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Symmetry of Some Properties of Lanthanides and Actinides with Respect to a Quarter of the f^N Shell

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Using the spin-polarized method it is shown that the periodicity of the various properties of lanthanides and actinides is related with the "electron-vacancy" symmetry for the ground state of the f^N shell. This symmetry remains approximately valid also taking into account some important terms and configuration mixing effects. The algebraic expressions for the ground-state energy and the ionization energies in terms of the number of f electrons are obtained and the interval rule is derived. The reason for the inclined *W* systematic or *L* dependence is the correlation between the values of the two quantities, depending almost linearly on the number of f electrons in the four quarters of this shell.

Introduction

Some chemical and physical properties of lanthanides and actinides, especially in the trivalent state, show periodic regularities depending on the number of electrons in the *n*f^N shell. Such regularities known as small periodicity and gadolinium break,[1−4] tetrad or double−double effect,[5−8] two zigzag segments or inner series periodicity,[9−12] interval rules,[13,14] *L* dependence, and inclined *W* systematics[15−17] have been widely investigated and discussed. The summary of these results and their analysis has been given in the review.[18] Various explanations of such regularities have been proposed: the extrastabilization in the crystal field,[19] the nepheleutic effect,[20] and spin−orbit[21] and Coulomb[8] interactions within the *n*f^N shell. The crystal field is relatively weak for the inner f^N electronic shell.[18,22] Thus at present the periodicity of the properties in the lanthanide and actinide series is usually related with the peculiarities of the atomic open f^N shell.[18] The atomic origin of the periodicity is supported by the similarity of dependence of chemical properties (oxidation potentials, cohesive energies, enthalpies of decomposition and disproportionation, etc.) for some simple compounds and of physical properties (ionization potentials, differences of energies for the ground state of configurations, etc.) on the number of f^N electrons in the lanthanides and actinides series.[18] Some examples of such similarity are presented in Figures 1 and 2. These regularities have been interpreted as the consequence of the variation of the spin-angular coefficients at the radial integrals in the expression for the energy of the ground state of the f^N shell.[8,18] However, a clear understanding of the nature of these regularities was absent. The later more complete and reliable results[23,25−27] support the regularities established in the 1970s on the basis of less numerous data.

The aim of this work is to reveal the reasons for such periodicity in terms of the symmetry properties of the f^N shell in its ground and higher multiplicity states, using the spin-polarized model. For chemical properties, related with the number of *n*f electrons, the physical origin of the periodicity can be modified to a smaller or larger extent and obtains various forms or even does not appear at all. In this work we investigate only the physical reasons, which can be important to understand the origin of the periodicity of various chemical properties.

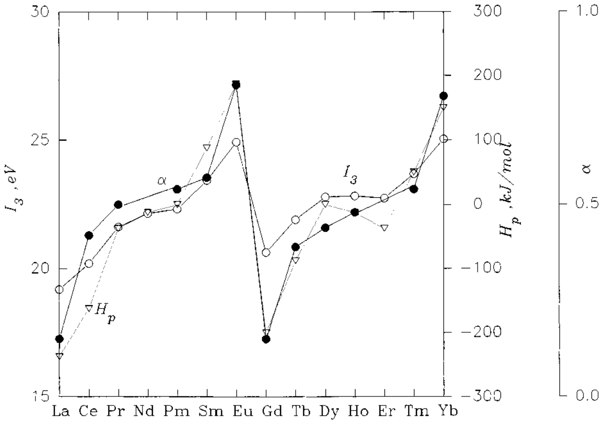

Figure 1. Variation of the third ionization potential I_3 (○) (experimental values[23]), the enthalpy of decomposition H_p (∇) (semiempirical data[24]), and the α parameter (●), calculated for the ionization equilibrium[24] (two last quantities correspond to the reaction $\mathrm{LnHal_2} \rightarrow 1/3\mathrm{Ln} + 2/3\mathrm{LnHal_3}$) in the lanthanide series.

Calculations have been performed using the pseudorelativistic Hartree−Fock (HFR) method (some principal relativistic corrections are taken into account calculating radial wave functions[28]).

Symmetry Properties of the *n*f^N Shell in Its Ground State

In the central field approximation only the radial wavefunction of an electron depends on the peculiarities of the field within an atom. The equation for the single-electron wavefunction is transformed to the one-dimensional equation for the radial function with the effective potential

$$V^{\mathrm{ef}}{}_{\mathrm{nl}}(r) = V_{\mathrm{nl}}(r) + \frac{l(l+1)}{2r^2} \qquad (1)$$

where $V_{\mathrm{nl}}(r)$ is the true potential, and the second term corresponds to the classical centrifugal energy. Due to this positive term, the effective potential for the f electron in a neutral atom and first ions obtains the form of two potential wells separated by a positive potential barrier.[29] The radial orbital of the 4f

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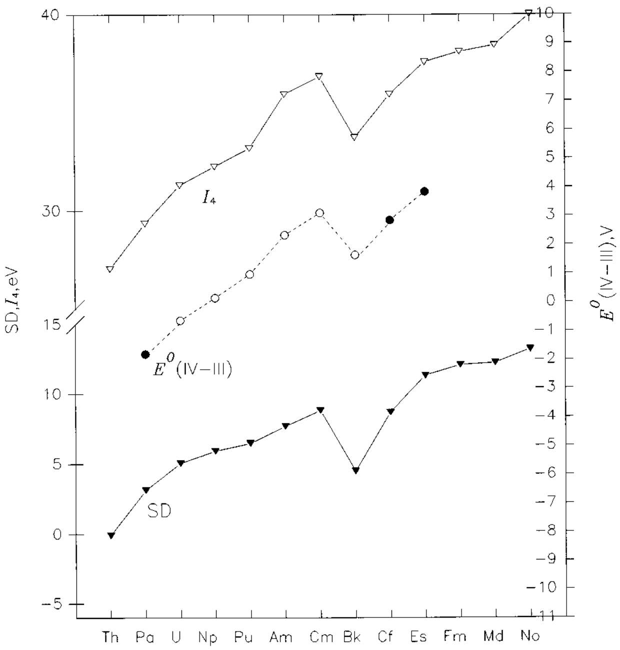

Figure 2. Variation of the fourth ionization potential I_4 (▽), the system difference SD (the difference between the energies of the ground levels of $5f^{N-1}6d$ and $5f^N$ configurations) for trivalent ions (▼) (both quantities calculated by the pseudorelativistic Hartree−Fock method), and the oxidation potential E^0(IV−III) (experimental (○) and empirical (●) values[26]) in the actinide series.

electron in lanthanides and of the 5f electron in actinides for the atom ground state is mainly localized in the narrow inner well. It causes the penetration of the corresponding f^N shell in the atomic core and a very strong Coulomb interaction between the electrons of this "compressed" shell, the importance of this interaction being for the atomic properties.

In the single-configuration central field model the approximate symmetry between the electrons and vacancies exist. The partially (l^N) and almost (l^{4l+2-N}) filled shells are described by the same many-electron terms and the spin-angular parts of the wavefunctions differ only by the phase factor for these complementary shells. This symmetry is violated only in the radial space due to the dependence of the radial wavefunction on the effective nuclear charge peculiarities of the field within the atom.[28]

The "electron-vacancy" symmetry for the wavefunctions leads to the symmetry relations for the matrix elements of atomic operators, which do not contain the scalar part (the matrix element of the scalar operator is directly proportional to the number of electrons and is not symmetric with respect to the replacement of electrons by vacancies). The average energy of the spin−orbit interaction is equal to zero, but the Coulomb interaction within the electronic shell has some nonzero average value. It can be excluded by expressing the energy with respect to the average energy. For the configuration with one open f^N shell it takes the form

$$E(f^N\gamma) = E_{av}(f^N) + \sum_i e_i'(f^N\gamma)E^i + \chi_f(f^N\gamma)\zeta_{nf} \qquad (2)$$

Here γ is the many-electron state, $E_{av}(f^N)$ is the average energy of configuration, E^i is the linear combination of the Slater radial integrals $F^k(nf,nf)$ introduced in ref 30 for the description of the f^N shell, e_i' is the spin-angular coefficient at E^i excluding its average value $\bar{e}_i$ ($e_i' = e_i - \bar{e}_i$), ζ_{nf} is the spin−orbit constant, and χ_f is the spin-angular coefficient at it.

For the coefficients e_i' and χ_f the "electron-vacancy" symmetry is expressed by the relations

$$e_i'(f^N\gamma) = e_i'(f^{14-N}\gamma) \quad (i = 1, 2, 3) \qquad (3)$$

$$\chi(f^N\gamma) = -\chi(f^{14-N}\gamma) \qquad (4)$$

Usually the f^N shell is in its ground state. The coupling within this shell is close to the LS coupling, and the ground state, according to Hund's rule, has the highest multiplicity. For such a state not only the quantum numbers of spin (S), orbital (L), and total (J) moments as well as the seniority ν but also the additional quantum numbers u_i, w_i (necessary for the characterization of the states of the f^N shell) can be expressed in terms of the number of electrons N:[31]

$$S = \frac{N}{2}; \quad \nu = N; \quad L = \frac{1}{2}N(7 - N) \qquad (5)$$

$$J = \begin{cases} \dfrac{N(2l - N)}{2} & \text{if } N \le 7 \\ \dfrac{(4l + 2 - N)(N - 2l)}{2}, & \text{if } N > 7 \end{cases} \qquad (6)$$

$$\omega_1 = \frac{N(7-N)}{2^4 \cdot 3^2 \cdot 5}[252 - 28N(7-N) + N^2(7-N)^2] \qquad (7)$$

$$\omega_2 = \frac{N(7-N)}{2^2 \cdot 3^2 \cdot 5}[-174 + 41N(7-N) - 2N^2(7-N)^2] \qquad (8)$$

$$\omega_3 = \frac{N(7-N)}{2^4 \cdot 3^2}[60 - 16N(7-N) + N^2(7-N)^2] \qquad (9)$$

$$u_1 = \omega_1 + \omega_3; \quad u_2 = \omega_2 - \omega_3 \qquad (10)$$

Here N is equal to the number of electrons N for the partially filled shell ($N \le 7$) and to the number of vacancies $14 - N$ for the almost filled shell ($N > 7$).

Quantum numbers L, ω_i and u_i describing the properties of the wavefunction in the orbital space show additional symmetry with respect to a quarter of the shell. This follows from the possibility of treating the shell in its highest multiplicity state as consisting of two subshells with spins of electrons directed up ($nl^N{\uparrow}$) and down ($nl^{N'}{\downarrow}$). The spin-polarized model has been elaborated in refs 32−34. However in general the partition of shell into subshells

$$l^N \rightarrow l^{N'}{}_{\downarrow} l^{N-N'}{}_{\uparrow} \qquad (11)$$

can be accomplished in various ways, differing by the number N'. All these subconfiqurations $l_{\downarrow}^{N'}\, l_{\uparrow}^{N-N'}$, $l_{\downarrow}^{N'+1}\, l_{\uparrow}^{N-N'-1}$, ..., are mixed between them by the spin−orbit interaction. This partition becomes unique only for the terms of highest multiplicity:

$$l^N \rightarrow \begin{cases} l_{\downarrow}^{N} & \text{for } N \le 2l + 1 \\ l_{\downarrow}^{2l+1}\; l_{\uparrow}^{N-2l-1} & \text{for } N > 2l + 1 \end{cases} \qquad (12)$$

The attribution of the projection of spin in the first subshell is conventional.

Instead of spin and orbital spaces, introduced in the traditional approach, the spin-polarized model uses two orbital spaces in which electrons have different projections of spins. Both subshells $l_{\downarrow}^{N}$ and $l_{\uparrow}^{N'}$ have the same number of single-electron states. The closed subshell l^{2l+1} has all quantum numbers, defined in the orbital space, equal to 0. The "electron-vacancy" symmetry for the subshell, having only half the states of the shell, manifests as the symmetry with respect to a quarter of the shell. Thus the coefficients at the radial integrals in the matrix elements of operators (whose average value is equal to zero) can differ for the highest multiplicity states γ_h of l^N and l^{2l+1-N} configurations only by a phase factor. In the case of the f^N shell the following relations take place:

$$e_3'(f^N\gamma_h) = e_3'(f^{7-N}\gamma_h), \quad e_3'(f^{7+N}\gamma_h) = e_3'(f^{14-N}\gamma_h) \quad (0 \le N \le 7) \tag{13}$$

$$\chi(f^N\gamma_h) = \chi(f^{7-N}\gamma_h), \quad \chi(f^{7+N}\gamma_h) = \chi(f^{14-N}\gamma_h) \quad (0 \le N \le 7) \tag{14}$$

For the states of the highest multiplicity the e_2' coefficient disappears. The e_1' coefficient has an average value nonequal to zero; thus the symmetry with respect to a quarter of the shell takes place only for the reduced coefficient e_1'', which is obtained by subtracting from e_1' its average value for the corresponding subshell. This value is equal to e_1'; thus,

$$e_1''(f^N\gamma_h) = 0 \tag{15}$$

There exist additional relations for the operators in the spin-polarized approach; thus this give the possibility to obtain the algebraic expressions of the matrix elements for the terms of higher multiplicity.[31] In the case of the ground state γ_g these formulas can be simplified and expressed in terms of the number of f electrons using expressions 5−10 for the quantum numbers of this state:

$$e_1'(f^N\gamma_g) = -\frac{9}{2\cdot 13}N(N-1); \quad e_2(f^N\gamma_g) = e_2'(f^N\gamma_g) = 0 \tag{16}$$

$$e_3(f^N\gamma_g) = e_3'(f^N\gamma_g) = -\frac{1}{2^3\cdot 3\cdot 5}N(7-N)[78 - 37N(7-N) + 4N^2(7-N)^2] \tag{17}$$

$$\chi(l^N\gamma_g) = \begin{cases} [N^2 - (2l+1)N - 2]/4 & 0 < N < 2l+1 \\ -(N-2l-1)(4l+2-N)/4 & N \ge 2l+1 \end{cases} \tag{18}$$

The formula for the spin−orbit coefficient χ holds not only for f electrons; thus, l in eq 18 is not definite.

The dependence of the coefficients e_1', e_3', and χ on the number of f electrons N is shown in Figure 3. As has been indicated above, the coefficients e_3' and χ, whose average value is equal to 0, show symmetry with respect to a quarter of the f^N shell, but the e_1' coefficient giving the contribution to the average energy is symmetric only with respect to a half shell. This coefficient gives the minimum value at $N = 7$ and determines the additional stability of the half-filled f^7 shell. On the other hand, coefficients e_3' and χ reach minimal values at $N = 3-4$ and $N = 10-11$ and give rise to additional stability for one-fourth and three-quarters of the shell.[8]

Of course, the true role of the various parts of the interaction essentially depends on the values not only of the coefficients but also of the radial integrals. The integral E^1 exceeds E^3 by approximately 2 orders; thus, the term-dependent part of the Coulomb interaction between nf electrons is mainly determined by the contribution of $e_1'E^1$. The Coulomb and the spin−orbit interaction parts of the ground-state energy (with respect to the average energy) for lanthanides and actinides are given in Figure 4. On going from lanthanides to actinides the Coulomb interaction within the nf^N shell decreases (the effect of the

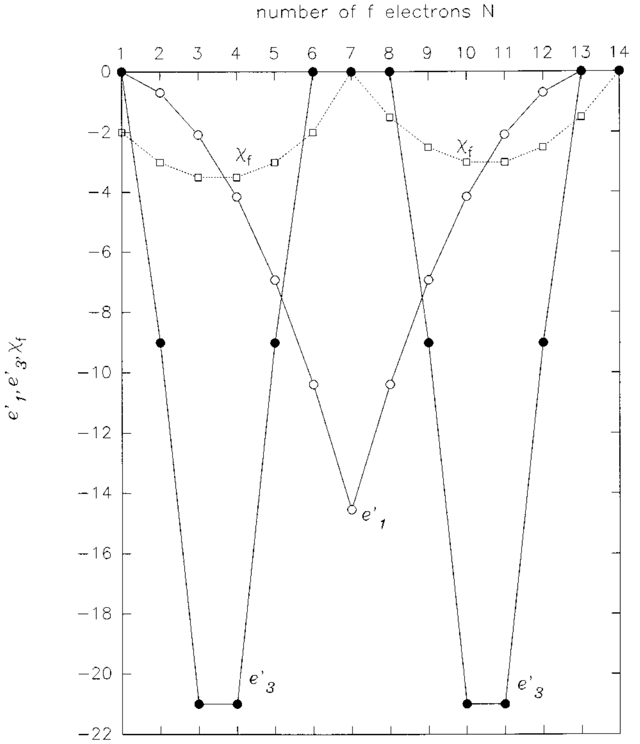

Figure 3. Dependence of the Coulomb interaction coefficients e_1' (○) (eq 16), e_3' (●) (eq 17), and the coefficient χ_f (□) (eq 18) at the spin−orbit constant ζ_f on the number of electrons in the f^N shell.

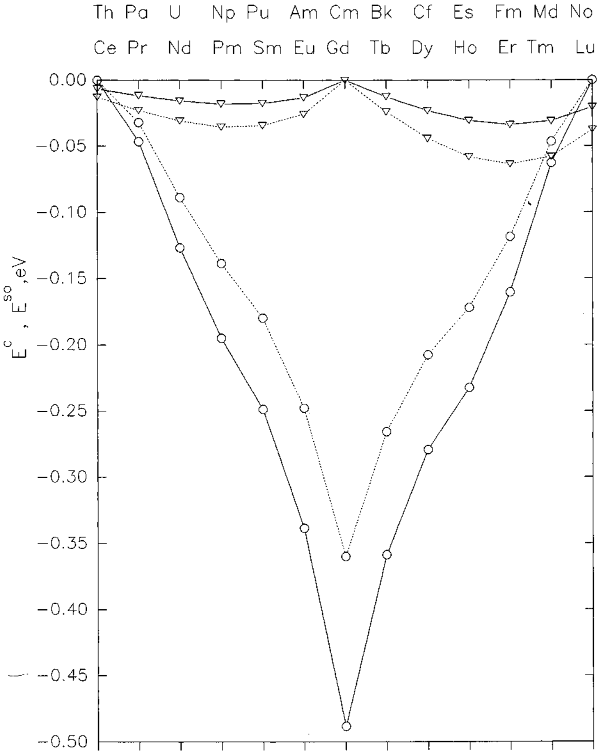

Figure 4. Variation of the energy of Coulomb interaction within the nf^N shell energy (with respect to the average energy) (○) and the spin−orbit interaction energy (▽) for the ground state of trivalent lanthanides (solid line) and actinides (dotted line).

potential barrier is less expressed); on the contrary the spin−orbit interaction increases for actinides approximately twice. However for the majority of elements it remains considerably smaller than the Coulomb interaction. Thus the *LS* scheme can be used for the description not only of the $4f^N$ shell in lanthanides but also of the $5f^N$ shell in actinides.

The main term e'_1E^1 of the term-dependent energy determines the small periodicity or the gadolinium break for some properties related with the ground-state energy, for example, for the ionic radii.

The ground state of the nf^N shell is usually separated energetically by about 1 eV from the other states with the same total momentum *J*. This reason together with the relatively small spin−orbit interaction within the $4f^N$ shell causes fairly pure coupling for the ground state of lanthanides with one open $4f^N$ shell.[22,35] Mixing of terms essentially increases for actinides, but due to the tendency of terms with higher multiplicity to lie lower in the spectrum, the ground term tends to mix mainly with the other terms of the same multiplicity. Such mixing does not violate the symmetry with respect to a quarter shell which takes place for all terms of highest multiplicity.

This symmetry is not violated also by some configuration mixing effects. It is known that the values of integrals E^i, calculated in the single-configuration approximation, essentially exceed their empirical values. This is caused by the interaction of the considered configuration with some type of distant configurations.[36] However the ratio $E^i_{\rm emp}/E^i_{\rm theor}$ remains almost constant for all lanthanides[28,37] (the systematic semiempirical investigation of actinides has not been performed yet).

The mixing of the considered configuration with some other distant configurations gives rise to the correlation corrections[36]

$$\Delta E^{\rm cor} = \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) \qquad (19)$$

where α, β, γ are the empirical parameters and $G(G_2)$, $G(R_7)$ are the eigenvalues of the Casimir operator for the special G_2 and R_7 groups. These corrections play a rather important role in the spectra of elements with an open f^N shell.[22,37] Some relativistic corrections like the part of the "orbit−orbit" interaction can also be presented in the form of eq 19. The quantities $G(G_2)$, $G(R_7)$ are expressed in terms of quantum numbers ω_i and u_i, which for the terms of highest multiplicity are symmetric with respect to a quarter of shell. For the ground term using the eqs 7−10 we obtain the following formula:

$$G(G_2) = \frac{N(7-N)}{2^2\cdot 3^3\cdot 5}[6 + 41N(7-N) - 2N^2(7-N)^2] \qquad (20)$$

$$G(R_7) = \frac{1}{2}N(7-N) \qquad (21)$$

Thus all three factors at the constants α, β, and γ in eq 19 are also symmetric with respect to a quarter and a half a shell (Figure 5).

Consequently the "electron-vacancy" symmetry not only takes place in the single-configuration pure term approximation but remains approximately valid also taking into account some term and configuration mixing as well as relativistic effects.

When a configuration of the rare earth atom contains $(n+1)$d or $(n+2)$s electrons above the nf^N shell ($n = 4$ for lanthanides and $n = 5$ for actinides), the Coulomb interaction within this shell remains dominant in the atom (it exceeds several times and even by an order of magnitude the interaction between the nf^N shell and $(n+1)$d or $(n+2)$s electrons). Thus usually in the ground state of such a configuration the *n*f electrons keep their many-electron quantum numbers according to Hund's rule. The energy of the direct Coulomb interaction between nf^N and other open shells also obeys the "electron-vacancy" symmetry for the nf^N shell, but this does not take place for the Coulomb exchange interaction.

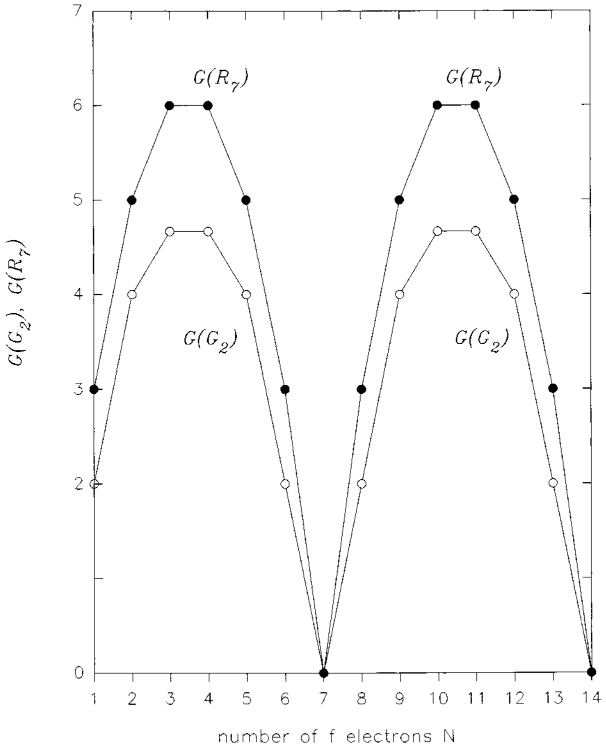

Figure 5. Symmetry of the eigenvalues of Casimir operators $G(G_2)$ (○) and $G(R_7)$ (●) for the ground state of the f^N shell. A few important configuration mixing effects are expressed in terms of these values (eq 19).

This reason together with the larger mixing for the ground state of such a configuration leads to additional deviations from the symmetry with respect to a quarter of the f^N shell.

The Symmetry for the Energy Differences. The Interval Rules and *L* Dependence

One of the principal atomic quantities, the ionization energy of a shell (the binding energy of an electron in the shell), is defined as the energy difference of the ion with vacancy nl^{-1} and the atom (or ion) without this vacancy in their ground states:

$$I_{nl} = E(nl^{-1}\gamma'_{\rm g}) - E(\gamma_{\rm g}) \qquad (22)$$

We will consider these quantities for the configurations with one open nf^N shell. When the nf^N shell has the smallest ionization energy among the atomic shells, $I_{n\rm f}$ gives the ionization potential (ionization energy) for the atom.

It is useful to separate the ionization potential into the parts corresponding to the contributions of the average energy ($I^{\rm av}_{n\rm f}$), the Coulomb interaction between *nf* electrons ($I^{\rm C}_{nf}$), and the spin−orbit interaction ($I^{\rm so}_{n\rm f}$):

$$I_{n\rm f} = I^{\rm av}_{n\rm f} + I^{\rm C}_{nf} + I^{\rm so}_{n\rm f} \qquad (23)$$

According to the Koopman's theorem, the average energy part approximately is equal to the single-electron energy and it depends almost linearly on the atomic number. For the qualitative investigation of the $I_{n\rm f}$ dependence on the number of electrons in the nf^N shell the radial integrals E^i and the spin−

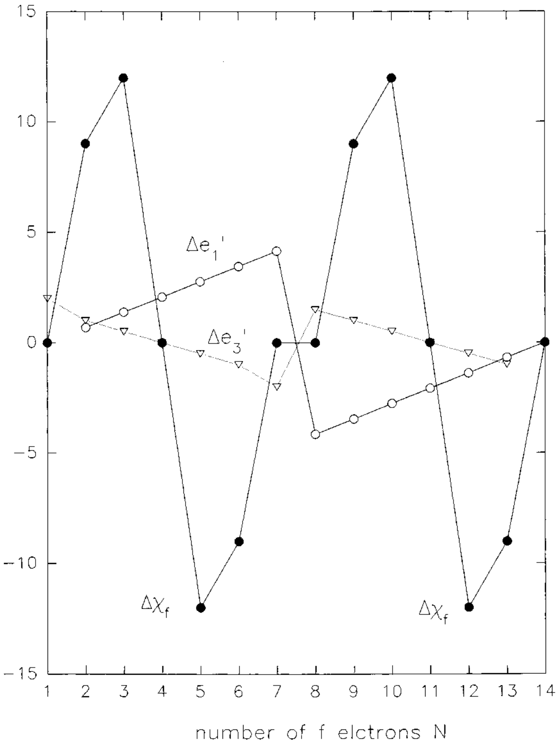

Figure 6. Dependence of the differences $\Delta e_i'(f^N)$ ($i = 1, 3$) (eq 26) and $\Delta\chi_f(l^N)$ (eq 27) on the number of electrons in the f^N shell.

orbit constant ζ_{nf} can be supposed for the configurations nf^N and nf^{N-1} to be equal; then the Coulomb and the spin−orbit parts in eq 23 can be presented as follows:

$$I^C{}_{nf} = \sum_i \Delta e_i'(f^N)E^i \tag{24}$$

$$I^{so}_{nf} = \Delta\chi_f(f^N)\zeta_{nf} \tag{25}$$

where

$$\Delta e_i'(f^N) = e_i'(f^{N-1}) - e_i'(f^N) \tag{26}$$

$$\Delta\chi_f = \chi_f(f^{N-1}) - \chi_f(f^N) \tag{27}$$

Taking the differences of the coefficients the symmetry $f^N \rightarrow f^{7-N}$ ($N \leq 7$) is changed into $f^N \rightarrow f^{8-N}$; thus the quantities $\Delta e_i'$ and $\Delta\chi_f$ become symmetric with respect to the numbers of electrons $N_0 = 4$ and 11 (Figure 6). Consequently, the following relation takes place for $\Delta e_i'$ and $\Delta\chi_f$:

$$X(f^{N_0-q}) + X(f^{N_0+q}) = 2X(f^{N_0}) \tag{28}$$

where $X \equiv \Delta e_i, \Delta\chi_f$; $N_0 = 4, 11$; and $q = 1, 2, 3$.

The values of $\Delta e_1(f^{N_0})$ and $\Delta\chi_f(f^{N_0})$ are equal to 0.

Namely the variation of the coefficient $\Delta e_1'$ determines the main trend of the periodicity for the ionization potential and other quantities related with the energy differences of two configurations with different numbers of f electrons (Figures 1, 2). The other coefficients $\Delta e_3'$ and $\Delta\chi_f$ only slightly modify this periodicity.

TABLE 1: Values of the Coefficients a_1, a_3, b, and e in the Expansions 29, 30, and 31 as well as the Deviation from the Interval Rule Δ (Eq 32) for Ln^{3+} and An^{3+} Ions

ions	$a_1 \times 10^4$, eV	$a_3 \times 10^4$, eV	$b \times 10^4$, eV	$e \times 10^2$, eV
Ln^{3+}	9.763	0.274	8.630	−3.504
An^{3+}	8.912	0.223	15.57	−2.442

$\Delta \times 10^3$

	$N_0 = 4$			$N_0 = 11$		
ions	$q = 1$	$q = 2$	$q = 3$	$q = 1$	$q = 2$	$q = 3$
Ln^{3+}	−1.80	−7.14	−16.08	−1.77	−7.10	−15.90
An^{3+}	−1.27	−5.05	−11.43	−1.25	−5.01	−11.22

The integrals E^i can be approximated by the linear series, the spin−orbit constant ζ_{nf}, and the average energy part of the binding energy (I^{av}_{nf}) by the quadratic series in terms of the number of electrons (for the ions Ln^{3+} and An^{3+} the accuracy of this approximation is better than 1%):

$$E^i(f^N) = E^i(f^{N_0}) + \mathrm{a}_i(N - N_0) \tag{29}$$

$$\zeta_{nf}(f^N) = \zeta_{nf}(f^{N_0}) + b(N - N_0) + c(N - N_0)^2 \tag{30}$$

$$I^{av}_{nf}(f^N) = I^{av}_{nf}(f^N) + d(N - N_0) + e(N - N_0)^2 \tag{31}$$

where a_i, b, c, d, and e are the numerical constants, obtained by the least-squares fitting.

Using the expansion 23 and the symmetry properties for the coefficients 26 and 27, the following expression for the ratio of the ionization energies is obtained:

$$\frac{I_{nf}(f^{N_0-q}) + I_{nf}(f^{N_0+q})}{I_{nf}(f^{N_0})} = 2 + \Delta \quad (N_0 = 4, 11;\ q = 1, 2, 3) \tag{32}$$

where the second term Δ on the right side of equation has the following expression:

$$\Delta = \left\{\frac{18}{13}a_1q^2 - \frac{1}{5}a_3q^2(2q^4 - 35q^2 + 153) - bq[q + \delta(q,3)\delta(N_0,4)] + 2eq^2\right\}I^{-1}_{4f}(f^{N_0}) \tag{33}$$

The coefficients c and d do not give contributions to Δ. The quantity Δ gives only a small correction to 2 for the neutral and several time ionized atoms (Table 1). Omitting Δ, the interval rule for the binding energies is obtained:

$$\frac{I_{nf}(f^{N_0-q}) + I_{nf}(f^{N_0+q})}{I_{nf}(f^{N_0})} = 2 \quad (N_0 = 4, 11;\ q = 1, 2, 3) \tag{34}$$

It can be presented in the other form

$$\frac{I_{nf}(f^{N_0-q}) + I_{nf}(f^{N_0+q})}{I_{nf}(f^{N_0-q'}) + I_{nf}(f^{N_0+q'})} = 1 \quad (N_0 = 4, 11;\ q, q' = 1, 2, 3) \tag{35}$$

Such interval rules for the ionization energies and oxidation potentials were obtained empirically[12] and grounded using the properties of the coefficients at the radial integrals.[18] It was indicated that the deviations from the interval rules can be caused only by the crystal field. As follows from eq 33, the spin−orbit and even Coulomb interaction within the nf^N shell as well as the nonlinearity in the variation of the average energies can also be the reason for such deviations. For neutral atoms and the first ions all these contributions are of the same order and partially compensate each other. The deviations from

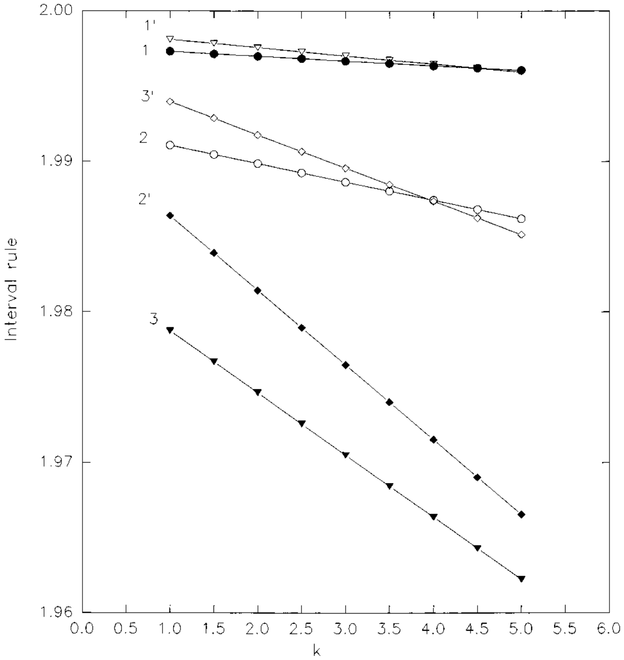

Figure 7. Deviation of the ratio of ionization energies from the interval rule with the increase of the contribution of the spin−orbit interaction with respect to the Coulomb interaction. Such increase is modeled multiplying the spin−orbit interaction constant ζ_{4f} by coefficient *k* at the constant values of Coulomb interaction integrals for Ln^{3+}. The number *q* is indicated near the corresponding curve (without prime for $N_0 = 4$ and with prime for $N_0 = 11$).

the interval rule in the free ion model become more significant only with the essential increase of the spin−orbit interaction (Figure 7).

The interval rule also approximately holds for the energy differences of the energies for the ground states of two nf^N and $nf^{N-1}n'l'$ configurations, differing by the number of *n*f electrons.[9] This energy difference between the two configurations is mainly determined by the change of the number of *n*f electrons and has symmetry properties similar to the ionization energy for the nf^N shell (Figure 2).

The interval rules take place also for the other physical and chemical properties of lanthanides and actinides, which can be related with the differences of the energies for configurations with different numbers of *n*f electrons in their ground state.[14,18,38]

Some attempts were made to relate the main properties of the ground state of lanthanide and actinide ions with the orbital quantum number *L* of this state. For ionization energies, radial integrals E^i and ζ_{nf}, ionic radii, and other quantities[16] such dependence has been found to be nearly linear.

As shown above, various properties of the ground state, including the orbital quantum number *L*, can be expressed in terms of the number *N* of f electrons. Thus it is possible to obtain the relations between these characteristics and *L*, but usually they are not simple. However, within the four intervals of the f electron numbers 1−3, 4−7, 8−10, and 11−14, the orbital quantum number *L* varies almost linearly (Figure 8). Consequently, every quantity that behaves in a similar manner within these intervals (its curve is a little convexed as for *L* (the ionization potential) or even is strictly linear (some quantity *X* in Figure 8)) can be represented by the "inclined *W*" plot consisting of four linear segments. This plot can sometimes be useful for the interpolation of values, but it shows only the correlation of two quantities, not their true linear dependence (taking into account excluded intervals 7−8 and 10−11, the relation becomes considerably more complex).

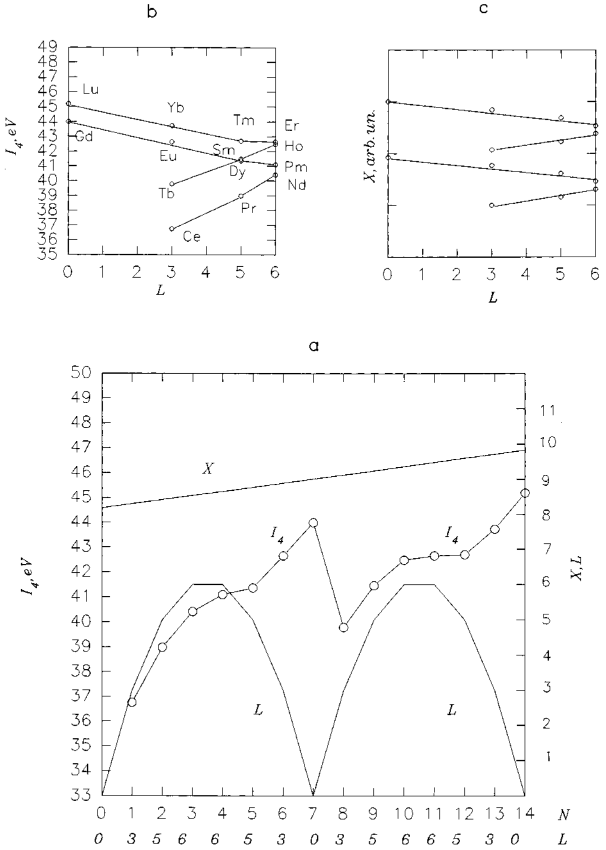

Figure 8. Variation of the orbital quantum number *L*, the fourth ionization potential I_4 (experimental values[17]), and some quantity *X* directly proportional to the number *N* of 4f electrons in the series of lanthanides (a) and the correlation between I_4, *X*, and *L* values (*L* dependence) (b, c).

Conclusions

We proceed from the predominant assumption that the periodicity of the chemical properties for lanthanides and actinides is mainly determined by the peculiarities of the inner atomic nf^N shell and investigate the symmetry properties for the characteristics of this shell and the related quantities. The electronic shell in its higher multiplicity state can be separated in a unique way into two subshells with spins of electrons directed up and down. The "electron-vacancy" symmetry for the subshell having only half states of the shell manifests as the symmetry with respect to a quarter of the shell. It is characteristic for the many-electron numbers *L*, *U*, *W*, defined in the orbital space, and for the matrix elements of operators, having no scalar part.

The symmetry with respect to a quarter of the shell not only takes place in the single-configuration pure term approximation but remains approximately valid also taking into account some term and configuration mixing as well as relativistic effects.

It is shown that all many-electron quantums numbers, energies, and some other characteristics for the ground state of the f^N shell can be expressed in terms of the number *N* of *n*f electrons. The interval rule for the ionization energies is obtained, and it is shown that the deviation from this rule in the free atom model becomes more significant only with the increase of spin−orbit interaction. The "inclined *W*" plot for some quantities is explained as the consequence of the near linear dependence of the corresponding quantity and *L* on electron numbers within four intervals.

Of course, the symmetry originating from the properties of the atomic nf^N shell is modified to a smaller or larger extent by the environmental effects and takes various forms or even does not appear at all. Thus our results show only the tendency for the manifestation of periodicity.

The main results obtained can be extended to the d^N shell, but the periodicity of properties for the elements with this shell is more modified by the chemical bonding and configuration mixing effects.

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