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Relativistic electron densities and isomer shifts in transition-metal ions*

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Relative isomer shifts of $3d$, $4d$, and $5d$ ions are obtained by calculation of atomic electron charge densities, using numerical Hartree-Fock and multiconfiguration Dirac-Fock theory, with exact exchange, to describe the ionic systems. The relativistic calculations, for both point and finite nucleus models, are compared with results obtained from the nonrelativistic calculations augmented by one-electron relativistic corrections. The relativistic charge densities and experimental isomer shifts are employed to deduce estimates of changes in mean square nuclear radii.

I. INTRODUCTION

With the discovery of the Mössbauer effect, it was widely recognized that the measurement of isomer shifts had great potential for becoming an important tool for the study of both nuclear and electronic properties of atoms in various environments.[1,2] The isomer shift provides a measure of the product of the difference of mean-square radii of two nuclear isomers and the difference in electron density in the region of the nucleus, between two isomeric atoms in different chemical environments. Whereas these quantities are impossible to measure by themselves, isomer-shift measurements coupled with independent information about either the isomeric radii or the electronic densities provides knowledge of the other. Thus, in principle, a measurement of the isomer shift between two ions in different environments, and an accurate calculation of the electronic charge densities would allow one to deduce the change in nuclear isomeric radii. Unfortunately, the enormous difficulties involved in determining theoretically either electron or nuclear densities has left the promised potential largely unfulfilled.

In the face of the greater difficulties inherent in the state of nuclear theory, some progress has been made in this field by assuming, as a first *crude* approximation, that the electronic charge difference between several ions in different chemical environments may be ascribed to a change in ionicity.[3,4] Thus, Hartree-Fock calculations have been performed, on various charge states of an atom[5] and the resultant electron charge densities at the nucleus are then used to estimate relative isomer shifts. Implicit in this procedure is the assumption that the difference in nuclear radii is the same for the various ionic states. Using these calibrations, comparison with experimental isomer shifts then provides estimates of other effects due to the chemical environment, such as ligand bonding and electron correlations.

The isomer shift S_{AB} between a source B and an absorber A is given by the well-known expression[2,6,7]

$$S_{AB} = (2\pi c/3E_\gamma) Z e^2 [|\psi_A(0)|^2 - |\psi_B(0)|^2] \delta\langle r^2\rangle , \tag{1}$$

where E_γ is the γ-ray energy, Z is the nuclear charge, $e|\psi_A(0)|^2$ and $e|\psi_B(0)|^2$ are the electron charge densities at the nuclei of the source and the absorber, respectively, and $\delta\langle r^2\rangle$ is the change in mean-square nuclear-charge radius between isomers. For a given pair of isomers, $\delta\langle r^2\rangle$ is constant, and $|\psi_A(0)|^2 - |\psi_B(0)|^2$ measures the change in electronic charge densities as the ions are placed in different compounds. Implicit in this formulation are the assumptions that the electron density is constant over the nuclear volume and that the change in electronic state (ψ_A to ψ_B) does not affect the nuclear densities. Thus, the calculated values of S_{AB} for various charge states of the same isomers yield the dependence of isomer shift on changes in atomic electron density; the differences between measured and calculated S_{AB} allow one to deduce the additional effects of the chemical environment.

This paper reports results of a study of the relativistic effects on charge densities and isomer shifts in open-shell d-electron ions. Both nonrelativistic and relativistic electronic wave functions have been calculated for a number of $4d$ and $5d$ ions. The relativistic calculations, for both point- and finite-nucleus models, are compared with results obtained from the nonrelativistic calculations augmented by one-electron relativistic corrections. The relativistic charge densities and experimental isomer shifts are employed to deduce estimates of changes in mean-square nuclear radii.

II. HARTREE-FOCK AND DIRAC-FOCK CHARGE DENSITIES AND ISOMER SHIFTS FOR $3d$, $4d$, AND $5d$ IONS

Hartree-Fock calculations, and Dirac-Fock calculations for point-nucleus ions, and in some cases for finite-nucleus ions as well, were performed using the fully relativistic numerical self-consistent field codes of one of us (J.P.D.).[8] In each case, we calculated the ionic ground states. For the Hartree-Fock problem, this was the single-configuration Hund's-rule ground state in Russell-Saunders coupling. In the relativistic treatment, on the other hand, the single particle wave functions are eigenfunctions of the total angular momentum, but not of the separate spin and orbital angular momenta; thus, the Dirac-Fock calculations are performed in j-j coupling; however, the total wave function is not a single j-j configuration, but rather a linear combination of j-j configurations of total angular momentum $J = L + S$. Thus, the Dirac-Fock wave function formally approximates as closely as possible the (L-S) Hartree-Fock wave function.

The importance of including all relevant j-j configurations has been discussed elsewhere[8] as has the validity of the L-S coupling model even for fairly heavy ions, where relativistic corrections are important. Available calculations[9] of the effect of coupling scheme on isomer shifts show effects of up to 10%; these are small, but are not negligible. Our Dirac-Fock wave functions contain multiconfiguration weights which are varied successively to minimize the total energy. Both the Hartree-Fock and Dirac-Fock calculations are "restricted," i.e., the radial wave functions are assumed independent of the magnetic quantum numbers (m_l and m_s for Hartree-Fock; $m_j = m_l + m_s$ for Dirac-Fock). Hartree-Fock wave functions for the various ions investigated were obtained by means of the numerical self-consistent field program of Froese-Fischer.[10]

The ions on which we have performed Dirac-Fock or Dirac-Fock and Hartree-Fock calculations are (in L-S coupling formalism) given in Table I.

TABLE I. Listing of ions for which Dirac-Fock or Dirac-Fock and Hartree-Fock calculations have been performed.

Fe^{+2}	$3d^6$	(^5D)	Pd^{+2}	$4d^8$	(^3F)
Fe^{+3}	$3d^5$	(^6S)	Os^{+4}	$5d^4$	(^5D)
Fe^{+4}	$3d^4$	(^5D)	Os^{+6}	$5d^2$	(^3F)
Ru^{+2}	$4d^6$	(^5D)	Os^{+8}	$5d^0$	(^1S)
Ru^{+3}	$4d^5$	(^6S)	Ir^{+2}	$5d^7$	(^4F)
Ru^{+4}	$4d^4$	(^5D)	Ir^{+3}	$5d^6$	(^5D)
Ru^{+5}	$4d^3$	(^4F)	Ir^{+4}	$5d^5$	(^6S)
Ru^{+6}	$4d^2$	(^3F)	Ir^{+5}	$5d^4$	(^5D)
Pd^{+0}	$4d^{10}$	(^1S)	Ir^{+6}	$5d^3$	(^4F)
Pd^{+1}	$4d^9$	(^2D)	Ir^{+7}	$5d^2$	(^3F)

The atomic contributions to $|\psi_A(0)|^2$ and $|\psi_B(0)|^2$ are simply the sums of the squared densities of those orbitals having nonzero probability densities in the region of the nucleus. For the nonrelativistic (Hartree-Fock) calculations, these are the s orbitals φ_{ns}, and their contribution is thus

$$4\pi|\psi(0)|^2 = 2\sum_{ns} |\varphi_{ns}(0)|^2 , \tag{2}$$

where n is the principal quantum number. The charge density for s orbitals at the nucleus is easily obtained as the square of the first coefficient of the series expansion near the origin, i.e., by writing the radial wave function as

$$\varphi_{nl} = r^l \sum_{i=0}^{\infty} a_i^{nl} r^i \tag{3}$$

one obtains

$$4\pi|\psi(0)|^2 = 2\sum_{ns} |a_0^{ns}|^2 . \tag{4}$$

In the relativistic (Dirac-Fock) case, the large and small components are also expanded near the origin as power series of r, the distance to the origin. But here we have to distinguish between the use of a finite and a point proton-charge distribution. For the *finite nucleus* the analog of Eq. (3) is

$$\varphi_{n\kappa} = r^{|\kappa|-1} \sum_{i=0} b_i^{(P \text{ or } Q)} r^i , \tag{5}$$

where P and Q stand for the large and small component, respectively. For s and $p_{1/2}$ shells $|\kappa| = 1$ and

$$(b_0^Q)_s = (b_0^P)_{p_{1/2}} = 0 . \tag{6}$$

Equation (6) expresses the well-known fact that only the large component of s orbitals and the small component of $p_{1/2}$ orbitals have nonvanishing charge density at the origin.[11] The total charge density is thus given by

$$|\psi(0)|^2 = 2\sum_{ns} (b_0^P)^2_{ns} + 2\sum_{n'p_{1/2}} (b_0^Q)^2_{n'p_{1/2}} . \qquad (7)$$

The coefficients b_0^P and b_0^Q are calculated by the Dirac-Fock program for a nucleus of radial extent $R = 1.2A^{1/3}$ fm (and A is the atomic mass number of the dominant isotope).

If, on the other hand, one uses a *point* nucleus, there is no obvious definition of the electronic charge density because of the singularity of the s and $p_{1/2}$ Dirac one-electron wave functions near the origin,

$$\varphi_{nl} = r^{\lambda-1}\sum_{i=0}^{\infty} C_i^{(P \text{ or } Q)} r^i , \qquad (8)$$

with

$$\lambda = [1 - (Z\alpha)^2]^{1/2} , \qquad (9)$$

and α is the fine structure constant. Nevertheless, as the nonrelativistic calculations are performed using point nuclei, we should expect a consistent estimate of the relativistic effects to result from using the same nuclear potential in both calculations. To overcome the singularity difficulty just mentioned, we may define, in the relativistic case, a charge density for the point nucleus by insisting that the (electron-nucleus) interaction energies formally agree for point and finite nucleus within the nuclear radius R. Therefore, we define effective coefficients $(B_0^P)_{ns}$ and $(B_0^Q)_{n'p_{1/2}}$ by the relation

$$[(C^P)^2 + (C^Q)^2] \int_0^R \frac{r^{2\lambda}}{r}\, dr = B^2 \int_0^R \frac{r^2}{r}\, dr . \qquad (10)$$

(Here the indices have been omitted for simplicity.) One obtains

$$B^2 = C^2(R^{2\lambda-2}/\lambda) . \qquad (11)$$

From the coefficients C calculated by the Dirac-Fock program we deduced the effective B coefficients and expressed the charge density for a point nucleus in the same way as for a finite one [cf. Eq. (7)].

Table II contains, as typical examples, the charge-density differences [see Eq. (1)] for adjacent ionic states in Fe, Ru, and Ir. The wave-function superscripts refer to the charge states. Contributions to the density differences are listed shell by shell [see Eqs. (2) and (7)], and, for the Dirac-Fock calculations, the total s and $p_{1/2}$ contributions are separately evaluated. The three examples of Table I share certain features common to all the ions calculated:

(i) The contribution of the $1s$ shell to the isomer shift is always negative (antishielding). This antishielding is a typical self-consistent effect which may be described by the following process. The removal of a d electron results in a contraction of the outermost s shell owing to the reduction in the external screening of the nuclear potential; this contraction will increase the internal screening factor for the inner s shells resulting in a small expansion of their charge density. As the external and internal screening variations will produce opposite effects on a given shell, it is rather difficult to predict *a priori*, what will be the net result. For some cases, such as Fe^{3d} and Fe^{2+}, the $2s$ electrons are slightly antishielded. This antishielding has been observed in other calculations.[12]

(ii) The valence s shell has a smaller charge density at the nucleus than do the core s shells; however, the valence s shell produces the largest *change* in density as the ionicity is increased. Since the valence s electrons are closest to the valence d shell, they feel this change in ionicity (i.e., in number of d electrons) most strongly, and thus produce the largest contribution to the isomer shift.

(iii) For the Dirac-Fock calculations, s contributions to the isomer shift dominate $p_{1/2}$ contributions. The total $p_{1/2}$ contributions is about 1% for $3d$ ions, 2% for $4d$ ions, and 10% for $5d$ ions. Calculations by Dunlap[13] and Ellis and Ros[14] on Np and Desclaux and Freeman[15] for the actinides show a 15% contribution by $p_{1/2}$ electrons.

(iv) Relativistic density differences are larger than their nonrelativistic counterparts by factors varying from about 1.3 for $3d$ ions to about 6 for $5d$ ions. This effect is well known,[1,2,14] and is due to the increase in density near the nucleus for relativistic electrons. The density *differences* scale approximately with the actual densities; thus, the isomer shift is enhanced to the same degree as the actual "amount of time spent" by the relativistic electrons in the nuclear region.

(v) The density differences calculated from the Dirac-Fock nucleus model are larger than those from the finite nucleus by about 2.5% for Fe to about 17% for Ir ions. This discrepancy is not to be attributed to our definition of the charge density for the point nucleus [cf. Eq. (11)], but may be explained by the fact that the nuclear potential is less attractive for the finite-nucleus case. This can be easily checked by performing a Dirac-Fock calculation with a finite nucleus having a radius which is only a few percent of the true radius. In the case of Ir^{2+} the results for the point nucleus and finite nucleus with a radius equal to 0.556 fm instead of the normal value of 5.6 fm agree to within less a percent. This good agreement gives us confidence in the use of our average density for the point nucleus.

Ellis and Ros[14] have shown, using Dirac-Slater

TABLE II. Sample shell-by-shell charge-density differences between different ionic states.

Shell	Dirac-Fock point nucleus	Dirac-Fock finite nucleus	Hartree Fock
Fe: $4\pi[\lvert\Psi^{+3}(0)\rvert^2-\lvert\Psi^{+2}(0)\rvert^2]$ (a.u.)			
1s	−5.317	−5.469	−4.281
2s	−0.936	−0.937	−0.576
3s	+41.537	+40.943	+32.756
Total s	+35.290	+34.537	+27.899
$2p_{1/2}$	+0.027	+0.026	
$3p_{1/2}$	+0.295	+0.291	
Total $p_{1/2}$	+0.321	+0.318	
Total	+35.611	+34.854	+27.899
Ru: $4\pi[\lvert\Psi^{+6}(0)\rvert^2-\lvert\Psi^{+5}(0)\rvert^2]$			
1s	−9.850	−9.440	−5.219
2s	+7.517	+7.214	+4.291
3s	+26.152	+25.070	+13.537
4s	+108.860	+104.367	+55.897
Total s	+132.680	+127.210	+68.506
$2p_{1/2}$	+0.166	+0.112	
$3p_{1/2}$	+0.536	+0.516	
$4p_{1/2}$	+2.638	+2.542	
Total $p_{1/2}$	+3.291	+3.171	
Total	+135.970	+130.381	+68.506
Ir: $4\pi[\lvert\Psi^{+3}(0)\rvert^2-\lvert\Psi^{+2}(0)\rvert^2]$			
1s	−15.091	−11.684	−1.718
2s	+6.270	+5.424	+1.404
3s	+16.287	−13.615	+2.494
4s	+8.582	+7.212	+1.868
5s	+273.262	+230.120	+47.696
Total s	+289.310	+244.686	+51.744
$2p_{1/2}$	−0.101	−0.099	
$3p_{1/2}$	+1.281	+1.084	
$4p_{1/2}$	+0.415	+0.362	
$5p_{1/2}$	+31.219	+26.719	
Total p	+32.813	+28.066	
Total	+322.122	+272.752	+51.744

TABLE III. Charge-density differences $4\pi[\Psi^{+N}(0)|^2-|\Psi^{+(N-1)}(0)|^2]$ (a.u.); finite-nucleus Dirac-Fock values are given in parentheses.

Ions	Dirac Fock		Hartree Fock	Dirac Fock/ Hartree Fock		$S'(Z)$
Fe: 2+,3+	35.611	(34.854)	27.899	1.276	(1.249)	1.29
3+, 4+	58.147		45.568	1.276		
Ru: 2+, 3+	64.090		33.296	1.925		1.92
3+, 4+	95.530		48.446	1.972		
4+, 5+	115.310		58.951	1.956		
5+, 6+	135.970	(130.381)	68.506	1.985	(1.903)	
Ir: 2+, 3+	322.122	(272.752)	51.744	6.225	(5.271)	
3+, 4+	435.016	(369.925)	62.672	6.941	(5.903)	6.21
4+, 5+	569.140		84.704	6.719		
5+, 6+	660.101					
6+, 7+	770.360					

calculations, that the charge densities calculated for a point nucleus have a steeper dependence on $r(<R)$ than do the finite-nucleus values, and this is precisely what we observe in Table II, and, in fact, in all of our calculations.

Table III shows the total-charge-density differences between various ions, as calculated by Dirac-Fock and Hartree-Fock theory: column 1 lists the ion pairs between which the densities have been calculated; column 2 lists the Dirac-Fock differences. These refer to the point-nucleus calculations; results of finite-nucleus calculations where performed, appear in parentheses. Column 3 contains the Hartree-Fock results and column 4 is the ratio of Dirac-Fock–to–Hartree-Fock results. The final column lists the factors $S'(Z)$ obtained from single-electron calculations of Shirley[1]; these may be compared directly with column 4.

We observe first the strong dependence of isomer shift on charge state. This is well known for Hartree-Fock states; not unexpectedly, the Dirac-Fock isomer shifts exhibit the same strong dependence. This large increase in the calculated ion isomer shifts as one goes to higher charge states is modified strongly by the chemical environment of the compounds in which the isomers are found.

In column 4 the "relativity correction" is given for ions of different nuclear charge Z and different ionicity. As is obvious, relativity corrections depend on both factors; nevertheless, it is useful to compare column 4 with the hydrogenic, purely-Z-dependent relativity corrections[1] of column 5. It is striking that the latter, although based on a very simple model, give rather accurate values for the correction, agreeing with our values to about 1% for Fe, to more than 4% for Ru and to within 15% of all values for Ir.

Although the relativity correction varies for different ionic pairs of the same Z, this variation appears not to exhibit any systematic behavior, as the results in column 4 show. However, there is a systematic dependence in the particular model used, viz., the finite-nucleus relativity corrections are considerably lower than the point-nucleus corrections since the finite-nucleus density shifts are lower (columns 1 and 2) as discussed above. We give in Table IV the shell-by-shell contributions to $4\pi|\varphi(0)|^2$ for the various ions studied here.

III. COMPARISON WITH EXPERIMENT: ESTIMATES OF CHANGES IN MEAN-SQUARE NUCLEI RADII

Numerous researchers[2,16,17] have discussed the difficulties encountered when attempting to apply free-ion calculated charge densities to the interpretation of experimental isomer shifts in solids. The free-ion calculations accurately describe the electronic charge density at the nucleus due to valence d shielding of core s and $p_{1/2}$ electrons. Even for ionic compounds, for which the free-ion charge state is a good approximation, the admixture of valence s, p, and d electrons from the ligand seriously affects the charge density at the ion nucleus; thus, for a series of ionic compounds of the same charge state, the spread in isomer-shift values can be large, and can, in fact, overlap the next-charge-state isomer shifts.

For covalent compounds, the comparison to free-ion calculations is even more dubious: the charge states are not easily characterized by ascribing a free-ion ionicity to the metal ion in the compound; low spin states are important (and thus Hund's-rule atomic calculations are of limited value); and delocalization of both metal and ligand orbitals strongly affect the charge densities at the metal-ion nucleus. Thus, comparison of relativistic free-ion results with experiment is, of necessity, limited; they cannot be expected to correctly predict accurate magnitudes of isomer shifts for an entire series of compounds of different charge states. Nevertheless, in the absence of accurate molecular-cluster calculations[18,19] for the heavy-metal ion systems, they can answer the following questions: (i) Does the sign of the calculated shift agree with experiment? (ii) Can one predict $\delta\langle r^2\rangle$, given either the relative isomer shifts between ionic compounds or between compounds exhibiting the same covalency? How do predicted values of $\delta\langle r^2\rangle$ compare with values from other relativistic calculations, and from "relativity corrected" $[S'(Z)]$ Hartree-Fock calculations? (iii) Is the discrepancy between computed free-ion isomer shifts and experimental values in the correct direction, i.e., is the free-ion value the limiting case as covalency and overlap effects decrease in a series of compounds? (iv) What are the systematics of isomer shifts in nd ions for $n=4, 5$?

The change in mean-square nuclear charge radii $\delta\langle r^2\rangle$ upon excitation can be extracted from Mössbauer-isomer-shift experiments if one has reliable estimates of the electron densities inside the nucleus. Systematics and tables of such $\delta\langle r^2\rangle$ values have been given by Kalvius and Shenoy[20] (KS) based on Dirac-Fock-Slater calculations. These authors have emphasized the difficulties attendant to such estimates because of the uncertainties in knowledge about the $\Delta\rho(0)$ values given by various theoretical methods. The mechanism for determining the charge density at the nucleus is the same in this free-ion model: shielding of

TABLE IV. One-electron and total contributions to the charge density $4\pi|\varphi(0)|^2$ at the nucleus determined by Dirac-Fock (point- and in some instances finite-nuclear radius) and by Hartree-Fock calculations.

	$Fe^{2+}(d^6)$			$Fe^{3+}(d^5)$			$Fe^{4+}(d^4)$	
	Dirac Fock		Hartree	Dirac Fock		Hartree	Dirac Fock	Hartree
Orbital	Point nucleus	Finite nucleus	Fock	Point nucleus	Finite nucleus	Fock	Point nucleus	Fock
1*s*	86 666.27	85 434.92	67 704.67	86 663.61	85 432.19	67 702.53	86 659.33	67 699.30
2*s*	8 211.16	8 094.29	6 226.06	8 210.70	8 093.82	6 225.76	8 212.14	6 227.04
3*s*	1 125.55	1 109.53	850.27	1 146.32	1 130.00	866.64	1 178.00	891.39
2*p**	44.00	43.47	...	44.01	43.49	...	44.03	...
3*p**	5.80	5.73	...	5.94	5.88	...	6.16	...
2 Σ *s*	192 005.96	189 277.48	149 562.00	192 041.26	189 312.02	149 589.86	192 098.94	149 635.46
2 Σ *p**	99.60	98.40	...	99.90	98.74	...	100.38	...
Total	192 104.56	189 375.88	149 562.00	192 141.16	189 410.76	149 589.86	192 199.32	149 635.46

	$Ru^{+2}(d^6)$		$Ru^{+3}(d^5)$		$Ru^{+4}(d^4)$	
Orbital	Point nucleus	Hartree Fock	Point nucleus	Hartree Fock	Point nucleus	Hartree Fock
1*s*	633 165.11	332 703.04	633 162.40	332 701.66	633 158.70	332 699.64
2*s*	71 027.21	34 122.43	71 027.77	34 122.81	71 029.48	34 123.79
3*s*	13 006.90	6 206.22	13 010.76	6 208.22	13 018.13	6 212.03
4*s*	2 130.97	1 013.86	2 160.35	1 029.52	2 201.46	1 050.97
2*p**	1 255.72		1 255.76		1 255.81	
3*p**	245.08		245.14		245.27	
4*p**	35.56		36.43		37.52	
s Total	1 438 660.38	748 091.10	1 438 722.56	748 124.42	1 438 815.54	748 172.86
*p** Total	3 072.72	...	3 074.66	...	3 077.20	...
Total	1 441 733.10	748 091.10	1 441 797.22	748 124.42	1 441 892.74	748 172.86

	$Ru^{+5}(d^3)$			$Ru^{+6}(d^2)$		
Orbital	Point nucleus	Finite nucleus	Hartree Fock	Point nucleus	Finite nucleus	Hartree Fock
1*s*	633 154.90	607 098.64	332 697.61	633 149.97	607 093.93	332 695.01
2*s*	71 032.19	68 096.52	34 125.34	71 035.95	68 100.13	34 127.48
3*s*	13 028.16	12 489.45	6 217.22	13 041.24	12 501.99	6 223.99
4*s*	2 249.33	2 156.31	1 075.74	2 303.76	2 208.50	1 103.69
2*p**	1 255.87	1 210.52	...	1 255.92	1 210.56	...
3*p**	245.47	236.60	...	245.73	236.85	...
4*p**	38.73	37.33	...	40.05	38.61	...
2 Σ *s*	1 438 929.16	1 379 681.84	748 231.82	1 439 061.84	1 379 809.10	748 300.34
2 Σ *p**	3 080.14	2 968.90	...	3 083.40	2 972.04	...
Total	1 442 009.30	1 382 650.74	748 231.82	1 442 145.24	1 382 881.14	748 300.34

TABLE IV *(Continued)*

	Os^{+4} "d^4"		Os^{+6} "d^2"		Os^{+8} "d^0"	
Orbital	Point nucleus		Point nucleus		Point nucleus	
1*s*	10 293 292.82		10 293 269.67		10 293 242.67	
2*s*	1 502 628.29		1 502 655.32		1 502 694.54	
3*s*	340 869.24		340 909.49		340 967.79	
4*s*	83 388.62		83 409.18		83 444.89	
5*s*	14 833.16		15 286.84		15 841.75	
2*p**	95 910.80		95 912.71		95 914.04	
3*p**	24 910.80		24 364.94		24 369.57	
4*p**	5 852.68		5 852.20		5 854.98	
5*p**	916.94		966.17		1 015.32	
2 Σ *s*	24 470 024.26		24 471 061.00		24 472 383.28	
2 Σ *p**	254 084.44		254 192.04		254 307.82	
Total	24 724 108.70		24 725 253.04		24 726 691.10	

		Ir^{+2}(d^7)			Ir^{+3}(d^6)	
Orbital	Point nucleus	Finite nucleus	Hartree Fock	Point nucleus	Finite nucleus	Hartree Fock
1*s*	11 213 803.02	9 455 717.13	1 799 923.71	11 213 795.47	9 455 711.28	1 799 922.84
2*s*	1 652 133.37	1 390 275.89	199 026.97	1 652 136.50	1 390 278.60	199 027.68
3*s*	376 086.82	316 399.17	44 466.48	376 094.97	316 405.98	44 467.73
4*s*	92 616.68	77 911.98	10 808.53	92 620.97	77 915.58	10 809.47
5*s*	16 540.27	13 911.95	1 843.79	16 676.91	14 027.01	1 867.63
2*p**	108 991.98	93 303.16		108 991.93	93 303.11	
3*p**	27 798.96	23 789.71		27 799.60	23 790.25	
4*p**	6 734.37	5 762.67		6 734.57	5 762.84	
5*p**	1 044.95	894.14		1 060.55	907.50	
2 Σ *s*	26 702 360.32	22 508 432.24	4 112 138.96	26 702 649.64	22 508 676.90	4 112 190.70
2 Σ *p**	289 140.52	247 499.36	⋯	289 173.30	247 527.40	⋯
Total	26 991 500.84	22 755 931.60	4 112 138.96	26 991 822.94	22 756 204.30	4 112 190.70

TABLE IV (*Continued*)

Orbital	Ir^{+4} (d^5)		Ir^{+5} (d^4)		Ir^{+6} (d^3)	Ir^{+7} (d^2)
	Point nucleus	Finite nucleus	Point nucleus	Hartree Fock	Point nucleus	Point nucleus
1*s*	11 213 785.79	9 455 702.86	11 213 774.41	1 799 920.37	11 213 761.27	11 213 746.71
2*s*	1 652 143.72	1 390 284.76	1 652 154.92	199 030.72	1 652 170.26	1 652 191.66
3*s*	376 107.78	316 416.76	376 126.68	44 472.18	376 150.47	376 180.44
4*s*	92 627.68	77 921.25	42 639.39	10 813.19	92 654.58	92 673.93
5*s*	16 856.09	14 177.87	17 083.89	1 932.59	17 342.34	17 634.37
$2p^*$	108 992.52	93 303.61	108 992.97		108 993.84	108 995.77
$3p^*$	27 800.61	23 791.12	27 802.13		27 804.05	27 806.48
$4p^*$	6 734.22	5 762.54	6 734.76		6 735.24	6 734.79
$5p^*$	1 082.59	926.35	1 106.43		1 133.60	1 166.67
$2\,\Sigma\,s$	26 703 042.12	22 509 007.00	26 703 558.58	4 112 338.10	26 704 157.84	26 704 854.22
$2\,\Sigma\,p^*$	289 219.88	247 567.24	289 272.58	...	289 333.46	289 407.42
Total	26 992 262.00	22 756 574.24	26 992 831.16	4 112 338.10	26 993 491.30	26 994 261.64

s and $p_{1/2}$ electrons by valence *d* shells.

The results obtained from the Dirac-Fock calculations allow some more accurate estimates to be made of changes in the mean-square radius $\delta\langle r^2\rangle$. Our results are not truly model-free, since the Dirac-Fock finite-nucleus calculations assume a uniform spherical nucleus, while the point-nucleus charge densities, as described in Sec. II, were obtained by postulating a formal equivalence to the spherical nucleus.

For the ^{99}Ru ions of Table IV, we chose (following Potzel *et al.*[17]) two rather covalent but similar Ru complexes: $[Ru(NH_3)_6]Cl_3$ for trivalent Ru and $[Ru(NH_3)_6]Cl_2$ for divalent Ru. We expect however that these will exhibit the same degree of covalency, thus the difference between their shifts should cancel. We obtain $\delta\langle r^2\rangle = 0.0283$, in excellent agreement with the value $+0.0288$ of Potzel *et al.*[17] using the same compounds, but using single-configuration Dirac-Fock calculations of Mann.[9] This may be compared with the KS[20] value $\delta\langle r^2\rangle = 0.0020$ fm^2 obtained from the Potzel *et al.*[17] isomer-shift data on RuF_5 and K_3RuF_6 and their Dirac-Fock-Slater $|\psi(0)|^2$ values. Our Dirac-Fock values for these isomer-shift data give $\delta\langle r^2\rangle = 0.0020$ fm^2 [because in this case our $\Delta|\psi(0)|^2$ values are close to the Dirac-Fock-Slater values of KS].

From the above comparison with Mann's single-configuration values, we observe that introducing a multiconfigurational approach to Dirac-Fock calculation causes small changes as long as we concentrate on the calculation of isomer shifts. This occurs because, whereas values of the charge density are each affected by about 2% when using the multiconfigurational approach, the difference in the charge density between various ions which determines the isomer shift is essentially model independent.

We must keep in mind that these changes are actually a small "tempest in a teapot" of large variations in isomer shifts within charge states, due to effects of the chemical environment. Measured Ru^{+3} isomer shifts alone span about 0.4 mm/sec which is comparable to our chosen relative shift between Ru^{+3} and Ru^{+2}.

^{189}Os exhibits a negative isomer shift in the direction of increasing charge state. Using the measured shifts of Bohn *et al.*[21] on OsF_6 and $K_2[OsF_6]$ our Dirac-Fock densities, we obtain $\delta\langle r^2\rangle = -0.0020$ fm^2. Thus, the excited nuclear state is somewhat smaller than the ground state. We expect this value to contain a sizable error: although our choices are the most ionic in their respective charge states, the ions are highly charged, probably very covalent, and separated by two charges rather than one. It is therefore somewhat surprising that the estimate of Kalvius and Shenoy[20] using the data of Bohn *et al.*[21] for the strongly covalent OsO_4 and K_2OsCl_6 systems (configurations $5d^0$ and $5d^4$) is also $\delta\langle r^2\rangle = -0.0020$ fm^2. Our Dirac-Fock values for the $5d^0$ and $5d^4$ configurations yield $\delta\langle r^2\rangle = -0.0018$ fm^2, again in remarkable agreement with the above values. What one sees then in the KS estimates is a case of a fortuitous cancellation of errors, i.e., approximate treatment of exchange on the one hand and lack of inclusion of bonding effects on the other.

Our final example is of ^{193}Ir ions: we choose the theoretical values of $|\psi(0)|^2$ for $Ir^{2+}(5d^7)$ and $Ir^{3+}(5d^6)$, select the most ionic species from Wagner *et al.*,[22] namely, $IrCl_6^{4-}$ in K_2IrCl_6 and K_3IrCl_6 and obtain a positive, but fairly small $\delta\langle r^2\rangle = 0.0057$ fm^2. This value again compares well to the Kalvius and Shenoy estimates $\delta\langle r^2\rangle = 0.0055$ fm^2 based on the Wagner *et al.*[22] data for the more highly charged Ir ions in $IrF_6(5d^3)$ and $K_2IrF_6(5d^5)$ their Dirac-Fock-Slater estimates of $\Delta\rho(0)$. However, if we use this data of Wagner *et al.*[22] for IrF_6 and K_2IrF_6 and our calculated Dirac-Fock values of $\Delta\rho(0)$ for Ir^{+6} and Ir^{+4} we obtain an estimate for $\delta\langle r^2\rangle = 0.0045$ fm^2 which differs by 20% from the KS estimate. If we use isomer-shift data of Potzel *et al.*[17] for the lower charge states represented by $IrF_5(d^4)$ and $K_2IrF_6(d^5)$ and our Dirac-Fock results we obtain $\delta\langle r^2\rangle = 0.0051$ fm^2. These estimates indicate the range in estimates of $\delta\langle r^2\rangle$ based on free ion $|\psi(0)|^2$ values and the significant role played by bonding effects.

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[1] D. A. Shirley, Rev. Mod. Phys. 36, 339 (1964).

[2] B. Dunlap and G. M. Kalvius, in *Mössbauer Isomer Shifts*, edited by G. K. Shenoy and F. E. Wagner (North-Holland, Amsterdam, 1975), Chap. II.

[3] L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Lett. 6, 98 (1961).

[4] S. DeBenedetti, G. Lang, and R. Ingalls, Phys. Rev. Lett. 6, 60 (1961).

[5] See for example, R. E. Watson, MIT report (unpublished); E. Clementi, IBM J. Res. Dev. Suppl. 9, 2 (1965); S. L. Ruby and G. K. Shenoy, Phys. Rev. 186, 326 (1969).

[6] See derivation by R. L. Mössbauer and M. J. Clauser, in *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic, New York, 1967), p.497 ff.

[7] G. M. Kalvius, in *Hyperfine Interactions in Excited Nuclei*, edited by G. Goldring and R. Kalish, (Gordon and Breach, New York, 1971), Vol. 2, p. 523.

[8] J. P. Desclaux, Atomic Data 12, 311 (1973), and references therein.

[9] J. B. Mann results quoted in Ref. 2; and Los Alamos Scientific report (unpublished).

[10] C. Froese-Fisher, Can. J. Phys. 46, 336 (1968).

[11] H. Bethe and E. Salpeter, Hand. Phys. 35, 149 (1957).

[12] B. Fricke and J. T. Waber, Phys. Rev. B 5, 3445 (1972).

[13] B. D. Dunlap, see Refs. 2.

[14] D. E. Ellis and P. Ros (unpublished).

[15] J. P. Desclaux and A. J. Freeman (unpublished).

[16] P. Ingalls, F. van der Woude and G. A. Sawatzky, see Ref. 2, Chap. VII.

[17] W. Potzel *et al* ., Z. Phys. 240, 306 (1970); 241, 179 (1971); 226, 103 (1969).

[18] K. J. Duff, Phys. Rev. B 9, 66 (1974).

[19] P. F. Walch and D. E. Ellis, Phys. Rev. B 7, 903 (1973).

[20] G. M. Kalvius and G. K. Shenoy, Atomic Data Nucl. Data Tables 14, 639 (1974); and G. K. Shenoy and G. M. Kalvius, see Ref. 7, p. 1201.

[21] H. Bohn, G. Kaindl, D. Kucheida, F. E. Wagner and P. Kienle, Phys. Lett. B 32, 346 (1970).

[22] F. Wagner, J. Klöckner, H. J. Körner, H. Schaller, and P. Kienle, Phys. Lett. B 25, 253 (1967); F. Wagner and U. Zahn, Z. Phys. 233, 1 (1970).