Many electron correlations and dynamics in atoms and multi-charged atomic ions

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Abstract. Electron correlations in atoms or atomic ions with multiple electrons are discussed extensively. The scheme of correlations between the electronic configurations are investigated in view of the (Dirac)-Hartree-Fock type variational calculations. In highly lying states realized by multiple inner-shell electron excitations, single electron orbitals have to be modified in accordance with the creation of electron vacancies near the atomic centre; the optimizations of orbitals for individual energy levels are indispensable to gain a good insight of such atomic states and their dynamics. Electronic configurations with the same total parities may interact each other even in the cases that the constituent single electron orbitals have opposit parities. Such configuration interactions may induce the hybridization of single electron orbitals providing us with characteristic interference structures in the optical emission or absorption spectra. Numerical examples have been illustrated for several atomic or ionic systems such as lithium hollow atomic states, neon core excited states, and 4d-open highly charged tin ionic states.

1. Introduction
In photoexcitation or photoionization of many electron atoms or ions, we sometimes observe excitations of multiple electrons from inner-shell orbitals as well as valence orbitals resulting with super excited states, hollow atomic states, or other exotic states. And furthermore we may find various excited ionic states also in the plasmas of heavy atomic species. In those excited states, we often have highly correlated multi-electronic states that end up with photo or electron emissions, providing us with anomalous photoabsorption or emission spectra. Recent progress of experimental technique has become to allow us to produce detailed spectral data which may deserve for the analysis of the electronic states in terms of the electronic correlations. The study of electron correlations in atoms or ions are quite important not only from the academic point of view but also from the view point of applications such as plasma diagnostics or extreme ultraviolet light source development. It is especially important to establish a way to understand the characteristics of the electronic correlations if we want to gain a deep insight of the multiple electron atoms or atomic ions.

In the present paper we illustrate several characteristic examples of correlatd electronic states of atoms and ionic ions. Firstly, we point out that the relaxation of single electron orbitals in a excited state may cause effects of electron correlations, and, secondly, we point out that another candidate of the electron correlation is the mixing of a configuration with other configurations containing two electrons with different parities. In the next section, we briefly
review the characteristics of (Dirac) Hartree Fock method. In section 3, we describe the electron correlations in lithium hollow atomic states, neon 1s2s double inner-shell electron excited states. And, furthermore, we discuss the mixing of the 4p and 4d excited configurations in 4d - open shell atomic ions. We give a concluding remark in section 4.

2. Characteristics of the (Dirac) Hartree Fock methods

To describe the (Dirac) Hartree Fock (DHF) method, we may refer to the formalism of Lipkin[1]. We consider an N-electron wavefunction under the independent particle model. We take \( a_{ki}^\dagger \) as a creation operator of the single electron orbital. The configuration state function (CSF) may be represented by

\[
|\Phi\rangle = \prod_{i=1}^{N} a_{ki}^\dagger |0\rangle, \tag{1}
\]

where \(|0\rangle\) represents the vacuum and the CSF \(|\Phi\rangle\) is anti-symmetrized with respect to the electronic coordinates. To diagonalize the Hamiltonian, \( H \), we apply a variational condition

\[
\delta \langle \Phi | H | \Phi \rangle = \langle \Phi | H | \delta \Phi \rangle = 0, \tag{2}
\]

under an ortho-normality constraint for single electron orbitals. We take \( \delta_{ki}^\dagger \) as a small variation of \( a_{ki}^\dagger \). Then, the variational condition in (2) may be represented as

\[
\langle \Phi | H | \delta \Phi \rangle = \sum_{j=1}^{N} (-1)^P \langle 0 | a_{kj} | H | \delta_{kj}^\dagger | 0 \rangle = 0 \tag{3}
\]

where \( P \) in \((-1)^P\) is the number of permutations that is required to place the operator \( \delta_{kj}^\dagger \) on top of the product.

The DHF method diagonalizes \( H \) with respect to the single electron displacements and may not diagonalize \( H \) with respect to the multiple electron displacements on the basis of independent particle view point. To consider the optimizations for multiple electron excitations, we, on one hand, need to include multiple CSF’s in a trial atomic wavefunction; the effect of electron correlations may be evaluated by means of multi-configuration Dirac Hartree Fock (MCDF) method. On the other hand, as a source of the electron correlations, we should further recognize that a single CSF \(|\Phi\rangle\) may be optimized for an atomic state independently of the other states. The orbital basis sets are not necessarily be orthogonal between the sets for different atomic states. For example, a 1s orbital \(|(1s)_1\rangle\) in the first set \(|\{(ns)_1\}\rangle\) may be a linear combination of the second set \(|\{(ns)_2\}\rangle\), we may here write as

\[
|(1s)_1\rangle = \sum_n |(ns)_2\rangle |(ns)_2\rangle |(1s)_1\rangle = \sum_n |(ns)_2\rangle s_n. \tag{4}
\]

Namely, a state that is described in terms of a set \( \{a_{1}(1)\} \) may be a state with multiple excitations if expanded in terms of a different basis set \( \{a_{2}(2)\} \). Thus, the effect of electron correlations may be evaluated by introducing separate optimizations for individual states.

To carry out actual numerical calculations, we can employ computer codes from a set of GRASP (General purpose Relativistic Atomic Structure Program)family such as GRASP92[2] and from its extensions such as RATIP(Relativistic Atomic Transitions and Ionization Properties)[3, 4, 5, 6, 7, 8, 9, 10, 11].
Figure 1. Schematic drawing of the contraction of single electron excited orbitals realized by a creation of $K$, $L$ inner shell vacancies. The photon incidence may excite multiple electrons from the inner shell orbitals to the excited state orbitals, which are created without the shielding of the nuclear attraction potentials due to the electrons in lower lying orbitals.

3. Electron correlations in atoms and atomic ions

3.1. Lithium $3s$ orbital contraction triggered by tripple electron escape from $K$ and $L$ shells by photoabsorption

In the last decade, there have been an extensive study of the lithium hollow atomic state excitations[12]. Azma et al have observed for the first time a $K$, $L$ double shell hollow atomic state in lithium atoms[13]. They observed the photoion spectra of Li $3s^23p$ photoexcitations from the ground state Li $1s^22s$. In these type of multiple electron excitations, we may have a considerable modification of the excited state single electron orbitals due to the dissapearance of the nuclear shieldings by the lower lying electronic orbitals. A schematic illustration of the effects is given in figure 1.

Azuma et al[13] found a photoion spectral profile of triple electron excitations centred at 175.25 eV of the incident photon energy. Figure 2 illustrate the spectrum by dots. We have also shown , in figure 2, a calculated resonance energy 175.05 eV by an arrow. Koike et al[14] have carried out an elaborate multi-configuration Dirac Fock calculation using GRASP92[2] and RATIP[8]. They have obtained a value 175.05 eV for the excitation energy of Li $3s^23p \ ^2S$ state; they have included 10,050 CSF’s for the ground state and 490 CSF’s for the excited state in their MCDF calculation. Note that the required number of configurations to obtain a desired numerical acuracy is much less in the excited state calculations; in the excited orbitals, the electrons spend most of the times far apart from others providing us with less correlation energies compared with the ones in the ground states. The calculated oscillar strength of the three electron excitation is about $10^{-6}$, which is still large enough to make the states experimentally observable. The larginess of the oscillator strengths originates from the $3s$ and $3p$ orbital contraction in the hollow atomic states. Due to the orbital contraction, we may have fairly large overlap of the $3s^23p \ ^2S$ state configuration with the ground state configuration. In figure 3, we can see the orbital contractions in the core excited states from the plot of the electron charge densities against the radial distance from the nucleous, which we have calculated using GRASP92[2] and RATIP[8] packages.
Figure 2. Experimental photoion spectra of Li $3s^23p^2\,^2S$ double $K, L$ hollow atomic state excitation[13] are given by dots. The solid curve is the result of profile fitting using the Fano-Beutler profile formula. The experimental resonance point energy 175.25 eV and the theoretical resonance point energy 175.05 eV[14] are indicated by arrows.

Figure 3. Calculated electron density distributions of various excited states of Li atoms. Type of the resonance is indicated in the figure by arrows with three digits that specify the combination of principal quantum numbers in the excited state configurations. For example, 233 denotes the $2\ell3\ell'3\ell''$ configurations.

3.2. Ne $1s$ and $2s$ resonant double photoexcitation
Recently, Oura et al have made an experiment on neon $1s$ and $2s$ resonant double photoexcitation processes[15], as shown in figure 4. They observed a pair of $1s^12s^1(^1S)2p^63s^13p^1$ and $1s^12s^1(^1S)2p^63s^13p^1$ double electron excitations at 924.78 eV and at about 935 eV of photon energies. Those two peaks are apart by about 10 eV each other. This value is somewhat large compared with the usual understanding of the singlet-triplet separation in neon $1s^12s^1$ configurations. To find out the origin of this largeness, we have calculated the electron density distribution of the Ne$^{2+}1s^12s^12p^6$ configuration using both the MCDF wavefunctions of neutral neon and the doubly charged neon atom. Figure 5 shows the charge density plots from those two sets of wavefunctions; the solid curve represents the charge density of Ne$^{2+}1s^12s^12p^6$ doubly charged.
Figure 5. Comparison of the calculated electron density distributions of Ne$^{2+}$1s2s2p$^6$ configurations using the sets of single electron orbitals with and without relaxations for the creation of double inner-shell holes. The solid line stands for the case without orbital relaxation, and the broken line stands for the case with orbital relaxation.

Ions with use of the wavefunctions that optimize the ground state of neutral neon atoms and the broken curve is the one using the optimized Ne$^{2+}$1s$^1$2s$^1$2p$^6$ ionic wavefunctions. We see that in the actual Ne$^{2+}$1s$^1$2s$^1$2p$^6$ ions, the electronic charges are relaxed to the atomic center. It may be concluded that this contraction of the electronic wavefunctions due to the 1s2s double hole creation is the cause of the enlargement of the singlet - triplet separation in Ne 1s$^1$2s$^1$(3,1S)$^2$p$^6$3s$^1$3p$^1$ states.

To gain a further insight of the excitation process and the subsequent non-radiative decay process, we are now in progress of numerical calculations for multi-step Auger decay processes using RATIP[8]. The results will be issued in one of our forthcoming papers.
3.3. Interactions between the configurations two pairs of single-electron orbitals with opposite parities

A pair of configurations with the same total symmetry may undergo configuration interactions and this is one of the sources of electron correlation effect. We should note here that there are no symmetry constraint for individual constituent electron orbitals. If we replace, in a configuration, two single electron orbitals by the ones with opposite parities, the total parity will not change. And we can consider the configuration interaction between such the pair of configurations. In the followings we illustrate a typical example in the case of optical emissions of highly charged heavy atomic ions.

In these decades, extreme ultra-violet (EUV) light emissions of many electron atomic ions have become of interest in relation to the light sources for semiconductor lithography technologies. The light emissions by intra $N$ shell ($n = 4$ shell) transitions or inter $N − O$ shell transitions of tin (Sn) or xenon (Xe) ions are considered to be as good candidates. It is normally indispensable, in general, 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. And, furthermore, we have to be aware that, in this type of the ions, especially of the Sn ions, the presence of a peculiar behaviour in the emission spectra has been discussed by O’Sullivan and his coworkers[16, 17]. They pointed out that narrowing and shift of the wavelength ranges would occur in the $4f − 4d$ emission spectra as due to the interactions between $4p^54d^{N−1}4f^1$ and $4p^54d^{N+1}4f^0$ configurations in $\text{Sn}^{(14−N)}$ atomic ions, where $N$ is an integer that runs from 1 to 9.

To gain a further insight of the effects, we have carried out careful MCDF calculations using GRASP92[2] and RATIP[8] for $4d^N$ ($N = 1$ to 9) atomic ions with atomic number $Z = 48$ to 56. We find, for example, that, in the case of Sn$^{12+}$, the major peak positions of the $4s$, $4p$, $4d$ and $4f$ single electron radial wavefunctions almost coincide; the wavefunctions may overlap...
strongly. And, furthermore, we also find that the differences of orbital energies between 4p and 4d orbitals, and, 4d and 4f orbitals coincide within the difference of 1 The configurations 4p^6 4d^3 4f^1 = (4p^5 4d^1) 4p^1 4f^1 and 4p^6 4d^3 4f^0 = (4p^5 4d^1) 4d^2 will mix strongly, and the optical 4p – 4d and 4f – 4d transitions take place coherently, providing us with quite a peculiar EUV emission spectrum. We can thus verify the discussions by O’Sullivan and his coworkers[16, 17] based on present elaborate MCDF calculations.

As noted already, we have carried out MCDF calculations for other ionic states Sn^{(14–N)} and also for atomic ions with other atomic numbers Z from 48 to 56. We may point out that quite a similar behaviour of the emission spectra is obtained for every combination of N and Z. As an example, we illustrate the calculated oscillator strength distributions of Sn^{10+} also for atomic ions with other atomic numbers Z.

In this case of N = 4, coherent transitions 4p^6 4d^4 – 4p^6 4d^3 4f^1 and 4p^6 4d^4 – 4p^5 4d^5 4f^0 will take place due to the mixing of excited state configurations 4p^6 4d^3 4f^1 and 4p^5 4d^5 4f^0; we may expect the interference between those two transitions. The upper entry in figure 6 illustrates the oscillator strength distribution for all the possible transitions between the Sn^{10+} 4p or 4d single electron excited states and the ground states. The configuration interaction between the 4p and 4d excited states are taken into account. The broken line in the lower entry illustrate the transitions from the 4d excited states only, and the solid line in the lower entry illustrate the transitions from the 4p excited states only. We can see in this figure that the wavelength range is narrow in the spectrum at upper entry compared to the the spectra for individual 4p – 4d and 4d – 4f transitions at lower entry. We can also see that the interference between the 4p – 4d and 4d – 4f transitions gives a spectral enhancement near 13.3 nm of the wavelength.

4. Conclusion
There are several sources of electron correlations in atomic and ionic excited states. One is the relaxation of single electron orbitals due to the removal of electrons in lower lying orbitals. This type of the correlation effects can be evaluated by optimizing the single electron orbitals individually for excited atomic states. The lithium K and L hollow atomic states and the neon 1s2s doubly excited states have been introduced as examples. Another is the mixing of a configuration with other configurations that contains two electrons with different parities. The mixing of 4p^6 4d^{N-1} 4f^1 and 4p^5 4d^{N+1} 4f^0 configurations in tin atomic ions has been introduced as an example. Sophisticated study of the correlation effects have been made possible by the use of the computer codes GRASP92[2] and RATIP[8].

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