Multiconfiguration Dirac-Fock calculations of the $2s^2\,{}^1S_0-2s2p\ {}^3P_1$ intercombination transition in C III

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(Received 2 April 1997; revised manuscript received 5 January 1998)

Multiconfiguration Dirac-Fock calculations for the $2s^2\,{}^1S_0-2s2p\ {}^3P_1$ intercombination transition in C III are revisited. To improve the accuracy, the orbital sets for the initial- and final-state wave functions were not restricted to be the same, but were optimized independently. The calculated $2s2p\ {}^3P$ fine-structure splitting and the $2s^2\,{}^1S_0-2s2p\,{}^3P_1$ transition energy are in good agreement with experiment. The predicted transition rate $A=102.9\pm1.5\ \mathrm{s}^{-1}$ is in agreement with a recent storage-ring measurement by Doerfert *et al.* [Phys. Rev. Lett. **78**, 4355 (1997)]. Results are also presented for the allowed $2s^2\,{}^1S_0-2s2p\ {}^1P_1$ transition and the $2s^2\,{}^1S_0-2s2p\ {}^3P_2$ magnetic quadrupole transition.
[S1050-2947(98)07306-5]

PACS number(s): 31.25.−v, 31.30.Jv, 32.70.Cs

In the recent multiconfiguration Dirac-Fock (MCDF) calculation for the $2s^2\,{}^1S_0-2s2p\ {}^3P_1$ intercombination (IC) transition in the Be-like sequence [1], the orbitals for the initial and final states were restricted to be the same. In the present work, this restriction has been removed using a biorthogonal transformation method [2]. As a test of the capability of the unconstrained MCDF method, new and more accurate calculations were performed for C III.

In the MCDF approach, as implemented in the GRASP92 code [3], the wave function for a state is expanded in terms of jj-coupled configuration state functions. The latter are antisymmetrized 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

$$\mathcal{H}_{\mathrm{trans}}=-\sum_{i<j}^{N}\left[\frac{\boldsymbol{\alpha}_i\cdot\boldsymbol{\alpha}_j\,\cos(\omega_{ij}r_{ij})}{r_{ij}}+(\boldsymbol{\alpha}_i\cdot\boldsymbol{\nabla}_i)\times(\boldsymbol{\alpha}_j\cdot\boldsymbol{\nabla}_j)\,\frac{\cos(\omega_{ij}r_{ij})-1}{\omega_{ij}^2 r_{ij}}\right] \tag{1}$$

may be included in the Hamiltonian. The photon frequency ω_{ij} used by GRASP92 [3] in calculating the matrix elements of the transverse photon interaction is taken to be the difference in the diagonal Lagrange multipliers associated with Dirac orbitals. In general, diagonal Lagrange multipliers are approximate electron removal energies only when orbitals are spectroscopic and singly occupied. Thus it is not known how well the code can determine the full transverse photon interaction when correlation orbitals are present. What can be obtained instead is the low-frequency limit $\omega_{ij}\to 0$ usually referred to as the Breit interaction. In the RCI calculations, some QED and finite nuclear mass effects can also be accounted for.

To illustrate the importance of different correlation effects, two separate sets of calculations were done; in the first, valence and core-valence effects were included and in the second also some core correlation was accounted for. For the core-valence calculations the configuration expansions were generated by allowing all single and double excitations from the multireference set of closely degenerate configurations to an active set of orbitals, with the restriction that there should be at most one excitation from the $1s^2$ electron core. For the $2s^2\,{}^1S_0$ state, the reference set was $\{2s^2,2p_{1/2}^2,2p_{3/2}^2\}$ whereas for $2s2p\ {}^1P_1$ and $2s2p\ {}^3P_{0,1,2}$ it was $\{2s2p_{1/2},2s2p_{3/2}\}$. To monitor the convergence of the calculated properties, the active set was then systematically increased to include orbitals with quantum numbers up to $n=8$ and $l\leqslant 6$. In these calculations the $1s$ orbitals were kept fixed from calculations including only the reference sets.

The $2s2p\ {}^3P$ term has three fine-structure levels, and there is a choice of how to optimize the orbitals. As shown by Ynnerman and Froese Fischer [1], optimizing on the $2s2p\ {}^3P_1$ state alone leads to an extremely oscillatory behavior of the $2s^2\,{}^1S_0-2s2p\ {}^3P_1$ transition rate as the active set is increased. The reason for this is not entirely understood, but is believed to be related to an incorrect nonrelativistic limit of the $2s2p\ {}^3P_1$ wave function. To overcome this problem, extended optimal level (EOL) calculations were performed. Here the optimization was on the $(2J+1)$ weighted energy average of the $2s2p\ {}^3P_{0,1,2}$ states. The Breit interaction, which has been shown to be extremely important for the intercombination rate [4,1], was accounted for in a sequence of RCI calculations. The results from these calculations are shown in the first part of Table I. From the table it is clear that most properties have converged, though not A_{IC}. The change, however, is smooth and can be extrapolated, as described below.

Based on the observation that core correlation is easily unbalanced between two states, the first step of the core correlation calculation was done in the EOL mode, optimizing simultaneously on the initial and final states in the transition. Thus for $2s^2\,{}^1S-2s2p\ {}^3P$ the optimization was on the weighted energy average of the $2s^2\,{}^1S_0$, $2s2p\ {}^3P_{0,1,2}$ states.

TABLE I. Energies (cm^{-1}), transition rates (s^{-1}), and gf values for the intercombination (IC), magnetic quadrupole ($M2$), and electric dipole ($E1$) transitions as functions of the active set (AS); B and C denote the Babushkin and Coulomb gauges.

AS	$\Delta E^{\rm fs}_{2-0}$	ΔE_{IC}	A^B_{IC}	A^C_{IC}	ΔE_{M2}	A_{M2} (units of 10^3)	ΔE_{E1}	gf^B_{E1}	gf^C_{E1}
				Core-valence calculation					
3	78.17	52 553	77.36	91.35	52 607	5.210	104 513	0.7699	0.7747
4	80.03	52 511	89.49	89.34	52 566	5.187	103 308	0.7606	0.7542
5	80.32	52 461	98.58	127.90	52 517	5.163	102 818	0.7584	0.7566
6	80.44	52 448	101.47	132.68	52 503	5.159	102 623	0.7579	0.7582
7	80.48	52 448	102.46	137.17	52 503	5.160	102 565	0.7585	0.7589
8	80.50	52 449	102.91	137.22	52 504	5.160	102 540	0.7589	0.7585
Norm.[a]			102.57			5.132		0.7575	0.7599
Extp.[b]	80.52		102.94						
				Core-core calculation					
3	77.32	52 393	66.12	3.14	52 446	5.172	104 362	0.7850	0.7401
4	79.46	52 223	81.45	80.99	52 278	5.089	102 982	0.7627	0.7414
5	79.59	52 298	95.95	136.78	52 353	5.089	102 656	0.7586	0.7537
6	79.74	52 357	100.92	157.55	52 412	5.119	102 528	0.7591	0.7559
7	79.81	52 373	102.38	158.86	52 428	5.128	102 496	0.7587	0.7568
8	79.84	52 382	102.72	160.14	52 437	5.134	102 480	0.7588	0.7571
Norm.[a]			102.77	160.17		5.139		0.7579	0.7581
Extp.[b]	79.86	52 394	102.85		52 449		102 464		
Corr.[c]	80.05	52 370	102.87		52 425	5.139	102 440	0.7579	0.7576
Expt.[d]	80.05	52 391			52 447		102 352		

[a]Normalized to observed transition energy (see text).
[b]Extrapolated Dirac-Coulomb-Breit values (see text).
[c]Corrected for QED and finite nuclear mass effects.
[d]NIST online database.

For the EOL calculations the expansions for the initial and final states were again obtained by allowing all possible excitations to $n=3$. As the next step core-valence orbitals were optimized separately on, respectively, the $^1S_0$, $^3P_{0,1,2}$, and $^1P_1$ states. The expansions for these calculations were obtained by augmenting the $n=3$ expansions by the core-valence expansions for the larger active sets. The MCDF core correlation calculations were followed by RCI calculations including the Breit interaction. The results from these calculations are shown in the second part of Table I. It is seen that the inclusion of core correlation results in a small, but significant, improvement of all energy differences. From the table it is also clear that the calculated energy differences and transition parameters change smoothly with respect to the increasing active set n, but that they have not yet converged. To extrapolate a sequence of values for a property, say P_n, we calculated $\Delta P_n = P_n - P_{n-1}$ and the ratios $r_n = \Delta P_n / \Delta P_{n-1}$ for the last few values of n. In the case of the fine-structure separation the ratios r_n were found to be rather constant between $n=7$ and 8. The assumption that r_n is also constant for the remainder of the series leads to an extrapolation correction $\Delta P_n r_n/(1-r_n)$ which, when evaluated, becomes $0.02\ cm^{-1}$. For the intercombination, magnetic quadrupole, and allowed electric dipole transition energies, the ratios for $n=8$ are larger than those for $n=7$, and an extrapolation becomes more uncertain. Based on the ratios for $n=8$ alone we obtain an increase of $12\ cm^{-1}$ for the two former lines and a decrease of $16\ cm^{-1}$ for the latter. A similar extrapolation procedure can be applied to the transition parameters. Before extrapolating the intercombination rate $A^B_{\rm IC}$, it is helpful to remember that this depends on $\Delta E^3_{\rm IC}$: in fact, quite a bit of the changing trend is due to the changing computed transition energy. By first normalizing each computed transition rate to the observed transition energy, extrapolation produces only a small change.

For completeness the frequency-dependent part of the Breit interaction also was investigated. This was done in a sequence of RCI calculations where now the full transverse photon interaction was included in the Hamiltonian. By comparing the results from these calculations with the ones from the Dirac-Coulomb-Breit calculations, it was seen that the frequency-dependent part of the transverse photon interaction decreases both the fine-structure splitting and the transition rate. The decrease was found to depend both on the orbital basis and the type of correlation included in the wave function. For the core correlation calculation the decreases were 0.40 cm and $2\ s^{-1}$, respectively, whereas for the core-valence calculation the corresponding values were 0.32 cm and $0.73\ s^{-1}$. In relativistic many-body calculations [5], the frequency dependence on the fine structure was negligible (private communication) [13].

For the intercombination transition the uncertainties in the calculation come mainly from the effects of the frequency-dependent Breit interaction. Because of the extensive cancellation of about three significant digits between the contributions to the transition matrix elements from the $2s_{1/2}2p_{1/2}\ J$

TABLE II. Comparison of experimental and theoretical values for energies (cm^{-1}) and rates (s^{-1}) in the intercombination (IC), magnetic quadrupole ($M2$), and the electric dipole ($E1$) transitions.

Source	ΔE^{fs}_{2-0}	ΔE_{IC}	A_{IC}	ΔE_{M2}	A_{M2} (units of 10^3)	ΔE_{E1}	gf_{E1}
MCDF+RCI[a]	79.86	52 394	102.8	52 449	5.139	102 464	0.7579(4)
Corr.[b]	80.05	52 370	102.9(15)	52 425		102 440	
MCDF+RCI[c]	78.56	52 372	100.3(40)			102 726	0.7571(20)
MCHF+BP[d]	79.72	52 357	103.0(4)			102 469	0.7563(20)
CIV3[e]	78.9	52 369	103.8			102 694	0.7587
MCRRPA[f]		53 327	118.2				
FCPC[g]	79.72	52 397				102 370	
RMBPT[h]	81.7	51 940				99 710	
NIST[i]					5.19		0.7586
Expt.[j]	80.05	52 391	102.94(14)	52 447		102 352	0.754(14)

[a]This work extrapolated and/or normalized to observed energy.
[b]This work corrected for QED and finite nuclear mass effects.
[c]Reference [1]; frequency-dependent transverse photon interaction included along with core correlation.
[d]Reference [6]; not corrected for QED.
[e]Reference [8]; the *ab initio value* 99.2 s^{-1} has been scaled using experimental energies.
[f]Reference [9]; Breit interaction is not included.
[g]Reference [10]; corrected for QED effects.
[h]Reference [5]; corrected for QED effects.
[i]Reference [11].
[j]NIST online database, and Refs. [7] (IC) and [12] ($E1$).

$=1$ and $2s_{1/2}2p_{3/2}$ $J=1$ (see Ref. [1]), small changes in mixing coefficients have an unusually large effect on the transition rate. An estimate is that these effects may alter the extrapolated Dirac-Coulomb-Breit value $A_{IC}=102.9\ s^{-1}$ by as much as $1\ s^{-1}$. Adding the uncertainty due to correlation effects which, based on the rather close agreement between the core-valence and core correlation values, are believed to be less than $0.5\ s^{-1}$, we end up with a total uncertainty of the order $\pm 1.5\ s^{-1}$.

In Table II the present values are compared with values from other theories. It is seen that the present transition rate for the intercombination line is somewhat larger than the rate from the MCDF and RCI calculations by Ynnerman and Froese Fischer [1]. The present calculation exhibits a substantial improvement in the fine-structure splitting. The convergence patterns for the calculated values are also much smoother, reflecting the great advantage of an independent optimization as compared to the previous MCDF calculations that were constrained to a simultaneous optimization of the $^1S_0$, $^3P_{0,1,2}$, and $^1P_1$ states. As before, the transition rates in the two gauges are not in good agreement, though for the core-valence calculation the present discrepancy is reduced by a factor of 2. The Coulomb gauge is sensitive to the core correlation, which has not been treated completely in this work. The present Dirac-Coulomb-Breit limit for the intercombination transition rate is $102.9\ s^{-1}$. This rate is in good agreement with rate from the most recent Breit-Pauli (BP) calculations [6]. Both are in excellent agreement with the storage-ring measurement by Doerfert *et al.* [7], giving $A_{IC}=102.94\pm 0.14\ s^{-1}$.

This study indicates that the MCDF+RCI method, with an allowance for independently optimized orbital sets, is capable of providing transition rates for intercombination lines in light atoms with accuracy at the 1% level. Because of the extensive cancellation between the contributions to the transition matrix elements from the $1s^22s_{1/2}2p_{1/2}$ $J=1$ and $1s^22s_{1/2}2p_{3/2}$ $J=1$, the uncertainty estimates for the MCDF calculation are larger than for the MCHF+BP result, but in fact the two computed results differ by only $0.1\ s^{-1}$.

We would like to thank M. Safronova and W. Johnson for their help in evaluating the importance of the frequency-dependent Breit interaction. This research was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy.

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