Relativistic, relaxation, and correlation effects in spectra of Cu II

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The influence of relativistic, relaxation, and correlation effects on the low-lying energy levels of the $3d^{10}, 3d^9 4s$, and $3d^9 4p$ configurations of Cu II have been investigated. Large-scale multiconfiguration Dirac-Fock wave functions were applied to calculate the excitation energies and the electric-dipole-allowed transition probabilities and to allow for a systematic improvement of the computations. From these calculations, the theoretical lifetimes of the $3d^9 4p$ levels are derived and compared with previous experiments and computations. Our results show that we provide not only an improved data basis for the low-lying levels of Cu II but also a useful computational model for studying other ions along the nickel isoelectronic sequence.

I. INTRODUCTION

During recent years, the emission spectra of Cu II have attracted considerable interest, in both theory and experiment. For a medium-heavy element like copper, for example, a rather strong interplay between the relativistic and correlations effects has to be expected already, and they cannot be treated independently of each other. Moreover, Cu II ions are known for having a $^1S_0$ ground state with a closed $3d^{10}$ valence configuration (as in the nickel isoelectronic sequence), where excitations of a single $3d$ electron may result in a polarization and rearrangement of the ionic core. From a theoretical viewpoint, therefore, the spectrum of Cu II is a good candidate to test our understanding of the electronic structure of medium-Z elements. Furthermore, measurements on the Cu II spectra have been found useful to determine the Cu abundances in interstellar H I clouds [1], for improving the gain of copper vapour lasers [2] as well as in the diagnostics of plasmas [3].

Over the years, a number of theoretical [4–10] and experimental [3,11–15] studies have been carried out on the spectrum of Cu II. Froese Fischer and Glass [4], for example, explored the correlation effects of the $3d^n$ core shell and their influence on the $3d^9 4p$-$3d^{10} E1$ resonance transitions of these ions. Later, Theodosiou [7] and Loginov [8] both calculated the $E1$ transition probabilities among the $3d^{10}$, $3d^9 4s$, and $3d^9 4p$ configurations from which the lifetimes of the $3d^9 4p$ levels were derived. Most of these earlier computations, however, have been performed either in a nonrelativistic approximation or by making use of semiempirical scalings. Although these approximations allowed the inclusion of some of the important correlation effects, they typically neglected the effects of relativity and the relaxation of the electron density on the spectrum of Cu II. Moreover, no systematically enlarged configuration basis was applied in all of these earlier computations. In fact, the dominant contributions of relativity were included only recently in two independent Breit–Pauli computations by Pinnington *et al.* [9] and Donnelly *et al.* [10], but were treated as (purely) *additive* to the electron-electron correlations.

Experimentally, the excitation energies of the low-lying $3d^9 4s$ and $3d^9 4p$ levels of Cu II have been known for a rather long time [11]. During the past three decades, a number of measurements on the lifetimes and transition probabilities have been carried out by Curtis *et al.* [12], Kono and Hattori [13], Prior [14], Cederquist *et al.* [15], Lopez-Urrutia *et al.* [3], and Pinnington *et al.* [9] using, for example, beam-foil spectroscopy, ion-trap measurements, and delayed-coincidence and laser-beam techniques. Yet, the experimental lifetimes and transition probabilities are rather incomplete and scatter—along with the available theoretical data—quite remarkably. Even for the strong $3d^9 4p \ ^1P_1^o$–$3d^{10} \ ^1S_0$ and $3d^9 4p \ ^1P_1^o$–$3d^9 4s \ ^1D_2$ transitions, for instance, the experimental transition probabilities still differ by about a factor of 2-3 [3,7–10,12,13]. Therefore, further experimental and theoretical investigations are required in order to understand the features of this spectrum.

Based on the widely used multiconfiguration Dirac-Fock (MCDF) method [16], additional tools and computational procedures have been developed recently by us [17,18], in which the effects of relativity, relaxation, and correlations can be treated consistently for various transition and ionization properties. Using these tools, for instance, we studied several complex spectra including atoms and ions with open p and d shells [19–23]. In the present work, the same techniques are applied to investigate the effects of relativity, relaxation and electron-electron correlations on the low-lying energy levels of the $3d^{10}, 3d^9 4s$, and $3d^9 4p$ configurations of Cu II. In Sec. II, we first provide a short description of the theoretical method and computational procedure. In Sec. III, the influences of the various effects on the spectra of Cu II are analyzed for several selected energy levels and transition probabilities. From these data, we also derived the lifetimes of the $3d^9 4p$ levels and compare them with previous experiments and computations. Finally, a few conclusions about the spectra of nickel-like ions are summarized in Sec. IV.

II. THEORETICAL METHOD

A. MCDF method

In this study, the wave functions were generated by the widely used atomic structure package GRASP92 [16]. In the

MCDF method, the Dirac-Coulomb Hamiltonian of a given atom or ion with N electrons is given by

$$\mathcal{H}^{\text{DC}} = \sum_{i=1}^{N} \mathcal{H}_i + \sum_{i \neq j}^{N} \frac{1}{r_{ij}} \qquad (1)$$

where $\mathcal{H}_i$ is the one-electron Dirac Hamiltonian including its kinetic energy and the interaction with the nucleus. This Hamiltonian has the form

$$\mathcal{H}_i = c \sum_{k=1}^{3} \boldsymbol{\alpha}_{\mathbf{k}} \cdot \mathbf{p}_{\mathbf{k}} + (\beta_i - 1)c^2 - \frac{Z}{r_i}. \qquad (2)$$

An atomic state function (ASF) of the system can be expressed by

$$\psi_\alpha(PJM) = \sum_{r=1}^{n_c} c_r(\alpha) |\gamma_r PJM\rangle, \qquad (3)$$

where n_c is the number of the configuration state wave function (CSF) and $c_r(\alpha)$ the configuration mixing coefficients corresponding to each single CSF. In a standard computation, the CSFs are antisymmetrized products of a common set of *orthonormal* orbitals which, together with the mixing coefficients, are optimized in a self-consistent field (SCF) procedure on the basis of the Dirac-Coulomb Hamiltonian.

B. Breit interaction and QED corrections

Apart from the Dirac-Coulomb Hamiltonian, the Breit interaction also plays an important role in understanding the electronic structure of medium and heavy atomic systems. The Breit interaction arises from the (relativistic) retardation and the current-current interaction of fast-moving charges

$$\mathcal{H}_{\text{trans}} = -\sum_{i \neq j}^{N} \left(\frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j \cos(\omega_{ij} r_{ij})}{r_{ij}} + (\boldsymbol{\alpha}_i \cdot \boldsymbol{\nabla}_i) \right.$$
$$\left. \times (\boldsymbol{\alpha}_j \cdot \boldsymbol{\nabla}_j) \frac{\cos(\omega_{ij} r_{ij}) - 1}{\omega_{ij}^2 r_{ij}} \right), \qquad (4)$$

and can be interpreted also as the exchange of a single transverse photon. Often, the contributions from the Breit interaction are calculated in the low-frequency limit ($\omega_{ij} \rightarrow 0$) by diagonalizing the Dirac-Coulomb-Breit Hamiltonian matrix. This procedure of diagonalizing the Hamiltonian matrix corrects the total level energies and mixing coefficient but not the wave functions as it is not included directly in the SCF procedure.

The dominant quantum-electrodynamical (QED) contributions, i.e., the self-energy and vacuum polarization corrections, are also included in the computations of the transition energy as suggested in Ref. [16]. Whereas the self-energy is estimated simply by a scaling of the hydrogenlike data with a proper screening due to the other $N-1$ electrons, the vacuum polarization is included into the Hamiltonian matrix and affects both the energies and mixing coefficients.

C. Systematic consideration of electron correlation

In order to include a sufficiently large number of CSFs in the expansion of the MCDF wave functions, the active space

(AS) method as discussed by Roos *et al.* [24] has been applied in order to generate the configuration state list systematically. In this method, we may start either from a single or from several reference configurations in line with the occupation of the atomic subshells and configurations of interest. From these reference configurations, the lists of CSFs with given total angular momentum J and parity P are generated systematically by replacing (exciting) electrons from the occupied shells into the unoccupied orbitals of a given active orbital set.

Using the AS method, one can easily generate very large wave function expansions including radial and angular correlations to a large extent. In practice, however, it is often impossible to include all of these CSFs in the self-consistent-field calculation due to the technical difficulties in solving the MCDF equations with a large number of (excited) one-electron orbitals at the same time. Therefore, a number of individual steps are usually carried out in order to obtain all the orbitals of the active set, starting from the innermost orbitals and by *adding* more and more (layers of) correlation orbitals. To obtain convergence of the correlation orbitals, the inner orbitals are often kept frozen as further orbitals are added outside.

D. Theoretical treatment of relaxation effects

The relaxation of the electron density refers to the change of the bound-state electron orbitals due to the emission or absorption of a photon. To include this effect in the wave functions of the initial, and final-state wave functions in a straightforward manner, a separate MCDF calculation is necessary for the atomic levels of interest. Such an independent computation of the wave functions, however, yields two sets of electron orbitals which are not quite orthogonal to each other.

To incorporate the effects of relaxation in the computation of transition amplitudes, the *overlap* of the initial- and final-state orbitals has to be treated properly in the evaluation of the many-electron matrix elements. Recently, two computational modules CESD and REOS have been developed by Fritzsche *et al.* [17,18] on the basis of the matrix expressions as derived by Löwdin [25]. These modules were designed to use the wave functions from the GRASP92 package [16] and to first carry out an expansion of the atomic states in a Slater-determinant basis.

Often, the transition probabilities are calculated for different gauges of the radiation field including, in the relativistic computations, the Babushkin and Coulomb gauges. In the nonrelativistic limit, these two gauges correspond to the length and velocity forms of the electron-photon interaction. While the length results usually reflect the behavior of the wave functions near the nucleus (i.e., for small radii r), the velocity gauge probes the character of the wave functions at larger distance. In principle, of course, the transition probabilities should be independent of the particular gauge form if the representation of the wave functions is accurate. Therefore, the agreement between the different gauges is sometimes taken as a *measure* for the accuracy of the computation. Note, however, that this is a necessary but not sufficient

TABLE I. Contributions of the relativistic and QED effects to the total energies E_t and the excitation energies E_e for three selected atomic states (in cm^{-1}).

Model	$^1S_0$		$^3D_1$		$^3P_1^o$	
	E_t	E_e	E_t	E_e	E_t	E_e
NR	−359658657	0	−359648332	10325	−359608602	50055
MCDF	−362838465	0	−362830573	7892	−362789881	48584
MCDF+Breit	−362690193	0	−362682301	7892	−362641561	48632
MCDF+Breit+QED	−362596324	0	−362588373	7951	−362547516	48808
Experiment [11]		0		23998		67916

criterion. For a larger part of the spectrum (set of transition amplitudes), the agreement of the different gauge forms still provides insight into the quality of the chosen approximation. For this reason, we have calculate all transition probabilities in both gauges. The results in length gauge are usually considered to be more reliable because they probe the wave functions in a similar (radial) region as does the optimization procedure on the total energy of the atoms or ions.

III. RESULTS AND DISCUSSIONS

In this section, the influence of the relativistic, relaxation, and correlation effects on the atomic state wave functions and energies is presented and discussed, including the electric-dipole transition probabilities among the low-lying levels of the $3d^94p$, and $3d^94s$ levels and the $3d^{10}$ ground-state configuration. From these computations, the lifetimes of the $3d^94p$ levels are derived and compared with previous theoretical and experimental results.

A. Relativistic effects

Relativistic effects are first investigated by comparing the relativistic computations with the corresponding nonrelativistic (NR) results. These nonrelativistic results were obtained by enlarging the speed of light, i.e., the inverse of the fine-structure constant ($1/c$), by a factor of 1000. In order to ensure a proper nonrelativistic limit, moreover, the important correlations within a nonrelativistic single-configuration calculation are included also in the MCDF computations.

Table I displays the total and excitation energies for the three selected levels $^1S_0$, $^3D_1$, and $^3P_1^o$ from the $3d^{10}$, $3d^94s$, and $3d^94p$ configurations, respectively. Different approximations have been used to demonstrate the relativistic and QED effects on the level energies. For comparison, moreover, we also list the experimental excitation energies as available from the literature [11].

As seen from this table, the relativistic MCDF calculations increase the total binding energy by about 320×10^4 cm^{-1}, when compared with the NR calculation for each state, while the Breit and QED interactions reduce the binding by 14.8×10^4 and 9.4×10^4 cm^{-1}, respectively. However, because these contributions are approximately the same for both the ground and excited states, we cannot obtain a reasonable excitation energy in the single-configuration approach, compared with experiment. It demonstrates the need to include correlation effects to a much larger extent for both the ground and excited states as discussed below.

In Table II, moreover, the influence of the various relativistic effects are shown for the transition probabilities of a few selected electric-dipole lines. To "exclude" the influence of the transition energy on the probabilities, the experimental energies were used in all these computations. As seen from this table, the MCDF results are always smaller than those from the NR approximation for the dipole-allowed transitions $^1P_1^o$-$^1S_0$ and $^3P_1^o$-$^3D_1$. For the spin–forbidden $^3P_1^o$-$^1S_0$ and $^1P_1^o$-$^3D_1$ transitions, in contrast, all results are reasonabley close to zero as expected from the (purely) NR limit of these lines. These transitions are mainly caused by the mixture between the singlet and triplet states where the mixing coefficients can become as large as about 0.4. As pointed out by Kim et al. [26] in studying the $2s2p$ $^3P_1^o$–$2s^2$ $^1S_0$ transition of Be I and C II, the transition probabilities of these intercombination lines should be zero in the NR limit of the MCDF computation but this often requires special care in the generation of the wave functions.

In addition, the Breit interaction which is included only in first-order perturbation theory in the Hamiltonian matrix leads to a change of the mixing coefficients and may reduce the transition probabilities by 10–40 % for the spin-forbidden (or intercombination) lines. For the allowed transitions, in contrast, the effect of the Breit interaction is small and often leads to an increase of the transition probabilities, a conclusion which is similar to those from previous studies for several light atoms [27,28].

TABLE II. Influences of relativistic effects on the transition probabilities of 4 selected transitions (in 10^5 s^{-1}).

Transition	NR	MCDF	MCDF+Breit	Experiment[a]
$^1P_1^o$-$^1S_0$	4810	4151	4424	3433
$^3P_1^o$-$^1S_0$	0.02	80	67	85
$^1P_1^o$-$^3D_1$	2.88	593	370	447
$^3P_1^o$-$^3D_1$	1215	749	772	635

[a]As obtained from the experimental lifetimes of Pinnington et al. [9] and the present theoretical branching ratios (see Table X of this work).

TABLE III. Mean orbital radii of the occupied orbitals in the ground and excited states (in atomic units).

Orbital	Level dependent			Level independent
	$3d^{10}$ $(J^P=0^+)$	$3d^94s$ $(J^P=1^+)$	$3d^94p$ $(J^P=1^-)$	$3d^{10}+3d^94s+3d^94p$ $(J^P=0^+,1^+,1^-)$
$3s$	0.713	0.710	0.710	0.710
$3p$-	0.747	0.741	0.740	0.741
$3p$	0.757	0.750	0.750	0.751
$3d$-	0.977	0.915	0.906	0.921
$3d$	0.987	0.917	0.911	0.924

B. Relaxation effects

As mentioned above, *relaxation effects* refer to the rearrangement of the electron density if the atom or ion undergoes a transition. Usually, these effects are taken into account by the separate generation of the wave functions for the initial and final states of a given transition and by evaluating the transition amplitudes with one-electron orbitals which are not quite orthogonal to each other. To demonstrate the effects of an independent optimization of the wave functions, Table III shows the mean orbital radii of the occupied $3s$, $3p$-, $3p$, $3d$-, and $3d$ valence orbitals for the two cases of a level-dependent and level-independent calculation. For the $1s$, $2s$, $2p$-, and $2p$ core orbitals, in contrast, the (shape and) radii of the orbitals are much less sensitive and, hence, have been omitted from the table.

As seen from Table III, there are quite remarkable differences in the orbital radii between the *level–dependent* and *level–independent* computations. Unlike what one might expect, the mean radii of the $3d^{10}$ $(J^P=0^+)$ ground-state orbitals (column 2) are always larger than for the $J^P=1^+$ and 1^- excited states of the $3d^94s$ and $3d^94p$ configurations. This feature is remarkable, in particular, for the active $3d$- and $3d$ orbitals. The difference in the mean radius of the $3d$- and $3d$ orbitals between the $3d^{10}$ $(J^P=0^+)$ and $3d^94s, 4p$ $(J^P=1^+,1^-)$ states reaches about 0.7%, while that between the $J^P=1^+$ and 1^- excited states remains rather small. When compared with the level-indendent computations, the largest changes occur for the $3d$- and $3d$ orbitals. For the transition probabilities, we may therefore expect a large influence for the $3d^{10}$-$3d^94l$ $(l=s,p)$ transitions, which include an excitation of a $3d$ electron, whereas the transitions among the $3d^94s$ and $3d^94p$ configurations are likely less affected by the rearrangement of the electrons.

The effect of relaxation on the transition rates of two selected $\Delta n=1$ and $\Delta n=0$ transitions are shown in Table IV. For each of these transitions, we display the transition probabilities as obtained *without* relaxation, i.e., from the level-independent generation of the initial- and final-state wave functions, and *with* relaxation (the level-dependent optimization of the wave functions). Again, in order to exclude the influence of the transition energy on the probabilities, all the rates have been calculated by using experimental energies. As expected, the largest influence of the rearrangement arises for the $\Delta n=1$ transitions, independent of whether the spin

TABLE IV. Influences of the relaxation effects on the transition probabilities A (in 10^5 1/s). Here the transition probabilities are presented only in the length gauge.

Transition	Without relaxation	With relaxation	Experiment[a]
	$3d^94p-3d^{10},\Delta n=1$		
$^3P^o_1$-$^1S_0$	2	67	85
$^1P^o_1$-$^1S_0$	270	4424	3433
	$3d^94p-3d^94s,\Delta n=0$		
$^3P^o_1$-$^3D_1$	786	772	635
$^1P^o_1$-$^3D_1$	75	370	447

[a]As obtained from the experimental lifetimes of Pinnington *et al.* [9] and the present theoretical branching ratios (see Table X of this work).

state of the levels (multipolarity) changes or not. For these transitions, the computations without relaxation yields pretty wrong results when compared with the experimental data available. For the $\Delta n=0$ transitions, in contrast, we observe a quite different behavior for the transition amplitudes of the spin-allowed and -forbidden lines concerning the effects of relaxation, as here only the $^1P^o_1$-$^3D_1$ intercombination transitions appears to be sensitive to the rearrangement of the electrons.

C. Correlation effects

From a theoretical viewpoint, relaxation and correlation effects are not independent of each other as the rearrangement of the electron density can be treated by configuration interaction or (many-body) perturbation techniques. In practice, however, it is often useful to distinguish between changes of the one-electron densities (i.e., the changes of the orbital functions) and the interaction of the (many-electron) configuration state functions. This distinction mainly arises from the fact that huge configuration expansions are usually required in order to incorporate the rearrangement of the density as obtained from an independent variation of the wave functions. Here, we adopt this *relaxation* picture by making use of independently generated orbitals for the $3d^{10}$ $^1S_0$ ground state and for the various J^P level groups of the $3d^94s$ and $3d^94p$ configurations. To investigate the effects of the size of the wave functions on the excitation energies and transition probabilities, a series of large-scale MCDF computations have been carried out for a few se-

TABLE V. Some possible correlation models and number of CSF, in the ASF expansion for several selected level groups.

Model	$3d^{10}$ $(J^P=0^+)$	$3d^94s$ $(J^P=1^+)$	$3d^94s$ $(J^P=2^+)$	$3d^94p$ $(J^P=1^-)$
SC	1	1	2	3
4SD	1016	915	1334	1876
4SD5SD	5821	5024	7364	11806
4SDT5SD	7310	7258	10562	15963

TABLE VI. Contributions of correlation effects on the excitation energies for several selected levels (in cm^{-1}).

Model	$^3D_1$	$^1D_2$	$^3P_1^o$	$^1P_1^o$
SC	7951	10800	48808	54742
4SD	21923	24516	65555	71284
4SD5SD	22780	25034	66532	72122
4SDT5SD	24906	27278	68703	74267
Experiment [11]	23998	26265	67916	73595

lected levels (and transitions among these levels) using different *correlation* models. Apart from the single-configuration (SC) model, all virtual single (S) and double (D) excitations from the occupied $3d$, $4s$, and $4p$ shells into the (unoccupied) $4l$ and $5l$ subshells have been taken account. In Tables V and VI, these models are denoted by 4SD and 4SD5SD, respectively. For the $4l$ layer, in addition, we also incorporated triple excitations (4SDT5SD). Table V shows the number of CSFs in Eq. (3) which are utilized in the wave function expansion of the corresponding J^P level groups with given total angular momentum and parity.

Table V displays the size of the wave function expansions in a symmetry-adapted basis, built from a set of orthonormal orbitals. For the representation of the $3d^94p$ ($J^P = 1^-$) levels, for instance, the 4SDT5SD correlation model results in a total of 15 963 CSFs as used for the diagonalization of the (Coulomb-Breit) Hamiltonian matrix. For the evaluation of the transition amplitudes, moreover, these expansions must be first transformed into a determinant basis in order to make use of Löwdin's expressions for Slater determinants which are constructed from not quite orthogonal orbitals. For the $J^P = 1^-$ levels from above, the 4SDT5SD model then gives rise to 156 298 determinants which is near to the limit of what is compuationally feasible today. The proper expansion of the wave functions help incorporate, however, the main correlation and relaxation effects in both the computation of the excitation energies and transition probabilities.

Table VI displays the excitation energies of four selected levels as the size of the wave function expansions is increased systematically. While the $^3D_1$ and $^1D_2$ levels here belong to the $3d^94s$ configuration, the $^{1,3}P_1^o$ levels are due to the $3d^94p$ configuration. In all these cases, the SC approximation only provides a rough estimate of the excitation en-

ergies which cannot be used for the analysis of experiments. Instead, the SD excitations into the $4l$ and $5l$ subshells are required at least to obtain theoretical energies in reasonable agreement with experiment. Both the excitations into the $5l$ layer as well as triple excitations into $4l$ strongly affect the ground-state representation and increase the excitation energies by about 1000 cm^{-1} or even more. From these computations, it becomes clear that excitations into higher subshells or even quadruple excitations might become necessary if one wishes to obtain theoretical excitation energies which are accurate to about 1% or less.

In Table VII, we display the influences of various correlation models on the transition probabilities of five selected lines. To emphasize the effects of the wave functions, independent of the energies as obtained in these models, the experimental transition energies were used in the computation of the probabilities. Both the (theoretical) transition rates in length and velocity gauges are shown to indicate the effects for the different "coupling" of the radiation field and to facilitate the data evaluation of these results in future case studies. In addition to our *ab initio* rates, we also display the semiempirical data of the transition probabilities as derived from the experimental lifetimes of Pinnington and co-workers [9] and the branching ratios from the 4SDT5SD model (see Table X of this work).

From the analysis of Table VII, two observations are apparent. (i) Although the transition probabilities change quite remarkably in going from the 4SD to the 4SD5SD models, they do not become very close to each other. Despite the importance of the single and double excitations into the $5l$ subshells, this indicates that a good deal of further correlation is needed in order to obtain an accurate description of these lines. Performing a number of test computations, we recognized that a reasonable agreement of the two gauges—to better than 4%—is obtained only if triple excitations are taken into account within the $4l$ layer. From the comparison of the different lines (columns), moreover, we see (ii) a rather different trend (and convergence) as the size of the wave functions is increased. While, for example, the transition probabilities increase for the $^3P_1^o$-$^1S_0$ and $^3P_1^o$-$^1D_2$ weak lines, they decrease for the other strong resonance lines, in line with the semiempirical data as obtained from the experimental lifetimes.

TABLE VII. Contributions of correlation effects on the transition probabilities for several selected transitions (in 10^5 s^{-1}). A_L and A_V are the probabilities in the length and velocity gauges, respectively.

Model	$^3P_1^o$-$^1S_0$		$^1P_1^o$-$^1S_0$		$^3P_1^o$-$^3D_2$		$^3P_1^o$-$^1D_2$		$^1P_1^o$-$^1D_2$	
	A_L	A_V	A_L	A_V	A_L	A_V	A_L	A_V	A_L	A_V
SC	67	72	4424	4757	3921	3570	47	47	5197	4251
4SD	73	83	3880	4395	3759	4198	64	80	4507	4707
4SD5SD	68	74	3651	4066	3422	3658	65	75	4203	4272
4SDT5SD	76	77	3990	4127	3425	3628	68	76	4183	4235
Experiment[a]	85		3433		3474		85		3582	

[a]As obtained from the experimental lifetimes of Pinnington *et al.* [9] and the present theoretical branching ratios (see Table X of this work).

TABLE VIII. Excitation energies and lifetimes of the $3d^9 4p$ levels.

| Level | Energy (cm^{-1}) | | Lifetime (10^{-9} s) | | |
	This calc.	Expt. [11]	Length	Velocity	Experiment
$^3P_0^o$	69061	68850	2.56	2.28	2.58±0.08[a]
$^3P_1^o$	68703	67916	2.39	2.21	2.36±0.05[a]
$^3D_1^o$	73856	73102	1.71	1.80	
$^1P_1^o$	74267	73595	1.15	1.13	1.34±0.22[a], 1.7±0.3[b], 1.8±0.2[c]
$^3P_2^o$	66984	66419	2.62	2.20	2.72±0.05[a]
$^3F_2^o$	70341	69868	2.31	2.67	2.8±0.3[d]
$^1D_2^o$	72204	71494	2.20	2.34	2.48±0.05[a], 3.0±0.3[d]
$^3D_2^o$	74033	73353	2.04	2.22	2.51±0.09[a]
$^3F_3^o$	69040	68448	2.42	2.78	2.39±0.07[a], 2.5±0.2[b]
$^1F_3^o$	71476	70842	2.37	2.59	2.53±0.06[a], 3.1±0.5[b], 3.1±0.3[d]
$^3D_3^o$	72619	71920	2.02	2.18	2.21±0.04[a], 2.1±0.3[b]
$^3F_4^o$	69080	68731	2.31	2.51	2.18±0.04[a], 2.5±0.3[b], 3.0±0.3[d]

[a]Pinnington *et al.* [9].
[b]Kono and Hattori [13].
[c]Curtis *et al.* [12].
[d]Cederquist *et al.* [15].

D. Excitation energies and lifetimes of the $3d^9 4p$ levels

Using our *best* 4SDT5SD correlation model, the excitation energies and lifetimes have been calculated for all $3d^9 4p$ levels as shown in Table VIII. In these computations, therefore, the most important effects from relativity and the correlation of the electron-electron interaction are taken into account. For comparison, moreover, the experimental excitation energies [11] as well as the lifetimes available [9,12,13,15] are also listed in this table. Overall, a good agreement between the calculated and the experimental energies is found for most of the lines. From the comparison of the lifetimes with the available experimental results, we see that our present computation is typically closer to the experiment of Pinnington *et al.* [9] than to the previous measurements [12,13]. Only for the $^1P_1^o$ and the $^{1,3}D_2^o$ levels, are the present computations about 10% smaller than the experiment by Pinnington *et al.* [9]. No measurements have been carried out (yet) for the $^3D_1^o$ level, while for the $^3F_2^o$ level there is only the early measurement by Cederquist *et al.* [15]. Since, typically, the lifetimes by Cederquist *et al.* are slightly larger than those by Pinnington and co-workers, we conclude that

our predicted $^3F_2^o$ lifetime still appears very reasonable. In most cases, in addition, the lifetimes in length and velocity gauges are found in good agreement with each other.

In Table IX, we compare our theoretical lifetimes (in both gauges) with a number of previous computations from the literature; they are shown for the four levels $^1P_1^o$, $^1D_2^o$, $^3D_2^o$, and $^3D_1^o$, respectively. The largest deviations occur for the $^1P_1^o$ level for which the computations of Donnelly *et al.* [10] is larger by about 20% while those by Pinnington *et al.* [9] and Loginov [8] are smaller by a similar amount. As discussed in Ref. [21], these deviations are mainly caused by the different computations for the two strong transitions $^1P_1^o$-$^1S_0$ and $^1P_1^o$-$^1D_2$.

E. Transition probabilities of the $3d^9 4p$-$3d^9 4s$ and $3d^9 4p$-$3d^{10}$ transitions

In Table X, we list the theoretical transition probabilities and branching ratios from the upper $3d^9 4p$ levels to the lower $3d^{10}$ ground state and the $3d^9 4s$ excited levels. Beside of these *ab initio* results, we also display a number of semi-

TABLE IX. Comparison of the calculated lifetimes with previous computations for four selected levels of the $3d^9 4p$ configuration (in 10^{-9} s).

| Author | $^1P_1^o$ | | $^1D_2^o$ | | $^3D_2^o$ | | $^3D_1^o$ | |
	Length	Velocity	Length	Velocity	Length	Velocity	Length	Velocity
This work	1.15	1.13	2.20	2.34	2.04	2.22	1.71	1.80
Donnelly *et al.* [10]	1.39	1.61	2.72	2.58	2.69	2.76	1.60	1.87
Pinnington *et al.* [9]	0.87		2.14		2.07		1.72	
Loginov [8]	0.94		1.80		1.67		1.53	
Theodosiou [7]	1.06		1.89		2.08		1.91	

TABLE X. Transition probabilities A (in 10^5 s^{-1}) and branching ratios of the $3d^94p$-$3d^{10}$, $3d^94s$ transitions in Cu II. A_L and A_V are the transition probabilities in the length and velocity gauges, respectively.

Transition	Ab initio		Branching	Semiempirical results			
i-f	A_L	A_V	ratio	This work	Pinnington et al. [9]	Crespo et al. [3]	Kono and Hattori [13]
$^3P_0^o$-$^3D_1$	3901	4368	1.00	3876	3875		3690
$^3P_1^o$-$^1S_0$	76	77	0.02	85	113		
$^3D_1^o$-$^1S_0$	830	866	0.14				
$^1P_1^o$-$^1S_0$	3990	4127	0.46	3433	4302		
$^3P_1^o$-$^3D_1$	629	716	0.15	635	629		540
$^3D_1^o$-$^3D_1$	3693	3385	0.62				3960
$^1P_1^o$-$^3D_1$	561	506	0.06	447	193		230
$^3P_1^o$-$^3D_2$	3425	3628	0.82	3474	3419		3080
$^3P_1^o$-$^1D_2$	68	76	0.02	85	77		78
$^3D_1^o$-$^3D_2$	979	849	0.16				930
$^3D_1^o$-$^1D_2$	420	453	0.07				
$^1P_1^o$-$^3D_2$	0	1	0.00		13		58
$^1P_1^o$-$^1D_2$	4183	4235	0.48	3582	2958		4090
$^3P_2^o$-$^3D_1$	16	19	0.00	15	15		
$^3F_2^o$-$^3D_1$	2744	2364	0.64			2370	2370
$^1D_2^o$-$^3D_1$	845	761	0.19	766	1206		980
$^3D_2^o$-$^3D_1$	845	753	0.17	677	526		840
$^3P_2^o$-$^3D_2$	265	313	0.07	257	264	340	210
$^3P_2^o$-$^1D_2$	17	22	0.00	15	15		
$^3F_2^o$-$^3D_2$	1522	1326	0.35			1550	1640
$^3F_2^o$-$^1D_2$	5	4	0.00				
$^1D_2^o$-$^3D_2$	1854	1723	0.41	1653	1586		1720
$^1D_2^o$-$^1D_2$	1739	1697	0.38	1532	1121		1480
$^3D_2^o$-$^3D_2$	1196	1058	0.24	956	632		1030
$^3D_2^o$-$^1D_2$	2592	2449	0.54	2152	2569		
$^3P_2^o$-$^3D_3$	3508	4173	0.92	3382	3382	3270	3340
$^3F_2^o$-$^3D_3$	50	43	0.01			8	
$^1D_2^o$-$^3D_3$	101	91	0.02	81	120	96	57
$^3D_2^o$-$^3D_3$	260	232	0.05	199	164		250
$^3F_3^o$-$^3D_2$	3125	2651	0.76	3180	3177	2540	2830
$^3F_3^o$-$^1D_2$	317	308	0.08	335	322	480	360
$^1F_3^o$-$^3D_2$	10	4	0.00	10	12		
$^1F_3^o$-$^1D_2$	2702	2419	0.64	2530	1851		2170
$^3D_3^o$-$^3D_2$	1319	1125	0.27	1222	1212	1410	1390
$^3D_3^o$-$^1D_2$	898	798	0.10	814	1580	1080	1100
$^3F_3^o$-$^3D_3$	676	628	0.16	669	686	800	640
$^1F_3^o$-$^3D_3$	1506	1439	0.36	1422	2089	2210	2210
$^3D_3^o$-$^3D_3$	2713	2657	0.55	2489	1732		1920
$^3F_4^o$-$^3D_3$	4324	3975	1.00	4587	4588	3330	4190

empirical transition probabilities in this table. These semiempirical data were derived from our theoretical branching ratios in length gauge and the experimental lifetimes of Pinnington et al. [9] as well as from the branching ratios of Cowan's code [29], and including further results by Lopez-Urrutia et al. [3] and Kono et al. [13].

As seen from Table X, a good agreement is found between the present *ab initio* computations and the semiempir-

ical estimations, using the lifetimes of Pinnington et al. [9]. A clear discrepancy only occurs for a few lines which arise from the (upper) $^1P_1^o$, $^1D_2^o$, $^3D_2^o$, $^1F_3^o$, and $^3D_3^o$ levels. In order to understand these deviations, Table XI displays a detailed comparison between the present results and previous computations for six selected lines, showing a rather wide scattering of the data. These differences indicate the sensitivity of the transition probabilities from the theoretical model

TABLE XI. Comparison of calculated transition probabilities A (in 10^5 s^{-1}). L and V here represent the length and velocity gauge forms, respectively.

Author	Gauge	$^1P_1^o$-^1S_o	$^1P_1^o$-$^1D_2$	$^1D_2^o$-$^3D_1$	$^3D_2^o$-$^3D_2$	$^1F_3^o$-$^3D_3$	$^3D_3^o$-$^3D_3$
This work	L	3990	4183	845	1196	1507	2713
	V	4127	4235	761	1058	1439	2657
Donnelly *et al.* [10]	L	3170	2890	890	568	461	3050
	V	2530	2550	918	511	422	2990
Pinnington *et al.* [9]	L	6626	4577	1400	786	2409	1853
Loginov [8]	L	4981	5452	1306	1306	2484	2887
Theodosiou [7]	L	4579	4890		3620		4660
Froese Fischer and Glass [4]	L	4432					
	V	4203					

and, hence, the need for taking a sufficiently large wave function expansion in order to include the important many-electron effects.

As pointed out before in Refs. [7,10], the lifetime of the $^1P_1^o$ level is determined by the two—similarly strong—transitions $^1P_1^o$-$^1S_0$ and $^1P_1^o$-$^1D_2$, which have remained as a puzzle for a long time. For the $^1P_1^o$-$^1S_0$ line, for example, Froese Fischer and Glass [4] originally obtained the probabilities 4432×10^5 s^{-1} (in length gauge) and 4203×10^5 s^{-1} (in velocity gauge) while, for the $^1P_1^o$-$^1D_2$ line, a theoretical transition probability of 1200×10^5 s^{-1} was obtained by Corliss *et al.* (see reference in Ref. [4]) and the experimental lifetime 1.8×10^{-9} s of the $^1P_1^o$ level was measured by Curtis *et al.* [12]. Later, Kono and Hattori [13] presented the rate 1792×10^5 s^{-1} for the $^1P_1^o$-$^1S_0$ transition according to the measured lifetime $(1.7 \pm 0.3) \times 10^{-9}$ s and the calculated rate of 4090×10^5 s^{-1} for the $^1P_1^o$-$^1D_2$ transition. In a recent experiment by Pinnington *et al.* [9], finally, the $^1P_1^o$ lifetime was determined to be $(1.34 \pm 0.22) \times 10^{-9}$ s. Using this measurement and the theoretical branching ratio from Cowan's code [29], Pinnington *et al.* presented the two probabilities 4302×10^5 and 2958×10^5 s^{-1} for the $^1P_1^o$-$^1S_0$ and $^1P_1^o$-$^1D_2$ transitions, respectively. These semiempirical data were, however, quite different from the theoretical values of Pinnington *et al.* [9] of 6626×10^5 and 4577×10^5 s^{-1}. In contrast, our present computations show a much better agreement with the experiment by Pinnington and co-workers and yield transition probabilities which are consistent with their semiempirical estimation.

IV. CONCLUSION

In summary, the influence of the relativistic, relaxation, and correlation effects has been investigated systematically for the low-lying level energies of the $3d^{10}$, $3d^94s$, and $3d^94p$ configurations of Cu II as well as for their transition probabilities by using large-scale MCDF wave functions. As found from this study, relativistic effects play an important role in the wave functions, the total binding energies, and the transition probabilities of Cu II. For several weak lines, in particular, the transition probabilities are strongly affected by the relativistic contraction of the wave functions and by the Breit interaction. The rearrangement of the electron density in course of the transitions, which is included by taking the nonorthogonality of the initial- and final-state wave functions into account, makes, moreover, a strong contribution to both the $\Delta n = 1$ and $\Delta n = 0$ transitions. An incorporation of the relativistic, relaxation, and correlation effects appears therefore necessary in order to obtain reliable theoretical results for the excitation energies and transition probabilities of Cu II.

For the levels of the $3d^94p$ configuration of Cu II, the transition probabilities and lifetimes are presented above. When compared with previous computations and experiments, the present results provide not only a consistent data set for these low-lying levels but also resolves the hitherto existing "puzzle" about the $^1P_1^o$-$^1S_0$ and $^1P_1^o$-$^1D_2$ transition probabilities. The present computations therefore tender a useful model for studying also other ions along the nickel isoelectronic sequence.

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