Study of inter sub-shell and inter shell electron correlations in 4d open-shell heavy atomic ions

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Abstract. The effect of correlations between 4p, 4d, and 4f has been studied extensively. The characteristic spectral structures of 4p−4d and 4d−4f optical transitions, due to the unique structures of \( N = 4 \) open sub-shells in heavy atomic ions, have been studied theoretically. To gain an insight of this effect, a series of careful MCDF calculations for 4d\(^q\) (\( q = 0 \) to 10) atomic ions with atomic numbers \( Z = 48 \) to 56 has been carried out. The difference of orbital energy differences between 4p and 4d orbitals and 4d and 4f orbitals coincidently falls within the range of a few % for almost all the atomic ions investigated. The 4p\(^5\)4d\(^4\)4f and 4p\(^5\)4d\(^3\) configurations may mix strongly, and the optical 4p−4d and 4d−4f transitions may take place coherently, providing us with quite a peculiar EUV emission spectrum. The effect of spectral narrowing and shift is expected to be quite common to the atomic species with the atomic numbers in the range \( Z = 48 \) to 56.

1. Introduction
The extreme ultra-violet light (EUVL) emissions of 4d open-shell atomic ions are of interest in relation to the semiconductor technologies and also to the study of highly charged heavy atomic ions in plasmas. Extensive efforts have been made in recent years for understanding the emission spectra from the plasmas [1—6]. Those spectral structures are of interest also from the view point of academic atomic spectroscopy, whereas they are obtained mainly on the purpose of EUV light source development.

During the last years, a series of sophisticated charge transfer experiments have been carried out for xenon ions [7,8] and for tin ions [8,9] by Tanuma and his co-workers. In these experiments, a beam of charge selected atomic xenon or tin ions has been introduced into the gas chamber and the EUV emissions from the excited atomic ions that were created by collisional electron capture from neutral gas atoms have been observed. Because the gas pressure has been kept as low as to maintain a single collision condition, their individual spectral data are of the ions with a unique charge state. This gives a great advantage for comparison of the data with theory.

To give a theoretical counterpart of these experimental data, we performed a set of accurate calculations of electronic states and optical processes based on a Multi-Configuration Dirac-Fock (MCDF) approximation. In these computations, the General purpose Relativistic Atomic Structure Program 92 (GRASP92) [10] and the Relativistic Atomic Transition and Ionization Properties (RATIP) [11] computer codes are used. An advantage of these programs is that we can treat the two electron non-local exchange integrals as they are [6]. In this context, we
can properly evaluate the electron correlations through configuration interactions including the excited orbitals in CSF’s in a sophisticated way.

To gain, especially, an insight of the role of the intra $N$-shell optical transitions, which are relevant for the 13.5 nm EUV emissions from 4$d$-open shell Sn ions, we calculated the $4p - 4d$ and $4d - 4f$ transitions for ions with atomic numbers $Z$ ranging 48 to 56. We have pointed out the important role of the configuration interactions between the 4$p$ sub-valence hole configurations and 4$f$ intra-shell excited configurations. It has been pointed out that the modifications of the optical emission spectral structures due to those type of configuration interactions are common to those ionic species.

We describe the procedure and the result of the present theoretical calculations in the next section. In section 3, we discuss the physical aspect of the electron correlations in the relevant system. And, finally, in section 4, we give a short summary of the present study.

2. The Calculation of $4p - 4d$ and $4d - 4f$ Transition Arrays of $Z = 46 - 56$ Ions

One of the best candidates for 13.5 nm region EUV light source are considered to be of the intra $N$ shell ($n = 4$ shell) transitions of tin (Sn) multiply charged atomic ions. It is normally indispensable to take into account the electron correlations if we are to evaluate the the transition energies within the accuracy of a few electron volts, because the correlation energy of the atomic valence electrons falls in this range. To gain an insight of the effects that are pointed out by O’Sullivan and Faukner [12], we have carried out careful MCDF calculations for 4$d^q$ ($q = 0$ to 10) atomic ions with atomic number $Z = 48$ to 56. Although, they argued only the Sn atomic ions, those effects should be present also in other atomic species. As an example, we show, in Fig.2, the single electron atomic orbital energies for Sr-like atomic ions of $Z = 48$ to 56. To obtain the single electron atomic orbitals and their energies, we have made their MCDF optimizations including the basis wavefunctions up to 6$p$, 5$d$, and 5$f$. In this figure,

![Figure 1. Atomic number $Z$ dependence of the energies of $N = 4$ atomic orbitals. The calculated range of the atomic number is $Z = 48$ to $Z = 56$. Dotted curve: 4$f$ orbital, Solid curve: 4$d$ orbital, Dot-dashed curve in upper entry: 4$p$ orbital, and Dot-dashed curve in lower entry: 4$s$ orbital.](image-url)
Figure 2. Atomic number $Z$ dependence of Einstein’s A-factors for $4d - 4f + 4p - 4d$ transitions of Y-like ions. The interference effects of $4d - 4f$ and $4p - 4d$ transitions are taken into account by configuration interaction calculations.

we can find that the differences of orbital energies between $4p$ and $4d$ orbitals, and $4d$ and $4f$ orbitals coincide within the range of a few %. The $4p^54d4f$ and $4p^54d^3$ configurations may mix strongly, and the optical $4p - 4d$ and $4f - 4d$ transitions may take place coherently, providing us with quite a peculiar EUV emission spectrum. The result of the orbital energy calculation stands for the argumentation made by O’Sullivan and FaulknerOSullivan1994. Also, we find, from this figure, that we may expect that the so called the effect of spectral narrowing and shift is quite common to the atomic species with the atomic numbers in the range $Z = 48$ to $56$. As an example of the effect of spectral narrowing and shift, we illustrate, in Fig.3 the calculated Einstein’s A-factor distributions of Y-like ions of atomic species with $Z = 49$, $50$, and $51$. In this figure, we can also observe the change of the spectral shape in the atomic number $Z$. Due to the interference between the $4p^64d^4 - 4p^64d^34f$ and $4p^54d^4 - 4p^54d^3$ transitions, we can observe a strong enhancement of the EUV emissions in 13.5 nm region of $Z = 50$, which provides us with the narrowing and shift in appearance of the emission spectra. Due to the term splitting both in the ground and the excited states, the spread of the A factor distribution would have been a couple of ten eV without the interference between the $4p - 4d$ and $4d - 4f$ transitions. Although the figures are not illustrated in the present paper, we have observed quite a similar interference effect in transitions for wide range of atomic numbers, say, for the range $Z = 48$ to $56$, and also for wide range of occupation numbers of $N$ shells.

3. Discussion
The precise and accurate theoretical data of the atomic structures and dynamics that includes the information about the relativistic effect and the electron-electron correlation effects provide us with a good base for precision analysis of highly charged atomic ions in a plasma. Owing to the general nature of many electron atoms or atomic ions, the inclusion of the effect of configuration interactions among virtually excited states is indispensable to obtain physically realistic atomic state wavefunctions. Especially, it is important to take into account the modification of the
atomic state wavefunctions due to the interactions among various many-electron configurations, which can be evaluated by only an SCF iterations in MCDF calculations. We can point out also that the spectral shift and narrowing should be the effects which are quite common to the 4d open shell atomic ion species with moderate atomic numbers. From the view point of atomic multi-configuration Dirac-Fock calculations, which can provide us with plausible shapes for the single electron orbitals by the procedure of non-linear numerical orbital SCF optimization, these effects are due to the coincident agreement of the orbital energy differences among the $N = 4$ sub-shells. This coincident agreement itself is the outcome of electron correlations, and a multi-configuration SCF can account for such correlations in the single electron orbital wavefunctions.

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