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Lifetimes and transition probabilities of the boron atom calculated with the active-space multiconfiguration Hartree-Fock method

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Systematic multiconfiguration Hartree-Fock results are presented for the transition probabilities and excited-state lifetimes in the term system of the boron atom. Particularly, the interaction between the $1s^22s2p^2$ configuration and the $1s^22s^2ns\,^2S$ and $1s^22s^2nd\,^2D$ Rydberg series is considered. Term energies and transition-matrix elements are calculated to convergence using increasing active sets of s, p, d, f, and g orbitals.

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I. INTRODUCTION

It is desirable to perform *ab initio* atomic-structure calculations in a systematic way. For variational calculations this can be done with the active-space method [1,2] so that the convergence of individual properties of the atom can be studied as the active space is being built up.

Systematic calculations using the multiconfiguration Hartree-Fock (MCHF) method have in many cases been performed for the study of hyperfine structures [3–9], but only few systematic active-space calculations exist for lifetimes [8,10]. Also, these calculations have only been performed for ground states or other states lowest of their symmetry. Here, the applicability of active-space MCHF for the study of lifetimes of states in Rydberg series is demonstrated.

The boron atom, with the ground state $1s^22s^22p\,^2P_{1/2}$, has an energy level structure similar to that of a one-electron system, formed by the excitation of the $2p$ electron. In addition to this, bound states are also formed by exciting one of the $2s$ electrons to a $2p$ orbital. The lowest term thus formed is $1s^22s2p^2\,^4P$, which is of little importance to the doublet states studied here. Also, three doublet terms are formed: ^2D which lies below $1s^22s^23d\,^2D$, ^2P which lies above the ionization limit, and ^2S which lies between $1s^22s^26s\,^2S$ and $1s^22s^27s\,^2S$. Since $1s^22s2p^2\,^2P$ and $1s^22s^2np\,^2P$ have opposite parity these do not interact. $1s^22s2p^2\,^2S$ and $1s^22s2p^2\,^2D$, however, interact with the Rydberg series of the same symmetry. Particularly $1s^22s2p^2\,^2S$, which lies in the middle of the ^2S series, can be expected to have a strong influence, something which is evident already from the irregular energies of the $1s^22s^2ns\,^2S$ states close to $1s^22s2p^2\,^2S$.

Several of the previous theoretical studies of transition probabilities in the boron atom do not include the interaction between the $2s^2nl$ and $2s2p^2$ configurations and must therefore be disregarded. Most of the remaining calculations were performed using different multiconfiguration self-consistent-field (MCSCF) or configuration-interaction (CI) procedures with expansions in the order of 10 or 20 configuration-state functions (CSF's) [11–17]. Only the CI calculation of [18] is considerably larger. The hyperfine structure of the ground state has recently been determined by systematic MCHF calculations [4,9] similar to those performed for the present lifetime study.

The lifetimes of some of the lower excited states of boron have been studied using different experimental techniques: beam-foil spectroscopy [19–24], the phase-shift method with electron-beam excitation [25,26], level-crossing spectroscopy [27], and laser-induced fluorescence [17,28,29].

II. METHOD OF CALCULATION

The wave functions were generated with the MCHF atomic-structure package of Froese Fischer [30].

A complete active space is not used, for two reasons. First, with five electrons, the wave function expansion would grow unmanageably large. Secondly, the existing programs for calculating transition moments [31,32] can only handle a limited degree of the nonorthogonality that arises from optimizing the orbitals of the different states separately. It has been suggested how this limitation could be overcome, using a biorthogonal transformation [33] and a new transition program is now being developed [34]. The restriction that is made in this study is that the $1s$ shell is kept closed and the $1s$ orbital, obtained from a Hartree-Fock calculation for the $1s^22s^2\,^1S$ state of B II, is not varied during the optimization.

Calculations have been performed for the $1s^22s^2ns\,^2S$, $n = 3$ to 6, $1s^22s^2np\,^2P$, $n = 2$ to 6, $1s^22s^2nd\,^2D$, $n = 3$ to 5, $1s^22s^24f\,^2F$, and $1s^22s2p^2\,^2D$ states. For each term calculations were performed with an increasing active set of orbitals, the smallest calculation in each case a Hartree-Fock calculation, the largest one in each case with the active set $7s6p5d4f3g$ which means seven s orbitals, six p orbitals, etc. Starting with the Hartree-Fock calculation, orbitals were added to the active set

TABLE I. Convergence of the term energies for increasing active sets of orbitals, in atomic units.

Term	HF	$3s2p1d$	$4s3p2d1f$	$5s4p3d2f1g$	$6s5p4d3f2g$	$7s6p5d4f3g$
$1s^22s^23s\,^2S$	-24.352104	-24.417944	-24.420551	-24.420974	-24.421121	-24.421174
$1s^22s^24s\,^2S$	-24.289374	-24.350550	-24.352532	-24.352857	-24.352979	-24.353030
$1s^22s^25s\,^2S$	-24.267136	-24.327224	-24.329107	-24.329434	-24.329564	-24.329611
$1s^22s^26s\,^2S$	-24.256684	-24.316373	-24.318257	-24.318653	-24.318747	-24.318819
$1s^22s^22p\,^2P$	-24.529036	-24.596002	-24.600564	-24.601683	-24.601923	-24.601999
$1s^22s^23p\,^2P$	-24.316261	-24.378547	-24.381214	-24.381761	-24.381956	-24.382027
$1s^22s^24p\,^2P$	-24.277493	-24.338642	-24.339843	-24.340184	-24.340311	-24.340360
$1s^22s^25p\,^2P$	-24.261773	-24.322647	-24.323365	-24.323659	-24.323739	-24.323781
$1s^22s^26p\,^2P$	-24.253815	-24.314586	-24.315112	-24.315372	-24.315435	-24.315472
$1s^22s2p^2\,^2D$	-24.311705	-24.369391	-24.380943	-24.382939	-24.383398	-24.383526
$1s^22s^23d\,^2D$	-24.293745	-24.350591[a]	-24.352361	-24.353540	-24.353822	-24.353912
$1s^22s^24d\,^2D$	-24.269170	-24.328838[a]	-24.329540	-24.330095	-24.330261	-24.330315
$1s^22s^25d\,^2D$	-24.257771	-24.318007[a]	-24.318453	-24.318842	-24.318958	-24.318996
$1s^22s^24f\,^2F$	-24.268828	-24.329583[b]	-24.329743	-24.330087	-24.330194	-24.330221
$1s^22s^2\,^1S$	-24.237575	-24.298330	-24.298647	-24.298767	-24.298802	-24.298811

[a] Active set $3s2p2d$.
[b] Active set $3s2p1d1f$.

one of each symmetry at a time, in the same way as orbitals appear in the shells in an atom. In each calculation all CSF's possible to form using the orbitals in the active set outside the $1s^2$ core and which have the correct parity and LS term were included. The lists of configurations were generated using the generation program of the MCHF package [35]. These CSF's are called the active space. In each calculation all orbitals except $1s$ were optimized. The active set was increased until a satisfactory convergence of the energy and transition-matrix elements was obtained. The largest active space, for the $4f\,^2F$ states, consisted of 4538 CSF's.

This type of calculation has previously been performed for states lowest of their symmetry. In such cases, the wave function is optimized for the lowest eigenvalue. For higher-lying states the eigenfunction must be orthogonal to all eigenfunctions belonging to lower states. In this study CSF's representing lower states were included in the expansions and by diagonalizing the interaction matrix the eigenvalue on which to optimize could be determined. For example, in the expansion of the $2s^23d\,^2D$ state, the second of its symmetry, the CSF representing the lowest state $2s2p^2\,^2D$ was also included. After the diagonalization of the interaction matrix the orbitals were optimized on the second eigenvalue.

For the next state above those included in the study, $2s2p^2\,^2S$, the attempted calculations were unstable when all orbitals were varied in the self-consistent-field procedure.

III. RESULTS AND DISCUSSION

Table I shows the convergence of the calculated term energies for increasing active sets. From the calculated

TABLE II. Convergence of the reduced electric dipole transition-matrix elements in the length (l) and velocity (v) forms for transitions to the ground state, for increasing active sets of orbitals, in atomic units.

Upper term		HF	$3s2p1d$	$4s3p2d1f$	$5s4p3d2f1g$	$6s5p4d3f2g$	$7s6p5d4f3g$
$1s^22s^23s\,^2S$	l	1.1292	1.3438	1.3785	1.3953	1.4002	1.4020
	$v/\Delta E$	1.2862	1.5169	1.4547	1.4317	1.4288	1.4290
$1s^22s^24s\,^2S$	l	0.3941	0.4958	0.5109	0.5221	0.5371	0.5388
	$v/\Delta E$	0.4361	0.5358	0.5315	0.5310	0.5476	0.5495
$1s^22s^25s\,^2S$	l	0.2266	0.3102	0.3414	0.3879	0.3980	0.4006
	$v/\Delta E$	0.2488	0.3294	0.3521	0.3956	0.4058	0.4085
$1s^22s^26s\,^2S$	l	0.1541	0.2314	0.3354	0.3914	0.4074	0.4133
	$v/\Delta E$	0.1687	0.2427	0.3438	0.3986	0.4154	0.4212
$1s^22s2p^2\,^2D$	l	-2.6468	-1.4650	-0.9027	-0.9146	-0.9139	-0.9133
	$v/\Delta E$	-2.6529	-1.6128	-0.9465	-0.9709	-0.9697	-0.9690
$1s^22s^23d\,^2D$	l	-1.3993	-1.6550[a]	-1.7523	-1.7641	-1.7683	-1.7688
	$v/\Delta E$	-1.3681	-1.6778[a]	-1.7648	-1.7750	-1.7816	-1.7825
$1s^22s^24d\,^2D$	l	-0.8827	-1.0669[a]	-1.1022	-1.0903	-1.0889	-1.0875
	$v/\Delta E$	-0.8529	-1.0577[a]	-1.1040	-1.0907	-1.0930	-1.0923
$1s^22s^25d\,^2D$	l	-0.6171	-0.7460[a]	-0.7477	-0.7553	-0.7515	-0.7512
	$v/\Delta E$	-0.5934	-0.7330[a]	-0.7409	-0.7526	-0.7530	-0.7536

[a] Active set $3s2p2d$ for the ^2D state.

wave functions transition-matrix elements were calculated. Table II shows, as an example, the convergence of the reduced transition-matrix elements for transitions to the ground state. Calculated values are given using both the length and velocity forms of the electric dipole operator. The velocity form values have been divided by the transition energy. In atomic units they should then, for the correct wave functions, equal the length form values. For the largest active sets the velocity values are on average 2% larger than the length values, with a larger difference for the transition from the $2s2p^2\,{}^2D$ states and a smaller difference for the transitions from the $2s^2nd\,{}^2D$ states. For the ${}^2S$ series the difference approaches a constant for the higher members, whereas for the ${}^2D$ series, the difference appears to be approaching zero. That it is the transition involving the $2s2p^2\,{}^2D$ states for which the velocity value differs the most from the length value is probably due to the single $2s$ electron of this configuration. This electron can be expected to cause a much stronger polarization of the $1s$ shell than any other single electron with higher n or l quantum numbers. This may also be the reason why the calculated energy of this term is too high compared with that of any other term, as can be seen in Table III, where the final values for the ionization energies can be compared with the experimental values. Table IV gives the final values for all electric dipole transition probabilities between the investigated states, calculated using either the length or velocity form of the electric dipole operator and using the calculated transition energies. The values of the length and velocity forms typically agree to within a few percent. The exception to this are the transitions with very small transition probabilities, for which the difference tends to be larger, and also most of the transitions involving the $2s2p^2\,{}^2D$ states. The velocity form, which depends more than the length form on the wave function close to the nucleus, may have been more affected by the closed $1s$ shell. The length form is therefore the more trusted one. To some extent the difference between the length and velocity values is due to their different dependence on the transition energy. With the velocity form the transition probability is proportional to the transition energy, with the length form it is proportional to the transition energy to the third. This may affect the results particularly for transitions between very near-lying states for which cases the relative error of the calculated transition energy may be large. These transition probabilities are small and have no appreciable effect on the calculated lifetimes. The oscillator strengths for transitions from the $2s^22p\,{}^2P$ ground state to the excited ${}^2S$ and ${}^2D$ states are given in Tables V and VI. These tables also include values obtained in previous calculations and experiments. On the whole, the agreement between the length and velocity forms is considerably improved in the present calculation.

TABLE III. Calculated and experimental ionization energies, in cm^{-1}. The fourth column lists the experimental energy minus the calculated one.

Term	Calculated	Experimental[a]	Difference
$1s^22s^23s\,{}^2S$	26856	26888.45	33
$1s^22s^24s\,{}^2S$	11900	11917.92	18
$1s^22s^25s\,{}^2S$	6760	6781.65	22
$1s^22s^26s\,{}^2S$	4391	4445.87	55
$1s^22s^22p\,{}^2P$	66542	66917.93	376
$1s^22s^23p\,{}^2P$	18264	18315.09	51
$1s^22s^24p\,{}^2P$	9119	9141.30	22
$1s^22s^25p\,{}^2P$	5480		
$1s^22s^26p\,{}^2P$	3657		
$1s^22s2p^2\,{}^2D$	18593	19070.98	478
$1s^22s^23d\,{}^2D$	12093	12160.36	67
$1s^22s^24d\,{}^2D$	6914	6934.67	20
$1s^22s^25d\,{}^2D$	4430	4442.63	13
$1s^22s^24f\,{}^2F$	6894	6897.07	3

[a] Reference [37].

Table VII gives the lifetime values, calculated from

TABLE IV. Transition probabilities for transitions between the investigated states, calculated using the length (l) and velocity (v) forms of the electric dipole operator and the calculated transition energies. Transition probabilities from the upper to the lower state are given. The numbers in brackets denote multiplicative powers of ten.

Term		$1s^22s^22p\,{}^2P$	$1s^22s^23p\,{}^2P$	$1s^22s^24p\,{}^2P$	$1s^22s^25p\,{}^2P$	$1s^22s^26p\,{}^2P$	$1s^22s^24f\,{}^2F$
$1s^22s^23s\,{}^2S$	l	2.489[8]	1.733[7]	2.066[5]	1.598[2]	7.328[3]	
	v	2.586[8]	1.747[7]	2.135[5]	3.675[2]	6.363[3]	
$1s^22s^24s\,{}^2S$	l	9.593[7]	1.640[7]	2.651[6]	1.574[5]	2.920[4]	
	v	9.979[7]	1.651[7]	2.666[6]	1.596[5]	2.984[4]	
$1s^22s^25s\,{}^2S$	l	6.947[7]	5.455[6]	3.722[6]	7.164[5]	8.155[4]	
	v	7.221[7]	5.501[6]	3.740[6]	7.176[5]	8.196[4]	
$1s^22s^26s\,{}^2S$	l	8.306[7]	2.518[6]	1.197[6]	1.112[6]	2.766[5]	
	v	8.629[7]	2.524[6]	1.198[6]	1.107[6]	2.783[5]	
$1s^22s2p^2\,{}^2D$	l	3.726[7]	2.900[2]	7.728[1]	1.501[4]	2.024[4]	2.624[6]
	v	4.194[7]	4.944[2]	6.165[2]	1.833[4]	2.329[4]	2.602[6]
$1s^22s^23d\,{}^2D$	l	2.046[8]	1.262[7]	1.708[6]	5.603[5]	2.923[5]	1.232[7]
	v	2.078[8]	1.265[7]	1.718[6]	5.672[5]	2.971[5]	1.234[7]
$1s^22s^24d\,{}^2D$	l	1.016[8]	1.917[2]	2.444[6]	7.730[5]	2.782[5]	1.873[0]
	v	1.025[8]	3.742[2]	2.458[6]	7.763[5]	2.796[5]	2.759[0]
$1s^22s^25d\,{}^2D$	l	5.478[7]	2.144[5]	8.757[4]	7.031[5]	3.346[5]	6.019[4]
	v	5.513[7]	2.231[5]	9.173[4]	7.076[5]	3.365[5]	6.027[4]

TABLE V. Weighted multiplet oscillator strengths, gf, for transitions between the ground state and excited ^2S states of boron.

Upper term	$1s^22s^23s\,^2S$	$1s^22s^24s\,^2S$	$1s^22s^25s\,^2S$	$1s^22s^26s\,^2S$
	Calculations			
This work, length	0.474	0.0963	0.0583	0.0645
This work, velocity	0.492	0.100	0.0606	0.0670
Ref. [11], length	0.402			
Ref. [11], velocity	0.444			
Ref. [12], length	0.372			
Ref. [12], velocity	0.408			
Ref. [13], length	0.216			
Ref. [18], length	0.417	0.188	0.0230	0.0533
Ref. [16], length	0.444	0.102	0.072	0.102
Ref. [16], velocity	0.540	0.108	0.078	0.114
	Experiments			
Ref. [19], beam foil	0.48 (0.03)			
Ref. [21], beam foil	0.33 (0.01)			
Ref. [26], phase shift	0.72 (0.15)			
Ref. [23], beam foil	0.54 (0.06)			
Ref. [24], beam foil	0.52 (0.03)			
Ref. [28], laser-induced fluorescence	0.47 (0.03)			

the transition probabilities given in Table IV, using the length form values. An interesting detail is that the $6s\,^2S$ state has a shorter lifetime than $5s\,^2S$. This can be understood from the interaction with the $2s2p^2\,^2S$ state. Table VIII gives the coefficients for the $2s2p^2$ CSF for each of the ^2S and ^2D states. This CSF gives a large contribution to the transition-matrix elements of the transitions to the ground state, thus making the lifetimes of these states shorter. In Table IX some of the most important contributions to the length form reduced transition-matrix elements for transitions to the ground state are detailed. It shows the cancellation in the matrix element for the transition to $2s2p^2\,^2D$, explaining the large variation in the theoretical gf values for this transition reported in Table VI.

In Table VII the lifetimes calculated in this study can be compared with those obtained in experiments. Without even being impartial one can say that a large part of the experimentally obtained values are either wrong or have too small error bars, not because they disagree with theory but because they disagree with each other.

Many of the experiments have been performed using

TABLE VI. Weighted multiplet oscillator strengths, gf, for transitions between the ground state and excited ^2D states of boron.

Upper term	$1s^22s2p^2\,^2D$	$1s^22s^23d\,^2D$	$1s^22s^24d\,^2D$	$1s^22s^25d\,^2D$
	Calculations			
This work, length	0.243	1.035	0.428	0.213
This work, velocity	0.274	1.051	0.432	0.214
Ref. [11], length	0.402	1.182		
Ref. [11], velocity	0.504	1.134		
Ref. [12], length	0.690			
Ref. [12], velocity	0.942			
Ref. [14], length	0.216			
Ref. [15], length	0.174			
Ref. [15], velocity	0.210			
Ref. [18], length	0.292	0.998	0.367	0.187
	Experiments			
Ref. [25], phase shift	0.28 (0.09)			
Ref. [19], beam foil	0.24 (0.01)			
Ref. [20], beam foil	0.30 (0.05)			
Ref. [21], beam foil	0.36 (0.02)			
Ref. [23], beam foil	0.30 (0.02)			
Ref. [24], beam foil	0.27 (0.02)			
Ref. [27], level crossing	0.28 (0.03)			
Ref. [28], laser-induced fluorescence	0.28 (0.02)			

TABLE VII. Calculated and experimental lifetimes, in ns. The calculated lifetimes were obtained using the length form of the electric dipole operator and the calculated energies.

Term	Calculated	Experimental
$1s^22s^23s\,^2S$	4.02	3.8(0.2)[a], 5.7(0.2)[b], 3.4(0.4)[c] 3.57(0.20)[d], 2.5(0.5)[e], 4.0(0.2)[f]
$1s^22s^24s\,^2S$	8.90	8.7(0.4)[f]
$1s^22s^25s\,^2S$	12.7	
$1s^22s^26s\,^2S$	11.4	
$1s^22s2p^2\,^2S$		3.6(0.3)[g]
$1s^22s^23p\,^2P$	57.7	52(5)[h]
$1s^22s^24p\,^2P$	219	218(20)[h], 360(50)[i]
$1s^22s^25p\,^2P$	450	
$1s^22s^26p\,^2P$	757	
$1s^22s2p^2\,^2D$	26.8	26.4(1.0)[a], 18.4(0.8)[b], 21.8(0.5)[c] 24.4(1.5)[d], 23.1(1.2)[f], 21.8(1.1)[j], 23.0(2.0)[k], 23.1(2.5)[l]
$1s^22s^23d\,^2D$	4.60	5.1(0.2)[c], 4.15(0.25)[d], 4.7(0.2)[f] 3.9(0.5)[g], 5.1(0.3)[j], 4.5(0.5)[k]
$1s^22s^24d\,^2D$	9.61	10.0(0.5)[f]
$1s^22s^25d\,^2D$	17.9	
$1s^22s^24f\,^2F$	66.9	

[a] Reference [19], beam foil.
[b] Reference [21], beam foil.
[c] Reference [23], beam foil.
[d] Reference [24], beam foil.
[e] Reference [26], phase shift with electron-beam excitation.
[f] Reference [28], laser-induced fluorescence.
[g] Reference [22], beam foil.
[h] Reference [17], laser-induced fluorescence.
[i] Reference [29], laser-induced fluorescence.
[j] Reference [20], beam foil.
[k] Reference [25], phase shift with electron-beam excitation.
[l] Reference [27], level crossing.

the beam-foil technique and these were all done before the necessity of a careful cascade analysis was fully understood. The same problem, repopulation from higher states due to the nonselective excitation, appears using electron-beam excitation.

Three of the experiments have been performed using pulsed laser excitation, two of them for ^2P states. Unfortunately these two studies give lifetime values for the $4p\,^2P$ states which differ by a factor of 1.65. In one of these experiments [17] two states were studied and for both the result agrees very well with that of the present calculation. In the second experiment [29] only one lifetime was measured. This experiment was performed at high pressure in a cell and the lifetime value was extrapolated after having performed the experiment at different pressures. This was a more complicated procedure than the one used in [17] and, it seems, one which did not work.

The most extensive experimental study of the boron

TABLE VIII. $2s2p^2$ admixture to the ^2S and ^2D states.

Term	Eigenvector coefficient
$1s^22s^23s\,^2S$	-0.108
$1s^22s^24s\,^2S$	-0.109
$1s^22s^25s\,^2S$	-0.136
$1s^22s^26s\,^2S$	-0.203
$1s^22s2p^2\,^2D$	0.891
$1s^22s^23d\,^2D$	0.255
$1s^22s^24d\,^2D$	0.107
$1s^22s^25d\,^2D$	0.066

TABLE IX. Contributions to the length form reduced transition-matrix elements for transitions to the ground state. The second column contains the contributions involving the $2s^2nl$ CSF of the excited state (for the $2s2p^2\,^2D$ states the sum of the contributions from all $2s^2nd$ CSF's) and the $2s^22p$ CSF of the ground state. The third column contains the contributions involving the $2s2p^2$ CSF of the excited state and the $2s^22p$ CSF of the ground state.

Upper state	$2s^2nl$-$2s^22p$	$2s2p^2$-$2s^22p$	Total
$1s^22s^23s\,^2S$	0.623	0.103	1.402
$1s^22s^24s\,^2S$	0.225	0.105	0.539
$1s^22s^25s\,^2S$	0.124	0.130	0.401
$1s^22s^26s\,^2S$	0.068	0.197	0.413
$1s^22s2p^2\,^2D$	0.917	-2.156	-0.913
$1s^22s^23d\,^2D$	-0.739	-0.549	-1.769
$1s^22s^24d\,^2D$	-0.549	-0.230	-1.088
$1s^22s^25d\,^2D$	-0.404	-0.141	-0.751

lifetimes is one of the five lowest even parity doublet terms using pulsed laser excitation [28]. For four of these five terms our calculated lifetimes are well within the 5% error bars of the experiment, the only term for which it is not is $2s2p^2\,{}^2D$. As discussed above, the discrepancy for this particular term could be explained by the neglected polarization of the $1s$ shell.

Finally, one of the measurements of the $1s^22s2p^2\,{}^2D$ states [27] was performed using level-crossing spectroscopy.

What has not been included in this study is the polarization of the $1s$ shell and the core-core correlation. This is expected to affect the transition energies more than the transition-matrix elements, as has been seen in a similar system in C III [36]. Since the calculated transition energies are correct typically to within 1% the neglected effects of the $1s$ shell should, for most of the states, be small, at least for the length form operator.

IV. CONCLUSION

The active-space multiconfiguration Hartree-Fock method has been extended to the study of Rydberg series. This has been done for boron, an atom in which two of the Rydberg series exhibit a strong configuration interaction due to the near degeneracy with states formed by excitation from an inner subshell.

The accuracy of the calculated transition probabilities is difficult to estimate. The convergence procedure, the accuracy of the transition energies, and the agreement between the length and velocity forms of the electric dipole operator indicate that the length form values may be accurate to within a few percent. Comparison with the most reliable experimental lifetime values [17,27,28] seems to indicate that the calculated values are at least accurate to within 5% or 10%, that is, as accurate as the experiments.

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[1] B.O. Roos, P.R. Taylor, and P.E.M. Siegbahn, Chem. Phys. **48**, 157 (1980).

[2] J. Olsen, B.O. Roos, P. Jørgensen, and H.J.Aa. Jensen, J. Chem. Phys. **89**, 2185 (1988).

[3] D. Sundholm and J. Olsen, Phys. Rev. A **42**, 2614 (1990).

[4] D. Sundholm and J. Olsen, J. Chem. Phys. **94**, 5051 (1991).

[5] D. Sundholm and J. Olsen, Chem. Phys. Lett. **177**, 91 (1991).

[6] J. Carlsson, P. Jönsson, and C. Froese Fischer, Phys. Rev. A **46**, 2420 (1992).

[7] J. Carlsson, P. Jönsson, L. Sturesson, and C. Froese Fischer, Phys. Scr. **46**, 394 (1992).

[8] M. Tong, P. Jönsson, and C. Froese Fischer, Phys. Scr. **48**, 446 (1993).

[9] P. Jönsson and C. Froese Fischer, Phys. Rev. A **48**, 4113 (1993).

[10] C. Froese Fischer, Phys. Scr. **49**, 51 (1994).

[11] A.W. Weiss, Phys. Rev. **188**, 119 (1969).

[12] Z. Sibincic, Phys. Rev. A **5**, 1150 (1972).

[13] C.A. Nicolaides, Chem. Phys. Lett. **21**, 242 (1973).

[14] O. Sinanoglu and S.L. Davis, Chem. Phys. Lett. **32**, 449 (1975).

[15] C.A. Nicolaides and D.R. Beck, Chem. Phys. Lett. **35**, 202 (1975).

[16] D.R. Beck and C.A. Nicolaides, Phys. Lett. **61A**, 227 (1977).

[17] H. Bergström, G.W. Faris, H. Hallstadius, H. Lundberg, A. Persson, and C.-G. Wahlström, Z. Phys. D **8**, 17 (1988).

[18] R.K. Nesbet, Phys. Rev. A **14**, 1065 (1976).

[19] T. Andersen, K.A. Jessen, and G. Sørensen, Phys. Rev. **188**, 76 (1969).

[20] I. Bergström, J. Bromander, R. Buchta, L. Lundin, and I. Martinson, Phys. Lett. **28A**, 721 (1969).

[21] J. Bromander, R. Buchta, and L. Lundin, Phys. Lett. **29A**, 523 (1969).

[22] I. Martinson, W.S. Bickel, and A. Ölme, J. Opt. Soc. Am. **60**, 1213 (1970).

[23] J. Bromander, Phys. Scr. **4**, 61 (1971).

[24] J.A. Kernahan, E.H. Pinnington, A.E. Livingston, and D.J.G. Irwin, Phys. Scr. **12**, 319 (1975).

[25] G.M. Lawrence and B.D. Savage, Phys. Rev. **141**, 67 (1966).

[26] W.H. Smith and H.S. Liszt, J. Opt. Soc. Am. **61**, 938 (1971).

[27] A. Hese and H.-P. Weise, Z. Phys. **215**, 95 (1968).

[28] T.R. O'Brian and J.E. Lawler, Astron. Astrophys. **255**, 420 (1992).

[29] X. Yang and P.J. Dagdigian, Chem. Phys. Lett. **200**, 217 (1992).

[30] C. Froese Fischer, Comput. Phys. Commun. **64**, 369 (1991).

[31] C. Froese Fischer, M.R. Godefroid, and A. Hibbert, Comput. Phys. Commun. **64**, 486 (1991).

[32] C. Froese Fischer and M.R. Godefroid, Comput. Phys. Commun. **64**, 501 (1991).

[33] P.Å. Malmqvist, Int. J. Quantum Chem. **XXX**, 479 (1986).

[34] M. Godefroid and J. Olsen (private communication).

[35] L. Sturesson and C. Froese Fischer, Comput. Phys. Commun. **74**, 432 (1993).

[36] J. Fleming, A. Hibbert, and R.P. Stafford, Phys. Scr. **49**, 316 (1994).

[37] G.A Odintzova and A.R. Striganov, J. Phys. Chem. Ref. Data **8**, 63 (1979).