

Isoelectronic Changes in the Core Radius of Fe³⁺ and Ru³⁺ 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 Fe³⁺ and Ru³⁺ 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).

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

$$E = AZ^2 + BZ + C + D/Z + \dots \tag{2}$$

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

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

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

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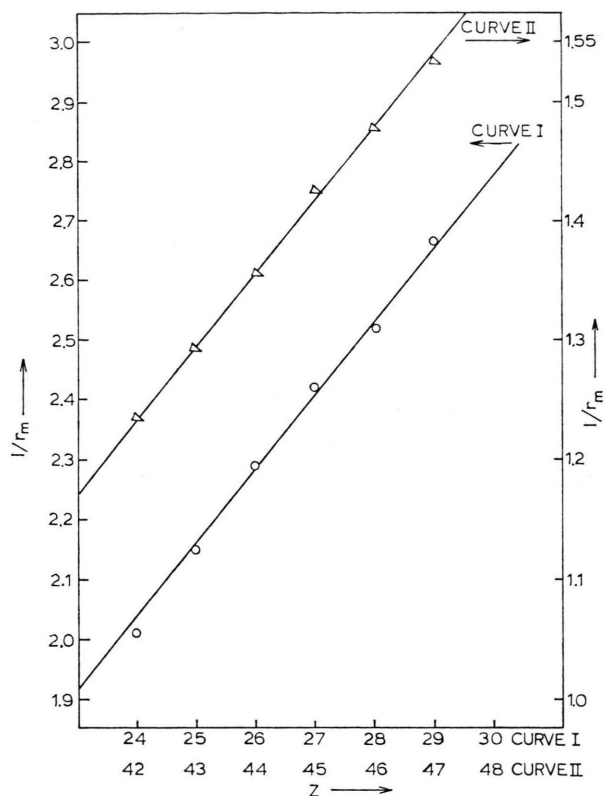


Fig. 1. Variation of the inverse core radius (in a.u.) with the nuclear charge within 3 d⁵ and 4 d⁵ isoelectronic series, shown by curve I and II, respectively.

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. $A' = 0.0618$, $B' = 1.3616$			

write

$$\int_0^\infty \varrho(r) r dr = \frac{V_{neZ}}{Z} \propto r_m^{-1} \dots \tag{4}$$

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



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) $3d^5$ and (Kr) $4d^5$ electronic configuration, respectively. In Fig. 1 we have plotted r_m^{-1} vs Z for $3d^5$ and $4d^5$ 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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