Isoelectronic Changes in the Core Radius of Fe^{3+} and Ru^{3+} Like Ions

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Isoelectronic changes in the core radius r_m, defined as the last minimum in the total radial charge density distribution function $4\pi r^2 \varrho(r)$, have been computed for Fe^{3+} and Ru^{3+} like ions using Hartree-Fock-Slater wave functions. It is found that a linear relationship $r_m^{-1} = A' Z + B'$ holds good within each series. An attempt is made to justify this empirical relationship.

Politzer and Parr [1] have shown that the position of the outermost minimum in the radial density funktion, $4\pi r^2 \varrho(r)$, based on Hartree-Fock (HF) wave functions can be used to define a core radius, r_m, of atoms and molecules. In this note we report that the isoelectronic changes in r_m^{-1} can be described empirically as

$$r_m^{-1} = A' Z + B', \tag{1}$$

where A' and B' are constants and Z denotes the atomic number. (1) can be justified if it is assumed that the changes in the values of $\langle 1/r \rangle$ within a given isoelectronic series bring about a proportional change in r_m^{-1}, see (4).

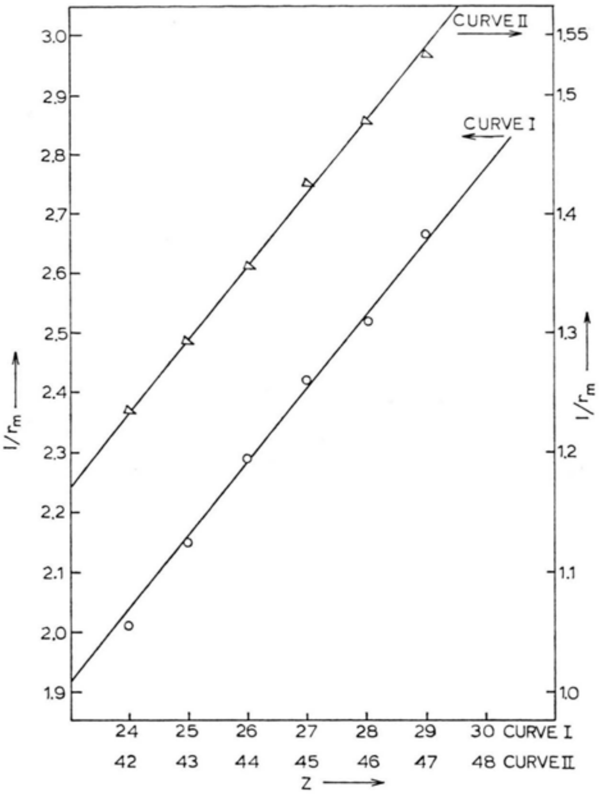

Fig. 1. Variation of the inverse core radius (in a. u.) with the nuclear charge within 3 d^5 and 4 d^5 isoelectronic series, shown by curve I and II, respectively.

Table 1. Comparison of r_m^{-1}, obtained from the wave functions, r_m^{-1} (w. f.), with the least squares fitted values from Equation (3). The predicted values are shown as starred. All values are given in a. u.

Ion	Z	r_m^{-1} (w. f.)	r_m^{-1} Eq. (1)
Cr^+	24	2.0120	2.0378*
Mn^{2+}	25	2.1505	2.1611
Fe^{3+}	26	2.2936	2.2844
Co^{4+}	27	2.4213	2.4077
Ni^{5+}	28	2.5189	2.5310
Cu^{6+}	29	2.6666	2.6543*
Coeff. $A' = +\,0.1233$, $B' = -0.9211$			
Mo^+	42	1.2346	1.2335*
Tc^{2+}	43	1.2937	1.2953
Ru^{3+}	44	1.3568	1.3571
Rh^{4+}	45	1.4245	1.4189
Pd^{5+}	46	1.4771	1.4807
Ag^{6+}	47	1.5314	1.5425*
Coeff. $A' = 0.0618$, $B' = 1.3616$			

According to the well known Z-expansion [2] of the total HF energy, we write,

$$E = A Z^2 + B Z + C + D/Z + \dots \tag{2}$$

where $A, B, \dots$ are constants. Using the first three terms in (2), and applying the Hellman-Feynman theorem [3] we obtain

$$\delta E/\delta Z = V_{neZ}/Z = 2 A Z + B \dots, \tag{3}$$

where V_{neZ} gives the total electron-nuclear attraction energy for an atom (or ion) with atomic number Z. We assume here as a working hypothesis that changes in $\varrho(r)$ would proportional change r_m and write

$$\int_0^\infty \varrho(r)\, r\, \mathrm{d}r = \frac{V_{neZ}}{Z}\, \alpha\, r_m^{-1} \dots \tag{4}$$

(4) and (3) lead to (1). In order to test the

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validity of (1) we have used Hartree-Fock-Slater (HFS) wave functions [4] to calculate r_m for the following isoelectronic series of ions: Mn^{2+}, Fe^{3+}, Co^{4+}, Ni^{5+}, and Tc^{2+}, Ru^{3+}, Rh^{4+}, and Pd^{5+}; in (Ar) $3\,d^5$ and (Kr) $4\,d^5$ electronic configuration, respectively. In Fig. 1 we have plotted r_m^{-1} vs Z for $3\,d^5$ and $4\,d^5$ series. A linear variation is obtained. In Table 1, we have presented the numerical values of r_m along with the least squares fitted estimates of A' and B'. In both cases the correlation factor is 0.99, which shows that the linear fittings are quite good. We have used (1) to predict r_m^{-1} in the cases of Cr^+, Cu^{6+} and Mo^+, Ag^{6+} in the two series, respectively. These values are found to be in good agreement with r_m^{-1} calculated directly using HFS wave functions. The present calculations show that (1) and (4) are good approximations for the isoelectronic changes in r_m.

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