

## Multiconfiguration Hartree–Fock calculations in $\text{Cr}^{5+}$ , $\text{Mn}^{6+}$ and $\text{Fe}^{7+}$

S N TIWARY, P KUMAR and R P ROY

Department of Physics, L.S. College, BRA Bihar University, Muzaffarpur 842001, India

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**Abstract.** The multiconfiguration Hartree–Fock (MCHF) method is used to calculate the excitation energies and oscillator strengths, of both the length ( $f_L$ ) and velocity ( $f_v$ ) forms, for  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 D \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^5 3d^2 \ ^2P^0, \ ^2D^0, \ ^2F^0$  transitions in  $\text{Cr}^{5+}$ ,  $\text{Mn}^{6+}$  and  $\text{Fe}^{7+}$  ions of the potassium isoelectronic sequence. Comparison is made with our earlier relevant results obtained by employing the configuration interaction (CI) method which is closely related to the MCHF method. Our present investigation demonstrates that the MCHF method is more accurate than the CI method in all ions of present consideration.

**Keywords.** Multiconfiguration Hartree–Fock; configuration interaction; excitation energies; oscillator strengths.

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### 1. Introduction

The study of ionized atoms has attracted special interest in modern atomic physics and other related fields such as astrophysics and plasma physics. Lines emitted from ionized atoms such as the first transition elements immersed in solar, stellar and laboratory plasmas have been playing a very important role in modelling these matters [1]. Development of experimental techniques such as electron-beam ion sources or ion accelerators has helped to study the spectroscopic properties and scattering cross-sections of various ion-collision processes with high accuracy [2]. In the analysis of the spectra observed in these experiments, accurate level structures and optical oscillator strengths for an atom in various charge states are required.

There has been growing interest in the inner-shell excitation of alkali metal atoms and alkali-like ions from both experimentalists [3–5] and theorists [6–16], because inner-shell excitation may lead to autoionization which has an important role in explaining the structure observed in the integrated ionization cross-section curves for electron impact. Consequently, the reliable theoretical calculation of position of the autoionizing level and hence the theoretical estimate of the excitation threshold, which is used in the calculation of the oscillator strengths, of both the length and velocity forms, is of special interest. The oscillator strength information is important to know the electronic probabilities for both valence and inner-shell excitation and ionization processes in many areas of application including plasmas, fusion research, lithography astronomy, astrophysics, space chemistry and physics, laser development, radiation

biology, dosimetry, health physics and radiation protection. Such information is also a crucial requirement for the development and evaluation of quantum-mechanical theoretical methods and for the modelling procedures used for various phenomenon involving electronic transitions induced by energetic radiation [17].

Recently, Tiwary [18] calculated the excitation energies and oscillator strengths, of both the length ( $f_L$ ) and velocity ( $f_V$ ) forms, for the inner-shell excitation  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 \ ^2D^e \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^5 3d^2 \ ^2P^0, \ ^2D^0 \ ^2F^0$  transitions using the configuration interaction (CI) method. There is a considerable discrepancy between the CI  $f_L$  and  $f_V$  which suggests further detailed calculation. In general, the multiconfiguration Hartree–Fock (MCHF) method yields better results than the CI method. The MCHF method has, over the years, been refined and generalized to treat a large variety of systems and it is also a very efficient method for treating correlation.

To test the accuracy of the MCHF method, we have performed the calculation for the inner-shell excitation  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 \ ^2D^e \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^5 3d^2 \ ^2P^0, \ ^2D^0 \ ^2F^0$  transitions, employing the same configurations as in our earlier CI method, using the MCHF method.

## 2. Method

The most widely used techniques to study the electron correlation in atoms, molecules and ions are the multiconfiguration Hartree–Fock (MCHF) method [19] and the closely related, but in general less accurate, configuration interaction (CI) method [20].

The basic assumption of both methods is that the atom is represented by an atomic state function (ASF),  $\Psi(\gamma LS)$ , which is a linear combination of configuration state function (CSF),  $\Phi(\alpha_i LS)$

$$\Psi(\gamma LS) = \sum_{i=1}^{NCSF} c_i \phi_i(\alpha_i LS). \quad (1)$$

Each CSF is constructed as a coupled, antisymmetric sum of products of one particle functions,  $\phi(nl)$ , called spin-orbitals,

$$\phi(nl) = \frac{1}{r} P_{nl}(r) Y_m^l(\theta\phi\chi_m) \quad (2)$$

according to the standard notations.

Equations (1) and (2) have two sets of unknowns, the  $c_i$  coefficients and the radial functions  $P_{nl}(r)$ . The difference between the MC and CI methods is now basically just the way the last set is obtained. In an MC calculation, the variational principle is used to derive a set of coupled integro-differential (ID) equations, one for each radial functions, while coefficients are obtained by solving a secular equation of the form

$$(H - EI)C = 0 \quad (3)$$

where the matrix  $H$  has the elements

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle \quad (4)$$

where  $H$  is the Hamiltonian operator.

**Table 1.** Important configurations used in the present calculation.

${}^2D$	${}^2P^0, {}^2D^0, {}^2F^0$
$3s^23p^63d$	$3s^23p^53d^2$
$3s^23p^64d$	$3s^23p^6np; n = 4, 7$
$3s^23p^43d^3$	$3s^23p^6nf; n = 4, 7$
$3s3p^63d^2$	$3s^23p^53d\ ns; n = 4, 5$
$3s^23p^53d4f$	$3s^23p^53d4d$
$3s^23p^53d5f$	$3s^23p^33d^4$
	$3s3p^53d^3$
	$3s^23p^43d^24f$
	$3s^2(3p^43d^2) {}^1S\ np; n = 4, 7$
	$3s^23p^54f\ np; n = 4, 7$
	$3s3p^63d\ np; n = 4, 7$

In CI calculations, on the other hand, the radial functions are predetermined and also the secular equation is solved for the coefficients.

We have used a nonrelativistic notation throughout, but the same discussion applies to a relativistic case. The main difference is that the good quantum number is a total  $J$ , and the ASF and CSF should be labeled  $\Psi(\gamma J)$  and  $\Phi(\alpha_i J)$ , respectively.

Once the MCHF initial state wavefunction  $\Psi_i$  and the final state wavefunction  $\Psi_f$  are determined, with energies  $E_i$  and  $E_f$  respectively, they can be used to obtain absorption oscillator strengths. We have two equivalent forms for the absorption oscillator strengths.

The length and velocity forms of the electric dipole oscillator strengths, for transition between initial and final states  $\Psi_i$  and  $\Psi_f$  respectively (assuming  $e = h = m = 1$ ) are

$$F_L = \frac{2\Delta E}{3g_i} \sum \left| \left\langle \Psi \left| \sum_{k=1}^N r_k \right| \Psi_i \right\rangle \right|^2 \quad (5)$$

$$f_v = \frac{2}{3\Delta E} \frac{1}{g_i} \sum \left| \left\langle \Psi \left| \sum_{k=1}^N p_k \right| \Psi_f \right\rangle \right|^2. \quad (6)$$

Important configurations used in the present MCHF calculations are given in table 1 for  ${}^2D^e$ ,  ${}^2P^0$ ,  ${}^2D^0$  and  ${}^2F^0$  states.

### 3. Results and discussion

Tables 2–4 display the Hartree–Fock (HF), our present multi-configuration Hartree–Fock (MCHF) and our earlier configuration interaction (CI), excitation energies ( $\Delta E$ ) as well as optical oscillator strengths (OOS), of both the length ( $f_L$ ) and velocity ( $f_v$ ) forms, of the inner-shell excitation  $1s^22s^22p^63s^23p^63d\ {}^2D^e \rightarrow 1s^22s^22p^63s^23p^53d^2\ {}^2P^0$ ,  ${}^2D^0$  and  ${}^2F^0$  transitions in  $Cr^{5+}$ ,  $Mn^{6+}$  and  $Fe^{7+}$  ions of the potassium iso-electronic sequence.

**Table 2.** Excitation energies ( $\Delta E$ ) and optical oscillator strengths (OOS), of both the length ( $f_L$ ) and velocity ( $f_V$ ) forms, of the inner-shell excitation  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 \ ^2D^e \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^5 3d^2 \ ^2P^o$  transition in  $Cr^{5+}$ ,  $Mn^{6+}$ ,  $Fe^{7+}$  ions of the potassium iso-electronic sequence.

	$Cr^{5+}$			$Mn^{6+}$			$Fe^{7+}$		
	$\Delta E^{a)}$	$f_L$	$f_V$	$\Delta E$	$f_L$	$f_V$	$\Delta E$	$f_L$	$f_V$
HF	( <sup>3</sup> P)	0.942	0.499	2.551	0.867	0.464	2.762	0.829	0.484
	( <sup>1</sup> S)	1.944	0.611 <sup>-5b)</sup>	0.465 <sup>-5</sup>	0.324 <sup>-4</sup>	0.246 <sup>-4</sup>	2.331	0.177 <sup>-4</sup>	0.145 <sup>-4</sup>
	( <sup>1</sup> D)	1.644	0.133 <sup>-2</sup>	0.142 <sup>-2</sup>	1.180	0.122 <sup>-2</sup>	1.981	0.119 <sup>-2</sup>	0.135 <sup>-2</sup>
MCHF	( <sup>3</sup> P)	2.236	0.434	0.438	2.469	0.651	2.705	0.560	0.583
	( <sup>1</sup> S)	1.918	0.468 <sup>-3</sup>	0.759	2.127	0.117 <sup>-2</sup>	2.318	0.579 <sup>-2</sup>	0.513 <sup>-2</sup>
	( <sup>1</sup> D)	1.624	0.486 <sup>-3</sup>	0.391 <sup>-4</sup>	1.758	0.210 <sup>-1</sup>	1.954	0.314 <sup>-2</sup>	0.178 <sup>-2</sup>
CI	( <sup>3</sup> P)	2.245	0.436	0.490	2.488	0.653	2.714	0.562	0.654
	( <sup>1</sup> S)	1.939	0.469 <sup>-3</sup>	0.994 <sup>-3</sup>	2.139	0.118 <sup>-2</sup>	2.329	0.580 <sup>-2</sup>	0.471 <sup>-2</sup>
	( <sup>1</sup> D)	1.641	0.488 <sup>-3</sup>	0.282 <sup>-4</sup>	1.799	0.211 <sup>-1</sup>	1.971	0.317 <sup>-2</sup>	0.181 <sup>-2</sup>

<sup>a)</sup>Excitation threshold  $\Delta E$  is in atomic unit (au). <sup>b)</sup>Abbreviations in table: 0.611<sup>-5</sup> means 0.611  $\times 10^{-5}$ .

**Table 3.** Excitation energies ( $\Delta E$ ) and optical oscillator strengths (OOS), of both the length ( $f_L$ ) and velocity ( $f_V$ ) forms, of the inner-shell excitation  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 D^e \rightarrow 1s^2 2s^2 2p^6 3s^2 3d^2 2D^0$  transition in  $Cr^{5+}$ ,  $Mn^{6+}$ ,  $Fe^{7+}$  ions of the potassium iso-electronic sequence.

	$Cr^{5+}$				$Mn^{6+}$				$Fe^{7+}$			
	$\Delta E^a$	$f_L$	$f_V$		$\Delta E$	$f_L$	$f_V$		$\Delta E$	$f_L$	$f_V$	
$3p^5 3d^2$												
HF	$(^3F)$ 2.383	1.947	0.987	2.606	1.789	0.918	2.821	1.709	0.957	2.821	1.709	0.957
	$(^3P)$ 1.808	0.106 <sup>-3b)</sup>	0.936 <sup>-4</sup>	1.989	0.886 <sup>-4</sup>	0.780 <sup>-4</sup>	2.171	0.976 <sup>-4</sup>	0.922 <sup>-4</sup>	2.171	0.976 <sup>-4</sup>	0.922 <sup>-4</sup>
	$(^1D)$ 1.599	0.704 <sup>-3</sup>	0.793 <sup>-3</sup>	1.760	0.724 <sup>-3</sup>	0.815 <sup>-3</sup>	1.929	0.683 <sup>-3</sup>	0.817 <sup>-3</sup>	1.929	0.683 <sup>-3</sup>	0.817 <sup>-3</sup>
MCHF	$(^3F)$ 2.307	1.616	1.322	2.534	1.463	1.190	2.749	1.357	1.159	2.749	1.357	1.159
	$(^3P)$ 1.819	0.552 <sup>-3</sup>	0.398 <sup>-3</sup>	2.013	0.561 <sup>-3</sup>	0.439 <sup>-3</sup>	2.183	0.474 <sup>-3</sup>	0.318 <sup>-3</sup>	2.183	0.474 <sup>-3</sup>	0.318 <sup>-3</sup>
	$(^1D)$ 1.625	0.251 <sup>-2</sup>	0.273 <sup>-4</sup>	1.805	0.2553 <sup>-2</sup>	0.667 <sup>-4</sup>	1.968	0.241 <sup>-2</sup>	0.503 <sup>-4</sup>	1.968	0.241 <sup>-2</sup>	0.503 <sup>-4</sup>
CI	$(^3F)$ 2.315	1.618	1.324	2.541	1.464	1.191	2.763	1.359	1.156	2.763	1.359	1.156
	$(^3P)$ 1.837	0.554 <sup>-3</sup>	0.396 <sup>-3</sup>	2.021	0.563 <sup>-3</sup>	0.434 <sup>-3</sup>	2.200	0.475 <sup>-3</sup>	0.315 <sup>-3</sup>	2.200	0.475 <sup>-3</sup>	0.315 <sup>-3</sup>
	$(^1D)$ 1.643	0.252 <sup>-2</sup>	0.276 <sup>-4</sup>	1.808	0.255 <sup>-2</sup>	0.669 <sup>-4</sup>	1.971	0.242 <sup>-2</sup>	0.507 <sup>-4</sup>	1.971	0.242 <sup>-2</sup>	0.507 <sup>-4</sup>

<sup>a)</sup>Excitation threshold  $\Delta E$  is in atomic unit (au). <sup>b)</sup>Abbreviations in table: 0.106<sup>-3</sup> means 0.106 × 10<sup>-3</sup>.

**Table 4.** Excitation energies ( $\Delta E$ ) and optical oscillator strengths (OOS), of both the length ( $f_L$ ) and velocity ( $f_V$ ) forms, of the inner-shell excitation  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 D^e \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^5 3d^2 {}^2F^0$  transition in  $Cr^{5+}$ ,  $Mn^{6+}$ ,  $Fe^{7+}$  ions of the potassium iso-electronic sequence.

$3p^5 3d^2$		$Cr^{5+}$			$Mn^{6+}$			$Fe^{7+}$		
		$\Delta E^a$	$f_L$	$f_V$	$\Delta E$	$f_L$	$f_V$	$\Delta E$	$f_L$	$f_V$
HF	( ${}^3F$ )	2.128	1.429	0.908	2.333	1.317	0.843	2.533	1.261	0.875
	( ${}^1D$ )	1.689	0.029	0.029	1.859	0.028	0.028	2.034	0.027	0.029
	( ${}^1G$ )	1.607	0.012	0.013	1.769	0.011	0.012	1.939	0.011	0.013
MCHF	( ${}^3F$ )	2.048	0.772	0.773	2.259	0.786	0.779	2.458	0.756	0.756
	( ${}^1D$ )	1.705	0.040	0.045	1.873	0.040	0.043	2.037	0.036	0.039
	( ${}^1G$ )	1.629	0.010	0.012	1.806	0.008	0.010	1.960	0.008	0.009
CI	( ${}^3F$ )	2.063	0.774	0.775	2.274	0.787	0.758	2.477	0.757	0.758
	( ${}^1D$ )	1.708	0.041	0.048	1.881	0.040	0.044	2.051	0.037	0.042
	( ${}^1G$ )	1.642	0.010	0.013	1.808	0.009	0.011	1.971	0.008	0.011

<sup>a)</sup>Excitation threshold  $\Delta E$  is in atomic unit (au).

Tables 2–4 have several important features. First, we notice that the HF  $f_L$  and  $f_V$  differ by about a factor of two which indicates that the HF description is not adequate for the determination of the oscillator strengths of the complex inner-shell excitation. Second, our earlier CI calculation has reduced the disagreement substantially but considerable discrepancy exists. This suggests further accurate calculation. Third, our present MCHF  $f_L$  and  $f_V$  are in agreement better than our earlier CI  $f_L$  and  $f_V$  which shows that the MCHF method is more accurate than CI method. However, it is also clear from tables 2–4 that there is disagreement between the MCHF  $f_L$  and  $f_V$ . This may be probably due to the neglect of the effect of relativity. Finally, our extensive investigation shows that in order to obtain the excellent agreement between  $f_L$  and  $f_V$ , it is indispensable to include the correlation and relativity simultaneously in heavy ions.

#### 4. Conclusion

We have demonstrated that (1) the inclusion of electron correlation is necessary but not sufficient for obtaining the accurate energy levels and oscillator strengths, (2) the incorporation of relativity is indispensable for reliable results, (3) the MCHF method is more accurate than the CI method, and (4) reliable theoretical predictions of energy levels and oscillator strengths require method that accounts for electron correlation, relativistic and quantum electrodynamic corrections simultaneously. We hope that our present theoretical investigation will stimulate interest for more accurate theoretical predictions and reliable experimental observations.

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