of energy radiated in the vuv region and the amount of energy associated with the Jesse effect. Quenching studies now in progress[10] seem to be consistent with the model suggested here. Thus, several other experiments all centered on the energy pathways following the interaction on swift charged particles with matter are compatible with the model developed here which relied mainly on time-dependent studies, supplemented by work with gas discharges, as input information.

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Expectation Values of $\langle r^n \rangle_{4f}$ for Rare-Earth Ions*

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The average values of the powers of r for the $4f$ orbital, $\langle r^n \rangle_{4f}$, were calculated using accurate analytical self-consistent-field wave functions. The results were compared with experimental and other theoretical values.

INTRODUCTION

Accurate analytical self-consistent-field wave functions for the ground states of Pr^{3+}, Nd^{3+}, and Dy^{2+} have appeared in the literature.[1] Accurate wave functions for Ce^{3+}, Eu^{3+}, Gd^{3+}, Tm^{3+}, Tm^{2+}, and Tm have also been calculated, and are to be published.[2]

These accurate wave functions were used in calculating the expectation values $\langle r^n \rangle$ for the $4f$ orbitals, with $n = -3$, 2, 4, and 6. The results for $\langle r^{-3}\rangle_{4f}$ are given in Table I and for $\langle r^n\rangle_{4f}$, ($n = 2$, 4, 6) in Table II. The $4f$ expectation values of $\langle r^{-3}\rangle$ are of interest since they are used to calculate nuclear magnetic moments of several lanthanide ions. The other $\langle r^n\rangle$ values are important in crystal field calculations. Our results are compared with experimental and theoretical values obtained by other research groups.

RESULTS AND DISCUSSION

Table I lists the $4f$ expectation values of $\langle r^{-3}\rangle$, which were obtained using several different approaches: from experimentally known spin-orbit coupling constants, from the nuclear magnetic moment and the hyperfine constants, and lastly from analytical Hartree-Fock wave functions.

Initially, when no accurate wave functions were available, estimates of $\langle r^{-3}\rangle$ were obtained from the spin-orbit coupling parameter ζ. A simple relationship between $\langle r^{-3}\rangle$ and ζ is available when the potential $V(r)$ is taken as purely Coulombic. Such a relationship was used by Elliot and Stevens[3] and Bleaney,[4] where they assumed hydrogenic wave functions to calculate $\langle r^{-3}\rangle$ for different lanthanide ions. Judd and Lindgren[5] used modified hydrogenic wave functions to calculate $\langle r^{-3}\rangle$; the radial part of their wave function is of the form

$$R(r) = Nr^4 e^{-ar} \cosh k(ar - 4) \quad .$$

Here a and k are two adjustable parameters which were chosen to match Ridley's Hartree-type $4f$ wave functions and experimental spin-orbit coupling measurements. Lindgren[6] improved this technique and extended it, using extrapolation and interpolation to include a great number of lanthanide ions. The values of $\langle r^{-3}\rangle$ calculated from the spin-orbit parameter depend on several assumptions[7,8] that are not justified in general. For example, Blume and Watson have shown[9] that the analytic form of the spin-orbit coupling constant contains, in addition to the one-body nuclear spin-orbit term ($\alpha\langle r^{-3}\rangle$), direct and exchange terms arising from the two-body mutual spin-orbit interaction. These terms have the effect of screening the nuclear charge and decreasing the coupling constant.[9-11] Hence one should not expect to obtain reliable estimates of the radial moment $\langle r^{-3}\rangle$ from the experimental values of the spin-orbit parameter. For a more detailed discussion of this point, see Freeman and Watson.[7,8]

Judd,[12] using a one-electron form of the spin-orbit operator, has attributed the discrepancy between theoretical and experimental spin-orbit coupling constants to shielding effects due to certain types of configuration interaction. His results provide confirmation of the work of Rajnak and Wybourne,[13] which indicates that configuration interaction leads to a scaling down of the spin-orbit parameter from the value obtained by means of single-configuration Hartree-Fock wave functions. However, in Judd's treatment, it should be noted that exchange effects in the coupling constant due to the two-body mutual spin-orbit interaction were neglected. Further quantitative work is needed to evaluate the importance of configuration mixing in determining the magnitudes of radial parameters such as $\langle r^{-3}\rangle$. An alternative suggestion, given by Blume *et al.*,[11] is that, for the rare earths, the $4f$ expansion due to increased screening by s and p electrons obtained in a relativistic treatment[14] would reduce the difference between theoretical values of $\langle r^{-3}\rangle$ calculated via nonrelativistic Hartree-Fock wave functions and values obtained

TABLE I. Average values $\langle r^{-3}\rangle_{4f}$ (a.u.) for the ground states of various lanthanide ions.

Ion and state	a	b	c	d	e	f	g	h
Ce^{3+}, $4f$, ^2F	4.881	4.8	3.66	4.72				
Pr^{3+}, $4f^2$, ^3H	5.518	5.5	4.26	5.37	5.4	5.0	5.06	
Nd^{3+}, $4f^3$, ^4I	6.166	6.2	4.86	6.03	6.0	5.6	5.64	$5.46 \pm 0.67^{(i)}$
Eu^{3+}, $4f^6$, ^7F	8.189	8.4					7.28	
Gd^{3+}, $4f^7$, ^8S	9.018	9.2	7.35	8.84			7.89	
Dy^{2+}, $4f^{10}$, ^5I	9.772							
Tm^{3+}, $4f^{12}$, ^3H	12.932	13.6	11.20		12.9	11.7	11.72	
Tm^{2+}, $4f^{13}$, ^2F	12.259							$10.95 \pm 0.44^{(ii)}$
Tm, $4f^{13}$, $6s^2$, ^2F							11.24	

[a] Present work.
[b] Reference 4.
[c] Reference 6.
[d] Reference 7.
[e] Reference 8.
[f] Experimental values quoted in Ref. 8.
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from experiment.

The average value of $\langle r^{-3} \rangle$ in combination with the hyperfine constant A were used to calculate the nuclear magnetic moment μ_I according to the following formula[3, 15]:

$$\frac{A}{g} = \frac{2\mu_B \mu_N \mu_I}{I} \langle r^{-3} \rangle \frac{\langle J \| N \| J \rangle}{\langle J \| \Lambda \| J \rangle} \quad ;$$

$\langle J \| N \| J \rangle$ and $\langle J \| \Lambda \| J \rangle$ are numerical factors given by Elliot and Stevens.[3] If the nuclear magnetic moment is known by independent means, the technique could be used to calculate $\langle r^{-3} \rangle$ using the experimental value of A. We used this method to calculate $\langle r^{-3} \rangle$ for Tm^{2+} in column h.

In our calculations core-polarization and relativistic effects were neglected. The values of $\langle r^{-3} \rangle$ including core-polarization effects for several lanthanide ions were calculated by Bleaney.[16] His results are given in column g, where $\langle r^{-3} \rangle$ for Nd^{3+} and Tm were calculated from measured values, and seem to be the most reliable experimental results in this table. He concludes that core-polarization effects can be neglected for atoms but play a more important role in the case of ions. The hyperfine constant A for the ion, after eliminating crystal field effects, is composed of two parts: $A = A_f + A_{\text{core}}$, where A_f is the hyperfine constant due to the open $4f$ shell and A_{core} is due to core polarization. The A_{core} is a small correction which often should be taken into account.

In a relativistic treatment, Sanders and Beck[17] have proposed an effective Hamiltonian which has three parameters that are dependent on the electron radial distribution: $\langle r_1^{-3} \rangle$, $\langle r_{sC}^{-3} \rangle$, and $\langle r_s^{-3} \rangle$. These three quantities are related to the interaction between the nuclear magnetic dipole moment and the electron orbit, the electron spin-orbit distribution outside the nucleus, and the electron density at the nucleus, respectively. The Hamiltonian is written as

$$H_{\text{hfs}} = \frac{2\mu_B \mu_N \mu_I}{I} \underline{\mathrm{I}} \cdot \sum_i \{ \underline{\mathrm{l}}_i \langle r_1^{-3} \rangle_i - (10)^{1/2} (\underline{\mathrm{sC}^2})_i^l \langle r_{sC}^{-3} \rangle_i + \langle r_s^{-3} \rangle_i \underline{\mathrm{s}}_i \} \quad .$$

Woodgate[18] used atomic-beam data on Sm to measure the nuclear magnetic moment and the three radial parameters. His experimental results appear to be the most accurate. He suggested that a nonvanishing $\langle r_s^{-3} \rangle$ can be derived using relativistic theory. In nonrelativistic theory we have $r_1^{-3} = r_{sC}^{-3}$ and $r_s^{-3} = 0$. The value of $\langle r_1^{-3} \rangle$ for Sm was found[12] to be 16.2% higher than Judd and Lindgren's value and 5% above Bleaney's[16] value. This brings the average values of $\langle r_1^{-3} \rangle$ and $\langle r_{sC}^{-3} \rangle$ closer to the Hartree-Fock values which are in general larger than those reported by Lindgren and by Bleaney.[16]

The values of $\langle r^n \rangle$ ($n = 2$, 4, 6) are important in calculations dealing with the crystal field theory. Table II gives the values we calculated as well as a comparison with other authors.[7, 8]

The average values of r^n are related to the crystal field parameters V_n^m which can be determined experimentally. Since $V_n^m = A_n^m \langle r^n \rangle$, a comparison of experimental and theoretical values of $\langle r^n \rangle$ is possible only if we can calculate A_n^m. Some attempts[19, 20] were made to calculate A_n^m assuming a point-charge model of the crystal lattice. For Pr^{3+} and Tm^{2+}, using such calculated A_n^m values and experimental V_n^m results, the values of $\langle r^n \rangle$ obtained were larger than those calculated using SCF wave functions. The point-charge model is inadequate in these cases partially because it fails to account for overlap between the rare-earth ions and the ligands. Hutchings and Ray[19] found considerable overlap between the $4f$ wave functions of Pr^{3+} and Cl^- in $PrCl_3$. Wybourne[21] summarizes the shortcomings of the pure electrostatic model in calculating crystal field parameters. To overcome these difficulties, additional calculations should be carried out to take into account configuration mixing[22–25] of the states of f^N with states from many excited configurations, as well as covalency[26–28] and other[29–31] effects.

Values of $\langle r^n \rangle$ using relativistic wave functions

TABLE II. Average values of $\langle r^n \rangle$ ($n = 2$, 4, 6) for different lanthanide ions.

Ion and state	$\langle r^2 \rangle$		$\langle r^4 \rangle$		$\langle r^6 \rangle$	
	Theoret.[a]	Theoret.[b]	Theoret.[a]	Theoret.[b]	Theoret.[a]	Theoret.[b]
Ce^{3+}, $4f$, ^2F	1.174	1.200	3.240	3.455	20.667	21.226
Pr^{3+}, $4f^2$, ^3H	1.064	1.086	2.623	2.822	14.666	15.726
Nd^{3+}, $4f^3$, ^4I	0.979	1.001	2.185	2.401	10.672	12.396
Eu^{3+}, $4f^6$, ^7F	0.812	0.832	1.514	1.697	5.917	7.442
Gd^{3+}, $4f^7$, ^8S	0.749	0.785	1.254	1.515	4.077	6.281
Dy^{2+}, $4f^{10}$, ^5I	0.806		1.704		7.982	
Tm^{3+}, $4f^{12}$, ^3H	0.623	0.646	0.949	1.067	3.141	3.647
Tm^{2+}, $4f^{13}$, ^2F	0.703	0.728	1.344	1.552	5.854	7.510

[a] Calculated using accurate analytical self-consistent-field wave functions in the present work.

[b] Reference 7.

were obtained by Lewis.[32] The values of $\langle r^n \rangle$ ($n=4$, 6), using relativistic wave functions, are considerably larger than those obtained from nonrelativistic wave functions. In calculating the powers of r using relativistic wave functions some of the accuracy was sacrified in order to use a much simpler approach which does not include the entirety of the exchange potential.[33] This is due to certain approximations[34] and an adjustment of the tail of the wave functions. This sacrifice may not have a great influence on the inner part of the atom, but it gives rise to an incorrect asymptotic form of the potential, which can introduce errors in the calculated $\langle r^4 \rangle$ and $\langle r^6 \rangle$, where the outer parts of the atoms or ions are most influential. It has not been possible to decide whether the adjusted relativistic or the ordinary Hartree-Fock results are in a better agreement with experiments, since no experimental results for this purpose have been found in the literature.

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