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The $2p^4\ ^3P_{1,2}$–$2p^33s\ ^5S_2^0$ and $2p^4\ ^3P_{1,2}$–$2s2p^5\ ^3P_2^0$ transitions in the oxygen isoelectronic sequence

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Abstract. Multiconfiguration Dirac-Fock results are reported for the $2s^22p^4\ ^3P_{1,2}$–$2s^22p^33s\ ^5S_2^0$ and $2s^22p^4\ ^3P_{1,2}$–$2s2p^5\ ^3P_2^0$ transitions in the oxygen-like sequence for $Z = 9, ..., 18$. Both transition energies and transition rates are included.

PACS. 31.10.+z Theory of electronic structure, electronic transitions, and chemical binding – 31.50.+w Excited states – 32.10.-f Properties of atoms and atomic ions

1 Introduction

Intercombination lines are important electron density diagnostic tools in astrophysics. An example of such a line is the one resulting from the $2s^2\ ^1S_0$–$2s2p\ ^3P_1^0$ transition in C III. The experimental measurement by Kwong *et al.* [1] of the decay rate of this transition stimulated extensive studies of many members of the Be isoelectronic sequence, both theoretically and experimentally. With the most recent multiconfiguration Dirac-Fock (MCDF) theoretical results and experimental values determined from fast ion beam and heavy-ion storage ring experiments [2], the sequence is now well-understood and theory and experiment are in excellent agreement [3]. But other intercombination lines could also be helpful diagnostics. Ne III lines observed in the extreme ultraviolet spectrum of a solar active region [4] provide one such possibility, where the intercombination lines are $2s^22p^4\ ^3P_{1,2}$–$2s^22p^33s\ ^5S_2^0$. The theoretical origin of these oxygen-like lines is quite different from the C III intercombination line which results from spin-orbit mixing of the singlet-triplet $2s2p$ states. In the oxygen-like $^5S_2^0$ case, within the different terms of the same configuration, there is spin-orbit and spin-other-orbit interaction with $2s^22p^33s\ ^3P_2^0$, but only a spin-spin interaction with $2s^22p^33s\ ^3D_2^0$ and $^1D_2^0$. At the same time, there is a coulomb interaction between $2s^22p^33s\ ^3P^0$ and $2s2p^5\ ^3P^0$ which both interact with $2s^22p^33s\ ^5S_2^0$ through a spin-other orbit interaction. Problems arise from the fact that the line strength of the $2p$–$3s$ transition from the ground state is an order of magnitude smaller than that of the $2s$–$2p$ transition to $2s2p^5\ ^3P_2^0$ which is the lowest odd $J = 2$ level for $Z > 8$. Thus the computed transition rates for decay from $2s^22p^33s\ ^5S_2^0$ will depend critically on the mixing with $2s2p^5\ ^3P_2^0$. Only for a few ions has the $^5S_2^0$ level been observed experimentally.

In this paper, we report decay rates from $2s^22p^33s\ ^5S_2^0$ and $2s2p^5\ ^3P_2^0$ to $2s^22p^4\ ^3P_{1,2}$ for the oxygen sequence over the range of $Z = 9$ to $Z = 18$. Because of the complex interactions between terms, a multiconfiguration Dirac-Fock (MCDF) approach was taken. For this work, an improved version of GRASP92 [5] was used, that dealt efficiently with expansions for different J-values. In addition, the initial and final states were optimized independently, with transition matrix elements evaluated using a biorthogonal transformation technique [6].

2 Theory

In the MCDF approach, as implemented in the GRASP92 code [5], the wave function for a state is expanded in terms of jj-coupled configuration state functions (CSF's). The latter are anti-symmetrized linear combinations of products of four-component Dirac-orbitals. In the self-consistent field procedure both the radial functions of the orbitals and the expansion coefficients are optimized to self-consistency. Once a set of radial orbitals has been obtained, relativistic configuration interaction (RCI) calculations can be performed. In the RCI calculations the transverse photon interaction

$$\mathcal{H}_{trans} = -\sum_{i<j}^{N} \Big[\frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j\ \cos(\omega_{ij} r_{ij})}{r_{ij}} + (\boldsymbol{\alpha}_i \cdot \nabla_i)(\boldsymbol{\alpha}_j \cdot \nabla_j) \frac{\cos(\omega_{ij} r_{ij}) - 1}{\omega_{ij}^2 r_{ij}} \Big] \cdot \qquad (1)$$

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Table 1. Fine-structure splittings for the initial state, $E(^3P_J)-E(^3P_2)$, compared with experiment (in cm^{-1}) [8].

	$Z =$	9	10	11	12	13	14	15	16	17	18
$^3P_1$:	MCDF	334.7	636.6	1096.8	1769.4	2719.2	3996.6	5706.5	7933.0	10782	14375
	Exp.	341.8	650	1106.3	1783.1	2732	4030	5760	7985	10880	
$^3P_0$:	MCDF	479.9	911.6	1563.4	2504.2	3847.2	5594.3	7851.7	10692.8	14184	18380
	Exp.	490.6	927	1576.0	2521.8	3829	5565	7822	10648		

may be included in the Hamiltonian. In this work only the low frequency limit $\omega_{ij} \to 0$ usually referred to as the Breit interaction, has been used. Neither quantum electrodynamic (QED) nor finite nuclear mass effects were included in the RCI calculations though the finite nuclear volume was included in the orbital optimization process.

3 Method of Computation

In a first stage, Dirac-Fock (DF) orbitals were obtained for the three lowest states of $1s^22s^22p^4$, $J = 0, 1, 2$ and the lowest $J = 2$ state for $1s^22s^22p^33s$, since our primary interest in this paper is the spin-forbidden transition. The $1s, 2s, 2p$ orbitals[1] obtained in this manner were then kept fixed, one set for $^3P_{0,1,2}$ and another set for both $^3P_2^0$ and $^5S_2^0$. The configuration expansions for subsequent MCDF and RCI calculations were obtained with the restricted active space method where CSFs of a specified parity and J symmetry are generated by single (S) and double (D) excitations from one or more reference configurations [7]. For the ground state, only the $1s^22s^22p^4$ configuration was considered, though expansions included CSFs with $J = 0, 1, 2$ quantum numbers so that orbital optimization was done simultaneously on all three levels of the term. No excitations from $1s^2$ were allowed and, consequently, the $1s$ orbitals are said to be *inactive*. For the $J = 2$ odd states, SD excitations with $1s$ inactive, were considered from both the $1s^22s2p^5$ and $1s^22s^22p^33s$ reference configurations. Because of the sensitivity to the mixing of these two configurations, the orbital optimization was now on both the lowest ($1s^22s2p^5\ ^3P_2^0$) and first excited ($1s^22s^22p^33s\ ^5S_2^0$) states. In order to study the convergence of the calculated atomic properties, the set of orbitals was increased in a systematic way leading to consecutively larger expansions. Three sets of orbitals were considered: for the first, referred to as the $n = 3$ calculation, the orbitals considered in SD excitations had principal quantum numbers restricted to $n \leq 3$; the second to $n \leq 4$, and the third to $n \leq 5$. No restrictions were placed on the angular quantum number. However, it should be remembered that, except for the reference configuration, the principal quantum numbers have no significance other than defining the order in which the orbitals are introduced. For the ground state, the largest expansion including the $J = 0, 1, 2$ quantum numbers contained 9.899CSFs whereas the odd states, with only the $J = 2$ quantum number, included 11.928CSFs. The large expansion size of the latter is a reflection of the many different couplings with the extra unfilled shell and the fact that two reference configurations were needed.

4 Results

Table 1 reports the computed fine-structure splittings of the initial state and compares these with experiment when available. Omitted in the present work are the QED corrections to the energies which become more important with increasing degree of ionization. In all cases the computed fine-structure splitting is too small. In C III, the inclusion of core-polarization by allowing double excitations where one electron replaces a $1s$ electron and the other an outer or valence electron, brought the theoretical values in much better agreement with observation [10]. The present results suggest that, in this case also, core-polarization has a small effect on the fine-structure splitting, though this needs to be confirmed.

In an MCDF calculation, the fine-structure splitting is not an *indicator of accuracy* [9], but rather a measure of how accurately a common orbital basis simultaneously represents the different J levels. A possible indicator is the accuracy of the allowed transitions to $2s2p^5\ ^3P_2^0$. The transition energy for these transitions, transition rates in both the Babushkin (length) and Coulomb (velocity) gauges, and convergence are reported in Table 2, with the transition energy compared with experiment. The $2s{-}2p$ transition is an *inner* transition, similar to $2s^2\ ^1S_0{-}2s2p\ ^1P_1^0$ for which core-polarization was found to affect the line strength. This correction is important for the Coulomb (velocity) gauge, but is a much smaller correction in the length form. Table 2 shows that there is fairly good convergence (typically to the 1% level) but the gauges for the allowed transition are not in agreement, indicating that some important correlation has been neglected. All transition energies are too large, also a sign that more correlation is needed for the $2s2p^5\ ^3P_2^0$ level, particularly at low Z.

For the spin-forbidden transition, an important indicator, in the present case, is the separation of the energy levels for the two lowest $J = 2$ eigenvalues, namely $2s2p^5$ $^3P_2^0$ and $2s^22p^33s\ ^5S_2^0$. In Table 3, the computed level separation is compared with experiment, using the NIST [8] tabulations. Whereas a smooth trend is expected, the error in the separation in Ne III is surprisingly large. Kastner *et al.* [11], on the basis of solar spectra, have predicted

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[1] For brevity we use the non-relativistic notation for the orbitals $1s, 2s, 2p$ meaning $1s_{1/2}, 2s_{1/2}, 2p_{1/2}, 2p_{3/2}$ *etc.*

Table 2. Transition trends for E1 decay from the $2s2p^5\ ^3P_2$ level for nuclear charges $9 \leq Z \leq 18$. Transition energies are in cm^{-1} and the A transition rates in 10^9 s^{-1}. The latter are reported in both the Babushkin (B) and Coulomb (C) gauges.

Z	AS	$2p^4\ ^3P_2$		$2p^4\ ^3P_1$	
		ΔE	A_B / A_C	ΔE	A_B / A_C
9	3	171106	3.2761 / 3.3769	170766	1.0684 / 1.0832
	4	168391	2.8560 / 2.7776	167963	0.8347 / 0.9027
	5	167916	2.7334 / 2.6504	167582	0.8973 / 0.8667
	Exp.	164798		164456	
10	3	208768	4.3173 / 4.6531	208129	1.4111 / 1.4969
	4	206034	3.9396 / 4.0914	205397	1.2926 / 1.3370
	5	205639	3.8455 / 3.9891	204993	1.2641 / 1.3101
	Exp.	204292		203642	
11	3	249639	5.7198 / 6.3374	248538	1.8648 / 2.0388
	4	246561	5.2944 / 5.6319	245465	1.7319 / 1.8345
	5	246157	5.1962 / 5.5085	245061	1.7028 /1.8035
	Exp.	243682		242576	
12	3	289585	7.1312 / 8.1508	287811	2.3169 / 2.6177
	4	285396	6.6933 / 7.3787	284627	2.1808 / 2.3973
	5	285997	6.5957 / 7.2451	284228	2.1520 / 2.3642
	Exp.	283212		265381	
13	3	330007	8.6316 / 10.125	327291	2.7906 / 3.2410
	4	326723	8.1792 / 9.2835	324013	2.6508 / 3.0039
	5	326330	8.0805 / 9.1350	323620	2.6219 / 2.9676
	Exp.	323002		320270	
14	3	370875	10.207 / 12.240	366873	3.2792 /3.9001
	4	36751	9.7396 / 11.329	363514	3.1359 / 3.6466
	5	367120	9.6384 / 11.162	363124	3.1063 / 3.6058
	Exp.	363170		359140	
15	3	412172	11.846 / 14.483	406460	3.7774 / 4.5880
	4	408740	11.363 / 13.502	403034	3.6305 / 4.3187
	5	408680	11.249 / 13.228	402973	3.5997 / 4.2530
	Exp.	403803		398043	
16	3	455311	13.676 / 17.415	447372	4.3241 / 5.4832
	4	451830	13.175 / 16.349	443899	4.1730 / 5.1948
	5	451418	13.065 / 16.128	443485	4.1411 / 5.1408
	Exp.	444987		437002	
17	3	498155	15.482 / 20.003	487368	4.8480 /6.2499
	4	494628	14.966 / 18.869	483849	4.6936 / 5.9474
	5	494519	14.845 / 18.536	483737	4.6614 / 5.8686
	Exp.	487000		476120	
18	3	541822	17.364 / 22.713	527444	5.3786 / 7.0359
	4	538261	16.832 / 21.512	523890	5.2212 / 6.7206
	5	537818	16.609 / 21.224	523442	5.1871 / 6.6528

Table 3. Energy separation between the lowest $2s2p^5\ ^3P_2^0$ and the second $2s^22p^33s\ ^5S_2^0$ level, compared with experiment (in cm^{-1}).

$Z =$	9	10	11	13
MCDF	7338	103332	226730	567049
Exp. [8]	11856	109856	230268	571298
Exp. [11]		105632		

a lower level, also shown in Table 3. Whatever the experimental value in Ne III, it is seen that the theoretical separation is always too small, but the relative difference (theory−observed) decreases rapidly from about 38% for F II to 7% for Al V. Since $2s2p^5$ is in a different complex (has different principal quantum numbers) the interaction with $2s^22p^33s$ will decrease with Z, and the excited state will interact more with the other terms of the $2s^22p^33s$ configuration. For the $2p-3s$ transition, an outer

Table 4. Transition trends for E1 decay from the $2s^22p^33s\ ^5S_2$ level for nuclear charges $9 \leq Z \leq 18$. Transition energies are in cm^{-1} and the A transition rates in 10^6 s^{-1}. The latter are reported in both the Babushkin (B) and Coulomb (C) gauges.

Z	AS	$2p^4\ ^3P_2$		$2p^4\ ^3P_1$	
		ΔE	A_B / A_C	ΔE	A_B / A_C
9	3	176275	0.0843/ 0.0854	175936	0.0296 / 0.0297
	4	174898	0.0190/ 0.0201	174561	0.0054 / 0.0078
	5	175254	0.0142/ 0.0031	174919	0.0039 / 0.0015
	Exp.	176654		176312	
10	3	310133	0.1843 / 0.2107	309493	0.0547 / 0.0623
	4	308650	0.2094 / 0.2098	308013	0.0628 / 0.0630
	5	308962	0.2203 / 0.2286	308326	0.0686 / 0.0659
	Exp.	309924		309281	
11	3	473888	1.040 / 1.076	472787	0.2906 / 0.2955
	4	472607	1.119 / 1.080	471510	0.3122 / 0.2986
	5	472887	1.170 / 1.166	471791	0.3271 / 0.3243
	Exp.	473950		472744	
12	3	668924	3.834 / 3.930	667150	1.040 / 1.050
	4	667562	4.081 / 3.938	665793	1.106 / 1.060
	5	667763	4.307 / 4.289	665993	1.171 / 1.160
13	3	894763	11.75 / 11.98	892048	3.068 / 3.080
	4	893284	12.49 / 12.07	890573	3.259 / 3.118
	5	893379	13.28 / 13.34	890669	3.462 / 3.496
	Exp.	894300		891568	
14	3	1151340	31.78 / 32.26	1147338	7.886 / 7.882
	4	1149720	33.78 /32.75	1145724	8.377 / 8.033
	5	1149697	36.52 / 36.36	1145700	9.109 / 9.017
15	3	1438655	77.72 / 78.61	1432942	18.79 / 18.76
	4	1436878	82.67 / 80.31	1431173	19.96 / 19.24
	5	1436768	98.46 / 98.84	1431061	23.87 / 23.88
16	3	1756739	177.6 / 179.2	1748800	39.67 / 39.46
	4	1754797	189.2 / 184.2	1746866	42.20 / 40.71
	5	1754543	207.5 / 206.6	1746610	46.69 / 46.33
17	3	2105645	382.5 / 385.3	2094858	77.71 / 76.99
	4	2103524	407.7 / 397.9	2092744	82.70 / 79.82
	5	2103179	494.9 / 495.4	4092396	101.6 / 101.1
18	3	2485364	783.4 / 788.6	2470986	142.3 / 140.5
	4	2483056	836.0 / 817.9	2468686	151.5 / 146.3
	5	2482544	960.1 / 961.6	2468168	176.0 / 175.2

transition, core-polarization is not expected to be nearly as important.

The transition data for decay from the $2s^22p^33s\ ^5S_2^0$ level to both the $2p^4\ ^3P_2$ and $2p^4\ ^3P_1$ levels are reported in Table 4. For F II ($Z = 9$) the results are not converged and it is clear that the MCDF values are sensitive to details of the calculation. Most surprising is the agreement in the two gauges for the $n = 3$ along with the excellent agreement with the observed transition energy. However, the energy separation between the two lowest $J = 2$ states is too small by almost a factor two and improves with increasing n, thereby affecting the transition rate significantly. The large transition rate for $n = 3$ arises from too large a mixing with $2s2p^5\ ^3P_2^0$. For $Z \geq 11$, the agreement in length and velocity forms improves dramatically for $n = 5$. Most discrepancies are less than 0.45%, but for Ne III ($Z = 10$) the discrepancy is about 3.8%, which is closer to the $n = 4$ discrepancies for higher members of the sequence. The convergence patterns indicate that the $n = 5$ results are lower bounds on the transition rate, so that for $Z \geq 10$ the correct decay rate may be higher by 5−10%. The generally excellent agreement between gauges for a forbidden transition at higher Z can be attributed to the decreasing importance of mixing with $2s2p^5\ ^3P_2^0$ and confirms that core-polarization is not important at this level of accuracy.

Looking at the transition energies it is seen that there is reasonable agreement between theory and experiment for F II, that the error decreases slightly for the more highly ionized ions. The experimental values for Ne III are those of Kastner *et al.* [11] whereas the others are from NIST tabulations [8].

Table 5. Comparison of present length results for decay $2s^22p^33s\ ^5S_2$ level for nuclear charges $9 \le Z \le 18$ with those reported by Kastner *et al.* [11]. The transition energies (ΔE) are in cm^{-1} and the A transition rates in 10^6 s^{-1}.

Z	Method	$2p^4\ ^3P_2$		$2p^4\ ^3P_1$	
		ΔE	A_B / A_C	ΔE	A_B / A_C
10	MCDF	308962	0.2203 / 0.2286	308326	0.0686 / 0.0659
	SUPER	309924	0.00773	309282	0.0185
12	MCDF	667763	4.307 / 4.289	665993	1.171 / 1.160
	SUPER	668941	0.627	666756	0.497
14	MCDF	1149697	36.52 / 36.36	1145700	9.109 / 9.017
	SUPER	1151012	8.11	1146921	4.42
16	MCDF	1754543	207.5 / 206.6	1746610	46.69 / 46.33
	SUPER	1757778	59.3	1749781	23.8
18	MCDF	2482544	960.1 / 961.6	2468168	176.0 / 175.2
	SUPER	2487562	312	2475248	91.6

Calculations for some part of this isoelectronic sequence have been reported by Kastner *et al.* [11] and are compared with the present values in Table 5. Their results were based on the SUPERSTRUCTURE program [12] where radial orbitals are obtained from a scaled Thomas-Fermi-Dirac potential. Though Breit-Pauli interactions (omitting orbit-orbit) were included between the different configurations of the multiplet, many correlation effects were omitted. Analyzing the values one sees that the transition rates for the two calculations differ by a factor ranging from 28.5 ($Z = 10$) to 3.1 ($Z = 18$). These large differences clearly indicate the complexity of the calculations and the sensitivity to correlation effects.

5 Summary and conclusion

Transition rates from MCDF calculations are reported for the $2p^4\ ^3P_{1,2}{-}2s2p^5\ ^3P^0_2$ and $2p^4\ ^3P_{1,2}{-}2p^33s\ ^5S^0_2$ transitions in the oxygen sequence. A restricted active space method was used for the generation of the configuration expansion, and the calculated values were studied as the active set of orbitals was increased to $n = 5$. The convergence patterns for the intercombination lines indicate that the calculated values are lower bounds on the transition rates and that the correct decay rates may be higher by 5−10%.

The present values differ appreciably from earlier values by Kastner *et al.* indicating the complexity of these calculations. For F II and Ne III, Breit-Pauli calculations may be able to yield more definitive results in that the expansions can be restricted to only the important terms and more correlation can be included, particularly core-valence correlation. An MCDF expansion as implemented in GRASP92, includes the equivalent of all possible terms. Thus calculations grow very rapidly and less correlation can be included.

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