

Oscillator strengths for K II $3p^6$ to $3p^5(4s+3d)$ $J = 1$ transitions

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Abstract.

The bottom three $J = 1$ K II levels are nearly degenerate, leading to strong interactions among them, which requires the simultaneous presence of relativistic and correlation effects in any *ab initio* treatment. Relativistic configuration interaction wavefunctions with $\sim 10\,000$ basis functions ($J = 1$) produce f -values in very good agreement with two of the three measured values. Improved predictions are made for the two uppermost $J = 1$ levels. Length and velocity gauge spreads average 1.3% for the five transitions. Landé g -values and hyperfine structure constants are also obtained.

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1. Introduction

We have been interested in the strong interactions among $p^n(s+d)^m$ basis functions and their effect on atomic properties. Early studies for oscillator strengths were for Nb II [1] and Cs II [2], while most recently, results for Ta II have been published [3]. It was not surprising to find that for nearly degenerate levels, interference effects can be quite large.

In 1997, Henderson *et al* published a combined experimental-theoretical paper on lifetimes of the three lowest K II $J = 1$ odd parity levels. The experimental values were the first for these levels which involve strong interactions, due to the plunging of the $3p^53d$ levels, associated with the collapse of the 3d radial, for the bottom two $3p^53d$ levels. The plunging effect is not observed in the adjacent isoelectronic Ar I or Ca III levels [4], although $3p^5(4s+3d)$ mixing is important in Sc IV [5].

Henderson *et al* [4] do two distinct theoretical calculations on these levels – the first using the semi-empirical Cowan approach, where a few configurations are used and radial integrals are scaled to match experimental energies (HFR/ADJ). These turn out to yield oscillator strengths in very good agreement with experiment. The second approach was to do a limited multiconfigurational Dirac-Fock (MCDF) calculation, but here the gauges were not in good agreement with each other, nor with experiment. Henderson *et al*'s conclusion was “An *ab initio* calculation of the level energies, g factors, and transition probabilities in this 4s-3d complex would be a significant test of theory because of the importance of both relativity and correlation”.

Soon after the Henderson *et al* paper appeared and following our relativistic many body perturbation theory (RMBPT) calculations [6] for the resonance transitions of the rare gases, RMBPT calculations were attempted for the K II transition. This time-limited RMBPT attempted failed [7] due to the convergence difficulties arising from the presence of nearly degenerate levels. In this work, we apply the relativistic configuration interaction (RCI) method to the K II problem; one of its strengths is its convergence for a given basis (i.e. almost any matrix can be diagonalized).

2. Methodology

We begin by separately solving the Dirac-Fock equations for the manifolds $3p^6$, $3p^54s\ ^3P_1$ and $3p^53d\ ^3P_1$ using the Desclaux algorithm [8] with the Dirac-Coulomb Hamiltonian. Now, as Figure 1 demonstrates, 3d radial functions for the 3D_1 and especially for the 1P_1 states are very different. While it did prove possible to generate a Dirac-Fock 3d solution for the 3D_1 ($3d'$), no such solution ($3d''$) proved possible for the 1P_1 state, despite careful attempts at Z extrapolation. This is in accordance with the experience of Lin *et al* [9]. Instead, we represent these functions ($3d'$, $3d''$, and $4s'$ for 1P_1) with correlation radials or virtuals. Virtuals (vl) are represented by relativistic screened hydrogenic functions, whose effective charge (Z^*) is determined during the energy variational process. More detail may be found in ref. 3.

The correlation function is built up by making single and double subshell excitations from the reference functions, which for $J = 1$ are $3p^5(4s+4s'+3d+3d'+3d'')$. The small variations among the $3p^5$ and core radials are included at the correlation stage, through single excitation. All single and double excitations from the $n = 3$ and $n = 4$ subshells were investigated, and all those important for energy differences, or with moderate or large coefficients were retained in the final wavefunctions.

The most important triple (quadruple) excitations are formally formed as products

of the most significant single and double (double and double) excitations. Here, these include the excitations $3d \rightarrow d$, $3p \rightarrow vf$, $3s \rightarrow d$ and $3p^2 \rightarrow d^2$. Triple and quadruple excitations $3p^4 \rightarrow d^4$, $3s 3p^2 \rightarrow d^3$, $3p^3 \rightarrow d^2 f$ and $3p^2 3d \rightarrow d^3$ were explored, but only the last was important enough to retain in the final wavefunctions.

For the oscillator strengths and Landé g -values, selected excitations from the $n = 2$ shell were investigated, but were not found to be significant. Included in this category are those which are potentially important to energy differences: (1) the single excitations $2p \rightarrow 3p+vp+vf$, (2) the core valence pairs, e.g. $e(2p,4s)$ and $e(2p,3d)$, and (3) exclusion effects, such as $2p3p \rightarrow 3d^2+3d4s+4s^2$. For the hyperfine structure single excitations from the $n = 2$ shell which make first order contributions to this structure, viz. $2s \rightarrow s+d$ and $2p \rightarrow p$, were included.

The magnetic part of the Breit operator was found to increase the $^1S \rightarrow ^3P_1$ f -values about 9%. This can be traced to the increase in the coefficient of the nearly degenerate $4s ^1P_1$ basis function in the 3P_1 wavefunctions. First order perturbation theory predicts the coefficient ratio is $H(1, i)/(H(i, i) - H(1, 1))$, where 1 refers to the $4s ^1P_1$ basis function, and i to either of the 3P_1 functions. Analysis shows that the magnetic Breit operator both decreases the denominator, and increases the numerator magnitudes. The former can be understood by realizing that the two particle magnetic Breit operator provides a shielding of the bare nucleus one particle Dirac operator, as specifically illustrated by Blume and Watson in their pioneering studies of the one and two particle low Z Pauli spin-orbit operators, which are generated from the Dirac-Breit Hamiltonian in the the $Z\alpha \rightarrow 0$ limit, for transition metal ions [10]. A separate analysis was done here for the retardation operator with the reference manifolds, but no significant contributions were detected.

The $J = 0$ and $J = 1$ wavefunctions are obtained entirely separately, so their radial functions are not mutually orthogonal. We explicitly include non-orthonormality (NON) effects using the method of King *et al* [11], based on the corresponding orbital method of Amos and Hall [12]. This determinantal based method, as originally applied for atomic oscillator strengths by Westhaus and Sinanoglu [13] was quite slow, as it involved diagonalization of two $n \times n$ matrices (n is the number of electrons) for each pair of determinants. Based on an extensive use of configurational and spinor symmetry, compression of all parents of a manifold into one, an adjustable core (which is excluded from the NON process), and doing all optical or near optical transitions in one pass [3, 14, 15], the NON calculations can be speeded up as much as 1000 times. In current practice, calculation times for the oscillator strengths are at least a few times less than wavefunction construction times.

3. Results

When levels are the same parity and J are closely spaced – say a few thousand cm^{-1} apart or less – one needs to produce wavefunctions that can accurately reproduce the observed separations. This helps ensure that the appropriate basis functions are properly mixed in each of the wavefunctions. This is particularly essential when properties associated with the nearly degenerate functions vary widely. For the K II $J = 1$ levels, the energy separations are [5, 16] 0, 1259, 3225, 17217 and 38724 cm^{-1} for the $3p^5 4s ^3P_1$, $3p^5 3d ^3P_1$, $3p^5 4s' ^1P_1$, $3p^5 3d' ^3D_1$ and $3p^5 3d'' ^1P_1$ levels, respectively. Clearly the correct positioning of the $4s'$ function with respect to the $4s$ and $3d$ functions is essential, as of the three, only it carries a non-zero oscillator strength. A second check on the accuracy of the wavefunction mixing is a comparison

of the computed and observed Landé g -values.

The $J = 1$ wavefunction produced with 9675 basis functions yields energy separations of 0, 1346, 3313, 17 873, and 39 258 cm^{-1} . Though the separation errors for the lowest three levels – the nearly degenerate ones are small, below 100 cm^{-1} , they do have a discernable impact on the oscillator strengths. While errors for separations of the two uppermost levels are 6-7 times larger, they are 10 times smaller than in the initial stages of the calculation. Their residual error is likely associated with the unexplored triple and quadruple excitations.

The $J = 0$ function is much smaller; it uses 359 basis functions. Nevertheless, all single and double excitations from the $n = 3$ shell are present, with the exception of double excitations from $3s^2$. The great decrease from $J = 1$ occurs because there is only one reference, and because J has its minimal value ($= 0$). As always the basis is built up in layers, working from the outer subshells inward. A total of five vd 's were used in the $J = 1$ calculations; two of them to represent $3d'$ and $3d''$, and the other three correlation radials.

In order to see the effect of improved $J = 1$ separations on the oscillator strengths, the diagonal matrix elements of the $3p^5(4s'+3d+3d'+3d'')$ basis functions were shifted by -.0011, -.0010, -.0036, and -.0030 a.u. (1 a.u. $\sim 219\,465\text{ cm}^{-1}$). This produced energy separations of 1238, 3241, 17 274 and 39 229 cm^{-1} , respectively. Note that the process is a non-linear one – the shifts are not equal to the separation errors. The main effect was on the $^1S \rightarrow 3d\ ^3P_1$ oscillator strength, increasing it from .0525 to .0648, i.e. towards experiment.

The RCI (shifted) oscillator strengths are shown in Table 1 along with the experimental values [4], Cowan type semi-empirical values [4], and some MCDF values computed by Lin *et al* [9]. These last values do not use correlated $J = 1$ states. While our length and velocity gauge values are in excellent agreement with each other, the oscillator strength for the $^1S \rightarrow 4s\ ^3P_1$ transition is more than twice that of experiment, but the Cowan value is also too high by 50%. Under certain conditions [17], when several upper (lower) levels are close together, the sum of the oscillator strengths may be nearly conserved as the calculation proceeds. Assuming the basis is large enough, the theoretical and experimental sums may agree better than the individual values. In the present instance, the RCI sum for the lowest three transitions is 0.461 and the experimental value is 0.469. Improved wavefunctions would likely redistribute individual oscillator strengths, while maintaining the sum. Table 1 also includes oscillator strengths to the upper two $J = 1$ states, and these are likely the best results currently available. It was not possible to convert experimental lifetimes to oscillator strengths, because of the multiple branches [4].

Results for Landé g -values are presented in Table 2. RCI values are in good agreement with the three known experimental values [5], though the semi-empirical values of Aymar and Schweighofer [5] are in somewhat better agreement. RCI results for the hyperfine structure constants – both magnetic dipole and nuclear quadrupole (relative to the quadrupole moment) are also in this table. These wavefunctions included excitations from the $n = 2$ subshells as noted in the text. The RCI hyperfine results appeared quite stable as the calculation proceeded.

Acknowledgments

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Table 1. K II $3p^6 \rightarrow 3p^5 4s/3d$ $J = 1$ f -values. RCI values are from this work, the bottom values in that column are the DF results for $3d'' \ ^1P$. MCDF[HF] values are from reference 9, the last entry is MCHF and the rest are MCDF. Numbers in parentheses are the percent spread in the velocity vs length gauges or, in the case of Expt, the experimental error [4] expressed as a percentage.

Final Level	RCI[DF] (v/l)	MCDF[HF] (v/l) [9]	HFR [4]	Expt [4]
$4s \ ^3P$	0.0419/0.0419 (0.1)	0.046/0.049 (3)	0.030	0.020 (20)
$3d \ ^3P$	0.0646/0.0648 (0.1)	1.0-5/3.3-5 (50)	0.057	0.069 (17)
$4s' \ ^1P$	0.354/0.355 (0.2)	0.304/0.337 (5)	0.39	0.38 (11)
$3d' \ ^3D$	3.5-3/3.6-3 (2)	4.1-4/1.5-3 (58)		
$3d'' \ ^1P$	1.612/1.729 (4) [1.226/2.028] (25)	[0.964/1.46] (20)		

Table 2. Hyperfine constants ($I=3/2$, $\mu=0.3914$) and Landé g -values for K II $3p^5 4s/3d$ $J = 1$ levels.

Level	Hyperfine constants		RCI	Landé g -values	
	A (MHz)	B/Q (MHz/b)		Expt [5]	Other theory [5]
$4s \ ^3P$	197	310	1.449	1.47	1.462
$3d \ ^3P$	50	37	1.437	1.38	1.441
$4s' \ ^1P$	572	-915	1.112	1.07	1.096
$3d' \ ^3D$	-39	433	0.5022		0.502
$3d'' \ ^1P$	-169	-126	0.9994		0.999

Figure captions

Figure 1. $3d_{3/2}$ radial functions (major component) for K II $J = 1$ states.

