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SERIES REPORT

(Laser, Atomic and Molecular Physics)

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OF THE CI OSCILLATOR STRENGTHS  
FOR THE LOWEST LYING AUTOIONIZING LEVEL  
IN THE Na ISOLECTRONIC SEQUENCE

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### A NEW STRATEGY FOR THE CALCULATION OF THE CI OSCILLATOR STRENGTHS FOR THE LOWEST LYING AUTOIONIZING LEVEL IN THE Na ISOELECTRONIC SEQUENCE\*

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#### ABSTRACT

We report Hartree-Fock and configuration-interaction calculations of both the length and velocity forms of the oscillator strengths for the resonance excitation  $1s^2 2s^2 2p^6 3s^2 S_j^e \rightarrow 1s^2 2s^2 2p^5 3s^2 {}^2P_j^o$  transition, which leads to autoionization (Auger transition), in several ions of the sodium isoelectronic sequence both in LS and intermediate coupling schemes employing a new strategy. The method is computationally economical and capable of yielding encouraging results.

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## 1 Introduction

Knowledge of both the length ( $f_L$ ) and velocity ( $f_V$ ) forms of the optical oscillator strengths is needed in astrophysics, plasma physics, atmospheric physics, laser physics, fusion research and space research; it is also required in testing the accuracy of the wave functions involved in the transitions under consideration. The agreement between  $f_L$  and  $f_V$  indicates the accuracy of the wave functions. Accurate wave functions are needed for the reliable study of collision processes in atoms, molecules, and ions.

There has been growing interest in the inner-shell excitation of atoms and ions from both experimentalists and theorists, because inner-shell excitation, in general, leads to autoionization which plays a very important role in explaining the structure observed in the total ionization cross section curve for electron impact.

Consequently, much of current theoretical as well as experimental work is devoted to evaluate the accurate oscillator strengths of the inner-shell excitation process in atoms and ions. From theoretical point of view, accurate oscillator strengths can be expected only if accurate wave functions are employed in the transition matrix elements. If the wave functions are exact, the length and velocity forms of the oscillator strengths ( $f_L$  and  $f_V$ ) will be equal. In general, the correct description of a transition depends on (a) the form of the dipole operator (b) correlations and (c) choice of basis orbitals used in the configuration-interaction calculations.

Very recently, Tayal and Henry<sup>1</sup> have calculated the configuration-interaction (CI) oscillator strengths for the resonance transition in the  $Fe^{13+}$  ion of the sodium isoelectronic sequence in the LS coupling scheme. They have not included the relativistic effects which may introduce some errors in their theoretical results. It is well known that the relativistic effects play an

\* A part of this work was done while the author was Research Director and Professor, CNRS Laboratory, University of Paris-Sud, Paris and Observatoire de Paris, Meudon, Paris, France.

extremely important role in obtaining accurate results especially in heavy ions. Consequently, it is indispensable to incorporate the relativistic effects in order to obtain reliable results. Tiwary et al<sup>2</sup> have investigated the length and velocity forms of the oscillator strengths using Hartree-Fock and large configuration-interaction wave functions for the inner-shell excitation of the  $P^{4+}$  ion but the agreement between the CI  $f_L$  and  $f_V$  is poor.

At the heart of the new strategy in the present calculation of the optical oscillator strengths in contrast to the so far known concepts and connections of the using orbitals obtained by the optimization method for the wave functions is that it is not required to optimize orbitals and to use large number of configurations which make the computation very cumbersome and expensive. As in our earlier *work*<sup>2</sup>, we have generated many orbitals by optimization method and used a large number of configurations. This calculation is computationally very expensive but the result is not very encouraging. In the present new strategy, we did not generate any orbital. We employed orbitals taken from Clementi and Roetti<sup>3</sup>. This choice of orbitals leads to perform a small CI calculations, which is computationally economic, and yields encouraging results.

Our purpose in this communication is to examine the effects of (1) relativity, (2) correlations and (3) inclusion of 3p and 3d orbitals, which satisfy the condition  $\langle r_{2p} \rangle \approx \langle r_{3p} \rangle \approx \langle r_{3d} \rangle$ , taken from Clementi and Roetti<sup>3</sup> (smaller exponents of 2p orbital of Clementi and Roetti are used for 3p and 3d orbitals) in our present CI calculations on both the length and velocity forms of the optical oscillator strengths for the inner-shell excitation, which leads to autoionization and plays an important role in explaining the structure observed in the total ionization cross sections curve by electron impact,  $1s^2 2s^2 2p^6 3s^2 S^o \rightarrow 1s^2 2s^2 2p^5 3s^2 {}^2P^o_j$ , transition in Na,  $Mg^+$ ,  $Al^{2+}$ ,  $Si^{3+}$ ,  $P^{4+}$ ,  $S^{5+}$ ,  $Cl^{6+}$ ,  $Ar^{7+}$ ,  $K^{8+}$ ,  $Ca^{9+}$ ,  $Sc^{10+}$ ,  $Ti^{11+}$ ,  $Fe^{15+}$ ,  $Cu^{18+}$ ,  $Zn^{19+}$ ,

$Br^{24+}$  and  $Kr^{25+}$  ions of the sodium isoelectronic sequence.

## 2 Method

We have performed our J-independent and -dependent calculations using the general configuration-interaction (CI) code CIV3 of Hibbert<sup>4</sup> and Glass and Hibbert<sup>5</sup>. The LS wave functions are written in the form

$$\Psi(LS) = \sum_{i=1}^M a_i \Phi_i(\alpha_i LS) \quad (1)$$

The coefficients  $a_i$  are the eigenvectors components of the Hamiltonian matrix with typical element

$$H_{ij} = \langle \Phi_i | H | \Phi_j \rangle \quad (2)$$

$\Phi_j$  are single-configuration functions constructed from one-electron functions, whose orbital and spin momenta are coupled to form the common total angular-momentum quantum numbers L and S according to a prescription denoted in (1) by  $\alpha_i$ .

We express the radial parts of the one-electron functions in analytical form as a sum of Slater-type orbitals, following Clementi and Roetti<sup>3</sup> :

$$P_{nl} = \sum_{j=1}^k C_{jnl} r^{I_{jnl}} e^{-\xi_{jnl} r} \quad (3)$$

The parameters in (3) can be varied to optimize the energy of any state, subject to the orthonormality conditions

$$\int_0^\infty P_{nl}(r) P_{n'l}(r) dr = \delta_{nn'} \quad (4)$$

Once the radial wave functions are determined, relativistic effects may be added to the Hamiltonian in the form of the Breit-Pauli interaction, of which we include the spin-orbit, spin-other-spin, spin-spin, mass correction, and one-body Darwin terms. The first three terms split LS states into J-dependent levels while the last two affect the overall energy of each term. The expansion (1) is then replaced by

$$\Psi(J) = \sum_i a_i \Phi_i(LSJ) \quad (5)$$

where the summation now includes single-configuration with different L and S (which can couple to form a common J value). The matrix which is diagonalized to give the eigenenergies and eigenvectors components  $a_i$  now contain the Breit-Pauli operators as well as the previous non-relativistic terms in the Hamiltonian. The parameters for the basis orbitals used in the present calculation chosen on the criterion  $\langle r_{2p} \rangle \approx \langle r_{3p} \rangle \approx \langle r_{3d} \rangle$  are shown in Table 1, and the configurations and their weights are given in Table 2 for the  $Fe^{15+}$  ion of the sodium isoelectronic sequence.

### 3 Results and discussion

Table 3 displays the J-independent and -dependent Hartree-Fock(HF) and configuration-interaction (CI) optical oscillator strengths, of both length ( $f_L$ ) and velocity ( $f_V$ ), of the resonance excitation (the inner-shell excitation which leads to autoionization)  $1s^2 2s^2 2p^6 3s^2 S_J^e \rightarrow 1s^2 2s^2 2p^5 3s^2 {}^2P_J^o$ , transition in the  $Fe^{15+}$  ion of the sodium isoelectronic sequence along with the other available theoretical results of Tayal and Henry<sup>1</sup>.

Several features of importance emerge from Table 3. First, relativistic ef-

fects lead to an increase of  $f_L$  values in both the HF and CI calculations whereas the situation is reverse in the case of the  $f_V$  values. Second, correlations effects enhance both  $f_L$  and  $f_V$  values which agree with the prediction of Tayal and Henry. Our present CI  $f_L$  is smaller than the CI  $f_V$  which disagrees with the prediction of Tayal and Henry. It is interesting to note that our CI  $f_L$  and  $f_V$  are exactly the same as that of Tayal and Henry CI  $f_V$  and  $f_L$ . We have exactly used the same set of configurations and orbitals. This may be probably due to different choices of 3p and 3d orbitals. Our 3p and 3d orbitals are taken from Clementi and Roetti<sup>3</sup> whereas Tayal and Henry have obtained by optimization. From the computational point of view, our present approach is much more economic than the Tayal and Henry approach, because we do not need to generate even the excited orbitals. Third, it is clear from Table 3 that the relativistic  $f_L$  and  $f_V$  values for the  $\Delta J = 0$  transition significantly smaller compare to the  $f_L$  and  $f_V$  values for the  $\Delta J = 1$  transition. Finally, our present results clearly demonstrate that the correlations have substantially larger influence than the relativity on the oscillator strengths, of both the length and velocity forms, of the inner-shell excitation, which leads to autoionization, in the  $Fe^{15+}$  ion of the sodium isoelectronic sequence. However, the effect of relativity is not negligible. This suggests that it is indispensable to incorporate the relativistic and correlations effects simultaneously in order to obtain the most reliable results.

Table 4 displays the present theoretical inner-shell excitation energies and oscillator strengths calculated using HF and small CI wave functions for the transition  $1s^2 2s^2 2p^6 3s^2 S_J^e \rightarrow 1s^2 2s^2 2p^5 3s^2 {}^2P_J^o$ , in Na,  $Mg^+$ ,  $Al^{2+}$ ,  $Si^{3+}$ ,  $P^{4+}$ ,  $S^{5+}$ ,  $Cl^{6+}$ ,  $Ar^{7+}$ ,  $K^{8+}$ ,  $Ca^{9+}$ ,  $Sc^{10+}$ ,  $Ti^{11+}$ ,  $Fe^{15+}$ ,  $Cu^{18+}$ ,  $Zn^{19+}$ ,  $Br^{24+}$  and  $Kr^{25+}$  ions of the sodium isoelectronic sequence obtained employing our present new strategy for the CI calculations. We notice that

(i) the oscillator strengths increase with increase of atomic number ( $Z$ ) up to  $S^{5+}$  ion and then decrease systematically, (ii) the correlation enhances the values of the oscillator strengths and (iii) the disagreement between the length and velocity forms of the oscillator strengths reduces with increase of  $Z$  for lowly ionized atoms and the situation is reverse for highly ionized atoms. This is probably due to the fact that the effect of relativity is not important for lowly ionized atoms, only correlation plays an important role whereas for highly ionized atoms, the effect of relativity is more important than the effect of the correlation.

Table 5 shows the relativistic optical oscillator strengths (OOS) for the above mentioned transition and systems. It is clear from Table 5 that the effect of relativity increases with increase of atomic number ( $Z$ ).

In order to see the general trend of the relativistic and non-relativistic oscillator strengths of the inner-shell excitation transition in the sodium isoelectronic sequence, we have plotted the  $f$ -value versus  $1/Z$  as shown in Figure 1. It is clear from Figure 1 that the trend of the oscillator strengths is regular and systematic.

#### 4. Conclusion

Our present theoretical relativistic and non-relativistic investigations of both the length and velocity forms of the optical oscillator strengths demonstrate the importance of correlations, relativity and our new strategy for the configuration-interaction calculations in the sodium isoelectronic sequence. We hope that this work will stimulate experimental and other elaborate theoretical investigations.

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#### References

1. S. S. Tayal and R. J. W. Henry, *Phys. Rev. A* **39**, 3890 (1989).
2. S. N. Tiwary, A. P. Singh, D. D. Singh and R. J. Sharma, *Can. J. Phys.* **66**, 405 (1988).
3. E. Clementi and C. Roetti, *At. Data Nucl. Data Tables* **14**, 177 (1974).
4. A. Hibbert, *Comput. Phys. Commun.* **9**, 141 (1975).
5. R. Glass and A. Hibbert, *Comput. Phys. Commun.* **16**, 19 (1978).

Table 1

Parameters for the bound orbitals used in the present calculation. Each orbital is a sum of Slater-type orbitals.

Orbital	Coefficient	Power of r	Exponent
1s	107.906937	1	15.3583002
	4.9286451	1	24.2626038
	0.4062686	2	5.6978903
	82.4930267	2	13.8613005
	0.0015250	3	2.3205605
	-0.1374697	3	4.7854404
2s	-28.9531403	1	15.3583002
	-1.7807064	1	24.2626038
	83.3355103	2	5.6978903
	-108.6022497	2	13.8613005
	-0.0020066	3	2.3205605
	19.0586395	3	4.7854404
3s	10.100811	1	15.3583002
	0.3680906	1	24.2626038
	-30.7731476	2	5.6978903
	38.0948639	2	13.8613005
	9.0910759	3	2.3205605
	-18.0962677	3	4.7854404
2p	31.1924896	2	4.3621998
	57.1310425	2	7.3200998
	17.4756317	2	13.3274002
3p	185.6664580	2	4.3621998
	-1805.6042500	3	7.3200998
3d	447.4538570	3	7.3200998

Table 2

Configurations used for the excited  ${}^2P^o$  state in the present calculation. The numbers below the configurations give their weights.

${}^2P^o$	$2p^5 3p^2 ({}^3P)$	$2p^5 3p^2 ({}^1D)$	$2p^5 3s^2$	$2p^5 3s ({}^3P) 3d$	$2p^5 3s ({}^1P) 3d$
$2p^5 3s^2$	0.00000121	-0.00000252	-0.99995983	-0.00701480	0.00516559
$2p^5 3s ({}^1P) 3d$	0.00070344	-0.00100292	-0.00825809	0.50439984	-0.86342931
$2p^5 3s ({}^3P) 3d$	-0.00190255	0.00294591	-0.00329976	0.86343771	0.50443131
$2p^5 3p^2 ({}^3P)$	0.79760921	0.60317397	-0.00000003	-0.00020427	-0.00016460
$2p^5 3p^2 ({}^1D)$	0.60317057	-0.79760313	0.00000134	0.00240037	0.00282430

Table 3.

J-independent and -dependent oscillator strengths of  $1s^2 2s^2 2p^6 3s^2 {}^2S_J^o \rightarrow 1s^2 2s^2 2p^5 3s^2 {}^2P_J^o$  in  $Fe^{15+}$

function	present results		other results		present results			
	$f_L$	$f_V$	$f_L$	$f_V$	$2J+1$	$2J'+1$	$f_L$	$f_V$
HF	0.064	0.060			2	2	0.022	0.019
					2	4	0.043	0.040
CI	0.084	0.087	0.087	0.084	2	2	0.031	0.028
					2	4	0.059	0.056

TABLE 4

OSCILLATOR STRENGTHS OF THE LOWEST-LYING  
AUTOIONIZING LEVEL IN Na ISO-ELECTRONIC SEQUENCE

$2p^6 3s^2 S^e \rightarrow 2p^5 3s^2 2p^0$	HF			CI		
	$\Delta E$	$f_L$	$f_V$	$\Delta E$	$f_L$	$f_V$
Na	1.266	0.044	0.033	1.266	0.047	0.039
Mg <sup>+</sup>	1.965	0.065	0.053	1.965	0.073	0.068
Al <sup>2+</sup>	2.814	0.073	0.062	2.814	0.085	0.083
Si <sup>3+</sup>	3.804	0.076	0.056	3.804	0.090	0.090
P <sup>4+</sup>	4.936	0.076	0.068	4.936	0.083	0.083
S <sup>5+</sup>	6.208	0.076	0.068	6.208	0.094	0.095
Cl <sup>6+</sup>	7.619	0.075	0.068	7.619	0.094	0.096
Ar <sup>7+</sup>	9.171	0.074	0.067	9.170	0.093	0.095
K <sup>8+</sup>	10.862	0.072	0.066	10.860	0.092	0.094
Ca <sup>9+</sup>	12.692	0.071	0.065	12.692	0.091	0.093
Sc <sup>10+</sup>	14.661	0.067	0.064	14.660	0.089	0.092
Ti <sup>11+</sup>	16.769	0.069	0.063	16.768	0.088	0.091
Fe <sup>15+</sup>	26.594	0.064	0.060	26.593	0.084	0.087
Cu <sup>18+</sup>	35.422	0.062	0.058	35.419	0.080	0.082
Zn <sup>19+</sup>	38.641	0.061	0.058	38.640	0.079	0.081
Br <sup>24+</sup>	56.831	0.058	0.055	56.826	0.074	0.076
Kr <sup>25+</sup>	60.885	0.057	0.055	60.882	0.073	0.076

$2p^6 3s^2 S^e \rightarrow 2p^5 3s^2 2p^2$	HF			CI		
	$\Delta E$	$f_L$	$f_V$	$\Delta E$	$f_L$	$f_V$
No J=0.5 → 0.5 J=0.5 → 1.5	1.273	0.015	0.011	1.273	0.015	0.013
	1.268	0.029	0.022	1.268	0.031	0.026
Mg <sup>+</sup>	1.976	0.022	0.018	1.976	0.024	0.023
	1.967	0.044	0.035	1.967	0.049	0.045
Al <sup>2+</sup>	2.829	0.025	0.021	2.829	0.028	0.027
	2.815	0.049	0.045	2.814	0.057	0.055
Si <sup>3+</sup>	3.827	0.026	0.022	3.825	0.030	0.030
	3.806	0.051	0.044	3.804	0.061	0.060
P <sup>4+</sup>	4.967	0.026	0.023	4.967	0.028	0.027
	4.937	0.051	0.045	4.937	0.056	0.055
S <sup>5+</sup>	6.251	0.026	0.023	6.251	0.032	0.032
	6.208	0.051	0.045	6.208	0.063	0.063
Cl <sup>6+</sup>	7.676	0.025	0.022	7.676	0.032	0.032
	7.619	0.050	0.045	7.619	0.063	0.064
Ar <sup>7+</sup>	9.245	0.025	0.022	9.245	0.032	0.031
	9.169	0.049	0.045	9.168	0.063	0.063
K <sup>8+</sup>	10.957	0.024	0.022	10.956	0.032	0.031
	10.857	0.048	0.044	10.856	0.063	0.063
Ca <sup>9+</sup>	12.813	0.024	0.023	12.813	0.032	0.031
	12.686	0.048	0.043	12.686	0.063	0.062
Sc <sup>10+</sup>	14.812	0.024	0.021	14.814	0.031	0.030
	14.651	0.047	0.043	14.652	0.062	0.061
Ti <sup>11+</sup>	16.956	0.023	0.021	16.959	0.031	0.028
	16.755	0.046	0.042	16.758	0.061	0.059
Fe <sup>15+</sup> <sub>e</sub>	26.989	0.022	0.019	27.010	0.031	0.028
	26.551	0.043	0.040	26.572	0.059	0.056
Cu <sup>18+</sup>	36.065	0.021	0.019	36.115	0.029	0.026
	35.344	0.041	0.039	35.396	0.057	0.053
Zn <sup>19+</sup>	39.387	0.021	0.019	39.450	0.029	0.026
	38.547	0.041	0.038	38.612	0.057	0.052
Br <sup>24+</sup>	58.290	0.019	0.018	58.507	0.029	0.024
	56.618	0.039	0.037	56.838	0.055	0.047
Kr <sup>25+</sup>	62.535	0.019	0.018	62.813	0.028	0.023
	60.640	0.038	0.037	60.918	0.054	0.046

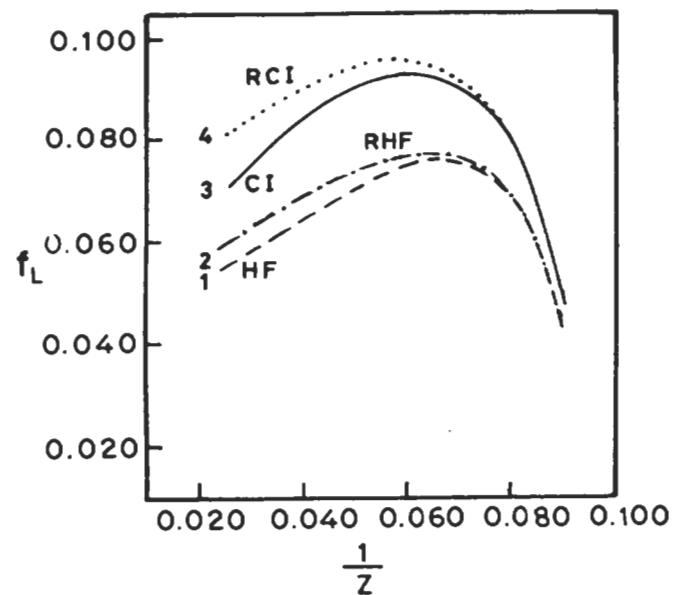


Figure 1. Theoretical oscillator strengths ( $f_L$ ) as a function of  $1/Z$  for the resonance excitation  $1s^2 2s^2 2p^6 3s^2 S_j^o \rightarrow 1s^2 2s^2 2p^5 3s^2 P_j^o$ , transition in Na,  $Mg^+$ ,  $Al^{2+}$ ,  $Si^{3+}$ ,  $P^{4+}$ ,  $S^{5+}$ ,  $Cl^{6+}$ ,  $Ar^{7+}$ ,  $K^{8+}$ ,  $Ca^{9+}$ ,  $Sc^{10+}$ ,  $Ti^{11+}$ ,  $Fe^{15+}$ ,  $Cu^{18+}$ ,  $Zn^{19+}$ ,  $Br^{24+}$  and  $Kr^{25+}$  ions of the sodium isoelectronic sequence. Curve 1, Hartree-Fock (HF); Curve 2, Relativistic Hartree-Fock (RHF); Curve 3, Configuration-interaction (CI); Curve 4, Relativistic configuration-interaction (RCI).