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# Relativistic configuration interaction calculations of energy levels, isotope shifts, hyperfine structures, and transition rates in the $2s^22p^2-2s2p^3$ transition array for the carbon-like sequence

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## Abstract

Energy levels, fine-structure separations, specific mass shift parameters, isotope shifts, hyperfine interaction constants, Landé  $g_J$ -factors and transition probabilities are reported for the  $2s^22p^2-2s2p^3$  transition array in N II, O III, F IV, Ne V and Ti XVII. Wavefunctions were determined using the multiconfiguration Dirac–Hartree–Fock method with account for valence, core–valence and core–core correlation effects. The transition energies and rates are compared with experimental data and with values from other calculations.

## 1. Introduction

Light atoms are important in astrophysical applications and transition data can be used in the determination of element abundances and plasma diagnostics [1–3]. A number of general computer codes such as SUPERSTRUCTURE, CIV3 and ATSP2K have been developed [4–6] to provide for these extensive data needs. These codes rely on the Breit–Pauli approximation [7, 8], in which the atomic state function  $\Psi(\gamma JM_J)$  is a linear combination of configuration state functions (CSF) of the form

$$\Psi(\gamma JM_J) = \sum_{LS} \sum_j c_j(LS) \Phi(\gamma_j LSJM_J), \quad (1)$$

where  $\gamma$  usually represents the dominant configuration and any additional quantum numbers required for uniquely specifying the state. The configuration state functions  $\Phi(\gamma_j LSJM_J)$  are built from a basis of one-electron spin-orbitals. The expansion coefficients  $c_j(LS)$  and the corresponding energy  $E(\gamma J)$  are an eigenvector and eigenvalue, respectively, of the interaction matrix of these CSFs as defined by the Breit–Pauli Hamiltonian. In accurate calculations the Hamiltonian includes the mass correction, the one- and two-body Darwin

terms, the spin-spin contact term, and the  $J$ -dependent spin-orbit, spin–other-orbit and spin–spin interactions. For massive calculations, where computational resources might be a problem, the operators are often limited to one-body mass correction, the Darwin term and the spin–orbit term [9].

For light elements the sum (1) is dominated by one  $LS$  term and the rate for an intercombination transition depends critically on the admixture of CSFs with different  $LS$  designations. A perturbation analysis shows that mixing of different  $LS$  terms is affected by term energy separations. Though it is possible, in simple cases, to correct a computed transition rate for such an error, it is simpler to first adjust the  $LS$  term energies in a Breit–Pauli calculation so that, for selected  $J$  values, the separation of terms is in close agreement with observed energies. Such a procedure is called fine-tuning. When judiciously applied, it has been shown to yield consistent sets of transition data even in cases where values from different uncorrected calculations are quite far away [10].

Although highly competitive for light atoms, especially when fine-tuning is applied, the Breit–Pauli approximation has some drawbacks. Relativistic effects manifest themselves qualitatively as orbital contractions (a *direct* relativistic effect), so that the inner electrons move in orbits closer to the

**Table 1.** Computed energies for F IV as functions of the increasing active sets, where  $n = 3$  denotes the orbital set with maximal principal quantum number  $n = 3$ , etc. MR denotes calculations using the  $n = 8$  active set, but with an enlarged multireference set. The experimental energies are those of [40].

Term	$J$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$	MR	QED	Exp
$2s^2 2p^2 \ ^3P$	0	0	0	0	0	0	0		0	0
	1	222.7	240.4	242.7	244.3	244.7	245.0	226.4	226.9	226.0
	2	608.7	615.1	616.1	615.1	615.1	615.0	611.6	613.2	614.0
$2s^2 2p^2 \ ^1D$	2	27 370.2	25 961.9	25 596.4	25 427.1	25 411.2	25 395.5	25 367.8	25 369.0	25 238.2
$2s^2 2p^2 \ ^1S$	0	56 739.8	54 472.1	53 885.7	53 653.6	53 633.0	53 616.0	53 746.2	53 744.8	53 541.2
$2s 2p^3 \ ^3S^o$	2	70 534.1	72 279.0	72 947.6	73 459.1	73 682.7	73 792.0	73 949.4	73 898.2	74 194.7
$2s 2p^3 \ ^3D^o$	3	149 981.6	148 424.7	148 178.4	148 149.8	148 142.0	148 131.6	147 964.2	147 911.2	147 843.0
	2	150 008.7	148 434.0	148 183.8	148 151.7	148 142.3	148 132.6	148 011.0	147 958.0	147 888.7
	1	150 023.3	148 447.5	148 197.1	148 164.6	148 155.0	148 144.1	148 023.7	147 970.7	147 903.5
$2s 2p^3 \ ^3P^o$	2	179 445.7	176 653.3	176 004.6	175 710.6	175 590.3	175 559.6	175 509.8	175 457.7	175 236.8
	1	179 446.6	176 655.6	176 006.0	175 712.8	175 592.6	175 562.4	175 513.7	174 461.6	175 241.9
	0	179 469.7	176 689.6	176 043.6	175 757.5	175 639.6	175 610.7	175 540.6	175 488.5	175 263.9
$2s 2p^3 \ ^1D^o$	2	234 577.1	230 902.7	230 115.2	229 863.4	229 764.2	229 693.6	229 263.2	229 205.2	228 903.8
$2s 2p^3 \ ^3S^o$	1	241 919.3	239 765.5	239 130.3	238 958.1	238 839.5	238 825.0	238 564.0	238 502.1	238 296.7
$2s 2p^3 \ ^1P^o$	1	265 416.8	260 294.5	259 085.7	258 565.7	258 407.6	258 318.9	257 929.5	257 873.0	257 386.5

nucleus. The amount of the contraction depends critically on the orbital symmetry—the largest contraction affects orbitals with the  $s$  angular symmetry. Orbital contraction has an important secondary, *indirect* relativistic effect on the more weakly bound high-angular-symmetry electrons [11], which undergo radial expansion and become, qualitatively, still less weakly bound. In fully relativistic methods based on the Dirac–Coulomb Hamiltonian these effects are described directly, through the shape of the radial orbitals. When methods based on the Breit–Pauli approximation are used, the *relativistic* rearrangement of the electrons is described in a less efficient way through the configuration expansion coefficients. The direct and indirect relativistic effects grow rapidly with increasing nuclear charge, and eventually the nonrelativistic orbital bases used in the Breit–Pauli calculations become inadequate in describing the system.

As alternatives to the general purpose codes in the Breit–Pauli approximation, fully relativistic codes, such as GRASP2K [12] and MCDFGME [13], can be used. Both are based on the multiconfiguration Dirac–Hartree–Fock method and can be applied to general systems with several open shells. In the present paper the GRASP2K package has been used. It implements a biorthogonal transformation technique that permits initial and final states in a transition array to be optimized separately [14], which, in many cases, leads to more accurate values of the calculated rates. The package also contains modules for computing diagonal and off-diagonal hyperfine interaction constants [15], isotope shifts [16], as well as Landé  $g_J$ -factors and splittings of magnetic substates in intermediate and strong magnetic fields [17].

The purpose of the present paper is threefold. Firstly, we provide data for plasma diagnosis and line profile modelling. We used the GRASP2K code to compute energy levels, fine-structure separations, specific mass shift parameters, hyperfine interaction constants, Landé  $g_J$ -factors and transition probabilities for the  $2s^2 2p^2$ – $2s 2p^3$  transition array in N II, O III, F IV, Ne V and Ti XVII. Nitrogen and oxygen are abundant elements in astrophysical objects and emission lines of carbon-like ions are useful in the diagnosis of

the solar, astrophysical and fusion plasmas [18]. There are very little data on hyperfine structure and isotope shifts available in the literature and computed parameters should support detailed modelling of the line profiles in high-resolution spectra [19]. The second purpose of the present paper is to test the capability of the GRASP2K code to produce large volumes of spectroscopic data with high accuracy necessary in astrophysical, plasma, spectroscopy, as well as other modern applications. In addition, in this paper transition data for N II, O III, F IV and Ne V are critically evaluated and compared with available experimental values and with the results from recent Breit–Pauli calculations [20–24], with the aim to establish an optimal combination of semi-relativistic Breit–Pauli and fully relativistic Dirac–Hartree–Fock methods in application to atomic spectroscopy *ab initio* calculations.

## 2. Computational procedure

The multiconfiguration Dirac–Hartree–Fock method is described in detail in a recent monograph by Grant [27] and here we only give a brief outline. Starting from the Dirac–Coulomb Hamiltonian

$$H_{DC} = \sum_{i=1}^N [c \alpha_i \cdot p_i + (\beta_i - 1)c^2 + V_i^N] + \sum_{i<j}^N 1/r_{ij}, \quad (2)$$

where  $V^N$  is the monopole part of the electron–nucleus Coulomb interaction, the atomic state functions describing different fine structure levels are obtained as linear combinations of symmetry adapted configuration state functions (CSFs)

$$\Psi(\gamma J M_J) = \sum_j c_j \Phi(\gamma_j J M_J). \quad (3)$$

Here  $J$  and  $M_J$  are the angular quantum numbers, while  $\gamma_j$  denotes other appropriate labelling of the configuration state functions, for example parity, orbital occupancy and coupling scheme. The configuration state functions  $\Phi(\gamma_j J M_J)$  are built from products of one-electron Dirac orbitals. In the relativistic self-consistent field procedure both the radial parts of the Dirac orbitals and the expansion coefficients

**Table 2.** Energies for N II, O III and F IV from multireference RCI calculations with QED corrections. The energies are given in units of  $\text{cm}^{-1}$  relative to a ground state energy of zero. Splitting of energy levels relative to the lowest level for the term. The experimental energies are those of [40].

Level	$J$	Level ( $\text{cm}^{-1}$ )			Splitting ( $\text{cm}^{-1}$ )		
		Theory	Observation	Difference	Theory	Observation	Difference
N II							
2s <sup>2</sup> 2p <sup>2</sup> <sup>3</sup> P	0	0	0	0			
	1	49.3	48.7	0.6	49.3	48.7	0.6
	2	129.2	130.8	-1.6	129.2	130.8	-1.6
2s <sup>2</sup> 2p <sup>2</sup> <sup>1</sup> D	2	15 458.8	15 316.2	142.6			
2s <sup>2</sup> 2p <sup>2</sup> <sup>1</sup> S	0	32 938.1	32 688.8	249.3			
2s2p <sup>3</sup> <sup>5</sup> S <sup>o</sup>	2	46 480.2	46 784.6	-304.4			
2s2p <sup>3</sup> <sup>3</sup> D <sup>o</sup>	3	92 356.0	92 237.2	118.8			
	2	92 367.9	92 250.3	117.6	11.9	13.1	-1.2
	1	92 369.0	92 251.8	117.2	13.0	14.6	-1.6
2s2p <sup>3</sup> <sup>3</sup> P <sup>o</sup>	2	109 693.1	109 217.6	475.5			
	1	109 693.2	109 216.6	476.6	0.1	-1.1	1.2
	0	109 709.4	109 223.5	485.9	16.3	5.9	10.4
2s2p <sup>3</sup> <sup>1</sup> D <sup>o</sup>	2	144 705.9	144 187.9	518.0			
O III							
2s <sup>2</sup> 2p <sup>2</sup> <sup>3</sup> P	0	0	0	0			
	1	113.6	113.2	0.4	113.6	113.2	0.4
	2	305.0	306.2	-1.2	305.2	306.2	-1.0
2s <sup>2</sup> 2p <sup>2</sup> <sup>1</sup> D	2	20 400.4	20 273.3	127.1			
2s <sup>2</sup> 2p <sup>2</sup> <sup>1</sup> S	0	43 393.4	43 185.7	207.7			
2s2p <sup>3</sup> <sup>5</sup> S <sup>o</sup>	2	60 022.8	60 324.8	-302.0			
2s2p <sup>3</sup> <sup>3</sup> D <sup>o</sup>	3	120 098.9	120 025.2	73.7			
	2	120 125.8	120 053.4	72.4	26.9	28.2	-1.3
	1	120 131.4	120 058.2	73.2	32.5	33.0	-0.5
2s2p <sup>3</sup> <sup>3</sup> P <sup>o</sup>	2	142 647.7	142 381.0	266.7			
	1	142 649.6	142 381.8	267.8	1.9	0.8	1.1
	0	142 669.7	142 393.5	276.2	22.0	12.5	9.5
2s2p <sup>3</sup> <sup>1</sup> D <sup>o</sup>	2	187 366.5	187 054.0	312.5			
2s2p <sup>3</sup> <sup>3</sup> S <sup>o</sup>	1	197 299.5	197 087.7	211.8			
2s2p <sup>3</sup> <sup>1</sup> P <sup>o</sup>	1	211 171.1	210 461.8	709.3			
F IV							
2s <sup>2</sup> 2p <sup>2</sup> <sup>3</sup> P	0	0	0	0			
	1	226.9	226.0	0.9	226.9	226.0	0.9
	2	613.2	614.0	-0.8	613.2	614.0	-0.8
2s <sup>2</sup> 2p <sup>2</sup> <sup>1</sup> D	2	25 369.0	25 238.2	130.8			
2s <sup>2</sup> 2p <sup>2</sup> <sup>1</sup> S	0	53 744.8	53 541.2	203.6			
2s2p <sup>3</sup> <sup>5</sup> S <sup>o</sup>	2	73 898.2	74 194.7	-296.5			
2s2p <sup>3</sup> <sup>3</sup> D <sup>o</sup>	3	147 911.2	147 843.0	68.2			
	2	147 958.0	147 888.7	69.3	46.8	45.7	1.1
	1	147 970.7	147 903.5	67.2	59.5	60.5	-1.0
2s2p <sup>3</sup> <sup>3</sup> P <sup>o</sup>	2	175 457.7	175 236.8	220.9			
	1	175 461.6	175 241.9	219.7	3.9	5.1	-1.2
	0	175 488.5	175 263.9	224.6	30.8	27.1	3.7
2s2p <sup>3</sup> <sup>3</sup> S <sup>o</sup>	1	229 205.2	228 903.8	301.4			
2s2p <sup>3</sup> <sup>1</sup> D <sup>o</sup>	2	238 502.1	238 296.7	205.4			
2s2p <sup>3</sup> <sup>1</sup> P <sup>o</sup>	1	257 873.0	257 386.5	486.5			

are optimized to self-consistency. In subsequent relativistic configuration interaction (RCI) calculations the transverse photon interaction

$$H_{\text{Breit}} = - \sum_{i < j}^N \left[ \alpha_i \cdot \alpha_j \frac{\cos(\omega_{ij} r_{ij}/c)}{r_{ij}} + (\alpha_i \cdot \nabla_i)(\alpha_j \cdot \nabla_j) \frac{\cos(\omega_{ij} r_{ij}/c) - 1}{\omega_{ij}^2 r_{ij}/c^2} \right] \quad (4)$$

may be included in the Hamiltonian [28]. The photon frequency  $\omega_{ij}$  used by GRASP2K in calculating the matrix elements of the transverse photon interaction is taken as the difference of the diagonal Lagrange multipliers  $\epsilon_i$  and  $\epsilon_j$  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

**Table 3.** Energies for Ne V and Ti XVII from multireference RCI calculations with QED corrections. The energies are given in units of  $\text{cm}^{-1}$  relative to a ground state energy of zero. Splitting of energy levels relative to the lowest level for the term. The experimental energies are those of [40].

Level	$J$	Level ( $\text{cm}^{-1}$ )			Splitting ( $\text{cm}^{-1}$ )		
		Theory	Observation	Difference	Theory	Observation	Difference
Ne V							
$2s^2 2p^2 \ ^3P$	0	0	0	0			
	1	411.3	411.2	0.1	411.3	411.2	0.1
	2	1 108.4	1 109.5	-1.1	1 108.4	1 109.5	-1.1
$2s^2 2p^2 \ ^1D$	2	30 289.9	30 290.7	-0.8			
$2s^2 2p^2 \ ^1S$	0	63 986.2	63 915.4	70.8			
$2s 2p^3 \ ^5S^o$	2	87 965.1	88 399.5	-434.4			
$2s 2p^3 \ ^3D^o$	3	175 779.2	175 832.3	-53.1			
	2	175 849.4	175 902.7	-53.3	70.2	70.4	-0.2
	1	175 873.0	175 925.0	-52.0	93.8	92.7	1.1
$2s 2p^3 \ ^3P^o$	2	208 217.6	208 151.3	66.3			
	1	208 222.1	208 153.3	68.8	4.5	2.0	2.5
	0	208 258.7	208 185	73.7	41.1	33.7	7.4
$2s 2p^3 \ ^3S^o$	1	270 715.1	270 552.9	162.2			
$2s 2p^3 \ ^1D^o$	2	279 434.6	279 371.2	63.4			
$2s 2p^3 \ ^1P^o$	1	304 127.1	303 819.2	307.9			
Ti XVII							
$2s^2 2p^2 \ ^3P$	0	0	0	0			
	1	29 647	29 658	-11	29 647	29 658	-11
	2	55 733	55 730	3	55 733	55 730	3
$2s^2 2p^2 \ ^1D$	2	140 771	140 660	111			
$2s^2 2p^2 \ ^1S$	0	242 313	242 180	133			
$2s 2p^3 \ ^5S^o$	2	333 487	333 660	-173			
$2s 2p^3 \ ^3D^o$	2	578 947	578 890	57			
	1	580 190	580 110	80	1243	1220	23
	3	586 836	586 760	76	7889	7870	19
$2s 2p^3 \ ^3P^o$	0	678 667	678 450	217			
	1	681 139	680 910	229	2472	2460	12
	2	686 982	686 780	202	8315	8330	-15
$2s 2p^3 \ ^3S^o$	1	838 569	838 340	229			
$2s 2p^3 \ ^1D^o$	2	845 454	845 140	314			
$2s 2p^3 \ ^1P^o$	1	943 866	943 500	366			

involved. In the RCI calculations some QED effects, such as vacuum polarization and self-energy correction, can also be accounted for [29, 30]. Calculations can be done for individual levels, but also for subsets of a spectrum in the extended optimal level (EOL) scheme, where optimization is on a weighted sum of energies [31]. In the latter scheme a balanced description of all the states in an  $LS$  term can be obtained in a single calculation.

### 3. Computation of atomic properties

Once the atomic state functions have been obtained, different properties like hyperfine structures, isotope shifts and oscillator strengths can be expressed in terms of reduced matrix elements of tensor operators of different rank

$$\langle \Psi(\gamma J) \| \mathbf{T}^{(k)} \| \Psi(\gamma' J') \rangle. \quad (5)$$

After inserting the CSF expansions, the expression above reduces to a sum over matrix elements between CSFs. With the use of the Racah algebra techniques these matrix elements, in turn, can be obtained as a sum over radial integrals [27].

**Table 4.** Computed magnetic dipole hyperfine interaction constants in MHz for  $2s^2 2p^2 \ ^3P_{1,2}$  and  $2s 2p^3 \ ^3P_{1,2}^o$  of F IV, as functions of the increasing active sets, where  $n = 3$  denotes the orbital set with maximal principal quantum number  $n = 3$ , etc. MR denotes calculations using the  $n = 8$  active set, but with an enlarged multireference set. The hyperfine constants are computed for  $^{19}\text{F}$  with  $I = 1/2$ ,  $\mu = 2.628\ 868$  nm.

$n$	$2s^2 2p^2 \ ^3P_{1,2}$		$2s 2p^3 \ ^3P_{1,2}^o$	
	$A_1$	$A_2$	$A_1$	$A_2$
3	-8.850+02	2.796+03	2.234+04	1.881+04
4	-2.813+02	3.565+03	2.245+04	1.875+04
5	3.952+01	3.800+03	2.243+04	1.875+04
6	-1.127+02	3.674+03	2.238+04	1.871+04
7	-6.741+01	3.718+03	2.234+04	1.867+04
8	-9.089+01	3.702+03	2.235+04	1.868+04
MR	-7.992+01	3.713+03	2.235+04	1.867+04

#### 3.1. Isotope shift

An isotope of an element is characterized by the mass  $M$  and the mean-square nuclear radius  $\langle r_M^2 \rangle$ . When effects of the finite nuclear mass and the extended nuclear charge distribution are

**Table 5.** Hyperfine interaction constants  $A_J$  and  $B_J$  in MHz and Landé  $g_J$ -factors of N II, O III, F IV, Ne V and Ti XVII from multireference RCI calculations. The hyperfine constants are computed for:  $^{15}\text{N}$  with  $I = 1$ ,  $\mu = 0.403\,761\,00$  nm,  $Q = 0.020\,01$  b;  $^{17}\text{O}$  with  $I = 5/2$ ,  $\mu = -1.893\,79$  nm,  $Q = -0.025\,78$  b;  $^{19}\text{F}$  with  $I = 1/2$ ,  $\mu = 2.628\,868$  nm;  $^{21}\text{Ne}$  with  $I = 3/2$ ,  $\mu = -0.661\,797$  nm,  $Q = 0.103$  b; and  $^{47}\text{Ti}$  with  $I = 5/2$ ,  $\mu = -0.788\,48$  nm,  $Q = 0.290$  b.

Level	$J$	$A_J$	$B_J$	$g_J$	$A_J$	$B_J$	$g_J$
				N II		O III	
$2s^2 2p^2 \ ^3P$	1	-1.229+00	3.392+00	1.501 04	5.536+00	-8.224+00	1.500 97
	2	9.284+01	-6.796+00	1.501 01	-3.227+02	1.649+01	1.500 91
$2s^2 2p^2 \ ^1D$	2	1.443+02	1.329+01	0.999 90	-5.080+02	-3.220+01	0.999 85
$2s2p^3 \ ^5S^o$	2	4.539+02	-6.579-05	2.002 15	-1.445+03	1.924-04	2.002 06
$2s2p^3 \ ^3D^o$	3	4.288+02	-7.700-01	1.333 97	-1.406+03	1.093+00	1.333 89
	2	2.394+02	-2.809-01	1.166 95	-7.935+02	8.806-02	1.166 90
$2s2p^3 \ ^3P^o$	1	-3.667+02	-2.176-01	0.498 80	1.127+03	1.541-01	0.498 79
	2	5.222+02	4.824-01	1.501 01	-1.698+03	-4.481-01	1.500 92
$2s2p^3 \ ^1D^o$	1	6.128+02	-3.496-01	1.500 99	-2.015+03	6.904-01	1.500 87
	2	1.379+02	-1.258-01	0.999 89	-4.975+02	4.537-01	0.999 83
$2s2p^3 \ ^3S^o$	1	-	-	-	1.741+03	3.024-04	2.001 92
$2s2p^3 \ ^1P^o$	1	-	-	-	-5.102+02	-6.827-01	0.999 98
				F IV		Ne V	
$2s^2 2p^2 \ ^3P$	1	-7.996+01		1.500 89	1.187+01	8.519+01	1.500 80
	2	3.713+03		1.500 76	-4.800+02	-1.709+02	1.500 55
$2s^2 2p^2 \ ^1D$	2	5.885+03		0.999 82	-7.615+02	3.360+02	0.999 83
$2s2p^3 \ ^5S^o$	2	1.575+04		2.001 95	-1.959+03	-4.281-03	2.001 82
$2s2p^3 \ ^3D^o$	3	1.561+04		1.333 80	-1.965+03	-5.287+00	1.333 70
	2	8.871+03		1.166 86	-1.122+03	9.321+00	1.166 85
$2s2p^3 \ ^3P^o$	1	-1.196+04		0.498 81	1.455+03	4.125+00	0.498 90
	2	1.867+04		1.500 78	-2.332+03	-6.820+00	1.500 59
$2s2p^3 \ ^1D^o$	1	2.235+04		1.500 71	-2.808+03	-8.641+00	1.500 47
	2	5.808+03		0.999 76	-7.561+02	-7.099+00	0.999 69
$2s2p^3 \ ^3S^o$	1	-1.874+04		2.001 64	2.300+03	-1.057-02	2.001 19
$2s2p^3 \ ^1P^o$	1	5.857+03		1.000 07	-7.567+02	6.092+00	1.000 29
				Ti XVII			
$2s^2 2p^2 \ ^3P$	1	3.422+02	4.271+03	1.49865			
	2	-7.593+03	-6.135+03	1.44744			
$2s^2 2p^2 \ ^1D$	2	-8.075+03	1.458+04	1.04823			
$2s2p^3 \ ^5S^o$	2	-2.190+04	2.631+01	1.99313			
$2s2p^3 \ ^3D^o$	3	-2.272+04	-2.958+01	1.33122			
	2	-1.493+04	8.403+03	1.19492			
$2s2p^3 \ ^3P^o$	1	1.351+04	4.592+03	0.55917			
	2	-2.320+04	-8.321+03	1.46142			
$2s2p^3 \ ^1D^o$	1	-2.992+04	-4.644+03	1.44806			
	2	-1.077+04	-3.029+02	1.00997			
$2s2p^3 \ ^3S^o$	1	1.788+04	2.995+01	1.90611			
$2s2p^3 \ ^1P^o$	1	-4.729+03	1.389+02	1.07843			

**Table 6.** Computed specific mass shift parameters  $S_{\text{sms}}$  in au and electron densities  $\rho(0)$  at the origin for  $2s^2 2p^2 \ ^3P_0$  and  $2s2p^3 \ ^3P_0^o$  in F IV as functions of the increasing active sets where  $n = 3$  denotes the set  $3s2p1d$  etc. MR denotes calculations using the  $n = 8$  active set, but with an enlarged multireference set.

$n$	$2s^2 2p^2 \ ^3P_0$		$2s2p^3 \ ^3P_0^o$		$2s2p^3 \ ^3P_0^o - 2s^2 2p^2 \ ^3P_0$	
	$S_{\text{sms}}$	$\rho(0)$	$S_{\text{sms}}$	$\rho(0)$	$\Delta S_{\text{sms}}$	$\Delta \rho(0)$
3	-3.938	470.635	-6.233	455.803	-2.295	-14.832
4	-4.012	470.619	-6.302	455.767	-2.290	-14.852
5	-4.006	470.684	-6.308	455.795	-2.302	-14.889
6	-4.004	470.709	-6.304	455.849	-2.300	-14.860
7	-4.009	470.722	-6.306	455.869	-2.297	-14.853
8	-4.010	470.734	-6.308	455.891	-2.298	-14.843
MR	-3.984	470.733	-6.277	455.913	-2.293	-14.820

**Table 7.** Specific mass shift parameters  $S_{\text{sms}}$  in au and electron densities  $\rho(0)$  at the origin for N II, O III, F IV, Ne V and Ti XVII from multireference RCI calculations.

Level	$J$	$S_{\text{sms}}$	$\rho(0)$	$S_{\text{sms}}$	$\rho(0)$	$S_{\text{sms}}$	$\rho(0)$
N II							
2s <sup>2</sup> 2p <sup>2</sup> 3P	0	-1.280	211.42	-2.473	323.50	-3.984	470.73
	1	-1.279	211.42	-2.471	323.50	-3.981	470.73
	2	-1.278	211.42	-2.468	323.50	-3.977	470.73
2s <sup>2</sup> 2p <sup>2</sup> 1D	2	-1.236	211.52	-2.422	323.61	-3.926	470.85
2s <sup>2</sup> 2p <sup>2</sup> 1S	0	-1.230	211.31	-2.415	323.29	-3.924	470.31
2s2p <sup>3</sup> 5S <sup>o</sup>	2	-2.487	206.29	-4.323	314.49	-6.631	456.27
2s2p <sup>3</sup> 3D <sup>o</sup>	3	-2.387	206.25	-4.208	314.29	-6.506	455.88
	2	-2.387	206.25	-4.208	314.29	-6.505	455.88
2s2p <sup>3</sup> 3P <sup>o</sup>	1	-2.387	206.25	-4.208	314.30	-6.504	455.88
	2	-2.250	206.31	-4.025	314.33	-6.277	455.91
	1	-2.250	206.31	-4.025	314.33	-6.277	455.91
	0	-2.250	206.31	-4.026	314.33	-6.277	455.91
2s2p <sup>3</sup> 1D <sup>o</sup>	2	-2.127	206.00	-3.918	313.50	-6.199	454.57
2s2p <sup>3</sup> 3S <sup>o</sup>	1	-	-	-3.592	312.64	-5.895	453.47
2s2p <sup>3</sup> 1P <sup>o</sup>	1	-	-	-3.569	313.50	-5.830	454.53
Ne V							
2s <sup>2</sup> 2p <sup>2</sup> 3P	0	-5.816	658.51	-53.279	8536.04		
	1	-5.810	658.51	-52.831	8535.95		
	2	-5.802	658.51	-52.647	8535.23		
2s <sup>2</sup> 2p <sup>2</sup> 1D	2	-5.748	658.64	-52.393	8534.76		
2s <sup>2</sup> 2p <sup>2</sup> 1S	0	-5.758	657.63	-52.897	8516.67		
2s2p <sup>3</sup> 5S <sup>o</sup>	2	-9.411	636.81	-80.082	8146.94		
2s2p <sup>3</sup> 3D <sup>o</sup>	3	-9.277	636.18	-79.832	8139.90		
	2	-9.276	636.18	-79.937	8140.17		
	1	-9.276	636.18	-79.936	8140.05		
2s2p <sup>3</sup> 3P <sup>o</sup>	2	-9.002	636.21	-78.863	8139.37		
	1	-9.001	636.21	-78.937	8139.53		
	0	-9.001	636.21	-78.946	8139.95		
2s2p <sup>3</sup> 1D <sup>o</sup>	2	-8.961	634.31	-79.407	8124.45		
2s2p <sup>3</sup> 3S <sup>o</sup>	1	-8.674	632.92	-79.405	8116.68		
2s2p <sup>3</sup> 1P <sup>o</sup>	1	-8.556	634.26	-78.355	8123.24		
Ti XVII							

taken into account, the energy of a level  $\gamma J$  can be written approximately as

$$E_M = E_0 - E_0 \frac{m}{M+m} + S_{\text{sms}} \frac{M}{(M+m)^2} + \frac{2}{3} \pi Z \rho(0) \langle r_M^2 \rangle, \quad (6)$$

where  $E_0$  is the calculated energy for infinite mass,  $S_{\text{sms}}$  is the specific mass shift parameter

$$S_{\text{sms}} = \langle \Psi(\gamma J M_J) | \sum_{i < j} \mathbf{p}_i \cdot \mathbf{p}_j | \Psi(\gamma J M_J) \rangle, \quad (7)$$

and  $\rho(0)$  the electron density at the site of the nucleus

$$\rho(0) = \langle \Psi(\gamma J M_J) | \sum_{i=1}^N \delta(\mathbf{r}_i) | \Psi(\gamma J M_J) \rangle. \quad (8)$$

The isotopic shift of an individual level is not a directly measurable quantity. What can be measured is the difference in transition energy between an upper and a lower level for different isotopes. Let  $\Delta E_0$  be the transition energy between an upper and a lower level for infinite mass. The difference in transition energy between two isotopes with masses  $M'$  and  $M$

is then given by

$$\begin{aligned} \Delta E_{M',M} = \Delta E_0 & \left[ \frac{m}{M+m} - \frac{m}{M'+m} \right] \\ & + \Delta S_{\text{sms}} \left[ \frac{M'}{(M'+m)^2} - \frac{M}{(M+m)^2} \right] \\ & + \frac{2}{3} \pi Z \Delta \rho(0) [\langle r_{M'}^2 \rangle - \langle r_M^2 \rangle], \end{aligned} \quad (9)$$

where the differences in the electronic parameters are between the values of the upper and lower levels in the transition. For light elements the transition isotope shift is dominated by the mass shift [32]. In practical calculations  $\Delta E_0$  is often replaced by the experimental transition energy (rather than the calculated transition energy for the infinite mass). All quantities in the above formulas are expressed in atomic units (au). The nuclear masses  $M$  and  $M'$  are usually given in units of the unified atomic mass (u) and must be converted to atomic units. We have used  $1 \text{ u} = 1822.888 51 \text{ au}$ .

### 3.2. Hyperfine structure and Landé factors

The fine-structure levels are split into closely spaced hyperfine levels in atoms with non-zero nuclear spin. The hyperfine

**Table 8.** Transition isotope shifts in  $\text{cm}^{-1}$  in N II, O III and Ne V. A positive sign of the transition isotope shift corresponds to a larger energy transition (i.e. a blue shifted line) for the heavier isotope.

Levels		Isotopic pair				
Upper	Lower	$^{15,14}\text{N}$	$^{18,16}\text{O}$	$^{17,16}\text{O}$	$^{22,20}\text{Ne}$	$^{21,20}\text{Ne}$
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^3P_0$	0.873	1.914	1.015	2.334	1.225
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^3P_0$	0.839	1.846	0.979	2.264	1.188
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^3P_0$	—	1.696	0.890	2.263	1.187
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^3P_0$	—	1.724	0.915	2.259	1.186
$2s2p^3\ ^5S_2^o$	$2s^22p^2\ ^3P_1$	0.812	1.783	0.946	2.192	1.150
$2s2p^3\ ^3D_2^o$	$2s^22p^2\ ^3P_1$	0.874	1.915	1.016	2.336	1.226
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^3P_1$	0.874	1.915	1.016	2.336	1.226
$2s2p^3\ ^3P_2^o$	$2s^22p^2\ ^3P_1$	0.839	1.847	0.980	2.266	1.189
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^3P_1$	0.839	1.847	0.980	2.266	1.189
$2s2p^3\ ^3P_0^o$	$2s^22p^2\ ^3P_1$	0.840	1.847	0.980	2.266	1.189
$2s2p^3\ ^1D_2^o$	$2s^22p^2\ ^3P_1$	0.861	1.928	1.023	2.400	1.259
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^3P_1$	—	1.693	0.898	2.265	1.188
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^3P_1$	—	1.725	0.915	2.261	1.187
$2s2p^3\ ^5S_2^o$	$2s^22p^2\ ^3P_2$	0.813	1.784	0.947	2.194	1.151
$2s2p^3\ ^3D_3^o$	$2s^22p^2\ ^3P_2$	0.874	1.916	1.017	2.339	1.228
$2s2p^3\ ^3D_2^o$	$2s^22p^2\ ^3P_2$	0.874	1.916	1.017	2.339	1.227
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^3P_2$	0.874	1.916	1.017	2.339	1.227
$2s2p^3\ ^3P_2^o$	$2s^22p^2\ ^3P_2$	0.840	1.848	0.981	2.269	1.191
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^3P_2$	0.840	1.848	0.980	2.269	1.191
$2s2p^3\ ^1D_2^o$	$2s^22p^2\ ^3P_2$	0.861	1.929	1.023	2.403	1.261
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^3P_2$	—	1.694	0.899	2.267	1.190
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^3P_2$	—	1.726	0.916	2.264	1.188
$2s2p^3\ ^5S_2^o$	$2s^22p^2\ ^1D_2$	0.797	1.747	0.927	2.151	1.129
$2s2p^3\ ^3D_3^o$	$2s^22p^2\ ^1D_2$	0.858	1.879	0.997	2.296	1.205
$2s2p^3\ ^3D_2^o$	$2s^22p^2\ ^1D_2$	0.858	1.879	0.997	2.296	1.205
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^1D_2$	0.858	1.879	0.997	2.295	1.205
$2s2p^3\ ^3P_2^o$	$2s^22p^2\ ^1D_2$	0.824	1.811	0.961	2.226	1.168
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^1D_2$	0.824	1.811	0.961	2.226	1.168
$2s2p^3\ ^1D_2^o$	$2s^22p^2\ ^1D_2$	0.845	1.892	1.004	2.359	1.238
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^1D_2$	—	1.657	0.879	2.224	1.167
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^1D_2$	—	1.689	0.896	2.220	1.165
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^1S_0$	0.816	1.797	0.953	2.206	1.158
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^1S_0$	0.782	1.729	0.917	2.136	1.121
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^1S_0$	—	1.575	0.836	2.135	1.120
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^1S_0$	—	1.607	0.852	2.131	1.118

shifts of the fine-structure levels may be to first order expressed in terms of magnetic dipole  $A_J$  and electric quadrupole  $B_J$  hyperfine interaction constants

$$A_J = \frac{\mu_I}{I} \frac{1}{\sqrt{J(J+1)(2J+1)}} \times \langle \Psi(\gamma J) \| - \sum_{j=1}^N i\sqrt{2}\alpha r_j^{-2} [\alpha_j \mathbf{C}_j^{(1)}]^{(1)} \| \Psi(\gamma J) \rangle, \quad (10)$$

$$B_J = 2Q \sqrt{\frac{J(2J-1)}{(J+1)(2J+1)(2J+3)}} \times \langle \Psi(\gamma J) \| - \sum_{j=1}^N r_j^{-3} \mathbf{C}_j^{(2)} \| \Psi(\gamma J) \rangle. \quad (11)$$

The hyperfine shifts of fine-structure levels are affected also by the off-diagonal hyperfine interaction [33]. However, this effect is small and has been neglected in the present study. The nuclear magnetic dipole moments  $\mu_I$  and the nuclear

quadrupole moments  $Q$  for the different isotopes were taken from a recent compilation by Stone [34].

The Landé  $g_J$ -factor determines the splitting of magnetic sub-levels in external magnetic fields and gives information about the coupling conditions [35]. The Landé  $g_J$ -factor has a tensorial form similar to the one for magnetic hyperfine interaction and it was calculated using a modified version of the hyperfine structure program [15].

### 3.3. Transition parameters

The transition parameters, such as rates of spontaneous decay, for electric dipole transitions between two atomic states  $\gamma JM_J$  and  $\gamma' J' M'_J$  can be expressed in terms of the reduced transition matrix element

$$\langle \Psi(\gamma J) \| \mathbf{D}^{(1)} \| \Psi(\gamma' J') \rangle, \quad (12)$$

where  $\mathbf{D}_q^{(1)}$  is the electromagnetic dipole operator in the Coulomb or Babushkin gauge [36]. Standard Racah algebra



**Table 9.** Transition rates (Babushkin and Coulomb gauge) in  $s^{-1}$  for  $2s^22p^2\ ^3P_0-2s2p^3\ ^3P_1^o$  and  $2s^22p^2\ ^1D_2-2s2p^3\ ^1P_1^o$  in F IV as functions of the active sets, where  $n = 3$  denotes the orbital set with maximal principal quantum number  $n = 3$ , etc. MR denotes calculations using the  $n = 8$  active set, but with an enlarged multireference set. Transition energies  $\Delta E$  are given in units of  $cm^{-1}$ . The experimental energies are those of [40].

$n$	$2s^22p^2\ ^3P_0-2s2p^3\ ^3P_1^o$			$2s^22p^2\ ^1D_2-2s2p^3\ ^1P_1^o$		
	$A_B$	$A_C$	$\Delta E$	$A_B$	$A_C$	$\Delta E$
3	8.10+08	7.82+08	179 447	1.11+10	9.50+09	238 047
4	8.54+08	8.51+08	178 036	1.11+10	1.04+10	234 333
5	8.32+08	8.30+08	176 006	1.12+10	1.06+10	233 489
6	8.29+08	8.22+08	175 712	1.12+10	1.06+10	233 139
7	8.33+08	8.26+08	175 592	1.12+10	1.07+10	232 996
8	8.27+08	8.15+08	175 562	1.12+10	1.07+10	232 923
MR	8.18+08	8.15+08	175 513	1.12+10	1.11+10	232 562
Exp			175 237			232 148

**Table 10.** Transition rates (Babushkin and Coulomb gauge) in  $s^{-1}$  for N II from multireference RCI calculations.  $A_{MCHF}$  transition rates from [21]. Transition energies  $\Delta E_{exp}$  are given in units of  $cm^{-1}$  and are those of [40].

Upper	Lower	$\Delta E_{exp}$	$A_B$	$A_C$	$A_{MCHF}$
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^3P_0$	92 251.80	2.11+08	2.13+08	2.095+08
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^3P_0$	109 216.60	4.11+08	4.06+08	4.226+08
$2s2p^3\ ^5S_2^o$	$2s^22p^2\ ^3P_1$	46 735.90	4.47+01	9.16+01	5.155+01
$2s2p^3\ ^3D_2^o$	$2s^22p^2\ ^3P_1$	92 201.60	2.84+08	2.87+08	2.823+08
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^3P_1$	92 203.10	1.56+08	1.57+08	1.545+08
$2s2p^3\ ^3P_2^o$	$2s^22p^2\ ^3P_1$	109 168.90	3.06+08	3.01+08	3.139+08
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^3P_1$	109 167.90	3.13+08	3.08+08	3.214+08
$2s2p^3\ ^3P_0^o$	$2s^22p^2\ ^3P_1$	109 174.80	1.24+09	1.22+09	1.273+09
$2s2p^3\ ^1D_2^o$	$2s^22p^2\ ^3P_1$	144 139.20	2.24+04	2.16+04	5.657+03
$2s2p^3\ ^5S_2^o$	$2s^22p^2\ ^3P_2$	46 653.80	1.10+02	2.55+02	1.266+02
$2s2p^3\ ^3D_3^o$	$2s^22p^2\ ^3P_2$	92 106.40	3.75+08	3.79+08	3.721+08
$2s2p^3\ ^3D_2^o$	$2s^22p^2\ ^3P_2$	92 119.50	9.18+07	9.25+07	9.097+07
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^3P_2$	92 121.00	1.01+07	1.01+07	9.963+06
$2s2p^3\ ^3P_2^o$	$2s^22p^2\ ^3P_2$	109 086.80	9.30+08	9.16+08	9.548+08
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^3P_2$	109 085.80	5.13+08	5.06+08	5.272+08
$2s2p^3\ ^1D_2^o$	$2s^22p^2\ ^3P_2$	144 057.10	1.18+05	1.14+05	4.141+04
$2s2p^3\ ^5S_2^o$	$2s^22p^2\ ^1D_2$	31 468.40	1.40−03	2.88−04	8.949−04
$2s2p^3\ ^3D_3^o$	$2s^22p^2\ ^1D_2$	76 921.00	4.09+03	5.17+03	4.140+03
$2s2p^3\ ^3D_2^o$	$2s^22p^2\ ^1D_2$	76 934.10	7.86+02	1.05+03	7.330+02
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^1D_2$	76 935.60	4.84+02	8.45+02	5.928+02
$2s2p^3\ ^3P_2^o$	$2s^22p^2\ ^1D_2$	93 901.40	1.93+03	1.55+03	2.297+03
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^1D_2$	93 900.40	5.41+03	5.87+03	5.158+03
$2s2p^3\ ^1D_2^o$	$2s^22p^2\ ^1D_2$	12 8871.70	3.25+09	3.21+09	3.143+09
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^1S_0$	59 563.00	3.78+02	4.31+02	3.619+02
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^1S_0$	76 527.80	2.01+03	2.71+03	2.057+03

assumes that the atomic state functions are built from the same orthogonal radial orbital set. However, this restriction can be relaxed with the use of the technique developed by Malmquist [37]. In order to compute transition matrix elements between two atomic state functions described by two independently optimized orbital sets, the wavefunction representations of the two states must undergo a *biorthogonal* transformation. The transformation of the atomic state functions is performed in such a way that the orbital sets become mutually orthogonal (*biorthogonal*), in which case the calculation of transition matrix elements can be handled using standard Racah techniques [14].

#### 4. Generation of configuration expansions

The calculations were done term by term for all terms belonging to the  $2s^22p^2$  and  $2s2p^3$  configurations. The atomic wavefunctions were generated separately for each term. Within a given term all fine structure levels were represented by wavefunctions optimized together in an EOL scheme. The fine structure levels within a term were weighted according to their statistical weights. For the terms belonging to the  $2s^22p^2$  ground configuration the configuration expansions were generated by single and double substitutions (SD expansion) from the  $\{2s^22p^2, 2p^4\}$  multireference set to an active set of orbitals. For the terms belonging to the  $2s2p^3$

**Table 11.** Transition rates (Babushkin and Coulomb gauge) in  $s^{-1}$  for O III.  $A_{\text{MCHF}}$ —from [21];  $A_{\text{CIv3}}$ —from [22];  $A_{\text{NIST}}$ —from NIST database [41]; in the last column we quoted only the values with NIST accuracy code ‘A’, i.e. better than 3%. Transition energies  $\Delta E_{\text{exp}}$  are given in units of  $\text{cm}^{-1}$  and are those of [40].

Upper	Lower	$\Delta E_{\text{exp}}$	$A_B$	$A_C$	$A_{\text{MCHF}}$	$A_{\text{CIv3}}$	$A_{\text{NIST}}$
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^3P_0$	120 058.20	3.50+08	3.51+08	3.489+08	3.505+08	3.41+08
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^3P_0$	142 381.80	6.11+08	6.07+08	6.112+08	6.595+08	6.06+08
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^3P_0$	197 087.70	1.59+09	1.58+09	1.588+09	1.718+09	1.61+09
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^3P_0$	210 461.80	5.09+04	5.25+04	6.279+04	2.400+04	
$2s2p^3\ ^5S_2^o$	$2s^22p^2\ ^3P_1$	60 211.60	2.15+02	3.79+02	2.308+02	1.668+02	
$2s2p^3\ ^3D_2^o$	$2s^22p^2\ ^3P_1$	119 940.20	4.71+08	4.73+08	4.693+08	4.716+08	4.58+08
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^3P_1$	119 945.00	2.55+08	2.56+08	2.542+08	2.564+08	2.48+08
$2s2p^3\ ^3P_2^o$	$2s^22p^2\ ^3P_1$	142 267.80	4.50+08	4.47+08	4.506+08	4.871+08	4.47+08
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^3P_1$	142 268.60	4.70+08	4.67+08	4.706+08	5.060+08	4.66+08
$2s2p^3\ ^3P_0^o$	$2s^22p^2\ ^3P_1$	142 280.30	1.84+09	1.83+09	1.845+09	1.987+09	1.83+09
$2s2p^3\ ^1D_2^o$	$2s^22p^2\ ^3P_1$	186 940.80	1.26+04	1.10+04	1.325+04	1.175+04	
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^3P_1$	196 974.50	4.77+09	4.74+09	4.765+09	5.157+09	4.82+09
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^3P_1$	210 348.60	8.40+05	8.29+05	8.959+05	4.937+05	
$2s2p^3\ ^5S_2^o$	$2s^22p^2\ ^3P_2$	60 018.60	5.35+02	1.03+03	5.765+02	4.148+02	
$2s2p^3\ ^3D_3^o$	$2s^22p^2\ ^3P_2$	119 719.00	6.17+08	6.19+08	6.138+08	6.182+08	5.99+08
$2s2p^3\ ^3D_2^o$	$2s^22p^2\ ^3P_2$	119 747.20	1.49+08	1.49+08	1.478+08	1.497+08	1.44+08
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^3P_2$	119 752.00	1.61+07	1.61+07	1.603+07	1.629+07	
$2s2p^3\ ^3P_2^o$	$2s^22p^2\ ^3P_2$	142 074.80	1.39+09	1.38+09	1.387+09	1.493+09	1.37+09
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^3P_2$	142 075.60	7.60+08	7.54+08	7.608+08	8.192+08	7.54+08
$2s2p^3\ ^1D_2^o$	$2s^22p^2\ ^3P_2$	186 747.80	2.78+05	2.65+05	2.811+05	1.885+05	
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^3P_2$	196 781.50	7.96+09	7.92+09	7.948+09	8.603+09	8.04+09
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^3P_2$	210 155.60	1.81+05	1.78+05	1.947+05	3.894+04	
$2s2p^3\ ^5S_2^o$	$2s^22p^2\ ^1D_2$	40 051.50	6.07−03	5.94−02	5.777−03	9.213−04	
$2s2p^3\ ^3D_3^o$	$2s^22p^2\ ^1D_2$	99 751.90	2.01+04	2.33+04	2.108+04	1.329+04	
$2s2p^3\ ^3D_2^o$	$2s^22p^2\ ^1D_2$	99 780.10	4.04+03	4.80+03	4.093+03	2.425+03	
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^1D_2$	99 784.90	2.13+03	3.42+03	2.358+03	2.239+03	
$2s2p^3\ ^3P_2^o$	$2s^22p^2\ ^1D_2$	122 107.70	6.71+03	5.62+03	7.088+03	2.524+03	
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^1D_2$	122 108.50	2.72+04	2.89+04	2.746+04	2.024+04	
$2s2p^3\ ^1D_2^o$	$2s^22p^2\ ^1D_2$	166 780.70	5.48+09	5.45+09	5.463+09	5.561+09	5.41+09
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^1D_2$	176 814.40	2.37+05	2.29+05	3.093+05	1.030+05	
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^1D_2$	190 188.50	9.23+09	9.09+09	9.380+09	1.071+10	9.60+09
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^1S_0$	76 872.50	1.86+03	1.65+03	1.699+03	8.307+02	
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^1S_0$	99 196.10	1.03+04	1.15+04	9.578+03	6.108+03	
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^1S_0$	153 902.00	6.56+04	6.73+04	6.975+04	2.168+04	
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^1S_0$	167 276.10	1.60+09	1.62+09	1.508+09	1.500+09	1.49+09

configuration the configuration lists were generated by SD substitutions from the single reference configuration to an active set of orbitals. In order to monitor the convergence of computed properties the active sets were systematically enlarged to include orbitals with principal quantum numbers  $n = 3 \dots 8$ , and orbital quantum numbers  $l = 0 \dots 5$  (i.e. angular symmetries s, p, d, f, g, h). Due to stability problems in the self-consistent field procedure the optimization of radial orbitals was done layer by layer. The configuration expansions involved valence, core–valence and core–core electron correlation effects and should be adequate to also describe inner properties, like hyperfine structure.

The self-consistent field calculations for each layer of orbitals were followed by relativistic configuration interaction (RCI) calculations, including the Breit interaction. At the final stage the multireference set for the terms of the  $2s^22p^2$  configuration was enlarged to include  $\{2s^22p^2, 2p^4, 2s2p^23d, 2s^23d^2\}$ . The multireference was chosen based on the criteria that it should contain the

configurations that had the largest weights in the preceding self-consistent field calculations. Among the states generated by SD-excitations from the multireference set only those interacting with the multireference states were kept. In the same way the multireference set for  $2s2p^3$  was enlarged to include the configurations  $\{2s2p^3, 2p^33d, 2s^22p3d, 2s2p3d^2\}$ . The leading QED effects—vacuum polarization and self-energy—were added, as perturbative corrections, to the results of the final multireference RCI calculations.

The configuration space was explored in two directions in the current work: through the enlarged active set of orbitals, and through the increased multireference set. It would be desirable to increase the size of both sets further, but it would cross the limit imposed by the computational resources at hand. All calculations were performed on a single processor machine with 3 Gb internal memory and the largest multireference expansion, the one for the  $2s2p^3\ ^3D_{1,2,3}^o$  states, contained almost 900 000 CSFs.

**Table 12.** Transition rates (Babushkin and Coulomb gauge) in  $s^{-1}$  for F IV.  $A_{MCHF}$ —from [21];  $A_{CIV3}$ —from [24];  $A_{HFR}$ —from [26]. Transition energies  $\Delta E_{exp}$  are given in units of  $cm^{-1}$  and are those of [40].

Upper	Lower	$\Delta E_{exp}$	$A_B$	$A_C$	$A_{MCHF}$	$A_{CIV3}$	$A_{HFR}$
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^3P_0$	147 903.50	5.00+08	5.01+08	5.051+08	5.045+08	5.06+08
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^3P_0$	175 241.90	8.18+08	8.15+08	8.277+08	8.779+08	8.84+08
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^3P_0$	238 296.70	1.99+09	1.98+09	2.002+09	2.118+09	1.87+09
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^3P_0$	257 386.50	6.12+04	6.42+04	6.329+04	3.180+04	
$2s2p^3\ ^5S_2^o$	$2s^22p^2\ ^3P_1$	73 968.70	7.78+02	1.25+03	8.225+02	6.211+02	
$2s2p^3\ ^3D_2^o$	$2s^22p^2\ ^3P_1$	147 662.70	6.71+08	6.72+08	6.778+08	6.773+08	6.77+08
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^3P_1$	147 677.50	3.59+08	3.58+08	3.618+08	3.630+08	3.58+08
$2s2p^3\ ^3P_2^o$	$2s^22p^2\ ^3P_1$	175 010.80	5.97+08	5.95+08	6.036+08	6.416+08	6.44+08
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^3P_1$	175 015.90	6.41+08	6.39+08	6.486+08	6.848+08	6.93+08
$2s2p^3\ ^3P_0^o$	$2s^22p^2\ ^3P_1$	175 037.90	2.48+09	2.47+09	2.508+09	2.654+09	2.67+09
$2s2p^3\ ^1D_2^o$	$2s^22p^2\ ^3P_1$	228 677.80	4.38+04	3.95+04	4.409+04	4.063+04	
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^3P_1$	238 070.70	5.96+09	5.94+09	6.007+09	6.357+09	5.65+09
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^3P_1$	257 160.50	2.07+06	2.04+06	2.091+06	1.406+06	
$2s2p^3\ ^5S_2^o$	$2s^22p^2\ ^3P_2$	73 580.70	1.95+03	3.34+03	2.072+03	1.562+03	
$2s2p^3\ ^3D_3^o$	$2s^22p^2\ ^3P_2$	147 229.00	8.69+08	8.71+08	8.767+08	8.785+08	8.81+08
$2s2p^3\ ^3D_2^o$	$2s^22p^2\ ^3P_2$	147 274.70	2.05+08	2.05+08	2.064+08	2.082+08	2.05+08
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^3P_2$	147 289.50	2.19+07	2.19+07	2.207+07	2.236+07	1.96+07
$2s2p^3\ ^3P_2^o$	$2s^22p^2\ ^3P_2$	174 622.80	1.87+09	1.86+09	1.889+09	1.998+09	2.02+09
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^3P_2$	174 627.90	1.01+09	1.01+09	1.026+09	1.086+09	1.10+09
$2s2p^3\ ^1D_2^o$	$2s^22p^2\ ^3P_2$	228 289.80	9.65+05	9.30+05	9.762+05	7.162+05	
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^3P_2$	237 682.70	9.96+09	9.92+09	1.003+10	1.062+10	9.45+10
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^3P_2$	256 772.50	3.10+05	3.03+05	3.076+05	1.055+05	
$2s2p^3\ ^5S_2^o$	$2s^22p^2\ ^1D_2$	48 956.50	4.43−02	2.32−01	4.568−02	1.406−02	
$2s2p^3\ ^3D_2^o$	$2s^22p^2\ ^1D_2$	122 604.80	7.31+04	8.18+04	7.694+04	5.269+04	
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^1D_2$	122 650.50	1.51+04	1.71+04	1.572+04	1.021+04	
$2s2p^3\ ^3D_0^o$	$2s^22p^2\ ^1D_2$	122 665.30	7.74+03	1.15+04	8.274+03	7.924+03	
$2s2p^3\ ^3P_2^o$	$2s^22p^2\ ^1D_2$	149 998.60	1.93+04	1.67+04	1.932+04	8.633+03	
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^1D_2$	150 003.70	9.64+04	1.01+05	1.000+05	7.639+04	
$2s2p^3\ ^1D_2^o$	$2s^22p^2\ ^1D_2$	203 665.60	7.52+09	7.50+09	7.581+09	7.710+09	7.00+09
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^1D_2$	213 058.50	3.90+05	3.80+05	4.273+05	1.988+05	
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^1D_2$	232 148.30	1.12+10	1.11+10	1.132+10	1.241+10	1.15+10
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^1S_0$	94 362.30	5.92+03	6.05+03	6.124+03	3.343+03	
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^1S_0$	121 700.70	3.32+04	4.00+04	3.381+04	2.299+04	
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^1S_0$	184 755.50	1.68+05	1.72+05	1.688+05	7.878+04	
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^1S_0$	203 845.30	2.37+09	2.38+09	2.354+09	2.342+09	1.94+09

## 5. Results and evaluation of data

Table 1 displays the experimental energy levels and the computed transition energies as functions of the increasing active sets and multireference sets for F IV. A saturation (or stabilization) of the calculated energy values in most cases occurred within the orbital sets with  $n = 8$ . There are three main exceptions:  $^5S_0^o$  term, for which the energy relative to the ground state is still increasing;  $^1D_0^o$  and  $^1P_0^o$  terms, for which the energies are decreasing. Increasing the multireference set changes energies in the correct direction, towards the experimental energies. The effect of the multireference set is comparatively large for the states which were not fully converged with respect to the orbital basis. We noted the large effects of the increased multireference set on the fine structure splittings of the terms. In tables 2 and 3 computed energies and fine-structure splittings for N II, O III, F IV, Ne V and Ti XVII are compared with experimental values. The overall agreement between theory and experiment is good. The larger energy differences for  $^5S_0^o$ ,  $^1D_0^o$  and  $^1P_0^o$  terms have been

discussed above. With respect to the fine-structure, splittings for the  $2s2p^3\ ^3P^o$  term remain problematic. The fine-structure for this term is highly irregular along the sequence and it is not described very well in the present calculations. The fine-structure splitting is strongly affected by the multireference set and it would be desirable to increase it further. When comparing with the energy differences reported by Tachiev and Froese Fischer [20], we see that the separations are somewhat better described in the Breit–Pauli approximation.

In table 4 magnetic hyperfine interaction constants  $A_J$  for  $2s^22p^2\ ^3P_{1,2}$  and  $2s2p^3\ ^3P_{1,2}^o$  in F IV are shown as functions of the increasing active sets and multireference sets. The hyperfine interaction constant for the  $2s^22p^2\ ^3P_1$  state is not converged with respect to the active set nor to the multireference set. The oscillatory behaviour can be explained by strong internal cancellation, where significant digits are lost. We can qualitatively explain this in terms of the non-relativistic theory, in which the orbital and spin-dipolar contributions to the interaction constant are both large but counteracting; therefore, the total value is mainly determined

**Table 13.** Transition rates (Babushkin and Coulomb gauge) in  $s^{-1}$  for Ne V.  $A_{MCHF}$ —from [21];  $A_{CIV3}$ —from [23];  $A_{SS}$ —from [25]. Transition energies  $\Delta E_{exp}$  are given in units of  $cm^{-1}$  and are those of [40].

Upper	Lower	$\Delta E_{exp}$	$A_B$	$A_C$	$A_{MCHF}$	$A_{CIV3}$	$A_{SS}$
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^3P_0$	175 925.00	6.63+08	6.63+08	6.741+08	6.701+08	7.250+08
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^3P_0$	208 153.30	1.03+09	1.03+09	1.050+09	1.102+09	1.247+09
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^3P_0$	279 371.20	2.39+09	2.38+09	2.416+09	2.520+09	2.855+09
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^3P_0$	303 819.20	8.62+04	9.19+04	8.572+04	4.998+04	1.781+05
$2s2p^3\ ^5S_2^o$	$2s^22p^2\ ^3P_1$	87 988.30	2.33+03	3.48+03	2.476+03	1.898+03	1.797+03
$2s2p^3\ ^3D_2^o$	$2s^22p^2\ ^3P_1$	175 491.50	8.87+08	8.88+08	9.019+08	8.970+08	9.709+08
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^3P_1$	175 513.80	4.64+08	4.64+08	4.717+08	4.716+08	5.033+08
$2s2p^3\ ^3P_2^o$	$2s^22p^2\ ^3P_1$	207 740.10	7.41+08	7.40+08	7.542+08	7.939+08	8.976+08
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^3P_1$	207 742.10	8.29+08	8.27+08	8.432+08	8.795+08	1.000+09
$2s2p^3\ ^3P_0^o$	$2s^22p^2\ ^3P_1$	207 773.80	3.15+09	3.14+09	3.200+09	—	3.804+09
$2s2p^3\ ^1D_2^o$	$2s^22p^2\ ^3P_1$	270 141.70	1.28+05	1.17+05	1.297+05	1.199+05	1.404+05
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^3P_1$	278 960.00	7.16+09	7.14+09	7.255+09	7.567+09	8.571+09
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^3P_1$	303 408.00	4.85+06	4.79+06	4.916+06	3.580+06	6.929+06
$2s2p^3\ ^5S_2^o$	$2s^22p^2\ ^3P_2$	87 290.00	5.84+03	9.16+03	6.233+03	4.776+03	5.124+03
$2s2p^3\ ^3D_3^o$	$2s^22p^2\ ^3P_2$	174 722.80	1.13+09	1.13+09	1.149+09	1.147+09	1.235+09
$2s2p^3\ ^3D_2^o$	$2s^22p^2\ ^3P_2$	174 793.20	2.58+08	2.58+08	2.622+08	2.639+08	2.774+08
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^3P_2$	174 815.50	2.71+07	2.70+07	2.751+07	2.783+07	2.874+07
$2s2p^3\ ^3P_2^o$	$2s^22p^2\ ^3P_2$	207 041.80	2.38+09	2.37+09	2.417+09	2.526+09	2.877+09
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^3P_2$	207 043.80	1.27+09	1.27+09	1.296+09	1.356+09	1.547+09
$2s2p^3\ ^1D_2^o$	$2s^22p^2\ ^3P_2$	269 443.40	2.72+06	2.64+06	2.770+06	2.126+06	2.970+06
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^3P_2$	278 261.70	1.20+10	1.19+10	1.214+10	1.266+10	1.435+10
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^3P_2$	302 709.70	5.30+05	5.15+05	5.324+05	2.190+05	1.271+06
$2s2p^3\ ^5S_2^o$	$2s^22p^2\ ^1D_2$	58 108.80	2.98−01	8.52−01	3.224−01	1.292−01	1.973−01
$2s2p^3\ ^3D_3^o$	$2s^22p^2\ ^1D_2$	145 541.60	2.18+05	2.38+05	2.310+05	1.653+05	2.061+05
$2s2p^3\ ^3D_2^o$	$2s^22p^2\ ^1D_2$	145 612.00	4.55+04	5.03+04	4.748+04	3.287+04	4.761+04
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^1D_2$	145 634.30	2.37+04	3.29+04	2.528+04	2.376+04	3.331+04
$2s2p^3\ ^3P_2^o$	$2s^22p^2\ ^1D_2$	177 860.60	4.88+04	4.30+04	4.909+05	2.450+04	8.085+04
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^1D_2$	177 862.60	2.78+05	2.89+05	2.893+05	2.292+05	3.027+05
$2s2p^3\ ^1D_2^o$	$2s^22p^2\ ^1D_2$	240 262.20	9.52+09	9.50+09	9.657+09	9.778+09	1.170+10
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^1D_2$	249 080.50	6.66+05	6.50+05	7.177+05	3.848+05	2.190+06
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^1D_2$	273 528.50	1.33+10	1.33+10	1.355+10	1.455+10	1.732+10
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^1S_0$	112 009.60	1.73+04	1.75+04	1.811+04	1.064+04	3.209+04
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^1S_0$	144 237.90	9.52+04	1.11+05	9.810+04	6.963+04	1.564+05
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^1S_0$	215 455.80	3.86+05	3.93+05	3.928+05	2.155+05	5.285+05
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^1S_0$	239 903.80	3.06+09	3.07+09	3.091+09	3.057+09	3.581+09

by the Fermi contact term. The contact term, in turn, is a sum of large and counteracting spin-polarization contributions from the 1s and 2s sub-shells. As a result the final value is very sensitive to correlation effects [38]. In contrast, the interaction constants for the other states are very stable and they are expected to be accurate to within a few parts in a thousand.

In table 5 magnetic dipole and electric quadrupole hyperfine interaction constants are displayed together with the Landé  $g_J$ -factors for all ions. The hyperfine shifts for the states belonging to the  $2s2p^3$  configuration are dominated by large magnetic dipole interaction constants. For the  $2s^22p^2$  states the electric quadrupole interaction constants are also important. The Landé  $g_J$ -factors are relatively insensitive to correlation effects. For light elements the values are close to what is expected from pure  $LS$  coupling. Only for Ti XVII there is a considerable deviation from the  $LS$  values. To the knowledge of the authors there are no experimental or theoretical data for the hyperfine interaction constants in the literature to compare with.

As noted by Clark [39] the  $2s^22p^n-2s2p^{n+1}$  transition arrays have large isotope shifts. This is due to the fact that both the normal and specific isotope shifts act in the same direction. In addition there is only a small cancellation for the specific mass shift parameters of the upper and lower state and difference  $\Delta S_{sms}$  remains comparatively large. In table 6 we display specific mass shift parameters  $S_{sms}$  and electron densities at the nucleus  $\rho(0)$  for  $2s^22p^2\ ^3P_0$  and  $2s2p^3\ ^3P_0^o$  in F IV as functions of the increasing active sets and multireference sets. Also the differences  $\Delta S_{sms}$  and  $\Delta\rho(0)$  are shown. The computed quantities, especially the differences, saturate quickly and there is excellent convergence. In table 7 the specific mass shift parameters and electron densities are shown for all ions. Most notable is perhaps how the specific mass shift parameters for  $2s2p^3\ ^3P^o$  and  $2s2p^3\ ^1P^o$  approach each other for large  $Z$ . For all ions except Ti there are only small effects of  $J$ , and the specific mass shifts are well described by term values. The elements N, O and Ne all have more than one stable isotope. Using the data in table 7 together with experimental values for the energy separations, transition isotope shifts for

**Table 14.** Transition rates (Babushkin and Coulomb gauge) in  $s^{-1}$  for Ti XVII.  $A_{\text{HFR}}$ —from [26];  $A_{\text{NIST}}$ —from NIST [41]. ‘Code’ is the accuracy code associated with the NIST data: C < 25%, D < 50%, E > 50%. Transition energies  $\Delta E_{\text{exp}}$  are given in units of  $\text{cm}^{-1}$  and are those of [40].

Upper	Lower	$\Delta E_{\text{exp}}$	$A_B$	$A_C$	$A_{\text{HFR}}$	$A_{\text{NIST}}$	Code
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^3P_0$	580 110.00	5.80+09	5.79+09	5.67+09	6.4+09	C
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^3P_0$	680 910.00	3.59+09	3.60+09	3.61+09	3.79+09	C
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^3P_0$	838 340.00	7.61+09	7.60+09	7.34+09	8.0+09	C
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^3P_0$	943 500.00	1.07+07	1.11+07			
$2s2p^3\ ^5S_2^o$	$2s^22p^2\ ^3P_1$	304 002.00	5.73+06	6.51+06		6.6+06	E
$2s2p^3\ ^3D_2^o$	$2s^22p^2\ ^3P_1$	549 232.00	6.00+09	6.02+09	5.91+09	6.6+09	D
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^3P_1$	550 452.00	1.19+09	1.18+09	1.14+09	1.3+09	D
$2s2p^3\ ^3P_2^o$	$2s^22p^2\ ^3P_1$	657 122.00	9.96+08	1.00+09	9.81+08	1.0+09	D
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^3P_1$	651 252.00	7.74+10	7.74+10	7.64+10	8.5+10	C
$2s2p^3\ ^3P_0^o$	$2s^22p^2\ ^3P_1$	648 792.00	1.47+10	1.46+10	1.46+10	1.63+10	C
$2s2p^3\ ^1D_2^o$	$2s^22p^2\ ^3P_1$	815 482.00	1.20+08	1.18+08	8.88+07	1.3+08	E
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^3P_1$	808 682.00	2.16+10	2.16+10	2.11+10	2.3+10	E
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^3P_1$	913 842.00	1.97+09	1.96+09	1.86+09	2.2+09	E
$2s2p^3\ ^5S_2^o$	$2s^22p^2\ ^3P_2$	277 930.00	7.73+06	9.02+06		8.3+06	E
$2s2p^3\ ^3D_3^o$	$2s^22p^2\ ^3P_2$	531 030.00	4.76+09	4.79+09	4.66+09	5.2+09	C
$2s2p^3\ ^3D_2^o$	$2s^22p^2\ ^3P_2$	523 160.00	1.02+08	9.98+07	7.27+07	8.8+07	E
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^3P_2$	524 380.00	2.03+07	2.11+07		1.5+07	E
$2s2p^3\ ^3P_2^o$	$2s^22p^2\ ^3P_2$	631 050.00	1.24+10	1.24+10	1.22+10	1.4+10	C
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^3P_2$	625 180.00	3.16+09	3.14+09	3.12+09	3.7+09	D
$2s2p^3\ ^1D_2^o$	$2s^22p^2\ ^3P_2$	789 410.00	2.73+09	2.72+09	2.82+09	3.0+09	E
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^3P_2$	782 610.00	4.38+10	4.39+10	4.28+10	4.6+10	C
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^3P_2$	887 770.00	1.38+07	1.41+07			
$2s2p^3\ ^5S_2^o$	$2s^22p^2\ ^1D_2$	193 000.00	1.51+05	1.94+05			
$2s2p^3\ ^3D_3^o$	$2s^22p^2\ ^1D_2$	446 100.00	3.01+08	3.12+08	3.27+08	3.2+08	E
$2s2p^3\ ^3D_2^o$	$2s^22p^2\ ^1D_2$	438 230.00	2.49+07	2.62+07	2.59+07	3.6+07	E
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^1D_2$	439 450.00	5.46+07	5.92+07		6.2+07	E
$2s2p^3\ ^3P_2^o$	$2s^22p^2\ ^1D_2$	546 120.00	7.16+07	6.94+07	8.02+07	1.1+08	E
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^1D_2$	540 250.00	1.73+08	1.72+08	1.96+08	1.9+08	E
$2s2p^3\ ^1D_2^o$	$2s^22p^2\ ^1D_2$	704 480.00	3.59+10	3.60+10	3.52+10	3.87+10	C
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^1D_2$	697 680.00	1.59+07	1.64+07			
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^1D_2$	802 840.00	4.74+10	4.74+10	4.63+10	5.2+10	C
$2s2p^3\ ^3D_1^o$	$2s^22p^2\ ^1S_0$	337 930.00	1.61+07	1.63+07		2.2+07	E
$2s2p^3\ ^3P_1^o$	$2s^22p^2\ ^1S_0$	438 730.00	5.84+07	6.24+07	4.27+07	6.8+07	E
$2s2p^3\ ^3S_1^o$	$2s^22p^2\ ^1S_0$	596 160.00	2.16+08	2.20+08	2.36+08	2.2+08	E
$2s2p^3\ ^1P_1^o$	$2s^22p^2\ ^1S_0$	701 320.00	1.26+10	1.26+10	1.21+10	1.35+10	C

the different isotopic pairs have been calculated for all  $E1$  transitions in the  $2s^22p^2$ – $2s2p^3$  transition array. The transition isotope shifts are displayed in table 8. A positive sign of the transition isotope shift corresponds to a larger energy transition (i.e. a blue shifted line) for the heavier isotope. These data together with hyperfine interaction constants allow line profiles in high-resolution spectra to be modelled in detail [19].

In table 9 the transition rates for  $2s^22p^2\ ^3P_0$ – $2s2p^3\ ^3P_1^o$  and  $2s^22p^2\ ^1D_2$ – $2s2p^3\ ^1P_1^o$  in F IV are shown as functions of increasing active sets and multireference sets. Whereas the values for the  $2s^22p^2\ ^1D_2$ – $2s2p^3\ ^1P_1^o$  transition are very stable, the values for  $2s^22p^2\ ^3P_0$ – $2s2p^3\ ^3P_1^o$  oscillate at the 1% level and, again, it would be desirable to increase the orbital basis further. Rates computed in two gauges, Babushkin and Coulomb, are brought in close agreement when the multireference set is increased. Rates for all  $E1$  transitions in the  $2s^22p^2$ – $2s2p^3$  transition array are given in tables 10–14. The values from recent MCHF and CIV3 Breit–Pauli [21–24] calculations are included in the tables for N II, O III,

F IV and Ne V for comparison. For F IV and Ti XVII we also display transition rates computed by the Hartree–Fock–Relativistic (HFR) program [26]. In table 13 values from SUPERSTRUCTURE calculations by Bhatia and Doschek [25] are added.

Rates for almost all transitions in the  $2s^22p^2$ – $2s2p^3$  array are also listed in the NIST database [41], but their accuracy classification renders them rather insufficient for the purpose of comparison with Breit–Pauli or current Dirac–Hartree–Fock results. The only exception is the O III, for which several entries are listed in [41] with NIST accuracy classification ‘A’ (i.e. better than 3%). We included these class ‘A’ data in the last column of table 11. With the exception of the two lines  $2s^22p^2\ ^1D_2$ – $2s2p^3\ ^1P_1^o$  and  $2s^22p^2\ ^1S_0$ – $2s2p^3\ ^1P_1^o$  the Dirac–Hartree–Fock results are in agreement with the NIST data within their specified error bounds. For Ti XVII, table 14 we added values from the NIST database [41] together with the accuracy classifications.

**Table 15.** Transition probabilities in  $s^{-1}$  for the  $2s^22p^2\ ^3P_J-2s2p^3\ ^5S_2^o$  intercombination lines in N II and O III, and lifetime  $\tau$  in ms for the  $^5S_2^o$  level.  $BR$  is the branching ratio.

A values ( $s^{-1}$ )		$BR$	$\tau$ (ms)	Source
$^5S_2^o-^3P_1$	$^5S_2^o-^3P_2$			
N II				
Theory				
44.7	110	2.46	6.46	RCI this work
51.55	126.6	2.456	5.61	MCHF-BP adjusted (2004) [21]
53.6	130.6	2.44	5.43	CIV3 adjusted (1997) [45]
Experiment				
			5.4(3)	Ion-trap (1991) [49]
			5.88(3)	Ion-trap (1998) [50]
Observation				
		2.31(40)		Solar (1977) [51]
		2.45(4)		Arc (1996) [52]
		2.27(23)		ICP (1996) [53]
		2.24(6)		Arc (1996) [54]
O III				
Theory				
215	535	2.49	1.33	RCI this work
230.8	576.5	2.498	1.239	MCHF-BP adjusted (2004) [21]
218	541	2.482	1.32	MCDF (1997) [46]
237	589	2.486	1.21	CIV3 adjusted (1997) [46]
166.8	414.8	2.487	1.719	CIV3 (1997) [22]
Experiment				
			1.22(8)	Ion-trap (1984) [55]
			1.250(13)	Ion-trap (2000) [56]
Observation				
		2.57		Solar (1996) [57]
		2.79(3)		RR Tel(GHRS) (1996) [58]

The agreement between the transition rates obtained in the Babushkin and Coulomb gauges is very good for strong transitions. In weak transitions the agreement between the gauges depends on a particular term under consideration. For some transitions the agreement is good but for others, e.g. the  $2s^22p^2\ ^3P_2-2s2p^3\ ^5S_2^o$ , there are substantial differences. The weakness of a transition frequently comes out as a result of cancellation between a number of large contributions or between different parts of the radial transition integrals [42]. A small unbalance due to correlation effects may thus change the calculated transition probabilities dramatically in one of the gauges. In weak transition there may be sizable effects from the negative energy states, not accounted for in the present calculation, which affect rates in the Coulomb gauge [43], and the general wisdom is that values in the Babushkin gauge should be used in such cases. The agreement between the present values and the Breit–Pauli values by Froese Fischer and Tachiev [21] is very good, especially for strong transitions. For Ne V the rates of strong transitions obtained from the fully relativistic Dirac–Hartree–Fock calculation are consistently smaller than the ones from the Breit–Pauli calculation. This might be due to the relativistic contraction effects which are better captured in the former calculation. The calculations by Aggarwal *et al* [22–24] are comparatively small in terms of electron correlation effects included. Nevertheless, the general agreement between these calculations and the Breit–Pauli calculations by Froese Fischer and Tachiev as well as the

present fully relativistic one is very satisfactory. There is a fair agreement between the SUPERSTRUCTURE calculations by Bhatia and Doschek [25] and the present calculations for Ne V. For Ti XVII the present values, which should be correct to within a few percent, are considerably more accurate than the values in the NIST compilation. The latter are mainly from the pioneering Dirac–Hartree–Fock calculations by Cheng *et al* [44]. The strongest transitions in Ti XVII have been calculated by Fawcett using the Hartree–Fock relativistic (HFR) method [26]. Although small, these calculations agree very well with the present calculation.

The  $2s^22p^2\ ^3P_J-2s2p^3\ ^5S_2^o$  transition is of considerable interest in astrophysical applications (see [45] and references therein). In table 15 we compare decay rates from  $2s2p^3\ ^5S_2^o$  to the two lower states  $2s^22p^2\ ^3P_J$  as well as lifetimes  $\tau$  of the  $^5S_2^o$  states in N II and O III. In addition the branching ratio

$$BR = \frac{A(^5S_2^o - ^3P_2)}{A(^5S_2^o - ^3P_1)}, \quad (13)$$

which is a measurable quantity, is given. The transition rates from the present calculations are somewhat smaller, especially for N II, than the ones from adjusted Breit–Pauli calculations [21, 45, 46], leading to a larger lifetime, as compared to accurate ion-trap measurements. All calculations give essentially the same value of the branching ratio  $BR$ . Considering weak intercombination transitions in general, the large cancellation of different contributions reduces the

accuracy of the calculated values and they are not of the same accuracy as the ones from the adjusted Breit–Pauli calculations of Froese Fischer and Tachiev [21]. As expected, the agreement between the present values and the values from Breit–Pauli calculations becomes better when  $Z$  increases.

## 6. Summary and conclusion

We have shown that fully relativistic multiconfiguration calculations have the capability to provide accurate hyperfine and isotope shift parameters for light atoms. The relativistic approach yields less accurate rates of intercombination transitions in light ions near the neutral end, but the accuracy improves rapidly with nuclear charge. Already for Ne V the relativistic transition rates compare very well with values from recent Breit–Pauli calculations. In contrast to the Breit–Pauli calculations, the relativistic computational scheme can be applied with good accuracy up to the high- $Z$  end of the iso-electronic sequence [48]. An optimal tool for calculations of atomic properties along an isoelectronic sequence would be a combination of a Breit–Pauli method and a fully relativistic Dirac–Hartree–Fock method. The former should be applied near the neutral end of the sequence, where it has the advantage in more accurate treatment of electron correlation effects. At some point along the sequence both methods yield results of comparable accuracy, and the Breit–Pauli approach begins to break down soon after. The Dirac–Hartree–Fock method would take over from there. To achieve a better description of energy separations it is desirable to develop systematic and automated procedures for selecting the multireference sets. Larger multireference sets make the configuration expansions grow very rapidly and the calculations would have to be run on parallel systems using the MPI version of the GRASP2K code [47]. Also, it would be of great interest to develop a fine-tuning scheme in  $jj$ -coupling. This is, however, not a straightforward task, since such a scheme—in contrast to the one in the Breit–Pauli approximation—involves also a modification of off-diagonal matrix elements in the Hamiltonian.

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