Isoelectronic Changes in the Behaviour of Nonrelativistic Electron Density Near the Nucleus in Free Ions

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It is shown numerically that the nonrelativistic Hartree-Fock-Slater total electronic density near the nucleus in $3d^5$, $4d^5$ and $5d^5$ ions can be approximately represented as $A_N Z^3 \exp(-2Zr)$ where A_N is a constant depending on the number of electrons.

The variation of the total electron density, $\varrho(r)$, near the nucleus in free atoms and ions is a relatively little studied property. It has been shown [1] that $\varrho(r)$ calculated within the spin-restricted approximation has a functional dependence near the nucleus as given by

$$\varrho(r) = \varrho(0) \exp(-2Zr), \tag{1}$$

where Z is the atomic number. This relationship has been tested [2] using Hartree-Fock (HF) wave functions for some light atoms. In this note we propose that within an isoelectronic series containing N electrons,

$$\varrho'(r) \cong A_N Z^3 \exp(-2Zr), \tag{2}$$

where $\varrho'(r)$ is the one electron density based on nonrelativistic restricted Hartree-Fock-Slater (HFS) wave functions, and A_N is a constant characteristic of the isoelectronic series. Equation (2) is based on the assumption that $\varrho'(0)$ is approximately hydrogenic in character. We have studied the isoelectronic changes in $\varrho'(0)$ for the following three series of positive ions in $3d^5$, $4d^5$, and $5d^5$ electronic configuration, respectively: Cr^+, Mn^{2+}, Fe^{3+}, Co^{4+}, Ni^{5+}, Cu^{6+}; Mo^+, Tc^{2+}, Ru^{3+}, Rh^{4+}, Pd^{5+}, Ag^{6+}; W^+, Re^{2+}, Os^{3+}, Ir^{4+}, Pt^{5+}, Au^{6+}.

The HFS radial wave functions, $R_{nl}(r)$, have been generated over a 441 point mesh using a modified Herman-Skillman program [3]. The radial wave functions corresponding to the various s-orbitals are expressed as

$$R_{ns}(r) = \sum_{i=0}^{3} a_{ni} r^i \tag{3}$$

at the first four points near the nucleus, and $R_{ns}(0)$ values have been obtained by the extrapolation $r \to 0$. Finally, $\varrho'(0)$ has been calculated according to

$$\varrho'(0) = \frac{1}{2\pi} \sum_{ns} R_{ns}^2(0). \tag{4}$$

Our results of $\varrho'(0)$ along with the shellwise contribution, $\varrho_{ns}'(0)$, are presented in Table 1. The values of $\varrho'(0)/Z^3$ are given in the last column. The

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Table 1. The total s-electron density, $\varrho(0)$, for the Fe^{3+}, Ru^{3+} and Os^{3+} like ions calculated using HFS wave functions. The hydrogen-like behaviour of $\varrho(0)$ is illustrated in the last column.

Ion	Z	$\varrho_{1s}(0)$	$\varrho_{2s}(0)$	$\varrho_{3s}(0)$	$\varrho_{4s}(0)$	$\varrho_{5s}(0)$	$\varrho(0)$	$\varrho(0)/Z^3$
Cr^+	24	8507.63	766.02	107.88			9381.53	0.68
Mn^{2+}	25	9626.76	877.08	126.78			10630.62	0.68
Fe^{3+}	26	10839.92	998.42	148.58			11986.92	0.68
Co^{4+}	27	12150.72	1130.63	173.20			13454.55	0.68
Ni^{5+}	28	13563.52	1274.07	200.83			15038.42	0.69
Cu^{6+}	29	15082.20	1429.36	231.54			16743.11	0.69
Mo^+	42	46173.73	4701.73	839.89	143.95		51859.30	0.70
Tc^{2+}	43	49570.70	5067.46	916.32	163.08		55717.57	0.70
Ru^{3+}	44	53131.34	5451.95	997.42	184.34		59765.01	0.70
Rh^{4+}	45	56859.39	5855.69	1083.47	207.50		64006.05	0.70
Pd^{5+}	46	60756.70	6278.97	1174.50	232.72		68442.89	0.70
Ag^{6+}	47	64828.88	6722.37	1270.66	258.38		73080.29	0.70
W^+	74	254617.88	28051.96	6200.14	1500.75	263.05	290633.77	0.72
Re^{2+}	75	265118.06	29251.41	6486.28	1579.28	287.28	302722.43	0.72
Os^{3+}	76	275907.07	30485.64	6781.37	1661.16	313.68	315148.91	0.72
Ir^{4+}	77	286981.76	31753.10	7085.30	1746.55	342.16	327908.87	0.72
Pt^{5+}	78	298350.62	33056.051	7398.24	1835.21	372.60	341012.72	0.72
Au^{6+}	79	310016.26	34394.11	7720.31	1927.44	404.75	354462.87	0.72

results suggest that the value of A_N in Eq. (2) is given by 0.68, 0.70 and 0.72, respectively, for the $3d^5$, $4d^5$ and $5d^5$ isoelectronic series. We note here that the relativistic effects are important, specially for the $5d^5$ series. However the fact that a simple approximate relationship such as Eq. (2) can be written for the isoelectronic variation of $\varrho'(r)$ near the nucleus is worth noticing.

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