Multiply Excited Three-Electron Systems Studied by Optical Emission Spectroscopy

Recent developments in the study of radiative multiply excited states in three-electron systems are reviewed. The progress concerns experimental and theoretical studies of the term schemes for quartet states in Li I, Be II, and B III, the first term schemes for doublet states in Li I and Be II, absolute term values for Li I, the existence of two bound states in Li I, and the first accurate autoionization widths for autoionizing resonances in Li I and Be II. This Comment concentrates on the low Z numbers for which strong effects of electron correlation and configuration interactions are important.

INTRODUCTION

Studies of atoms with two or more electrons excited relative to the ground state configuration have for a long time yielded important new information about the structure and dynamics of atoms. If an atom has two electrons excited relative to its ground state configuration, in a single configuration description, the atom is classified as being in a doubly, or more generally, a multiply excited state.

A three-electron system with two excited electrons, such as the Li I isoelectronic systems, will always possess more energy than it needs to completely remove a single electron from the ground state, i.e., more energy than the first ionization potential. Thus a doubly excited three-electron system is energetically able to autoionize. Since photon emission ($\tau \approx 10^{-5}$ s) generally is a much slower process than the electron emission taking place during autoionization ($\tau \approx 10^{-14}$ s), it is only under special circumstances that optical emission from
multiply excited states can be observed. Only when the selection rules for fast autoionization are violated does the multiply excited atom exist long enough to be observed via photon emission.

Autoionizing states are characterized by having, at the same energy as the discrete state, a continuum which is an eigenfunction of the atomic Hamiltonian with the same quantum numbers as the discrete state. The discrete and continuum configurations can then mix to allow the radiationless transitions to take place under the selection rules: no change in total angular momentum \((\Delta J = 0)\) and no change of parity \((\Delta \pi = 0)\). Provided LS coupling holds, \(\Delta L = \Delta S = 0\).

The multiply excited states may be divided into two groups: *weakly quantized states*, which are subject to autoionization in the single configuration nonrelativistic approximation, and which have lifetimes less than \(10^{-12}\) s, and *exactly quantized states*, which form real bound states not imbedded in continua of the same spin, total angular momentum and parity, and which thus cannot autoionize by pure Coulombic interactions. Optical emission can yield information not only about the properties of the exactly bound states (energies, fine and hyperfine structures, lifetimes, branching ratios, etc.) but also in some cases about weakly bound states (energies, autoionization width) provided the weakly bound states can be populated by photon emission from exactly bound states. The much higher resolution obtainable in photon spectroscopy than in electron spectroscopy makes the optical emission studies attractive for the testing of theoretical predictions.

Figure 1 gives a schematic representation of the energies of the radiative, doubly excited doublet and quartet states in a three-electron atom such as Li I, Be II, etc. A large number of quartet states may be located below the lowest triplet state of the ion, \(1s2s^3S\), and thus in the LS approximation be energetically metastable toward autoionization. Above the \(1s2s^1S\) level fast Coulombic autoionization may take place, but the selection rules may favor the radiative quartet states. Above the \(1s^2^1S_0\) ground state of the ion, radiative doublets may appear when the selection rules for fast autoionization are violated.

Within the last few years the radiative states of three-electron systems have attracted a good deal of interest both experimentally and theoretically. Most of the recent work has dealt with the low \(Z\) numbers of the Li I isoelectronic sequence. For a review of the
radiative states covering the period before 1975, the reader is referred to the article by Berry; the autoionizing states in these systems have been discussed very recently in this journal.

Light sources based upon heavy-ion collisions as the fast beam-foil/gas sources have been shown to efficiently populate multiply excited states. In spite of the fact that the beam-foil light source
causes severe line broadening due to multiple scattering and energy straggling of the ion beam in the foil, it has recently been proven applicable for term scheme studies of the relatively complicated core-excited Be II system (see below) and for determination of the first accurate autoionization widths in Li I and Be II (see below). Photoabsorption experiments\textsuperscript{5,6} seem so far to be the only alternative method to gain experimental information about the radiative doublets. This technique, however, is not applicable for the quartet states.

Recently, the properties of the radiative states, such as energies, lifetimes, and branching ratios, have been studied theoretically by a variety of methods: model potential,\textsuperscript{7} variational Hylleraas method,\textsuperscript{8} multiconfiguration Hartree–Fock,\textsuperscript{9} and accurate configuration interaction calculations.\textsuperscript{10}

H\textsuperscript{2−}, He\textsuperscript{−}

Calculations performed for the negative ions, H\textsuperscript{2−} and He\textsuperscript{−}, have revealed that only He\textsuperscript{−} possesses bound states.\textsuperscript{11} Of these, the 2p\textsuperscript{3} \textsuperscript{4}S\textsuperscript{0} state may be observable by optical emission spectroscopy, since this state is predicted to decay to the (1s 2p)\textsuperscript{3}P + e\textsuperscript{−} continuum by radiative autoionization with a broad emission peak near 323.15 Å. So far, it has not been possible to verify these predictions experimentally, but very recently the 2p\textsuperscript{3} \textsuperscript{4}S\textsuperscript{0} state in Li I and Be II was identified in an experiment reported by Agentoft \textit{et al.}\textsuperscript{12}

Li I

The identification of the optical emission spectrum of doubly excited Li I was progressing rapidly at the end of the 1960's, when beam-foil spectroscopy was applied to the study of doubly excited systems. Within a few years several tentative assignments resulted in a fairly complete level scheme for the Li I quartets. The results from this period were reviewed by Berry.\textsuperscript{3} The large amount of new experimental data initiated a series of theoretical studies.\textsuperscript{6,13} It was proved that the \textsuperscript{4}P\textsuperscript{0} energies originally calculated by Holøien and Geltman\textsuperscript{14} were incorrect, which implied the dismissal of a number of previously performed assignments. The theoretical studies, however, did not lead to the identification of the remaining spectral lines, most noticeably the line at 3490 Å already observed in the first beam-foil study of lithium.
At the end of the 1970's the study of the Li I quartet system progressed as a result of the interaction between the very accurate calculations by Bunge and co-workers\textsuperscript{15-18} and the experimental work performed in Stockholm\textsuperscript{19}. The system was finally established by Mannervik and Cederquist\textsuperscript{20} (see Fig. 2), who also presented a comparison between the experimental and theoretical results obtained so far. Since then the 2\(p^1\) 4\(S\) state has also been identified.\textsuperscript{12} It should be noted that only the 2\(p^3\) configuration lies below the 1\(s^2\) 3\(S\) limit leaving the 1\(s^2 3n\) 4\(S\) and 1\(s^2 3n\) 4\(D\) Rydberg series unperturbed. This fact was utilized as the basis for a quantum defect analysis\textsuperscript{20} of the 1\(s^2 2p\) 4\(P\)-1\(s^2 3nd\) 4\(D\) (\(n = 3-10\)) Rydberg series to determine the energy difference between the series limit (1\(s^2\) 3\(S\) in Li II) and the metastable 1\(s^2 2p\) 4\(P^0\) to be 56.473 \(\pm\) 5 cm\(^{-1}\) resulting in an absolute term value for 1\(s^2 2p\) 4\(P^0\) of 463.050 \(\pm\) 5 cm\(^{-1}\) (57.4113 \(\pm\) 0.0006 eV). Previously the value obtained from electron spectra,\textsuperscript{21} 57.41 \(\pm\) 0.015 eV, was considered the most reliable experimental value, whereas theory\textsuperscript{16} predicted 57.4128 \(\pm\) 0.0002 eV.

Very recently, Chung\textsuperscript{22} has performed a detailed calculation of the energy of the Li I 1\(s^2 2p\) 4\(P\) term including relativistic and mass polarization effects. The Pauli approximation of the Breit equation was applied in order to obtain a relativistic treatment of the problem. In this formulation, the relativistic effects are treated by perturbation theory. The nonrelativistic part of the energy was, however, less accurate than the value given by Bunge,\textsuperscript{16} but a combination of the

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![Figure 2: Energy level diagram of the quartet levels of Li I.](image-url)

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two calculations yields an absolute term value for \(1s2s2p^4P^0\) of 463,046 cm\(^{-1}\) in close agreement with experiment. The predicted mass polarization effects have been tested and found to agree very well with the experimental values.\(^\text{23}\)

The identification of the 3490 Å line was due to calculations by Bunge,\(^\text{24}\) who assigned the line to the \(1s2s2p^2\,^5P-1s2p^1\,^5S^0\) transition in Li\(^-\). The electron affinity for attaching an electron to the \(1s2s2p^4P^0\) or \(1s2p^2\,^4P\) states was predicted to be positive indicating that the 3490 Å line could be considered as a satellite to the quartet "resonance" line at 3714 Å. This theoretical prediction of the first optical emission line in a negative atomic ion was readily confirmed experimentally.\(^\text{25}\) The fine and hyperfine structure of the quintet states of the \(^7\)Li\(^-\) ion are predicted\(^\text{26}\) to be of comparable magnitude, but experimental data are lacking. Several other optical transitions in atomic negative ions have been predicted\(^\text{27}\) but none of these have so far been confirmed experimentally.

The doubly excited Li I system is currently being studied\(^\text{28}\) as a potential source for energy storage for extreme-ultraviolet (XUV) lasers. The storage level considered, \(1s2s2p\,^4P_{3/2}\), is stable against decay in the absence of spin–spin interaction. By means of a tunable, picosecond-time-scale laser the stored population can be transferred to the \(1s2p^2\,^2P\) state, which decays primarily to \(1s^2p\,^2P\) by emission at 207 Å. Intense discharges leading to higher Li\((1s2s2p\,^4P)\) population than reported\(^\text{29}\) to date will be needed to demonstrate the XUV laser.

Only a very limited number of Li I core-excited radiating doublets are known,\(^\text{30}\) since the doubly excited configurations forming doublets are embedded in the \(1s^2\ell\,^2L\) continua. Experimentally eight core-excited doublets\(^\text{30}\) have been established with an accuracy of 10 cm\(^{-1}\) or better. For the bound states the theoretically predicted values\(^\text{17,18}\) are in good agreement with the experimental observations, whereas the accuracy of the calculations for the autoionizing states is considerably lower.

Be II and B III

Spectral lines from doubly excited Be II were first observed in 1971 by Berry \textit{et al.}\(^\text{31}\) when the 2324 Å line was assigned to the \(1s2s2p\,^4P-1s2p^2\,^4P\) transition on the basis of variational calculations by Holøien and Geltman.\(^\text{14}\) Shortly after, Hontzeas \textit{et al.}\(^\text{32}\) made a comprehensive
study of the quartet system, but lack of precise VUV wavelengths invalidated all attempts up to 1981 to establish unambiguously the Be II-quartet term scheme. In 1979 Larsson et al.\textsuperscript{8} dismissed most of the experimental assignments on the basis of Hylleraas calculations and left only four states, 1s2s2p \(^4P\), 1s2p\(^2\) \(^4P\), 1s2s3s \(^4S\), and 1s2p3s \(^4P\), firmly established.

The key to the quartet system is the position of the 1s2s3p \(^4P\) level, which Larsson et al.\textsuperscript{8} predicted. The Hartree–Fock calculations of \(^4D\) states by Ali\textsuperscript{13} and the very accurate configuration interaction calculations for a few \(^4D\) and \(^4F\) states by Galán and Bunge,\textsuperscript{10} provided sufficient theoretical support to allow identification of a large part of the Be II \(^4L\) system provided more accurate spectral data and lifetimes of quartet states could be obtained. Bentzen et al.\textsuperscript{34} and Mannervik et al.\textsuperscript{15} presented such data in 1981 allowing identifications of nearly all 2s3l, 2p3l, and 2s4l quartet states. Strong effects of electron correlation and configuration interactions are present in the Be II-quartet system. The low \(^4F\) states of odd parity, 2p3d and 2s4f, are so strongly mixed that single configuration notation makes practically no sense and strong configuration interaction is present in many of the series.

In order to establish the 2p4l and some of the 2s5l and 2p5l states, close cooperation has taken place between experiment\textsuperscript{7,8,37} and theory.\textsuperscript{7,8,37} This cooperation demonstrated the strong need for theoretical support in order to identify the multiply excited levels, but also revealed the limitations of the two methods used, i.e., the model potential and the multiconfiguration Hartree–Fock. Subsequent large-scale calculations with configuration interaction wave functions\textsuperscript{10} have improved the agreement between theory and experiment, but have not led to reassignment of any line. Figure 3 shows the established Be II-quartet term scheme. It does not include the highly excited 2p\(^3\) \(^4S\) state,\textsuperscript{12} which decays to 1s2p\(^2\) \(^4P\) at 80.85 Å.

For B III the lesson is much the same! The quartet states were first studied by To et al.\textsuperscript{38} but the line identification was hampered by the lack of even moderately accurate theoretical predictions of term energies and transition wavelengths. Calculations performed by various methods (Hylleraas,\textsuperscript{8} model potential\textsuperscript{19} or MCHF\textsuperscript{20}) all indicated that the main part of the published B III \(^4L\) term scheme was incorrect. However, these calculations were not sufficiently accurate to allow experimentalists to identify unambiguously the quartet transitions in the rather complicated boron beam-foil spectrum.
FIGURE 3. Energy level diagram of the quartet levels of Be II. These levels lie about 100 eV above the Be III ground state. All the transitions indicated are observed in beam-foil experiments. None of these lines has appeared in other light sources.

On the basis of more accurate configuration-interaction calculations by Chung et al., it has very recently been possible experimentally to establish a large part of the lower lying quartet states in Be III.

The complete revision needed for the Be II and Be III quartet schemes from those established only five years ago makes it very likely that serious errors are present in the quartet schemes for the higher Z members. Possible errors should now be predictable on the basis of the theoretical calculations as applied to Be II and Be III.

As a spinoff effect from the studies of the Be II \( ^4L \) system it has also been possible to establish the radiative transitions in the doubly excited Be II \( ^{2}L \) and Be I \( ^{2}L \) systems. Recent configuration interaction calculations have confirmed the experimental assignments which were based upon MCHF calculations.
Systems with $Z > 5$

For systems with $Z > 5$ recent studies have concentrated on the two lower quartet states $1s2s2p^2P^0$ and $1s2p^2^4P$, for which transition energies, fine structure splittings and level lifetimes have been the objects. The main goal of the experimental\textsuperscript{45} and theoretical\textsuperscript{46} work has been to explore the complexities of the multielectron correlation effects along the isoelectronic sequence and the importance of the relativistic contributions in simple atomic systems as the core-excited three-electron systems.

AUTOIONIZATION WIDTHS

Recently, it has been possible to obtain accurate autoionization widths for doublet resonance states in Li I\textsuperscript{47} and Be II\textsuperscript{48} from optical emission spectra. The $[1s(2s2p)^3P]^{2}P^0$ and $[1s2p2p)^3D$ resonances have been studied for both Li I and Be II, whereas the $[(1s2s)^5S3d]^{2}D$ resonance is studied only in Li I. These widths have been obtained by analyzing the broadened line profiles resulting from optical transitions connecting the autoionizing state with a radiating state, e.g., $[1s2p2p)^3P]^{2}P^0$ to $[1s2s2p)^3P]^{2}P^0$. Figure 4 gives the Be II doubly excited term scheme\textsuperscript{37} which indicates four autoionizing states populated from radiating states. So far only two of these widths have been studied.

The total width of these lines is the sum of the radiative and autoionization widths of the upper and lower states. In the energy region of interest, the relativistic spin-induced autoionization rates of the upper states are very small. The radiative widths of the upper and lower states can be neglected for Li with the experimental resolution obtained so far, but for the $[1s2p2p)^3P]^{2}P^0$ transition in Be II those widths have a small but non-negligible effect.\textsuperscript{48} As $Z$ increases along the isoelectronic sequence the contribution to the width from radiative decay will grow rapidly.

The experimental procedure for obtaining accurate linewidths from beam-foil spectra involves a careful determination of the spectral line profile with a proper normalization for beam fluctuations over the profile. The data analysis\textsuperscript{48} is done by deconvolution of the Lorentzian profile from the experimental line using an experimental response function obtained from sharp lines.

The experimental values for Li I and Be II have led to new the-
energy levels, fine-structure splittings and lifetimes of multiply excited states in three-electron systems. The progress made in recent years is clearly a result of a joint experimental and theoretical effort in order to establish the doublet and quartet term schemes and to study the properties of their radiative and autoionizing states.

Acknowledgment

One of us (T.A.) acknowledges the Danish Natural Science Research Council for a travel grant.

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