MCDF calculations for EUV-emissions of 4d-open shell ions based on the features of non-local exchange integrals

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Abstract. Wavelengths and intensities of extreme ultra-violet optical emissions are studied for 4d – 5p transitions of Xe^{10+} ions in plasmas. The electronic states of the ions have been calculated employing a method based on the multi-configuration Dirac-Fock approximation. Dipole transition rates have been calculated allowing the non-orthogonal orbital wavefunctions between the initial and final electronic states. Single and double electron virtual excitations have been taken into account to evaluate the electron correlations. The orbital relaxations and electron correlations have substantial effects on the formation of the transition arrays.

1. Introduction
Extreme ultra-violet (EUV) emissions from 4d open shell atomic ions in plasmas have received a lot of interest both by experiment and theory as a potential light source relevant to the development of semiconductor technologies. Extensive efforts have been made for understanding the emission spectra from plasmas [1, 2, 3]. A comprehensive data compilation on the emission spectra of xenon ions has been carried out by Salomon et al [4].

During the last years, a series of sophisticated charge transfer experiments have been carried out for xenon ions [6] and for tin ions [7] 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) [8] and the Relativistic Atomic Transition and Ionization Properties (RATIP) [9] computer codes are used. An advantage of these programs is that we can treat the two electron non-local exchange integrals as they are.

In the present paper, we consider the EUV emission wavelengths and transition rates of Xe$^{10+}$ ions. We calculate the $4p^64d^8 - 4p^64d^75p$ electric-dipole transition array.

2. Theory

In a standard treatment of the MCDF method, an atomic state function (ASF) is responsible for representing the individual multi-electron atomic state. An ASF is expanded in terms of configuration state functions (CSF), which are antisymmetrized products of a common set of orthonormal single electron orbitals. Including the excited orbitals in CSF’s, we can evaluate the electron correlations through configuration interactions.

Einstein spontaneous emission rates, i.e., the $A$-factors, have been calculated for all the combinations of excited and ground states relevant to the $4d - 5p$ electric dipole transitions. Firstly, we calculate the $4d - 5p$ transition probabilities of Xe$^{10+}$ ions including only the minimal set of orbitals, say, $1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d,$ and $5p$. The ground configuration is $1s^22s^22p^63s^23p^64d^8$ of 14 multiplet levels. The excited configuration is $1s^22s^22p^63s^23p^64d^75p^1$ and consists of, in contrast, already 110 multiplet levels. Secondly, we calculate them including the correlation configurations. In these computations, we start from the $4p^64d^8$ and $4p^44d^{10}$ reference configurations and include all the single and double excitations into the $4f, 5p, 6s, 6p, 6d, 6f,$ and $6g$ sub-shells from the $4p^64d^8$ configuration. This approach then results in 16140 CSF. A similar scheme of virtual excitations is employed also for the excited states. Owing to the size of the calculations, the total computation required more than 750 hours ($\approx$ 1 month) of CPU time on a present-day high-end PC.

3. Results and Discussion

![Figure 1](image1.png)

**Figure 1.** $A$-factor distributions for $4d - 5p$ transitions of Xe$^{10+}$ ions. The broken curve: the minimal base calculation. The solid curve: the large basis set calculation with correlation orbitals $4f, 5p, 6s, 6p, 6d, 6f$ and $6g$.

In Figure 1, the calculated distribution of the $A$-factors is plotted as a function of the wavelengths of optical emission. In order to synthesize the ‘real’ spectra, the calculated lines have
been convoluted with a Lorentzian profile for the natural width \( \text{width} = 0.02 \text{ nm} \) and a triangular profile for the spectrometer \( \text{width} = 0.02 \text{ nm} \). The broken curve is of the minimal base calculation and the solid curve is of the basis set with large scale correlation functions. It can be seen that, on the level of individual peaks, the two curves appear to be quite different. The electron correlation has a substantial influence on the populations of \( A \)-factors with respect to the combination of total angular momenta of the upper and lower levels.

Table 1. Wavelengths and rates of \( 4d - 5p \) electric dipole transitions in the region 12 to 15 nm.

| Upper level angular momentum | Lower level angular momentum | Wavelength present calc. (nm) | \( A \)-factor Coulomb gage \( \times 10^{10} \text{ (1/s)} \) | \( A \)-factor Babushkin gage \( \times 10^{10} \text{ (1/s)} \) | Wavelength Saloman [4] (nm) | Intensity Saloman [4] (arb. unit) |
|-----------------------------|-----------------------------|-------------------------------|---------------------------------|---------------------------------|-----------------------------|--------------------------------|
| 1                           | 2                           | 12.7251                       | 1.68824                         | 2.00702                         | –                           | –                             |
| 1                           | 0                           | 12.8409                       | 5.25589                         | 6.62560                         | –                           | –                             |
| 4                           | 4                           | 13.0243                       | 2.10509                         | 1.61826                         | –                           | –                             |
| 0                           | 1                           | 13.0295                       | 4.41445                         | 4.68371                         | –                           | –                             |
| 1                           | 0                           | 13.0703                       | 7.25224                         | 7.91344                         | –                           | –                             |
| 1                           | 1                           | 13.0735                       | 3.54107                         | 3.78470                         | –                           | –                             |
| 4                           | 4                           | 13.1224                       | 4.68160                         | 4.73013                         | –                           | –                             |
| 3                           | 4                           | 13.1313                       | 1.07094                         | 1.04687                         | 13.1515                     | 156                           |
| 1                           | 2                           | 13.1871                       | 4.19585                         | 4.38572                         | –                           | –                             |
| 5                           | 4                           | 13.1964                       | 5.73363                         | 5.48372                         | –                           | –                             |
| 2                           | 2                           | 13.1983                       | 3.57149                         | 3.81152                         | –                           | –                             |
| 2                           | 2                           | 13.2288                       | 2.93902                         | 3.06610                         | –                           | –                             |
| 3                           | 3                           | 13.2340                       | 1.59934                         | 2.06908                         | –                           | –                             |
| 1                           | 2                           | 13.2521                       | 2.10563                         | 2.14668                         | –                           | –                             |
| 1                           | 0                           | 13.2775                       | 2.76620                         | 2.76423                         | –                           | –                             |
| 3                           | 4                           | 13.2800                       | 1.74243                         | 1.83735                         | 13.2573                     | 170                           |
| 0                           | 1                           | 13.2836                       | 2.83040                         | 2.83080                         | –                           | –                             |
| 3                           | 4                           | 13.2981                       | 2.20060                         | 2.20617                         | –                           | –                             |
| 2                           | 2                           | 13.3063                       | 3.95639                         | 4.08706                         | –                           | –                             |
| 1                           | 2                           | 13.3081                       | 2.15152                         | 1.92982                         | –                           | –                             |
| 1                           | 2                           | 13.3086                       | 3.97931                         | 3.67144                         | –                           | –                             |
| 3                           | 2                           | 13.3247                       | 2.91888                         | 2.23569                         | –                           | –                             |
| 1                           | 2                           | 13.3275                       | 3.32820                         | 3.99064                         | –                           | –                             |
| 2                           | 2                           | 13.3296                       | 3.16620                         | 2.83941                         | –                           | –                             |
| 2                           | 2                           | 13.3350                       | 2.99325                         | 3.29167                         | –                           | –                             |
| 4                           | 3                           | 13.3395                       | 4.17141                         | 4.26180                         | 13.4987                     | 392                           |
| 5                           | 4                           | 13.3406                       | 6.19201                         | 6.45949                         | 13.5072                     | 518                           |
| 2                           | 3                           | 13.3463                       | 2.43870                         | 2.65455                         | –                           | –                             |
| 3                           | 2                           | 13.3551                       | 2.85879                         | 2.95628                         | 13.5100                     | 179                           |
| 1                           | 2                           | 13.3656                       | 5.65392                         | 5.82819                         | –                           | –                             |
| 3                           | 2                           | 13.3763                       | 2.01688                         | 2.13407                         | 13.5334                     | 165                           |
| 2                           | 2                           | 13.3770                       | 2.43871                         | 2.47897                         | –                           | –                             |
| 4                           | 3                           | 13.3827                       | 2.43699                         | 2.26594                         | –                           | –                             |

In table 1 and 2, we have listed our results from the calculation including the correlation effects, and also listed the corresponding values by Saloman [4] for comparison. We may say that the overall agreement is reasonable. Also, the agreement with the charge selected data of Tanuma et al [6] was found to be fairly well. However, the line by line comparison would not be appropriate from currently available data.
Table 2. Continued from Table 1.

| Upper level angular momentum | Lower level angular momentum | Wavelength (nm) | $A$-factor Coulomb gage $\times 10^{10} (1/s)$ | $A$-factor Babushkin gage $\times 10^{10} (1/s)$ | Wavelength Saloman [4] (nm) | Intensity Saloman [4] (arb. unit) |
|------------------------------|-----------------------------|----------------|-----------------------------------|-----------------------------------|-------------------------------|----------------------------------|
| 3                            | 2                           | 13.4220        | 4.15326                           | 4.03751                           | –                             | –                                |
| 4                            | 4                           | 13.4453        | 4.53258                           | 4.4106                            | –                             | –                                |
| 2                            | 2                           | 13.4550        | 3.29967                           | 3.45749                           | 13.5334                       | 165                              |
| 2                            | 3                           | 13.4608        | 1.41478                           | 1.42233                           | 13.4962                       | 222                              |
| 1                            | 0                           | 13.4628        | 7.33049                           | 7.06751                           | –                             | –                                |
| 3                            | 3                           | 13.4808        | 3.63103                           | 3.33794                           | 13.4037                       | 390                              |
| 1                            | 2                           | 13.4895        | 2.09521                           | 2.08123                           | 13.4927                       | 218                              |
| 1                            | 0                           | 13.5113        | 2.51755                           | 2.38080                           | –                             | –                                |
| 3                            | 4                           | 13.5291        | 1.47865                           | 1.49451                           | 13.4091                       | 156                              |
| 4                            | 4                           | 13.5340        | 4.82794                           | 4.98559                           | 13.5614                       | 339                              |
| 4                            | 4                           | 13.5354        | 2.13754                           | 2.10283                           | 13.6401                       | 236                              |
| 1                            | 1                           | 13.6304        | 3.85344                           | 3.93575                           | –                             | –                                |
| 3                            | 4                           | 13.6625        | 4.65111                           | 4.49136                           | –                             | –                                |
| 4                            | 4                           | 13.7317        | 1.48114                           | 1.49973                           | 13.6605                       | 315                              |
| 5                            | 4                           | 13.7339        | 3.47433                           | 2.96986                           | 13.6401                       | 236                              |
| 1                            | 0                           | 13.7446        | 1.91193                           | 2.05482                           | –                             | –                                |
| 2                            | 1                           | 13.7627        | 1.05335                           | 1.08050                           | 13.6605                       | 315                              |
| 1                            | 0                           | 14.0077        | 2.53333                           | 1.83530                           | –                             | –                                |
| 1                            | 0                           | 14.0452        | 3.45158                           | 3.80649                           | –                             | –                                |
| 1                            | 0                           | 14.4596        | 2.64676                           | 2.33983                           | –                             | –                                |

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