper Kα and Kβ diagram lines, satellite spectra, and ab initio determination of single and double shake probabilities, Phys. Lett. A (2022) **426** 127900

[3] J. W. Dean, H. A. Melia, L. F. Smale, C. T. Chantler, High accuracy characterisation for the absolute energy of scandium Kα, J. Phys. B (2019) **52** 165002

[4] H. A. Melia, C. T. Chantler, L. F. Smale, A. J. Illig, The characteristic radiation of copper $K\alpha_{1,2,3,4}$, Acta Cryst. (2019) **A75** 527-540