

IFUSP/P-73

MULTIPLIET SPLITTING OF THE 4s ELECTRONS
OF THE EARTHS

by

B.I.F. - USP

A.C.Pavão - Instituto de Química - USP

and

J.R.Leite - Instituto de Física - USP

MULTIPLY SPLITTING OF THE 4s ELECTRONS OF THE RARE EARTHS *

A.C. Pavão

Instituto de Química, Universidade de São Paulo
C.P. 20780, São Paulo, Brazil

and

J.R. Leite

Instituto de Física, Universidade de São Paulo
C.P. 20516, São Paulo, Brazil

ABSTRACT

The 4s multiplet splittings in the trivalent rare earths were calculated. Such theoretical calculations are in good agreement with experiment, provided that the electronic Coulomb correlations effects, the dependence of the exchange term on the electronic local velocity and relaxation effects are taken into account.

(*) Work supported by Conselho Nacional de Desenvolvimento Tecnológico e Científico and Fundação de Amparo à Pesquisa do Estado de São Paulo.

The 4s photoelectron spectra of the trivalent rare earths (RE) show doublet structures due to multiplet coupling of the final 4s hole state with the partly filled 4f shell. We report here the calculations of these splittings using the spin polarized Hartree-Fock (SPHF) with an approximation to the exchange term based on the mass operator of the many body theory.

Dealing with the 3d-group transition elements, Bagus et.al. (1) showed that correlation effects must be taken into account for understanding the magnitude of the s doublet splitting. We can estimate the electronic Coulomb correlation on the splitting by comparing calculations with Liberman approximation (X_L) to the exchange term and experiment. This can be done because it is well known that the Liberman approximation reproduces the one electron Hartree-Fock energy eigenvalues (2). Table 1 indicates the importance of correlation effects as well as relaxation effects. In order to include the Coulomb screening in the SPHF formalism we used a single particle description of manybody systems based on effective wave equation, with the mass operator (X_M) instead of the simpler exchange operator of the Hartree-Fock Theory. Using this formalism we have already obtained good results for 3d-transition metal core electron splittings (4). This is also verified for rare earths serie.

Insert Table 1

A local approximation to the mass operator can be obtained from the real part of the eigenvalue of this operator

in the free electron gas (5). For an excitation with wavevector k in a gas with Fermi momentum k_F one obtains the exchange correlation energy in atomic units

$$\begin{aligned}
 X_M(k) = & \left[-\frac{2}{\pi} \left\{ k_F + \frac{k_F^2 + k_{FT}^2 - k^2}{4k} \ln \frac{(k + k_F)^2 + k_{FT}^2}{(k - k_F)^2 + k_{FT}^2} \right. \right. \\
 & \left. \left. + k_{FT} \left(\tan^{-1} \frac{k - k_F}{k_{FT}} - \tan^{-1} \frac{k + k_F}{k_{FT}} \right) \right\} \right] \\
 & + \{ 0.054 k_F \theta (129 - k_F) \ln (k_F/129) \} \quad (I)
 \end{aligned}$$

where $k_{FT} = (4k_F/\pi)^{1/2}$ is the Thomas-Fermi wavenumber, $k_F = (3\pi^2 n)^{1/3}$, and n is the electron gas density.

The first term inside the brackets in Equation I can be interpreted as the exchange energy when the Coulomb interaction is screened by the Thomas-Fermi dielectric constant. The second term comes from the imaginary part of the RPA dielectric constant and can be interpreted as a shift in the excitation frequency due to the absorption in the electron gas.

The spin polarization effects are taken into account in the first term of the right hand side of Equation I supposing two electronic gases, each one with different Fermi wave numbers, that is

$$k_{F\uparrow} = (6\pi^2 n_{\uparrow})^{1/3}$$

$$k_{F\downarrow} = (6\pi^2 n_{\downarrow})^{1/3}$$

where $n\uparrow$ and $n\downarrow$ are the electronic densities for up and down spins.

In the present work we used the approximate form of the mass operator in the SPHF formalism. In this way the Coulomb correlation effect and the exchange-correlation dependence on the local electronic velocity are included in the theory.

In order to take into account the relaxation effects (Table 1) we evaluated the 4s splittings taking the total energy difference between the two RE^{4+} free ion states.

In Fig. 1 we present the results of our calculations with the correspondent experimental data.

Insert Figure 1

The small differences between experience and theory can be attributed to covalence effects.

The plotted theoretical data show that the splitting is proportional to $2S + 1$ where S is the f-shell spin of the trivalent metal.

The results reported here are typical for the rare earths elements. Calculations were done for 4s (divalent) and 5s (divalent and trivalent) splittings and the general conclusion is that the magnitude of the core electrons splittings depends critically of the electron Coulomb correlation effects. On the other hand, the relaxation effects are also important and has to be considered in order to have an agreement with experiment, for both 4s and 5s splittings.

REFERENCES:

- (1) P.S. Bagus, A.J. Freeman and F. Sasaki, Phys. Rev. Lett. 30, 850 (1973).
- (2) D.A. Liberman, Phys. Rev. 171, 1 (1968).
- (3) R.L. Cohen, G.K. Wertheim, A. Rosencwaig and H.J. Guggenheim, Phys. Rev. B5, 1037 (1972).
- (4) J.C. Rodrigues, A.C. Ferraz, A.C. Pavão and J.R. Leite - to be published in Journal of Physics.
- (5) J.R. Leite and L.G. Ferreira, Phys. Rev. A3, 1224 (1971).

Table 1 - Calculated and Observed Splitting for Gd

		4s splitting (eV)	5s splitting (eV)
Observed (a)	GdF ₃	8.2	3.7
X _L	ΔE	12.68	5.97
	Δε	17.99	9.29
X _M	ΔE	9.17	3.16
	Δε	11.37	3.78

(a) According reference (3)

ΔE is the total energies differences between the ⁹S and ⁷S states of the Gd⁴⁺ ion. Δε is the difference of SPHF energy eigenvalues (Gd³⁺).

FIGURE CAPTION

Fig. 1 - 4s core-electron splittings for RE^{3+} as a function of $2S + 1$ (S is the trivalent ion spin). Experimental data are from reference (3).

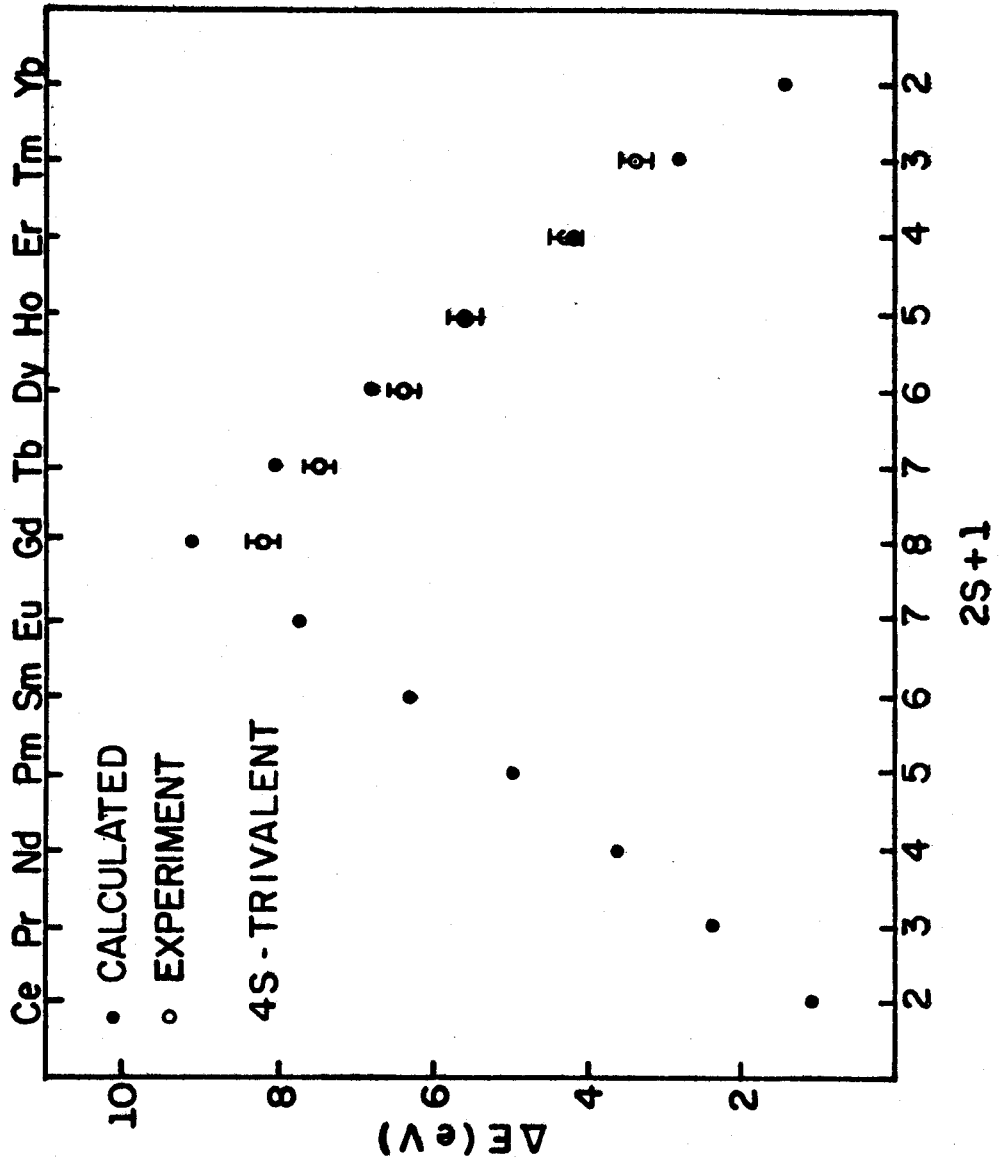


Figure 1