Improvement of the calculation method for X-ray Emission Spectroscopy based on Slater's transition state theory

Yuika Watari[a] and Osamu Takahashi[b]

[a]Graduate School of Advanced Science and Engineering, Hiroshima Univ.
[b]Research Institute for Synchrotron Radiation Science, Hiroshima Univ.

Our group is actively working on theoretical calculations of core-excited states using the density functional theory. For X-ray emission spectroscopy (XES) calculations our code estimates the state based on Koopmans' theorem. This theorem has the advantage that the relative energy difference can be evaluated to some extent by the orbital energy, but it has the disadvantage that the orbital relaxation due to the electron number change is not taken into account, which leads to large errors.

Recently, Hirao et al. calculated ionization potentials (IP) using three different methods that extend Slater's transition state theory [1]. The three methods are called the AVG, STS, and RPT3 methods. In these methods, to calculate the IP of one orbital, orbital energies are required for the ground state, the monovalent ionic state with one electron missing from the orbital for which the IP is to be calculated, and the divalent ionic state with one half electron missing. Therefore, while this method is highly accurate, it has the disadvantage of requiring a large amount of computational effort when obtaining IPs for multiple energy levels. In this study, we aim to improve the theoretical calculations of XES so as to eliminate such effort and to establish a practical theoretical calculation method.

Our procedure how to calculate the XES is described. In order to easily calculate IPs for all valence orbitals, we propose a method to remove electrons from the entire valence orbital. For example, consider the case of H_2O. H_2O has four valence electron orbitals, so if we remove 0.25 electrons from all valence electron orbitals, one electron is removed from the entire orbital. In the same way, 0.125 electrons are removed from all valence electron orbitals, resulting in a total of 0.5 electrons removed. By this improvement, the IPs of all levels can be calculated by calculating these three electronic states, which saves a lot of time and effort.

The improved method of XES calculation was validated on 28 molecules, and the errors compared to the experimental values were compared with Koopmans' theorem and the three methods. The results showed that the three methods were more accurate than Koopmans' theorem. Especially for the IP of HOMO, the average error from the experimental data was -0.14 eV for oxygen and -0.10 eV for carbon by the AVG method. In addition, XES spectra were calculated, and spectra with good reproducibility were produced for the peak positions.

TABLE 1. Average of error between calculated and experimental IP from HOMO in eV.

core level	Koopmans	AVG	STS	RPT3
C	-3.73	-0.14	-0.18	-0.17
N	-3.52	-0.10	-0.15	-0.13
O	-4.30	-0.34	-0.41	-0.39

REFERENCES

1. K. Hirao et al., *J. Chem. Phys.* **155**, 034101(2021).