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Variation of core-electron contributions to Mössbauer isomer shift with ionic size

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Using nonrelativistic Hartree-Fock-Slater wave functions, the core s-electron densities at the nucleus have been calculated for several nd^5 ($n = 3, 4, 5$) ions. The results show a significant variation of core densities with the ion size.

I. INTRODUCTION

The purpose of this paper is to calculate the change in core s-electron density $\rho_c(0)$ at the nucleus with the ionic size. Such a theoretical study is of some interest since the shellwise contributions to the total contact density can now be measured in conversion-electron-spectroscopy experiments.[1] Apart from this, the calibration of Mössbauer isomer shifts based on free-ion calculations[2] generally assume that the difference in core contributions of two Mössbauer systems can always be neglected. The present calculations predict that this is not generally valid. In Sec. II we outline the details of our calculations. In Sec. III our results are presented with conclusions.

II. CALCULATIONS

We used the nonrelativistic Hartree-Fock-Slater (HFS) wave functions[3] to calculate $\rho_c(0)$ for the following nd^5 ($n = 3, 4, 5$) systems: Cr^+, Mn^{2+}, Fe^{3+}, Co^{4+}, Ni^{5+}, Cu^{6+}; Mo^+, Tc^{2+}, Ru^{3+}, Rh^{4+}, Pd^{5+}, Ag^{6+}; and W^+, Re^{2+}, Os^{3+}, Ir^{4+}, Pt^{5+}, Au^{6+}, respectively. $\rho_c(0)$ values have been obtained according to

$$\rho_c(0) = \sum_{n}^{\text{core}} \psi_{ns}^2(0) \qquad (1)$$

$\psi_{ns}^2(0)$ values have been obtained by expanding the radial wave functions at the first four points near the nucleus in terms of the appropriate polynomial and

TABLE I. Shellwise contributions to the total electron density at the nucleus, and the position of outermost maxima in the radial density distribution function for $3d^5$, $4d^5$, and $5d^5$ ions. All the results are given in a.u.

Ion	$\psi_{1s}^2(0)$	$\psi_{2s}^2(0)$	$\psi_{3s}^2(0)$	$\psi_{4s}^2(0)$	$\psi_{5s}^2(0)$	$\sum_{ns} \psi_{ns}^2(0)$	ρ_m
Cr^+	8 507.63	766.02	107.88			9 381.53	0.767
Mn^{2+}	8 626.76	877.08	126.78			10 630.62	0.721
Fe^{3+}	10 839.92	998.42	148.58			11 986.92	0.675
Co^{4+}	12 150.72	1 130.63	173.20			13 454.55	0.643
Ni^{5+}	13 563.52	1 274.07	200.83			15 038.42	0.600
Cu^{6+}	15 082.20	1 429.36	231.54			16 743.11	0.571
Mo^+	46 173.73	4 701.73	839.89	143.95		51 859.30	1.014
Tc^{2+}	49 570.70	5 067.46	916.32	163.09		55 717.57	0.986
Ru^{3+}	53 131.34	5 451.95	997.42	184.34		59 765.01	0.938
Rh^{4+}	56 859.39	5 855.69	1 083.47	207.50		64 006.05	0.891
Pd^{5+}	60 756.70	6 278.97	1 174.50	232.72		68 442.89	0.865
Ag^{6+}	64 828.88	6 722.37	1 270.66	258.38		73 080.29	0.819
W^+	254 617.88	28 051.96	6 200.14	1 500.75	263.05	290 633.77	
Re^{2+}	265 118.06	29 251.41	6 486.41	1 579.28	287.28	302 722.43	
Os^{3+}	275 907.07	30 485.64	6 781.37	1 661.16	313.68	315 148.91	
Ir^{4+}	286 981.76	31 753.10	7 085.30	1 746.55	342.16	327 908.87	
Pt^{5+}	298 350.62	33 056.05	7 398.24	1 835.21	372.60	341 012.717	
Au^{6+}	310 016.26	34 394.11	7 720.31	1 927.44	404.76	354 462.87	

solving the simultaneous equations by Crouts method.

The outermost maximum ρ_m in the radial charge-density distribution function has been chosen as the size parameter within an isoelectronic series

$$\rho_m = \sum_{nl} \int \psi_{nl}^2 r^2 \, d\Omega \quad . \tag{2}$$

We note here that such a choice of ρ_m has been used earlier[3,4] in connection with the variation of multipole polarizabilities and shielding factors with the ionic size.

III. RESULTS AND CONCLUSIONS

Our results are presented in Table I. In the case of $5d^5$ ions, ρ_m values could not be located accurately owing to a flat distribution function in the outer regions. Our calculations show that $\rho_c(0)$ is inversely proportional to ρ_m. The variation can be satisfactorily represented by

$$\rho_c(0) = A(1/\rho_m) + B \quad . \tag{3}$$

The least-squares-fitting values of A and B are obtained as 15 789 and −11 251 for the $3d^5$ series, and 91 541 and −37 890 for the $4d^5$ series, respectively. It is estimated that a ~10% change in ρ_m for Fe^{3+} would alter the value of $\rho_c(0)$ by ~20% in the opposite sense. Similar results are also obtained in the cases of Ru^{3+} and Os^{3+} ions. We therefore suggest that in highly ionic systems where some independent experiments such as single crystal x-ray data indicate a substantial change in ρ_m, it is not advisable to neglect the difference in $\rho_c(0)$ between the two Mössbauer systems.

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