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Theoretical investigations on the $3d^9 4p - 3d^{10}$ spectrum of CuII

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Abstract

The low-lying level structure and the $3d^9 4p - 3d^{10}$ resonance and intercombination transitions of the spectrum CuII have been studied by using large-scale multiconfiguration Dirac–Fock wavefunctions. Excitation energies and transition probabilities are calculated by including all dominant effects of relativity, correlation, and of the rearrangement of the electron density within the same framework. Comparison with experiment and previous computations is made which shows a remarkable improvement in the accuracy of the theoretical results.

Keywords: MCDF method; Oscillator strength; Relativistic, relaxation and correlation effects; Transition probability

1. Introduction

The emission spectra of CuII has attracted considerable interest during the last years, both theoretically and experimentally. For a medium heavy element like copper, a rather (strong) interplay between relativistic and correlation effects has to be expected and is the reason that these effects cannot be treated independently of each other. Cu^+ ions, moreover, have a particular electronic structure so that even low-lying excitations from the stable $3d^{10}$ ground state (of the nickel sequence) immediately result in open *d*-shell configurations. Therefore, the low-lying spectrum of these ions are affected by strong relaxation effects when transitions occur from the ground state into some excited configuration. From a theoretical view point, the spectrum of CuII is thus a good candidate for testing our understanding of the electronic structure of medium-*Z* elements. Furthermore, measurements on the CuII spectrum have been found useful to determine the Cu abundance in interstellar H I clouds [1], for improving the gain of copper vapour lasers [2] as well as for the diagnostics of plasmas [3].

Over the years, a number of theoretical [4–9] and experimental [3,8,11–14] case studies have been carried out on the spectrum of CuII. Froese Fischer and Glass [4], for example, explored correlation effects of the $3d$ shell and its influence on the $3d^9 4p - 3d^{10}$ E1 resonance transitions of these ions; Theodosiou [6] and Loginov [7] both calculated the E1 transition probabilities among the $3d^{10}$, $3d^9 4s$ and $3d^9 4p$ configurations from which they were able to derive lifetimes for the $3d^9 4p$ levels. Most previous computations, however, have been performed in a rather nonrelativistic or even semiempirical approximation. While the mixing with some nearby lying configurations were often taken into account,

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neither the effects of relativity and relaxation on the spectrum of CuII nor any systematically enlarged basis have been included in these early calculations. Two recent computations in Breit–Pauli approximation were carried out by Pinnington et al. [8] and Donnelly et al. [9] who treated (at least) the dominant relativistic effects *in addition* to the dominant electron–electron correlations.

The low-lying $3d^9 4s$ and $3d^9 4p$ energy levels of Cu^+ are known experimentally for a long time; for instance, see Ref. [10]. Later measurements on the lifetimes and transition probabilities have been carried out by Curtis et al. [11], Kono and Hattori [12], Prior [13], Cederquist et al. [14] and Pinnington et al. [8] in using different techniques like beam–foil spectroscopy, ion trap techniques, delayed-coincidence, as well as laser-beams, respectively. Yet, the experimental lifetimes and transition probabilities are rather incomplete and scatter – along with the theoretical data available – quite remarkably. For the $^1P^o_1 - ^1S_0$ strong resonance line, for example, experimental lifetimes still differ by a factor of about 2 [4,6–9,12]. Therefore, further experimental and theoretical investigations are required to understand the features of this spectrum.

Below, we report on a large-scale multiconfiguration Dirac–Fock computation on the $3d^9 4p - 3d^{10}$ E1 resonance and intercombination transitions. In this investigation, we made use of our recently revised package RATIP [15–18] which now allows to incorporate most of the (dominant) physical effects of relativity, correlation, and of the rearrangement of the electron density consistently within the same framework. Our revised program [18] now supports (accurate) ab-initio computations even for atoms with open *p*- and/or *d*-shells which were not at all feasible in the past. In this contribution, we utilized this recently developed code to analyze the influence of electron correlations up to a large extent.

2. Method of computation

To calculate the Cu^+ low-lying level structure and transition probabilities, we applied wave functions from the known atomic structure code GRASP92 [19], an implementation of the multiconfiguration Dirac–Fock (MCDF) method. There is no need to repeat much about this method and its implementation since they have been utilized (although mainly for simpler shell structures) in a large variety of applications; for details, see Grant [20] or Ref. [21] for another application to a similar complex shell structure. In the MCDF model, electron correlations are treated by taking a linear combination of configuration state functions (CSF) of the same symmetry

$$|\psi_\alpha(PJM)\rangle = \sum_r^{n_c} c_r(\alpha)\ |\gamma_r PJM\rangle \qquad (1)$$

in order to approximate an atomic state with given angular momentum and parity (J^P). The number of CSF, n_c, and a proper choice of this (many-electron) basis will eventually determine to which extent correlations are included and will help distinguish between different *correlation* models (see below). In contrast to atoms and ions with only open *s* and *p* shells, however, open *d*-shell configurations are indeed very demanding regarding their size of the wave function expansions. Typically, expansions of several ten thousand CSF or of even larger size in Eq. (1) are required for describing the atomic levels of such shell structures properly. To generate the wave functions in ansatz (1), the CSF are constructed as antisymmetrized products of one-electron orbital functions and optimized on the basis of the Dirac-Coulomb Hamiltonian. Further relativistic contributions to the representation $\{c_r(\alpha)\}$ due to (transverse) Breit interactions were added later by diagonalizing the Dirac–Coulomb–Breit Hamiltonian matrix. We also analyzed the dominant QED corrections of the total energies. With regard to excitation energies, however, these contributions are still insignificant when compared with neglected correlations.

Many atomic transitions in the inner-shell and optical region are now known to be affected by the rearrangement of the electron density due to the emission or absorption of photons. While its influence on the wavefunctions is simple to incorporate by a separate optimization of the initial and final states of the transitions, special care has to be taken in calculating probabilities from these wavefunctions. In the computations below, we divided the levels – according to their total symmetry J^P – into two groups, one for the $3d^{10} J = 0$ ground state and

another for the three $J = 1$ levels of the excited $3d^9 4p$ configuration. Independent calculations have been carried out for these two groups. For calculating the probabilities with not quite orthogonal wave functions, we applied two (new) modules of RATIP [18]. Both modules utilize the wavefunctions as generated by the GRASP92 package [19]. In systematically enlarged wave function expansions, the inclusion of relaxation effects typically leads to improved transition probabilities and often require smaller expansions to achieve a certain accuracy when compared with a single *orthogonal* set for constructing the initial and final states together.

Different correlation models have been analyzed for the two level groups with symmetry $J^P = 0^+$ and 1^- by using the active space (AS) method. Apart from a single-configuration computations (SC), we included all virtual single (S) and double (D) excitations from the occupied $3d$ and $4s$ or $4p$ shells into the (unoccupied) $4l$ and $5l$ shells (below, these two correlation models are denoted by 4SD and 5SD, respectively). In our best representation of the atomic states, in addition, we incorporated also all triple excitations within the $4l$ layer (4SDT5SD).

3. Results and discussions

We first analyze the influence of electron correlations on the $3d^9 4p$–$3d^{10}$ resonance transitions. Wavefunction expansions of different complexity were explored to obtain the transition energies and probabilities.

In Table 1, the excitation energies in four different correlation models (see Section 2) are shown for the odd-parity levels $^3P^o_1$, $^3D^o_1$ and $^1P^o_1$. For these levels, any simple calculation in single-configuration approximation (SC) only yields a very rough estimate of the excitation energies which is not useful for experimental analysis. Virtual excitations within the $4l$ and $5l$ layers are required to obtain theoretical energies in reasonable agreement with experiment. Both, SD excitation into the $5l$ shells as well as triple excitation into $4l$ have a strong effect on the representation of the $3d^{10}$ ground state and increase the excitation energies by about 1000 cm^{-1} or even more. From the 4SDT5SD correlation model, it becomes clear that quadruple excitations (for the excited levels) and excitations in even higher layers might also play an essential role in obtaining energies which are accurate well below the 1% level.

Table 2 exhibits the influence of various models on the $^3P^o_1$–$^1S_0$, $^3D^o_1$–$^1S_0$, and $^1P^o_1$–$^1S_0$ transition probabilities. To emphasize the wave function effects on the decay probabilities, all data have been calculated by using experimental transition energies. Transition probabilities are displayed both in length and velocity gauge to facilitate the evaluation of our results in future work. For comparison, we also show the semiempirical transition probabilities of the $^3P^o_1$–$^1S_0$ intercombination and $^1P^o_1$–$^1S_0$ resonance lines as derived by Pinnington and coworkers [8] from the experimental lifetimes and HFX branching ratios (from Cowan's code [22]). We also display the value where this branching ratio was taken from the present computation in the 4SDT5SD model.

Table 1
Excitation energies (in cm^{-1}) of the $3d^9 4p$ $^3P^o_1$, $^3D^o_1$, and $^1P^o_1$ levels in different correlation models[a]

Models	$^3P^o_1$	$^3D^o_1$	$^1P^o_1$
SC	48 808	54 245	54 742
4SD	65 555	70 907	71 284
4SD5SD	66 532	71 707	72 122
4SDT5SD	68 703	73 856	74 267
Experiment [10]	67 916	73 102	73 595

[a] All excitation energies are taken relative to the total energy of the $3d^{10}$ $^1S_0$ ground state.

Table 2
Transition probabilities A (in 10^5 s^{-1}) of the $3d^9 4p$–$3d^{10}$ intercombination and resonance lines from different correlation models – the length and velocity gauge of the probabilities are denoted by A_L and A_V, respectively

	$^3P^o_1$–$^1S_0$		$^3D^o_1$–$^1S_0$		$^1P^o_1$–$^1S_0$	
Models	A_L	A_V	A_L	A_V	A_L	A_V
SC	67	72	502	549	4424	4757
4SD	73	83	992	1145	3880	4395
4SD5SD	68	74	732	823	3651	4066
4SDT5SD	76	77	830	866	3990	4127
Experiment	113[a], 85[b]				4302[a], 1792[c]	3433[b],

[a] Transition probabilities as derived from the experimental lifetimes and the theoretical HFX branching ratios of Pinnington et al. [8].

[b] Obtained from the same lifetimes as in [a] but using branching ratios according to this work.

[c] Kono et al. [12].

Table 2 gives rise to two observations: (i) Although the transition probabilities change quite remarkably for the 4SD and 5SD correlation models, showing the importance of these contributions, the two gauge forms do not get close to each other. A much better agreement of the two gauges (i.e. better than 4 %) is obtained only if triple excitation within the 4*l* layer are also included. (ii) A different convergence behaviour occurs for different transitions. For the two $^3P_1^o$–$^1S_0$ and $^3D_1^o$–$^1S_0$ weak lines, correlations among the electrons slightly increase the transition probabilities. In contrast, the decay rate of the $^1P_1^o$–$^1S_0$ resonance line decreases by including further excitations into higher shells. This trend of the transition probabilities – as the size of the basis is increased – is in very good agreement with the semiempirically derived data using experimental lifetimes. For both, the $^3P_1^o$–$^1S_0$ intercombination and the $^1P_1^o$–$^1S_0$ resonance lines, the theoretical branching ratio from our extensive computations is in reasonable and better agreement with our ab-initio results [23] than those obtained by HFX theory [22].

Further comparison of the transition probabilities of this work with previous computations is shown in Table 3. In fact, the transition probabilities of the various models which are known from the literature scatter quite remarkably, in particular for the medium and intercombination lines. Note, however, that the early (nonrelativistic) calculation by Froese Fischer and Glass [4] agrees well with our result for the resonance transition.

As pointed out before [6,8], the $^1P_1^o$–$^1S_0$ transition probability and the $^1P_1^o$ lifetime have been a puzzle for a long time. For the $3d^9 4p\ ^1P_1^o$ excited level, the lifetime is governed by the two $^1P_1^o$–$^1S_0$ and $^1P_1^o$–$^1D_2$ strong decay modes which lead either to the $3d^{10}$ ground state or to the $3d^9 4s$ metastable level. Knowing the branching ratio for these two decay modes and determining the lifetimes, Pinnington et al. [8] derived 4302×10^5 s^{-1} and 2958×10^5 s^{-1} as the probabilities of the $^1P_1^o$–$^1S_0$ and $^1P_1^o$–$^1D_2$ transitions, respectively. These values are rather different from their semiempirical estimates of 6626×10^5 s^{-1} and 4577×10^5 s^{-1}. Our present computations show in contrast a much better agreement with the experimental values of Pinnington et al. [8] and yield transition probabilities which are consistent with a semiempirical estimate.

4. Summary

Theoretical transition probabilities have been calculated for the $3d^9 4p$–$3d^{10}$ resonance and intercombination transitions. By applying MCDF wavefunctions of large size and a level-dependent generation of the wave functions, we are able to show a satisfactory *agreement* with recent measurements for both, the excitation energies and the transition probabilities. The present computations clearly improve the available data basis for Cu^+ ions and resolves the long-standing 'puzzle' about the $^1P_1^o$–$^1S_0$ resonance line in the CuII spectrum.

Table 3
Comparison of transition probabilities A (in 10^5 s^{-1}) from this work with previous calculations[a]

Author	Gauge form	$^3P_1^o$–$^1S_0$	$^3D_1^o$–$^1S_0$	$^1P_1^o$–$^1S_0$
This work	L	76	830	3990
	V	77	866	4127
Donnelly et al. (1999) [9]	L	223	2130	3170
	V	167	1650	2530
Pinnington et al. (1997) [8]	L	117	760	6626
Loginov (1993) [7]	L	64	177	4981
Theodosiou (1986) [6]	L			4579
Froese Fischer (1981) [4]	L			4432
	V			4203

[a] The length and velocity gauge forms of these probabilities are denoted by L and V, respectively.

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