Configuration-interaction In the Neutral Copper Atom

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Configuration interaction in the neutral copper atom

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The configuration interaction in the odd states of the copper atom and its effects on energy levels and transition probabilities have been studied with the multiconfiguration Hartree-Fock method. Relativistic effects have been included to first order. Good agreement is found between the results of the present work and available experimental data. The origins of observed irregularities in the energy-level structure and lifetime trends are explained. Properties of importance for the possible generation of additional lines in the copper-vapor laser are discussed.

I. INTRODUCTION

The electronic structure of the copper atom is similar to that of the potassium atom but copper has ten additional electrons. In the ground state these occupy the $3d$ shell. The ground state of copper, as of potassium, is $4s\ ^2S_{1/2}$ and copper has the same $nl\ ^2L$ Rydberg series as the alkali-metal atoms. An energy-level diagram of the copper atom is shown in Fig. 1. The presence of the $3d$ electrons causes a number of effects which are not found in the alkali-metal atoms and which make theoretical calculations for the copper atom rather more complicated.

Since the $3d$ orbitals are more extended in space than the $3p$ or other inner-shell orbitals, the $3d$ shell is more strongly influenced by the valence electron. This effect is different in different states. Therefore, in a theoretical calculation, it will be a much too crude approximation to include the $3d$ shell in a fixed core. On the other hand, not to include it and treat copper as an eleven electron problem, would make the calculations impractical.

The energy needed to excite an electron from a $3d$ to a $4s$ or $4p$ state is less than the ionization energy, so, in addition to the $3d^{10}nl\ ^2L$ states copper has a number of bound state belonging to the configurations $3d^94s^2$ and $3d^94s4p$. These may interact with states in the $3d^{10}nl\ ^2L$ Rydberg series. The $3d^94s^2$ configuration gives rise to a ^2D term only, which is situated far below any of the $3d^{10}nd\ ^2D$ states with which it could possibly interact. The $3d^94s4p$ configuration gives rise to nine different terms[1] of which $3d^94s(^3D)4p\ ^4P$, ^4D, ^4F, ^2P, ^2D, and ^2F

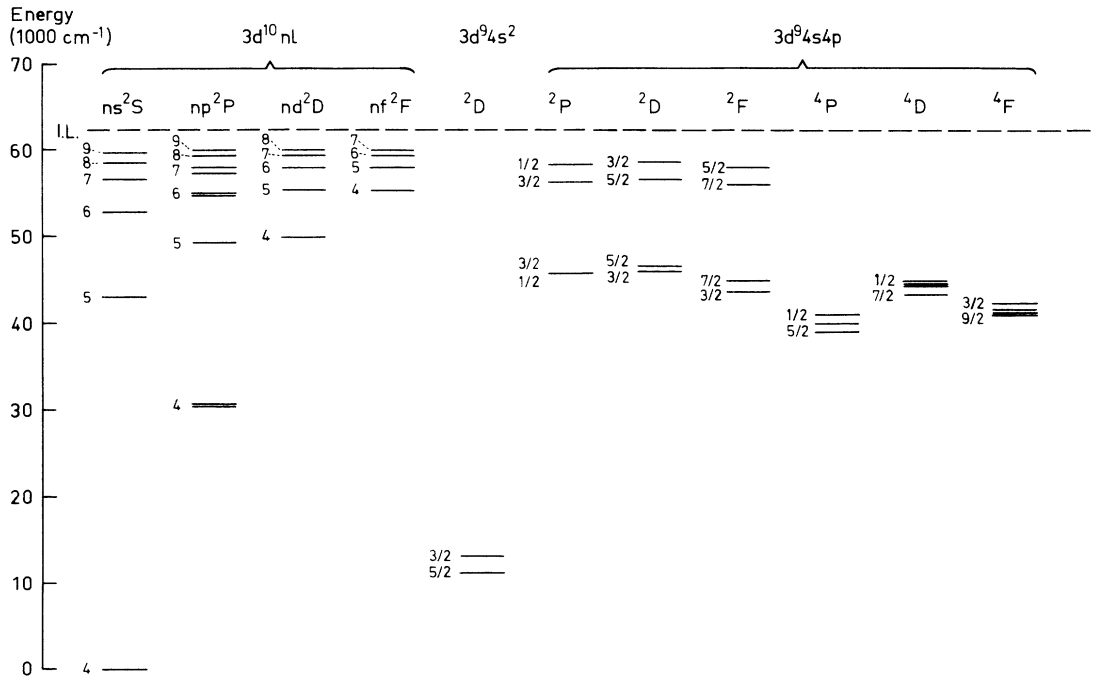

FIG. 1. Energy-level diagram for the copper atom. The numbers next to the levels are for the Rydberg series the values of n, for the other states the values of J.

are situated between the $3d^{10}4p\ ^2P$ and $3d^{10}5p\ ^2P$ levels and $3d^9 4s(^1D)4p\ ^2P$, ^2D, and ^2F are situated between the $3d^{10}6p\ ^2P$ and $3d^{10}8p\ ^2P$ levels. It has been pointed out[2] that a more correct way of naming these doublets would be to label the lower ones $3d^9 4s4p(^3P)\ ^2L$ and the upper ones $3d^9 4s4p(^1P)^2L$. The coupling is not pure in either scheme but the states are much more strongly mixed in the former. Whichever scheme one chooses to work with in a theoretical calculation does not have any effect on the results as long as all interactions are included. For computational reasons the left-to-right coupling has been used in this work.

The $3d^9 4s4p$ states interlap the $3d^{10}np\ ^2P$ and $3d^{10}nf\ ^2F$ series and have the same parity and therefore a strong configuration interaction with these states can be expected. The ^2P series was once called "probably the most distorted series known."[3] The fine-structure splittings are very irregular in the ^2P series and quite regular in the ^2D series. Measurements of the lifetimes in the ^2P series[4-8] show that some of them are extraordinarily short and that they are strongly J dependent.

In unperturbed Rydberg series the lifetimes are expected to scale as $(n^*)^3$, where n^* is the effective principal quantum number. Recent measurements of the lifetimes in the ^2S and ^2D series[8] show that neither of these follow such a trend.

The $3d^{10}4s\ ^2S - 3d^{10}4p\ ^2P$ transition has been studied with the multiconfiguration Hartree-Fock method[9] and with a core-polarization model potential in a relativistic Hartree-Fock calculation.[10] It seems that the greater success of these two calculations compared with Hartree-Fock[9] or relativistic Hartree-Fock[10] calculations, which both give approximately 1.8 times too large transition probabilities, primarily comes from a better description of the $3d$ shell.

The Rydberg series of copper have been studied with the pseudopotential method[11] and with the numerical Coulomb approximation.[12] As is said in the latter of these two works, but which applies to both, the ^2P states cannot be expected to be well described since the interaction with the $3d^9 4s4p$ states has not been included.

Calculations for the $3d^9 4s4p$ states have been performed with the method of varying the values of the radial integrals in order to fit the calculated energy-level values to the experimental ones.[13,14] Unfortunately neither of these calculations includes any $3d^{10}np\ ^2P$ or $3d^{10}nf\ ^2F$ states above $3d^{10}4p\ ^2P$. The interaction with these states is, as has often been suggested[2,3,15] and will be shown in this work, of the greatest importance. Both calculations do, however, include interaction with the $3d^8 4s^2 4p$ states. So far, these states have not been found experimentally and they are expected to lie in the continuum.

In the present work, wave functions are calculated for all states of the copper atom with $L \leq 3$ and an energy of less than 60 100 cm^{-1} above the energy of the ground state. The calculations were performed using the multiconfiguration Hartree-Fock (MCHF) method[16] with relativistic effects included in the Breit-Pauli approximation. For some states a term energy correction is made. The intention of this work is to study the configuration interaction and its effects and to explain the irregularities mentioned above. Particular attention is paid to the radiative properties. Transition probabilities for all allowed transitions between the investigated states are calculated and compared with experimental data.

II. METHOD OF CALCULATION

The J-dependent lifetimes and irregular fine-structure splittings indicate that the calculated wave functions, or at least wave-function compositions, should be J dependent. At the same time it is necessary to include the configuration interaction. This has been done in the present work by using computer programs in the MCHF package of Froese Fischer.[17] Nonrelativistic wave functions have been calculated using the configuration expansions listed in Table I. In all calculations the $1s$, $2s$, $2p$, $3s$, $3p$, and $3d$ orbitals were taken from a Hartree-Fock calculation of the ground state of Cu III, $3d^9\ ^2D$, and kept fixed. This fixed-core approximation will influence the calculated energies of the states. In particular it will have different effects on states with nine or ten $3d$ electrons. In the cases where we have configuration interaction between neighboring states with different numbers of $3d$ electrons this is not acceptable since the configuration interaction depends critically on the relative position of the states. The tenth $3d$ electron, when there is one, is allowed to be different from the nine others and is varied in the MCHF calculation. This is the same approach as has been used in the MCHF study of the $3d^{10}4s\ ^2S - 3d^{10}4p\ ^2P$ transition.[9] The configuration $3d^9 3d'\ ^1S$, where $3d'$ is different from $3d$, is expressed as $(3d^{10} + 3d^9 3d_2)\ ^1S$ with orthogonal orbitals. This makes it possible to include some of the polarization of the $3d$ shell. In the relativistic calculation which is to follow, one has, with the present computer program, to use orthogonal orbitals. This means that the $4s$ and $4p$ orbitals used in $3d^{10}4p\ ^2P$ and in all the different $3d^9 4s4p$ states have to be the same. Since they can only be optimized for one state—in this work $3d^{10}4p\ ^2P$ has been chosen—they will cause a too high energy of the other states. The problem with the wrong relative position of interacting states, which is caused by the fixed-core approximation and by the orthogonal orbitals, is circumvented by manually changing the average energy of each of the $3d^9 4s4p$ terms.

A further worry is that the shape of the $4s$ and $4p$ orbitals is crucial for the calculation of matrix elements for the transition probabilities and of mixing coefficients for the configuration interaction. That they really vary from one state to another can be seen in Table II, where the expectation values of the radius of $4s$ and $4p$ orbitals, optimized for different states, are listed. The calculation for $3d^{10}4p\ ^2P$ is the same MCHF calculation as is used in the rest of the work, the calculations for $3d^9 4s4p\ ^2L$ are two-configuration calculations of $3d^9 4s(^{1,3}D)4p\ ^2L$ and the ones for $3d^9 4s4p\ ^4L$ are single-configuration calculations. The fixed core previously described was used. A simple test of the effect on the transition probabilities has been made by calculating transition matrix elements between the $3d^9 4s4p$ states and the $3d^9 4s^2\ ^2D$ and $3d^{10}4s\ ^2S$ states.

TABLE I. Wave-function expansions.

MCHF
$3d^{10}ns\ ^2S$, $n=4$ to 9
$[3d^{10}ns + 3d^9 3d_2(^{1,3}S)ns + 3d^9(4p^2+4p4f)]\ ^2S$
$3d^{10}np\ ^2P$, $n=4$ to 9
$[3d^{10}np + 3d^9 3d_2(^{1,3}S)np + 3d^9 4s4p + 3d^8 4s^2 4p]\ ^2P$
$3d^{10}nd\ ^2D$, $n=4$ to 8
$[3d^{10}nd + 3d^9 3d_2(^{1,3}S)nd + 3d^9(4s^2 + 4p^2 + nd^2 + 4s4d + 4p4f)]^2D$
$3d^{10}nf\ ^2F$, $n=4$ to 7
$[3d^{10}nf + 3d^9 3d_2(^{1,3}S)nf + 3d^9 4s4p + 3d^8 4s^2 4p]\ ^2F$
$3d^9 4s^2\ ^2D$
$[3d^9(4s^2+4p^2 + 4d^2 + 4s4d + 4p4f) + 3d^{10}4d + 3d^9 3d_2(^{1,3}S)4d]\ ^2D$
Ionization limit
$(3d^{10} + 3d^9 3d_2)\ ^1S$
CI
Odd states
$[3d^{10}np + 3d^9 3d_2(^{1,3}S)np + 3d^{10}mf + 3d^9 3d_2(^{1,3}S)mf + 3d^9 4s4p + 3d^9 4s4f + 3d^8 4s^2 4p]$
All possible couplings
$n=4$ to 9, $m=4$ to 7
Even states
^2S
$[3d^{10}ns + 3d^9 3d_2(^{1,3}S)ns + 3d^9(4p^2 + 4p4f)]$
All couplings which can give $J=\frac{1}{2}$
$n=4$ to 9.
^2D
The same expansions as in the MCHF calculations
Ionization limit
The same expansion as in the MCHF calculation

The latter two were, in this case, calculated as $3d^9 4s^2\ ^2D$ and $[3d^{10}4s + 3d^9 3d_2(^{1/3,}S)4s]\ ^2S$, respectively. All allowed transition matrix elements were calculated in the length form using 4*s* and 4*p* orbitals in the odd state optimized either for the state itself or for $3d^{10}4p\ ^2P$. Judging from this simple test, the effect of using the same 4*s* and 4*p* orbitals in all odd states is that the transition matrix elements to the ground state become 12% too small for the lower $3d^9 4s4p\ ^2P$ states and 27% too large for the upper ones and those to $3d^9 4s^2\ ^2D$ 3% too small for the lower ^2L states and 11% too large for the upper ones. In the rest of this work, where all the odd states are described using one set of orthogonal orbitals, it seems, judging from the mean radii of the 4*s* and 4*p* orbitals, to be advantageous to optimize these for the $3d^{10}4p\ ^2P$ state rather than any of the $3d^9 4s4p$ states which have the more divergent values.

TABLE II. Test of different 4*s* and 4*p* orbitals in the odd states. Columns 2 and 3 give the expectation values of the radius, in atomic units, of the 4*s* and 4*p* orbitals optimized for the states in column 1. "Own" and "other" indicate whether the 4*s* and 4*p* orbitals used in the odd state have been optimized for the states itself or for $3d^{10}4p\ ^2P$.

			Transition matrix element to $3d^{10}4s\ ^2S$		$3d^9 4s^2\ ^2D$	
State	$\langle r\rangle_{4s}$	$\langle r\rangle_{4p}$	Own	Other	Own	Other
$3d^{10}4p\ ^2P$	2.647	4.751				
$3d^9 4s(^3D)4p\ ^4P$	2.870	3.771				
$3d^9 4s(^3D)4p\ ^4F$	2.868	3.855				
$3d^9 4s(^3D)4p\ ^4D$	2.863	4.012				
$3d^9 4s(^3D)4p\ ^2F$	2.915	3.903			0.252 21	0.245 23
$3d^9 4s(^3D)4p\ ^2P$	2.916	3.994	1.341 92	1.180 13	0.109 90	0.106 66
$3d^9 4s(^3D)4p\ ^2D$	2.911	4.003			0.330 08	0.320 53
$3d^9 4s(^1D)4p\ ^2F$	2.650	6.071			6.060 81	6.711 98
$3d^9 4s(^1D)4p\ ^2P$	2.467	6.011	0.351 79	0.447 77	4.018 47	4.424 99
$3d^9 4s(^1D)4p\ ^2D$	2.649	6.293			4.966 74	5.632 20

A. Odd states

The MCHF procedure was used to produce a set of orthogonal orbitals. First a calculation was performed for the $3d^{10}4p\ ^2P$ state in which one $3d$ orbital was allowed to be different from the nine others and where the configuration interaction with the $3d^9 4s4p\ ^2P$ and $3d^8 4s^2 4p\ ^2P$ states was included. The configurations are listed in Table I. In this calculation the $3d_2$, $4s$, and $4p$ orbitals were varied. Keeping these orbitals fixed the rest of the np orbitals ($n=5$ to 9) were calculated in consecutive MCHF calculations in which only the new np orbital was varied and where it was made orthogonal to all previously calculated p orbitals. The same procedure was then followed for the $3d^{10}nf\ ^2F$ states ($n=4$ to 7).

With the thus obtained orbitals a configuration-interaction (CI) calculation was performed. In this all relativistic contribution to the Hamiltonian except orbit-orbit interaction were included and a much larger wave-function expansion than previously was used (73 configuration state functions, see Table I). In this calculation the mixing coefficients are calculated with the orbitals kept fixed and all the odd states are obtained in one calculation. For comparison the ionization limit has been calculated using the same procedure as for the bound states and the wave-function expansion $(3d^{10}+3d^9 3d_2)\ ^1S$ where $3d_2$ was varied in the MCHF calculation. The energies of the bound states, relative to the ionization limit, are given in Table III under the heading *ab initio*. In this table the experimental energies[1] are also included. For the $3d^{10}6f\ ^2F$ and $3d^{10}7f\ ^2F$ states the experimental energy has been estimated by assuming $n^*=n-0.01$, which is justified from a study of the quantum defect of the lower $3d^{10}nf\ ^2F$ states. The position of the $3d^8 4s^2 4p$ states is not known from experiments but from comparison with other spectra it has been estimated[14] that the center of gravity of this configuration lies approximately 50 000 cm^{-1} above that of $3d^9 4s4p$. This is in good enough agreement with the distance 61 782 cm^{-1} found in this calculation between the lowest states of each of the two configurations, $3d^9 4s4p\ ^4P_{5/2}$ and $3d^8(^3F)4s^2 4p\ ^4D_{7/2}$.

As has been discussed above, the energy of the $3d^9 4s4p$ states relative to the Rydberg series, or to the ionization limit which has been calculated in the same manner, was not expected to be correct. To give the $3d^9 4s4p$ states reasonably correct positions (reasonably correct meaning a difference of the same order of magnitude as for most of the states of the Rydberg series, approximately 100 cm^{-1}) a new calculation, or rather two new calculations, were performed. In these, the average energy of each of the $3d^9 4s4p$ basis functions was lowered by the amount the states of the corresponding term, on average, were too high in the *ab initio* calculation. The reason why two calculations had to be performed is that the upper and lower $3d^9 4s4p\ ^2L$ terms were out of place by different amounts and that both the upper and lower states contain approximately equal portions of the two different $3d^9 4s4p\ ^2L$ configuration state functions. Hence, one calculation was performed where for each L the energies of both $3d^9 4s4p\ ^2L$ basis functions were lowered by the amount the lower ^2L states where too high and one where they were lowered by the amount the upper ^2L states were too high. In both calculations each $3d^9 4s4p\ ^4L$ basis function was lowered by the amount the states of the corresponding term, on average, were too high in the *ab initio* calculation. The adjustments are given in Table IV. The wave function compositions from the first of the two adjusted calculations were used for $3d^{10}5p\ ^2P$ and the states below it, those from the second for the states above it. The energies from these two calculations are given in Table III under the heading "adjusted."

B. Even states

In the even states the possibility of configuration interaction is much more limited than in the odd, the only obvious possibility being the interaction between the $3d^9 4s^2\ ^2D$ states and the $3d^{10}nd\ ^2D$ series. These are, however, very far apart, more than 35 000 cm^{-1}, so the effect can be expected to be much smaller than in the odd states.

For the $3d^{10}ns\ ^2S$ states a set of orthogonal orbitals was produced using the MCHF method in a similar way as for the odd states. The same fixed core was used and the configurations included in the expansion are given in Table I. The first MCHF calculation was optimized for the $3d^{10}4s\ ^2S$ state. In this calculation the $3d_2$, $4s$, $4p$, and $4f$ orbitals were varied. In the subsequent calculations for $3d^{10}ns\ ^2S$ ($n=5$ to 9) only the new ns orbital was varied and it was made orthogonal to those previously calculated. With these orbitals and all couplings of the configurations given in Table I which have a $J=\frac{1}{2}$ state, a total of 35, a relativistic CI calculation was performed. The calculated energies relative to the ionization limit are listed in Table III. The energy of the ground state is, in atomic units, $-1939.067\,487$ in the nonrelativistic MCHF calculation and $-1952.777\,896$ in the relativistic CI calculation.

Because of convergence problems when trying to produce a set of orthogonal orbitals for the $3d^{10}nd\ ^2D$ states, a separate calculation was performed for each of the even ^2D terms, $3d^9 4s^2$ and $3d^{10}nd$, $n=4$ to 8. For each term an MCHF calculation was performed in which the $3d_2$, $4s$, $4p$, $4d$, $4f$, and nd orbitals were varied. Then for each term a CI calculation was performed using the relativistic Hamiltonian and the same 20 configuration state functions as in the MCHF calculation. The calculated energies are listed in Table III. These calculations show that there is practically no mixing of $3d^9 4s^2$ and $3d^{10}nd$ states. The calculated energies of the $3d^9 4s^2\ ^2D$ states are more than 7000 cm^{-1} too high, i.e., too close to the $3d^{10}nd\ ^2D$ states, but since there is no mixing between them and an increased separation could only make the mixing smaller, this should not have affected the wave-function compositions. No term energy correction was made for any of the even states.

III. RESULTS AND DISCUSSION

The experimental and calculated fine-structure splittings are given in Table V. Of particular interest is the $3d^{10}np\ ^2P$ series where the highly irregular fine-structure

TABLE III. Calculated and experimental (Ref. 1) ionization energies, in cm^{-1}.

State	Experiment	*Ab initio*	Experiment − *Ab initio*	Adjusted	Experiment − Adjusted
$3d^{10}4s\ ^2S_{1/2}$	62 317	60 946	1371		
$3d^{10}5s\ ^2S_{1/2}$	19 180	18 344	836		
$3d^{10}6s\ ^2S_{1/2}$	9468	8959	509		
$3d^{10}7s\ ^2S_{1/2}$	5646	5232	414		
$3d^{10}8s\ ^2S_{1/2}$	3748	3373	375		
$3d^{10}9s\ ^2S_{1/2}$	2669	2313	356		
$3d^{10}4p\ ^2P_{1/2}$	31 782	29 188	2594	29 407	2375
$3d^{10}4p\ ^2P_{3/2}$	31 534	29 001	2533	29 232	2302
$3d^{10}5p\ ^2P_{1/2}$	12 934	12 755	179	12 296	638
$3d^{10}5p\ ^2P_{3/2}$	12 934	12 624	310	12 286	648
$3d^{10}6p\ ^2P_{1/2}$	7289	6771	518	6974	315
$3d^{10}6p\ ^2P_{3/2}$	7533	6762	771	7228	305
$3d^{10}7p\ ^2P_{1/2}$	4898	4329	569	4697	201
$3d^{10}7p\ ^2P_{3/2}$	4368	4332	36	4096	272
$3d^{10}8p\ ^2P_{1/2}$	2994	2981	13	2706	288
$3d^{10}8p\ ^2P_{3/2}$	3042	2986	56	2825	217
$3d^{10}9p\ ^2P_{1/2}$	2232	2166	66	2018	214
$3d^{10}9p\ ^2P_{3/2}$	2247	2171	76	2077	170
$3d^{10}4d\ ^2D_{3/2}$	12 382	12 230	152		
$3d^{10}4d\ ^2D_{5/2}$	12 375	12 224	151		
$3d^{10}5d\ ^2D_{3/2}$	6930	6867	63		
$3d^{10}5d\ ^2D_{5/2}$	6926	6864	62		
$3d^{10}6d\ ^2D_{3/2}$	4424	4392	32		
$3d^{10}6d\ ^2D_{5/2}$	4422	4391	31		
$3d^{10}7d\ ^2D_{3/2}$	3068	3050	18		
$3d^{10}7d\ ^2D_{5/2}$	3066	3049	17		
$3d^{10}8d\ ^2D_{3/2}$	2252	2240	12		
$3d^{10}8d\ ^2D_{5/2}$	2251	2240	11		
$3d^{10}4f\ ^2F_{5/2}$	6887	6769	118	6772	115
$3d^{10}4f\ ^2F_{7/2}$	6891	6769	122	6785	106
$3d^{10}5f\ ^2F_{5/2}$	4412	4301	111	4334	78
$3d^{10}5f\ ^2F_{7/2}$	4409	4301	108	4298	111
$3d^{10}6f\ ^2F_{5/2}$	3058[a]	2959	99	2957	101
$3d^{10}6f\ ^2F_{7/2}$	3058[a]	2959	99	2958	100
$3d^{10}7f\ ^2F_{5/2}$	2246[a]	2150	96	2149	97
$3d^{10}7f\ ^2F_{7/2}$	2246[a]	2150	96	2150	96
$3d^9 4s^2\ ^2D_{3/2}$	49 072	41 405	7667		
$3d^9 4s^2\ ^2D_{5/2}$	51 115	43 487	7628		
$3d^9 4s4p\ ^4P_{1/2}$	21 373	14 335	7038	21 413	−40
$3d^9 4s4p\ ^4P_{3/2}$	22 203	15 113	7090	22 175	28
$3d^9 4s4p\ ^4P_{5/2}$	23 299	16 037	7262	23 142	157
$3d^9 4s4p\ ^4F_{3/2}$	20 015	13 488	6527	19 906	109
$3d^9 4s4p\ ^4F_{5/2}$	20 754	14 173	6581	20 666	88
$3d^9 4s4p\ ^4F_{7/2}$	21 164	14 693	6471	21 168	−4
$3d^9 4s4p\ ^4F_{9/2}$	21 408	15 106	6302	21 574	−166
$3d^9 4s4p\ ^4D_{1/2}$	17 402	11 783	5619	17 683	−281
$3d^9 4s4p\ ^4D_{3/2}$	17 773	12 138	5635	17 771	2
$3d^9 4s4p\ ^4D_{5/2}$	17 911	12 798	5113	17 933	−22
$3d^9 4s4p\ ^4D_{7/2}$	18 803	13 390	5413	18 950	−147
$3d^9 4s4p\ ^2F_{5/2}$	18 591	11 328	7263	18 659	−68
$3d^9 4s4p\ ^2F_{7/2}$	17 354	10 648	6706	17 500	−146
$3d^9 4s4p\ ^2P_{1/2}$	16 496	10 251	6245	16 712	−216
$3d^9 4s4p\ ^2P_{3/2}$	16 438	9747	6691	16 718	−280
$3d^9 4s4p\ ^2D_{3/2}$	16 144	10 213	5931	16 003	141

TABLE III. (*Continued*).

State	Experiment	*Ab initio*	Experiment − *Ab initio*	Adjusted	Experiment − Adjusted
$3d^9 4s4p\ ^2D_{5/2}$	15 719	9541	6178	15 543	176
$3d^9 4s4p\ ^2F_{5/2}$	4198	−4826	9024	4188	10
$3d^9 4s4p\ ^2F_{7/2}$	6287	−2545	8832	6357	−70
$3d^9 4s4p\ ^2P_{1/2}$	3952	−4422	8374	3566	386
$3d^9 4s4p\ ^2P_{3/2}$	5973	−2550	8523	5588	385
$3d^9 4s4p\ ^2D_{3/2}$	3626	−5927	9553	3441	185
$3d^9 4s4p\ ^2D_{5/2}$	5666	−3736	9402	5564	102

[a]Calculated from the assumption $n^* = n - 0.0.1$

splittings are caused by the interaction with different $3d^9 4s4p$ states. The degree to which the calculated fine-structure agrees with experiment can here be believed to reflect the degree to which the configuration interaction is correctly reproduced. The fact that the fine-structure splittings are so irregular is, to some extent, due to the large fine-structure splitting of the $3d^9 4s(^1D)4p\ ^2P$ term, −2021 cm^{-1}. The strongest admixture of $3d^9 4s4p\ ^2P$ into the Rydberg series is in the states close to the perturbers, which are not the same for the $J = \frac{1}{2}$ and the $J = \frac{3}{2}$ states. Another important feature is that not only the ^2P states of $3d^9 4s4p$ interact with the ^2P series, but all states which have the same J value. In particular, $3d^9 4s4p\ ^2D_{3/2}$ gives large admixtures in the $3d^{10}np\ ^2P_{3/2}$ states.

In the $3d^{10}nf\ ^2F$ series we have a similar effect with the $3d^9 4s(^1D)4p\ ^2F_{5/2}$ state mixing most strongly with $3d^{10}5f\ ^2F_{5/2}$ and $3d^9 4s(^1D)4p\ ^2F_{7/2}$ with $3d^{10}4f\ ^2F_{7/2}$. This explains the inverted fine structure of the $3d^{10}4f\ ^2F$ term. Comparing the calculated and experimental fine-structure splittings, it seems that the degree of mixing in the ^2F states is somewhat too high in the calculation.

For the lower states, $3d^{10}4p\ ^2P$ and $3d^{10}5p\ ^2P$, which primarily interact with the $3d^9 4s(^3D)4p$ states, the mixing is not as strongly J dependent as for the upper states. $3d^9 4s(^3D)4p\ ^2P$ has a fine-structure splitting of only 58 cm^{-1} and mixes more or less equally into the $J = \frac{1}{2}$ and the $J = \frac{3}{2}$ states.

Transition probabilities for all allowed transitions between the investigated states have been calculated from the calculated radial wave functions and eigenvector compositions. A list of the transition probabilities and also of the eigenvector compositions of the odd states can be obtained on request.[18] The transition probabilities were calculated in the length form using experimental transition energies. From these transition probabilities, lifetimes of the excited states have been calculated. These are given in Table VI together with the most recent experimental lifetime values. The experimental lifetimes have been obtained either by pulsed laser excitation,[7,8]

TABLE IV. The amounts with which the average energy of the $3d^9 4s4p$ basis functions have been lowered, in cm^{-1}.

Quartets	Lower doublets	Upper doublets
^4P 7130	^2F 6985	^2F 8928
^4F 6470	^2P 6468	^2P 8449
^4D 5445	^2D 6054	^2D 9478

TABLE V. Experimental[1] and calculated fine-structure splittings, in cm^{-1}. For the quartets are given first the splittings between the levels with the lowest values of J.

Term	Experiment	Calculation
$3d^{10}4p\ ^2P$	248.384	174.7
$3d^{10}5p\ ^2P$	−0.31	10.6
$3d^{10}6p\ ^2P$	−243.68	−253.6
$3d^{10}7p\ ^2P$	529.40	600.7
$3d^{10}8p\ ^2P$	−47.84	−115.9
$3d^{10}9p\ ^2P$	−14.6	−58.7
$3d^{10}4d\ ^2D$	6.857	5.48
$3d^{10}5d\ ^2D$	3.624	2.88
$3d^{10}6d\ ^2D$	2.05	1.60
$3d^{10}7d\ ^2D$	1.26	0.97
$3d^{10}8d\ ^2D$	0.82	0.62
$3d^{10}4f\ ^2F$	−3.5	−12.4
$3d^{10}5f\ ^2F$	3.5	36.2
$3d^{10}6f\ ^2F$		−1.3
$3d^{10}7f\ ^2F$		−0.46
$3d^{10}4s\ ^2D$	−2042.858	−2082.0
$3d^9 4s(^3D)4p\ ^4P$	−829.74	−762.6
	−1095.34	−966.7
$3d^9 4s(^3D)4p\ ^4F$	−739.57	−760.5
	−409.462	−501.7
	−244.295	−406.4
$3d^9 4s(^3D)4p\ ^4D$	−371.46	−87.8
	−137.885	−162.2
	−892.32	−1017.2
$3d^9 4s(^3D)4p\ ^2F$	1237.032	1159.0
$3d^9 4s(^3D)4p\ ^2P$	58.31	−5.6
$3d^9 4s(^3D)4p\ ^2D$	425.50	460.4
$3d^9 4s(^1D)4p\ ^2F$	−2089.33	−2169.8
$3d^9 4s(^1D)4p\ ^2P$	−2020.99	−2021.8
$3d^9 4s(^1D)4p\ ^2D$	−2039.38	−2122.7

TABLE VI. Calculated and experimental lifetimes, in ns. xEy means $x \times 10^{y}$.

	Calculation	Experiment		
		Pulsed laser excitation	Electron beam excitation	Other methods
$3d^{10}5s\ ^2S_{1/2}$	16.9			
$3d^{10}6s\ ^2S_{1/2}$	45.9	53[a]	49[b]	
$3d^{10}7s\ ^2S_{1/2}$	96.0	103[a]	86[b]	
$3d^{10}8s\ ^2S_{1/2}$	169	204[a]		
$3d^{10}9s\ ^2S_{1/2}$	240	283[a]		
$3d^{10}4p\ ^2P_{1/2}$	6.87	7.4[c]	7.0[d]	
$3d^{10}4p\ ^2P_{3/2}$	6.68	7.1[c]	7.0[d]	
$3d^{10}5p\ ^2P_{1/2}$	19.5		27.1[b,e]	
$3d^{10}5p\ ^2P_{3/2}$	16.5	23[a]	27.9[b]	
$3d^{10}6p\ ^2P_{1/2}$	19.5		23[f]	
$3d^{10}6p\ ^2P_{3/2}$	4.92		6.2[f]	
$3d^{10}7p\ ^2P_{1/2}$	4.37		5.8[f]	
$3d^{10}7p\ ^2P_{3/2}$	5.76		17[f]	
$3d^{10}8p\ ^2P_{1/2}$	5.19			
$3d^{10}8p\ ^2P_{3/2}$	10.6			
$3d^{10}9p\ ^2P_{1/2}$	8.51			
$3d^{10}9p\ ^2P_{3/2}$	22.7			
$3d^{10}4d\ ^2D_{3/2}$	9.69		14.5[b]	11.4[g]
$3d^{10}4d\ ^2D_{5/2}$	9.82		14.2[b]	11.6[g]
$3d^{10}5d\ ^2D_{3/2}$	24.8	37[a,e]	30.9[b]	25[g]
$3d^{10}5d\ ^2D_{5/2}$	25.4		29.8[b]	26[g]
$3d^{10}6d\ ^2D_{3/2}$	49.8	67[a,e]		50[g]
$3d^{10}6d\ ^2D_{5/2}$	49.5		55.6[b]	56[g]
$3d^{10}7d\ ^2D_{3/2}$	84.8	99[a,e]		
$3d^{10}7d\ ^2D_{5/2}$	85.2			
$3d^{10}8d\ ^2D_{3/2}$	127	150[a,e]		
$3d^{10}8d\ ^2D_{5/2}$	121			
$3d^{9}4s(^3D)4p\ ^4P_{1/2}$	334			479[h]
$3d^{9}4s(^3D)4p\ ^4P_{3/2}$	242		329[b]	344[h]
$3d^{9}4s(^3D)4p\ ^4P_{5/2}$	17.9*E*6			
$3d^{9}4s(^3D)4p\ ^4F_{3/2}$	37.6 *E*3			
$3d^{9}4s(^3D)4p\ ^4F_{5/2}$	5.21*E*3			
$3d^{9}4s(^3D)4p\ ^4F_{7/2}$	5.35*E*3			
$3d^{9}4s(^3D)4p\ ^4F_{9/2}$				
$3d^{9}4s(^3D)4p\ ^4D_{1/2}$	12.6			
$3d^{9}4s(^3D)4p\ ^4D_{3/2}$	212		376[b]	386[h]
$3d^{9}4s(^3D)4p\ ^4D_{5/2}$	1.10*E*3			1.21*E*3[h]
$3d^{9}4s(^3D)4p\ ^4D_{7/2}$	3.95*E*3			
$3d^{9}4s(^3D)4p\ ^2F_{5/2}$	1.08*E*3			1.37*E*3[h]
$3d^{9}4s(^3D)4p\ ^2F_{7/2}$	331		424[b]	404[h]
$3d^{9}4s(^3D)4p\ ^2P_{1/2}$	16.1			
$3d^{9}4s(^3D)4p\ ^2P_{3/2}$	8.36		13.2[b]	
$3d^{9}4s(^3D)4p\ ^2D_{3/2}$	55.3		20.0[b]	
$3d^{9}4s(^3D)4p\ ^2D_{5/2}$	173			167[h]
$3d^{9}4s(^1D)4p\ ^2F_{5/2}$	1.56			
$3d^{9}4s(^1D)4p\ ^2F_{7/2}$	1.24			
$3d^{9}4s(^1D)4p\ ^2P_{1/2}$	2.62			
$3d^{9}4s(^1D)4p\ ^2P_{3/2}$	1.86			
$3d^{9}4s(^1D)4p\ ^2D_{3/2}$	1.35			
$3d^{9}4s(^1D)4p\ ^2D_{5/2}$	1.20			

[a]Reference 8.
[b]Reference 4.
[c]Reference 7.
[d]Reference 5.
[e]For both fine-structure components.
[f]Reference 6.
[g]Reference 19.
[h]Reference 20.

electron beam excitation,[4-6] beam-foil excitation[19] or an electric discharge in the atomic vapor created in a hollow-cathode discharge.[20] Of the experimental lifetimes, those obtained by selective excitation[7,8] can be assumed to be the most accurate. These have been given with errors of 3% to 9%. In most cases, the calculated lifetimes are between 5% and 25% shorter than the experimental ones. One explanation of this may be that polarization and correlation effects have been included to the greater part but not completely. When these effects were not included at all a transition probability for the $3d^{10}4s\ ^2S-3d^{10}4p\ ^2P$ transition of almost a factor of 2 too large was obtained, as was discussed in the Introduction.

From these calculations the origin of many irregularities in the lifetime trends of the excited states of the copper atom can be found. The lifetimes of the $3d^{10}np\ ^2P$ series are J dependent, since the mixing with different $3d^9 4s4p$ states is J dependent. Most of them are very short since the $3d^9 4s4p$ parts of the wave functions give very large contributions to the transition matrix elements both to $3d^{10}4s\ ^2S$ and to $3d^9 4s^2\ ^2D$. The transition from $6p\ ^2P_{1/2}$ to the ground states is very weak because of cancellation in the transition matrix element.

The $3d^9 4s4p\ ^4L$ states would also be metastable if they did not interact with doublet states. The $^4P_{1/2}$, $^4P_{3/2}$, $^4D_{1/2}$, and $^4D_{3/2}$ states have strong transitions to the ground state because of the $3d^{10}4p\ ^2P$ and $3d^9 4s4p\ ^2P$ admixture. All quartet states (except $^4F_{9/2}$) also have transitions to the $3d^9 4s^2\ ^2D$ states because of the $3d^9 4s4p\ ^2L$ admixture.

The lower $3d^9 4s4p\ ^2L$ states have allowed transitions to the $3d^9 4s^2\ ^2D$ states but the ones with $J=\frac{1}{2}$ or $\frac{3}{2}$ can also decay to the ground state. The transitions to the ground state are enhanced by the admixture of $3d^{10}4p\ ^2P$. The states with high enough energy also decay to the $3d^{10}5s\ ^2S$ state because of the $3d^{10}4p\ ^2P$ and $3d^{10}5p\ ^2P$ admixture.

The upper $3d^9 4s4p\ ^2L$ states have very short lifetimes because of strong transitions to the $3d^9 4s^2\ ^2D$ states. Here it is worth recalling that, according to the test of different 4s and 4p orbitals described in connection with Table II, these transition matrix elements may be typically 11% too large which would make the transition probabilities 1.23 times too large. The $J=\frac{1}{2}$ and $\frac{3}{2}$ states also have strong transitions to the ground state. These transitions are enhanced by the $3d^{10}np\ ^2P$ admixture. Furthermore, they have quite strong transitions to the excited $3d^{10}ns\ ^2S$ and $3d^{10}nd\ ^2D$ states, in many cases as strong as some of the $3d^{10}np\ ^2P$ states and this is caused by the mixing with these states.

The $3d^{10}ns\ ^2S$ and $3d^{10}nd\ ^2D$ states are unperturbed but recent accurate measurements[8] of their lifetimes show that neither of the two series has the $(n^*)^3$ dependence expected for unperturbed series: going up these series the lifetimes become increasingly too short compared with $(n^*)^3$. The same is found in this work. The reason for this is to be found not in the series members themselves but in the states to which they decay. Because of the configuration interaction in the odd states they can decay not only to the $3d^{10}np\ ^2P$ and the $3d^{10}nf\ ^2F$ states, but to many of the $3d^9 4s4p$ states as well. Without the configuration interaction these would have been two-electron transitions but since many of the $3d^9 4s4p$ states have large admixtures of $3d^{10}np\ ^2P$, allowed one-electron transitions can be made. So when we go up the ^2S and ^2D series we successively pass the $3d^9 4s4p$ states, thus opening up extra decay channels which shorten the lifetimes of the $3d^{10}ns\ ^2S$ and $3d^{10}nd\ ^2D$ states. As has been found experimentally, the present calculation shows that the lifetime of the $3d^{10}nd\ ^2D$ states do not have an appreciable J dependence.

IV. APPLICATION TO THE COPPER-VAPOR LASER

The ideal energy-level structure of the active medium of a cyclic gas-discharge laser,[21] is an upper laser level which is connected to the ground state by a strong, allowed transition (A typically $10^8\ s^{-1}$), connected to the lower laser level by a somewhat weaker allowed transition (A typically 10^4 to $10^7\ s^{-1}$) but which has no other, or at least no other strong, competing decay channels. In a system like this inverted population can be achieved by an electric discharge which populates the upper laser level more than the lower one since the lower one has the same parity as the ground state. These lasers are pulsed, often with high repetition rates, since the lower laser level is metastable. One such system is the copper atom with either one of the $3d^{10}4p\ ^2P$ levels as the upper level and one of the $3d^9 4s^2\ ^2D$ levels as the lower one. This is used in the copper vapor laser[21] and gives yellow or green light. If one of the higher-lying odd states could be used instead of the $3d^{10}4p\ ^2P$ states the laser transition would be in the ultraviolet. It seems that it is not possible to use the $3d^{10}5p\ ^2P$ states because of the decay to the $3d^{10}5s\ ^2S$ state. However, higher up in the ^2P series the decay is dominated by the $3d^9 4s4p$ parts of the wave function which gives strong transitions to $3d^{10}4s\ ^2S$ and $3d^9 4s^2\ ^2D$ only. The most promising of these states, judging from the calculated transition probabilities, are $3d^{10}7p\ ^2P_{1/2}$ and $3d^{10}8p\ ^2P_{1/2}$ which have branching ratios of only 0.5% and 1.5% to states other than the ground state and the supposed lower laser level. Unfortunately, both these upper states have stronger transitions to $3d^9 4s^2\ ^2D$ than to $3d^{10}4s\ ^2S$ which would make the inverted population difficult to attain. More promising are the $3d^9 4s4p$ states, particularly $3d^9 4s(^3D)4p\ ^2P_{1/2}$ and $^2P_{3/2}$ which have transition probabilities to the ground state of 0.62×10^8 and $1.19\times10^8\ s^{-1}$, to the $3d^9 4s^2\ ^2D_{3/2}$ state of 0.39×10^5 and $5.85\times10^5\ s^{-1}$ and all other transitions together contributing less than 0.1% to the total decay. This is very similar to what is found for $3d^{10}4p\ ^2P$ and indeed also to what was said about the ideal cyclic gas-discharge laser.

The important question which now remains, but which cannot be answered here, is whether the population of these levels, by a discharge, can be made efficient enough and whether the competition with the strong transitions in green and yellow can be overcome. If so, it may be possible to construct a copper-vapor laser operating at 288 or 307 nm, or, if $3d^{10}8p\ ^2P_{1/2}$ can be used, at 217 nm.

V. CONCLUSIONS

In this study it has been possible to explain a number of irregularities in the energy-level structure and in the radiative properties of the copper atom. Some of these irregularities are in the even, unperturbed series and the major cause of all of the irregularities is shown to be the configuration interaction in the odd states. It has not been possible to describe the correlation in the $3d$ shell completely *ab initio* because of the limitation of using orthogonal orbitals. However, with a term energy correction it has been possible to describe even such a complex configuration as $3d^9 4s4p$ in a way which gives results in a good agreement with experiment.

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