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Free-electron-gas exchange correlation in the calculated multiplet splittings of s-core levels in $3d$ transition metals and rare-earth elements*

J. R. Leite, J. C. Rodrigues, and A. C. Ferraz
Instituto de Física, Universidade de São Paulo, Caixa Postal 20516, São Paulo, Brazil

A. C. Pavão
Instituto de Química, Universidade de São Paulo, Caixa Postal 20780, São Paulo, Brazil

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A local approximation to the exchange-correlation effects is used in a detailed calculation of the s-core binding-energy splittings for the $3d$ transition elements and rare-earth series. Our approach to the many-body problem is a single-particle model based on an effective wave equation with the mass operator instead of the simpler exchange operator of Hartree-Fock theory. By treating the exchange-correlation effects (mass operator) in a form of an effective local potential in the free-electron gas, the splittings are calculated in the framework of the self-consistent-field method applied to free ions. The results are in good agreement with x-ray photoemission experimental data taken for $3d$ transition and rare-earth ionic compounds and metals.

I. INTRODUCTION

Photoelectron spectroscopy in x-ray energy region (XPS) has been used as a technique in studying the multiplet structure of core-electron binding-energy splittings in the $3d$ transition-metal ions[1-9] and the rare-earth (RE) series.[10-14] Since the first observation of multiplet splitting of core levels in XPS spectra of solids by Fadley *et al.*,[15] many investigations have been made in order to understand the phenomenon.[16-18] Special attention has been made to the s-core level splittings of atoms in free[16,17] and compounded[19] states. The spin polarization effects due to the $3d$ or $4f$ incomplete shells give rise to the s-core electron doublet structure observed in the spectra of $3d$ transition-metal complexes or RE elements. Comparison with free ion[16,17] and cluster Hartree-Fock calculations[1,2] has been reported for the $3d$ transition elements. The calculated $2s$ splittings for free ions show good agreement with experiment but the calculated $3s$ splittings are larger by a factor of 2 than those measured. Analogous results to that were obtained for the s-core level splittings in RE series. By using Van Vleck's theorem[13] it has been shown that the $5s$ splittings are calculated quite well while the $4s$ splittings are systematically predicted with 80% deviation from the experimental results. Relativistic effects on these splittings calculated by the relativistic Dirac formalism are found to be small.[17] Bagus *et al.*, by using the configuration-interaction (CI) method, have incorporated the effect of correlation and showed it to be of great importance in explaining the $3s$ splitting observation in Mn.[16] This correlated multiplet hole theory has been applied recently to calculate the $3s$ splittings for other $3d$ transition-metal free ions.[20] In all cases analyzed one obtains a splitting that is less than the measured value in fluoride compounds. The covalency effects are small for these compounds; however, their inclusion should decrease the calculated values further.[19] Furthermore the CI results reported in Ref. 20 show that, in disagreement with experiment, the $3s$ splitting increases with decreasing number of unpaired $3d$ electrons. Another important point related to this subject is the theoretical interpretation of the experimental data for the RE elements. It has been pointed out that the large calculated values for the $4s$ splittings in these elements can be reduced by taking into account the electron correlation effects.[13]

In this work we present the calculated values for the $2s$ and $3s$ splittings of the $3d$ transition-metal elements and for the $4s$ and $5s$ splittings of the RE series. In all cases the influence of the correlation effects on the calculated splittings is analyzed. Our results confirm that the correlation effects are of great significance in predicting the correct magnitude of s-core level splittings in the RE series. We are adopting a single-particle description of many-body systems based on an effective wave equation with the mass operator instead of the simpler exchange operator of the Hartree-Fock theory. An approximate value for the mass operator was already proposed based on the eigenvalue of this operator for the free-electron gas.[21,22] This paper shows how successful the free-electron gas approximation is when used in inhomogeneous systems if one also includes into the exchange operator the effects due to the Coulomb correlation.

In Sec. II we reintroduce the theory on which this paper is based. Section III gives our calculated results for the magnitude of the 2s and 3s splittings for the 3d transition-metal ions. Section IV gives the 4s and 5s splittings for the RE elements. Our main conclusions are shown in Sec. V.

II. EXCHANGE-CORRELATION ENERGY IN THE FREE-ELECTRON GAS MODEL

In this section we present a brief review of the way we introduce the correlation effects in inhomogeneous systems, as well as the method used to calculate the s-core level binding-energy splittings.

A local approximation to the mass operator of the many-body theory can be obtained from the real part of the eigenvalue of this operator in a free-electron gas.[21] For an excitation with wave vector $\vec{k}$ in a gas with Fermi momentum k_F one obtains the exchange-correlation energy, in a.u.,

$$X_M(\vec{k}) = \left\{ -\frac{2}{\pi}\left[k_F + \frac{k_F^2 + k_{FT}^2 - k^2}{4k} \ln \frac{(k+k_F)^2 + k_{FT}^2}{(k-k_F)^2 + k_{FT}^2} + k_{FT}\left(\tan^{-1}\frac{k-k_F}{k_{FT}} - \tan^{-1}\frac{k+k_F}{k_{FT}} \right) \right] \right\} + \left[0.054\, k_F\, \theta(129 - k_F) \ln\left(\tfrac{1}{129} k_F\right) \right], \qquad (2.1)$$

where

$$k_{FT} = (4k_F/\pi)^{1/2} \qquad (2.2a)$$

is the Thomas-Fermi wave number,

$$k_F = (3\pi^2 n)^{1/3}, \qquad (2.2b)$$

and n is the electron gas density.

The first term inside the large curly brackets in equation (2.1) can be interpreted as the exchange energy where the Coulomb interaction is screened by the Thomas-Fermi dielectric constant ϵ. The second term comes from the imaginary part of the random-phase-approximation (RPA) dielectric constant and can be interpreted as a shift in the excitation frequency due to the absorption in the electron gas. As far as the spin polarization effects are concerned, it has been shown that the second term inside the small square brackets in the right-hand side of equation (2.1) is not changed by any reasonable degree of spin alignment.[22] For this term k_F is calculated from the total (up and down spin) electronic density. The effects of the spin polarization are taken into account in the first term of the right-hand side of equation (2.1) supposing two electronic gases, each one with different Fermi wave numbers: $k_{F\uparrow}$ and $k_{F\downarrow}$. These Fermi wave numbers are to be calculated from

$$k_{F\uparrow} = (6\pi^2 n\uparrow)^{1/3}, \qquad (2.3a)$$

$$k_{F\downarrow} = (6\pi^2 n\downarrow)^{1/3}, \qquad (2.3b)$$

where $n\uparrow$ ($n\downarrow$) are the electronic densities for up (down) spins. Thus for each electronic gas with a different spin direction, the first term of the mass operator should be calculated from equation (2.1) with $k_{F\uparrow}$ (or $k_{F\downarrow}$) instead of k_F, but with k_{FT} calculated from the total electronic density ($n\uparrow + n\downarrow$) through Eqs. (2.2). When using $X_M(\vec{k})$ in atomic, molecular, or band calculations as the exchange-correlation energy for an electron with spin "up," for example, one considers its kinetic energy $k_\uparrow^2$ as function of the position through

$$k_\uparrow^2 = E_\uparrow - v(\vec{r}) - X_M(\vec{k}_\uparrow), \qquad (2.4)$$

where $E_\uparrow$ is the electron energy eigenvalue and $v(\vec{r})$ is the Coulomb potential. Thus one obtains a local approximation for the mass operator in the form of a potential energy. If one makes the RPA dielectric constant $\epsilon = 1$, Eq. (2.1) becomes the well-known expression for the exchange energy in a free-electron gas $X_L(\vec{k})$.[23] The second term inside small square brackets in the equation (2.1) vanishes and k_{FT} is equal to zero in the first term. $X_L(\vec{k})$ is the Liberman approximation to the Hartree-Fock exchange term. Thus in the Liberman approximation, the exchange energy is also made dependent on the local electronic speed and the electronic correlation effects are neglected. In the present investigation we are interested in obtaining the magnitude of the s-core level splittings for the 3d transition elements and the RE series by using the approximate form $X_M(\vec{k})$ to the exchange-correlation energy. By comparing the results obtained with $X_M(\vec{k})$ and $X_L(\vec{k})$ we will be able to estimate the importance of the Coulomb correlation in explaining important features of the s-core splitting observations.

Our interpretation of the photoelectron spectra of ionic 3d transition- or RE-metal compounds starts by first considering the metal ion in the initial ${}^{2S+1}L$ state. For an RE element we have

$$[(\text{core})\ 4s^2\, 4p^6\, 4d^{10}\, 4f^n 5s^2\, 5p^6\,]^{2S+1}L\,. \qquad (2.5)$$

If an s electron is ejected, say, a 4s electron, two final ground states will be formed:

$$[(\text{core})\ 4s(^2S)\, 4p^6\, 4d^{10}\, 4f^n\, (^{2S+1}L)\, 5s^2\, 5p^6\,]^{2(S+1)}L\,; \qquad (2.5a)$$

$$[(\text{core})\ 4s(^2S)\, 4p^6\, 4d^{10}\, 4f^n (^{2S+1}L)\, 5s^2\, 5p^6\,]^{2S}L\,. \qquad (2.5b)$$

In a physically simple model the ejected electron is supposed to have a spin parallel [Eq. (2.5a)] or antiparallel [Eq. (2.5b)] to the $4f^n$ spin. For each state indicated by Eqs. (2.5) we determine the one-particle wave functions and energy eigenvalues by solving the spin polarized effective wave equations[22] where the mass operator is approximated by Eq.

TABLE I. Calculated and observed splittings for Mn. X_M is the mass operator approximation to the exchange-correlation energy. X_L is the Liberman approximation to the Hartree-Fock exchange term. ΔE are the energy differences between the two final ground states of the Mn^{3+} ion. $\Delta\epsilon$ are the differences between spin polarized energy eigenvalues of Mn^{2+}.

		3s splitting (eV)	2s splitting (eV)
Observed[a]	MnF_2	6.5	5.85
	MnO	5.7	···
CI[b]	Internal	4.71	···
	Semi-internal	8.2	···
X_M	ΔE	6.96	5.00
	$\Delta\epsilon$	7.49	3.98
X_L	ΔE	12.84	7.80
	$\Delta\epsilon$	16.18	5.55

[a] Reference 4.
[b] Reference 16.

(2.1). We may then evaluate the 4s (5s) splitting in two ways: (i) assuming the difference ($\Delta\epsilon$) between the energy eigenvalues of 4$s\uparrow$ (spin up) and 4$s\downarrow$ (spin down) of the ion initial state (Koopmans's theorem method); (ii) taking the total energy difference (ΔE) between the two final ground states. The latter procedure is more correct since the relaxation effects are taken into account. The results reported in this work were obtained by means of a program described by Herman and Skillman.[24] This program, which calculates atomic orbitals and energy levels, was modified by us in order to handle self-consistent potentials dependent on the energy eigenvalue, and extended to include spin polarization effects.

One could argue that one source of error in our method should be the comparison between core-electron binding-energy splittings calculated for free ions, with the experimental results taken when the ions are under the influence of chemical surroundings. Recent investigations[19] with the multiple scattering X_α method in a cluster of the 3d transition-metal ion and six neighboring ligands in octahedral geometry [$MnX_6{}^{4-}$ (X = F, Cl, Br)] show that the environmental effects are usually small. The difference between the 3s splitting for the free ion Mn^{2+} and for the complex is a few tenths electron volts. This difference is very small (0.2 eV) if the ligands are F. All the experimental data quoted in the present paper for the 3d transition elements are taken from photoelectron spectra of fluoride compounds. For the RE elements, besides the experimental results in trifluoride compounds, we are also considering s-core splittings obtained from photoelectron spectra of metals. It has been shown earlier[13] that the XPS spectra of the 4f region of the metals compare well with XPS results on the trifluorides.

III. RESULTS FOR THE 3d TRANSITION ELEMENTS

In Table I we analyze the calculated and observed s-core level binding-energy splittings for Mn. The results of a CI calculation, according to Ref. 16, is included for comparison with our calculations. The entries in Table I show a definite reduction of the 3s splitting when the correlation effects are considered. The best Hartree-Fock multiplet-hole-theory (MHT) results for 3s splitting is 14.3 eV.[16] The entries quoted by X_L and X_M are the results of our calculations with the approximations to the exchange and correlation based on the free-electron gas model. They are typical for all 3d transition elements. The electron relaxation effects are noted by comparing the entries quoted as $\Delta\epsilon$ and ΔE. The results quoted as ΔE are obtained taking the relaxation effects into account. The results obtained when one uses the free-electron gas approximation to the Hartree-Fock exchange term X_L deviate strongly from experiment (100% for the 3s splitting). Once the correlation effects are included in the model through the mass operator a definite improvement in the results are obtained. A good agreement between theory and experiment is obtained for the s-core binding-energy splittings. We can conclude also from Table I that correlation effects are more important for the 3s than for the 2s levels. However they are not negligible effects as far as the 2s energy levels are concerned. The relaxation effects are less important but must be considered in order to get a better agreement with experiment. In Table II we show our calculated results for the 3s splittings (ΔE) obtained with X_M approximation to the exchange-correlation energy. The MHT entries are from the best Hartree-Fock multiplet-hole theory.[17] The CI results are from Ref. 20. Table II has an interesting feature: our calculated results predict

TABLE II. 3s splittings of the 3d transition-metal ions (energies in eV).

Ion	Initial-state spin (S)	MHT[a]	CI[b]	X_M[c]	Expt.[d] (Fluoride compounds)
Mn^{2+}	$\frac{5}{2}$	14.3	4.3	6.96	6.5(6.6)[e]
Fe^{2+}	2	12.4	4.5	5.88	5.85(6.1)[a]
Co^{2+}	$\frac{3}{2}$	10.3	5.5	4.70	5.05(5.0)[f]
Ni^{2+}	1	8.1	3.9	3.18	3.1(4.0)[f]

[a] Reference 17.
[b] Reference 20.
[c] This work.
[d] Reference 4.
[e] Reference 6.
[f] Reference 3.

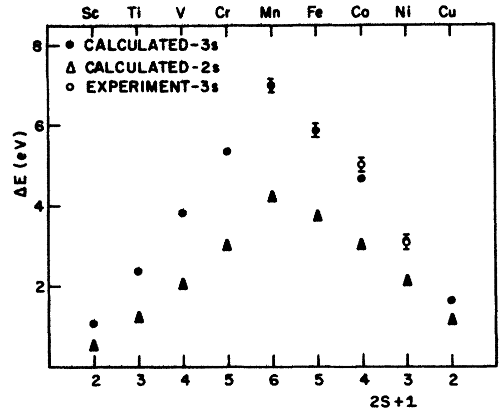

FIG. 1. 2s- and 3s-electron binding-energy splittings for the 3d transition elements. The calculated values were obtained by using the X_M approximation to the exchange-correlation energy. S is the initial-state spin of the divalent ion. The open circles are the XPS results on fluoride compounds (Ref. 4).

a decreasing of the splitting with the decreasing of the ion initial-state spin (according with the experiment but in disagreement with CI calculations). The splittings are roughly proportional to the ion initial-state spin. This behavior is observed in the spectra of 3d transition and RE fluoride complexes and confirmed by our results. In Fig. 1 are shown the results of our study of the 2s- and 3s-core binding-energy splittings for the 3d transition-metal elements. Also shown is the magnitude of the splittings obtained with the X_M approximation to the exchange-correlation energy as a function of $2S+1$, where S is the initial-state spin of the divalent ion. All the calculated values refer to ΔE, thus the relaxation effects are taken into account. The experimental results were taken in fluoride compounds[4] and the errors quoted in the figure refer to the least-squares fit of the experimental data. Our main conclusion related to the results shown in Fig. 1 is that the correlation effects are of great importance in describing correctly the s-core level splittings in the 3d transition elements. Once the correlation effects are neglected in the free-electron gas model, the calculated results deviate drastically from experiment. A typical situation was shown in Table I. Figure 1 also shows a proportionality between the magnitude of the splittings and the spin S.

TABLE III. Calculated and observed splittings for Gd. ΔE are the differences between the two final ground-state energies of the free Gd^{4+} ion. $\Delta\epsilon$ are the differences between spin polarized energy eigenvalues of Gd^{3+}.

		4s splitting (eV)	5s splitting (eV)
Observed[a]	GdF_3	8.2	3.7
X_M	ΔE	9.20	3.16
	$\Delta\epsilon$	11.37	3.78
X_L	ΔE	12.68	5.97
	$\Delta\epsilon$	17.99	9.29

[a] Reference 10.

IV. RESULTS FOR THE RARE EARTH ELEMENTS

In Table III are shown the observed and calculated 4s- and 5s-core level binding-energy splittings for Gd. Our calculated results with the X_L and X_M approximations to the exchange-correlation energy are typical for the RE elements. Once the correlation effects are included in the free-electron gas model, a good agreement between theory and experiment is obtained. The correlation effects have influence on both the calculated 4s and 5s splittings. The relaxation effects are of course important for the 4s splittings, being small for the 5s splittings.

From Figs. 2–5 we present our calculated values for the 4s and 5s binding-energy splittings for the RE elements obtained with the approximation X_M to the exchange-correlation energy. All values refer to ΔE. In Fig. 2 we show the magnitude of the 4s splittings as a function of $2S+1$, where S is the trivalent ion initial-state spin.

The experimental results for Ce, Pr, Nd, Sm, and Eu are for the metals according to Ref. 13. The other experimental results shown were obtained from photoelectron spectra of trifluoride compounds according to Ref. 10. Our main con-

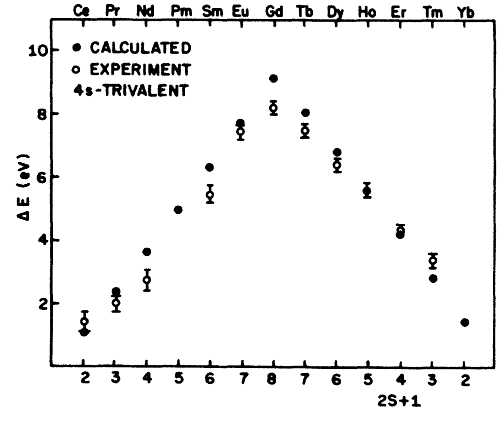

FIG. 2. 4s-electron binding-energy splittings for the RE elements. The calculated values were obtained by using the X_M approximation to the exchange-correlation energy. S is the initial-state spin of the trivalent ion. The open circles are the XPS results: from Ce to Eu they refer to experiments in metals (Ref. 13); from Gd to Tm they refer to experiments in trifluoride complexes (Ref. 10).

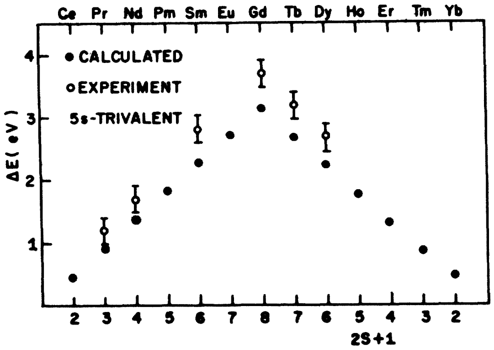

FIG. 3. 5s binding-energy splittings for the RE elements. The calculated values were obtained by using the X_M approximation to the exchange-correlation energy. S is the initial-state spin of the trivalent ion. The open circles are the XPS results on trifluoride compounds (Ref. 10).

clusion is that the calculated results are improved significantly when the correlation effects are included. By neglecting the electron correlation in the theory we obtain 4s splittings in some cases twice as big as the experimental ones. Figure 2 also shows a proportionality between the magnitude of the calculated splittings and the ion initial-state spin. Our results indicate an ion-core-like character in the RE elements in trivalent metals.

In Fig. 3 is shown the 5s splittings for the RE elements as a function of $2S+1$, where S is the initial-state spin of the trivalent ion. The experimental data are from Ref. 10 and refer to trifluoride compounds. The calculated splittings agree with experiment within 1 eV. The correlation effects are critical in determining such agreement. If we neglect the correlation effects the results become poorer, as is shown in Table III. The experimental results for the magnitude of 5s splittings are, for Ce, 1.0 eV (trivalent metal) and zero (trifluoride compound). Our calculated result shown in Fig. 3 is 0.46 eV. The 5s splittings obtained from photoemission spectra of RE metals[13] were not shown in Fig. 3 because they are similar to those obtained from trifluoride compounds.[10] In Fig. 4 is shown the magnitude of the 4s splitting for the divalent RE elements. For each element from Gd to Yb the calculations were performed supposing the divalent free ions in two initial configurations: (Xe) $4f^n$ and (Xe) $4f^{n-1}5d$. The configurations considered for the initial state of the Gd^{2+} free ions were: (Xe) $4f^8, S=3$ and (Xe) $4f^7 5d, S=4$. The differences between the plotted values (circle and triangle) for the same element is a measurement of the polarization effects on the 4s splitting due to the increasing by two of the number of unpaired spins in the system. These differences are roughly constant for the series. The difference between the plotted 4s splittings for an element (circle) and the plotted value for the next element (triangle) is the measurement of the polarization effects due to the inclusion of a 5d unpaired electron in the system. These influences decrease with increasing atomic number. The experimental results quoted in the literature at the moment of this writing that are comparable with our calculated values shown in Fig. 4 are those from Ref. 13. They were taken from photoemission experiments in divalent metals. Our calculated 4s splitting for La^{2+} is a small number, in agreement with experiment. La^{2+} has an initial state whose spin is $\frac{1}{2}$. If the only unpaired electron should fill a 4f level we estimate from Fig. 4 a 4s splitting with magnitude less than 1 eV. This value is close to zero if 5d is the occupied level. Also the calculated value of the 4s splitting for Lu^{2+} is very small. The only unpaired electron for this ion occupies a 5d level, therefore implying small polarization effects. Finally in Fig. 5 we show the magnitude of the 5s splittings for the RE series as a function of $2S+1$, where S is the divalent ion initial-state spin. The experimental results are quoted according to Ref. 13 and were taken from the photoemission spectra of metals. The splittings were calculated by considering one electron filling one d level of the divalent ions, from Gd to Yb. The calculated results with X_M approximation to the exchange-correlation energy are in good agreement with the experimental ones. Once the correlation effects are neglected this agreement becomes poorer.

The analyses of the results in Fig. 5 imply an

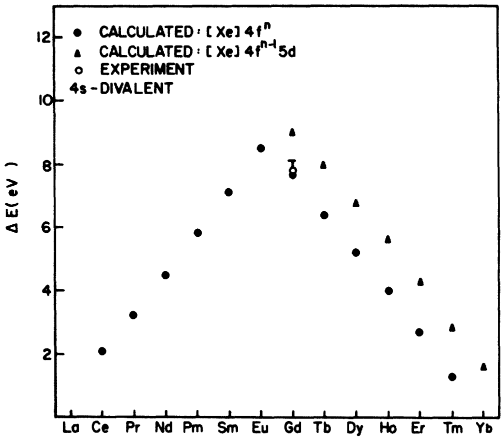

FIG. 4. 4s-electron binding-energy splittings for the RE elements. The calculated values were obtained by using the X_M approximation to the exchange-correlation energy. The initial state refers to the divalent ion. The open circle is the XPS result on the divalent metal Gd (Ref. 13).

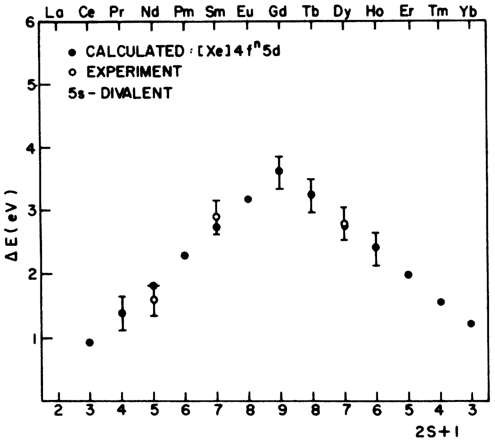

FIG. 5. 5s-electron binding-energy splittings for the RE elements. The calculated values were obtained by using the X_M approximation to the exchange-correlation energy. S is the initial-state spin of the divalent ion. The open circles are the XPS results on the divalent metals (Ref. 13). The splittings were calculated by considering one electron filling one d level from Gd to Yb.

ion-core-like character for the RE elements in divalent metals with a well-localized 4f shell. They also seem to indicate the presence of an occupied 5d level in the ion core state of the elements with atomic number greater than 63. However, more experimental determinations of 4s splittings in divalent metals (Fig. 4) are needed in order to clarify this point.

V. CONCLUSION

In the present investigation we show that the use of a local approximation to the exchange and correlation effects (mass operator) gives accurate s-core electron binding-energy splittings in 3d and 4f transition elements. Our results show how well the free-electron gas model can be used in inhomogeneous systems provided the Coulomb correlation effects are included in the theory. Similarly with what happens in 3d transition elements, the calculated magnitude of s-core electron energy splittings in RE elements depends critically on the Coulomb correlation effects. These effects have influence on both the 4s and 5s calculated splittings. The relaxation effects are important for the 4s splittings and small for the 5s splittings.

The theory on which this paper is based is a one-electron theory, and thus we are not able to explain some features of the s-core photoelectron spectra of the analyzed elements. It is clear that a simple one-electron model is insufficient to describe the fine structure observed in the s-core spectra,[16] therefore no attempt was made by us to compare calculated intensity ratios with experimental results. However, by dealing with the exchange-correlation effects in a form of an effective potential in the framework of a one-electron self-consistent-field theory, we were able to reproduce realistically the separation between the two main peaks in the spectra. That means we have already well correlated one-electron wave functions.

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