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Simple rules for determining valencies of f-electron systems

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Abstract

The electronic structure of f-electron systems is calculated with the self-interaction-corrected local-spin-density (LSD) approximation. This scheme allows for a splitting of the f-electron manifold into an integral number of localized electrons and self-consistently determined fractional number of band electrons. Therefore, in comparison with the LSD approximation, where all f states are pinned at the Fermi energy, only a maximum of one f band is left at the Fermi energy. We show that this band is partially occupied with occupancy n_f , and the f-electron fluctuations are reduced compared with the LSD approximation. When n_f exceeds a critical value of approximately 0.6, it becomes energetically more favourable to localize this state, and the number of valence bands is reduced by one.

1. Introduction

The classification of the rare earths and their compounds in terms of their valencies provides an elementary explanation of their physical properties. In particular, dramatic changes in the lattice parameters of the rare earths can be related to valency changes [1]. Most of the rare earths in the solid state are trivalent; this is in contrast to the atomic state, where the rare earths are divalent. However, some compounds involving Eu, Sm, Tm and Yb can become divalent. Ce compounds, on the other hand, can be either trivalent or tetravalent. Not all rare-earth compounds can be classified in this simple manner and some of the materials with the most interesting magnetic and superconducting properties are of intermediate-valence character, i.e. no integer valency can be associated with the system. In this article we will show how to calculate the valency of f-electron systems and from this derive a simple physical picture of valencies in the solid state [2].

Valency is a chemical concept but is also very effective in describing the rare earths in the solid state. The valency of a rare earth can vary from divalent to trivalent and tetravalent. This

signifies that two, three or four electrons, respectively, of the rare-earth ion are chemically active. We will show in this article that in the solid-state context this means that respectively two, three or four electrons are part of the valence band. Furthermore, these valence band electrons have s, p, d and even f character. The formalism presented below allows the *ab initio* determination of energy differences of the various valencies and represents the evaluation of the valency as a competition between an energy gain upon band formation and localization of the f electron.

Almost 30 years ago, Gschneidner Jr [3] postulated, on the basis of the analysis of the rare-earth crystal structures, melting points and heats of sublimation, that there are two types of f electron in rare-earth compounds, namely an integer number of atomic f electrons and a fractional number of band-like f electrons. The results of the present *ab initio* calculations confirm this picture of localized f electrons which determine the valency and a fractional number of hybridizing, band-like f electrons at the Fermi level. These calculations also predict that if the number of fractional f electrons exceeds approximately a value of 0.6, then it becomes energetically more favourable for these band-like electrons to localize and the valency decreases [4]. Pressure can change the physical properties of the rare earths profoundly: both structural and valency changes can occur. However, since the application of our methods to this has been reviewed recently [5], it will not be discussed in this article.

The valency concepts apply also to the actinides. Like in the case of the rare earths, the electronic structure of the actinides is of considerable interest due to the correlated nature of the 5f electrons [6–8]. In the early actinide elements, from Th to Pu, the f electrons play an active role in the cohesion, as manifested by the low-symmetry crystal structures, low specific volumes and large bulk moduli. In contrast, in the later actinides, from Am to Es, the f electrons are non-bonding, high-symmetry crystal structures are attained, the specific volumes are large and the bulk moduli are relatively small. The change in the f-electron character is due to the large on-site Coulomb interactions which cause the f electrons to localize from Am onwards. In the lighter actinides the energy gain due to band formation is larger than the localization energy. Pu is on the borderline, with a rather complex phase diagram [9] and several anomalous phases. Of these, the ground-state α -phase (monoclinic) is characterized by actively bonding f electrons, while the high-temperature δ -phase (fcc) is believed to be associated with localized f electrons. When external pressure is applied to the late actinide elements, f-electron bonding eventually sets in [10]. The trends in the physical properties of the actinides are therefore similar to the behaviour in the lanthanides, where the localization–delocalization transition takes place around Ce [11].

The outline of the remainder of the article is as follows. Section 2 introduces the formalism, section 3 deals with the study of the valency of the rare earths and section 4 is concerned with the application to the actinides. Section 5 contains our summary.

2. Formalism

Density functional theory constitutes a very versatile tool for studying the ground-state properties of many-electron systems. It expresses, in a compact form, the total energy as a functional of the order parameters. Taking the charge density as the order parameter, the structural properties can be studied. However, using the charge density in conjunction with the magnetization density allows also for detailed studies of the magnetic properties of solids. Replacing the magnetization density by the pairing amplitude leads to a material-specific theory of the electronic structure in the superconducting state. In the present contribution, we will express the total energy as a functional of the charge density and the magnetization density, but with an exchange and correlation energy which can describe both Bloch-like single-particle

states and localized Heitler–London single-particle states. This will allow us to differentiate between the band-like valence states and the localized states.

The self-interaction-corrected local-spin-density approximation [12] is an *ab initio* electronic structure scheme which is capable of describing localization phenomena in solids [13–18]. In this scheme the spurious self-interaction of each occupied electron state is subtracted from the conventional LSD approximation to the total-energy functional, leading to a greatly improved description of static Coulomb correlation effects over the LSD approximation. This has been demonstrated in studies of the Hubbard model [19–22], and in applications to 3d monoxides [14, 15, 23], La_2CuO_4 [24, 25], f-electron systems [2, 4, 5, 16–18, 26–29] and hydrogen solid [30].

In the LSD approximation the total energy of a many-electron system is found as the minimum of an energy functional which approximates the exchange and correlation contribution by a simple local expression:

$$E_{xc}^{LSD}[\bar{n}] = \int \epsilon_{xc}^{hom}(\bar{n}(\mathbf{r}))n(\mathbf{r}) \, d^3r \quad (1)$$

where \bar{n} is the total electron spin density of the system

$$\begin{aligned} \bar{n}(\mathbf{r}) &= (n^\uparrow(\mathbf{r}), n^\downarrow(\mathbf{r})) \\ n(\mathbf{r}) &= n^\uparrow(\mathbf{r}) + n^\downarrow(\mathbf{r}) \end{aligned}$$

and $\epsilon_{xc}^{hom}(\bar{n})$ is the exchange–correlation energy density of a homogeneous electron gas with spin density \bar{n} [31, 32]. The exact exchange–correlation energy functional, E_{xc} , of density functional theory has the property that for *any* single-electron density, \bar{n}_α , it exactly cancels the static Coulomb interaction energy for that density:

$$U[n_\alpha] + E_{xc}[\bar{n}_\alpha] = 0 \quad (2)$$

where

$$U[n] = \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d^3r \, d^3r'. \quad (3)$$

Atomic Rydberg units ($\hbar = 2m_e = e^2/2 = 1$) are used throughout. The cancellation in equation (2) is not complete in the LSD approximation, and the residual

$$\delta_\alpha = U[n_\alpha] + E_{xc}^{LSD}[\bar{n}_\alpha] \quad (4)$$

is interpreted as the self-interaction of the electron in state ψ_α .

Perdew and Zunger [12] suggested constructing a self-interaction-free total-energy functional by subtracting the self-interaction of each occupied electron state from the LSD total-energy functional, which defines the SIC-LSD total-energy functional:

$$E^{SIC}[\{\psi_\alpha\}] = \sum_\alpha \langle \psi_\alpha | -\Delta | \psi_\alpha \rangle + U[n] + E_{xc}^{LSD}[\bar{n}] + V_{ext}[n] - \sum_\alpha \delta_\alpha. \quad (5)$$

Here, $U[n]$ and $E_{xc}^{LSD}[\bar{n}]$ are defined in equations (3) and (1), while $V_{ext}[n]$ denotes the energy of interaction with the lattice of ions:

$$V_{ext}[n] = \int V_{ext}(\mathbf{r}) n(\mathbf{r}) \, d^3r. \quad (6)$$

As written in equations (1)–(6), E^{SIC} appears to be a functional of occupied orbitals, ψ_α , rather than a functional of just the total spin density, like E^{LSD} . By a reformulation it may be shown [12, 33] that E^{SIC} can in fact be regarded as a functional of the total spin density only. The corresponding exchange–correlation energy functional $E_{xc}^{SIC}[\bar{n}]$ is, however, only implicitly defined [33], for which reason the respective Kohn–Sham equations would be

impractical to exploit. For periodic solids the SIC-LSD approximation can be considered an extension of the LSD approximation in the sense that the self-interaction correction is only finite for localized states, which means that for Bloch-like single-particle states E^{SIC} coincides with E^{LSD} . Therefore, the LSD minimum is also a local minimum of E^{SIC} . In some cases another set of single-particle states may be found, not all having Bloch form, to provide a local minimum for E^{SIC} . For this to happen some states must exist which can benefit from the self-interaction term without losing too much band formation energy. This will usually be the case for rather well localized states like the 3d states in transition metal oxides or the 4f states in rare-earth compounds. In rare earths different valency scenarios may be investigated, corresponding to different localized f^n configurations of the rare-earth ions, and their energies compared. Thus, E^{SIC} is a density functional, which may be used to describe localized as well as delocalized electron states.

In the present work we have used two different, yet equivalent, implementations of the SIC-LSD approach [13, 16, 34]. Both are based on the linear muffin-tin-orbital (LMTO) method [35, 36], i.e., the electronic wave functions are expanded in terms of muffin-tin orbitals, and the minimization of E^{SIC} becomes a non-linear minimization problem in the expansion coefficients. The atomic sphere approximation (ASA) is used, according to which the polyhedral Wigner–Seitz cell is approximated by slightly overlapping atom-centred spheres with a total volume equal to the actual crystal volume. Inside each sphere the potential is assumed spherically symmetric.

3. Valency of the rare earths

The separation of the f-electron manifold into localized and band states means that the number of valence bands will be determined by the subset of band states only. On the basis of this we can introduce the following definition of the valency: $N_{valency} = Z - N_{core} - N_{SIC}$, where Z is the atomic number, N_{core} is the number of atomic core electrons and N_{SIC} is the number of f states for which the self-interaction has been removed. The SIC-LSD approach allows an *ab initio* determination of N_{SIC} . In particular, $N_{valency}$ equal to three or two describes a trivalent or divalent configuration respectively. The theoretical ground-state configuration is determined by exploring all values of N_{SIC} , and finding the number N_{SIC} which results in the lowest value of the total energy.

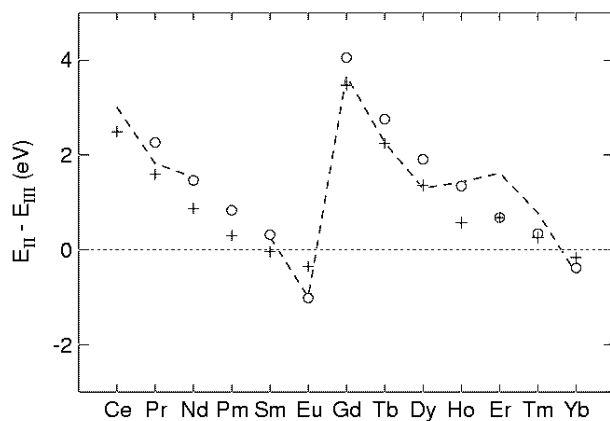


Figure 1. The energy difference in eV between the divalent and trivalent states of rare-earth materials. The dashed line shows the experimental values for the rare-earth metals. The open circles and crosses show the calculated values for the rare-earth metals and the rare-earth sulphides, respectively. As the calculated divalent–trivalent energy differences were too negative, they were uniformly shifted by 43 mRyd to agree with the observed valence transition pressure of 6 kbar in SmS. This shift also fixes the energy differences for all the other rare-earth materials. (After [2].)

Figure 1 shows the energy difference between the ground state and the configuration with the lowest excitation energy for all the rare earths together with their sulphides. We find

reassuringly that for all rare earths and their sulphides the trivalent and divalent configurations are giving rise to the ground state and the lowest excited states. The LSD state, which is obtained by putting N_{SIC} equal to zero, is in all cases unfavourable. The divalent–trivalent energy difference is large and positive at the beginning of the series, indicating that the trivalent state is well favoured. The energy differences then fall sharply and become negative for elemental Eu and for EuS and SmS, which means that the divalent state is the more stable one. There is a large discontinuous jump at Gd and GdS which are trivalent and in the latter half of the rare-earth series the values fall fairly steeply again, becoming negative at Yb for both the metal and the sulphide.

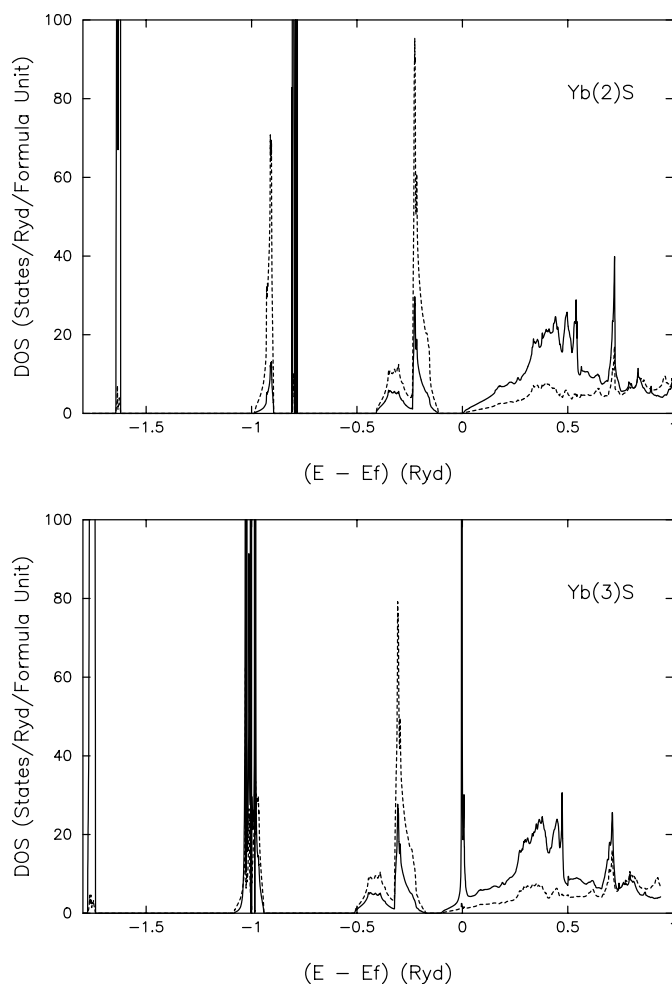


Figure 2. The density of states of YbS in the divalent configuration (a) and the trivalent configuration (b). The full and dashed lines are the Yb and S local densities of states respectively. The energies are with respect to the Fermi energy.

In figures 2(a) and 2(b) we display the densities of states of divalent and trivalent YbS respectively. These pictures show the SIC in action on the one-electron spectrum. Divalent YbS is seen to be semiconducting with a band gap of 1.5 eV. The valence bands, i.e. the first manifold of states below the band gap, contain six S-derived p states. Below this, at

approximately -0.8 Ryd, occur the fourteen f states which are bunched together in a very narrow peak; further down at -0.9 Ryd and -1.6 Ryd are the S 2s states and the Yb 5p semicore states respectively. Trivalent YbS has one more valence state, which is the very sharp f state which is pinned to the Fermi energy and which is also separated from the manifold of six states just below it. There are now thirteen localized f states and these localized f states occur at a slightly higher binding energy than in the divalent case. These densities of states show the same common features of the f states split into two sub-bands: the SIC-localized f states and the band f states. The SIC-localized f-electron states form a narrow energy band which lies well below the valence bands, while the f-band states lie just at and above the Fermi energy. These f bands hybridize with the s-d bands which cross the Fermi energy. The result of this process is that the s-d bands acquire some f character, creating a different type of f electron which can participate in electronic bonding.

It is for these systems which are characterized by a single sharp peak at the Fermi energy that very interesting physics can occur. For the rare earths it becomes energetically favourable to either localize this particular state, giving rise to a divalent configuration, or become of intermediate valence [29]. When the number of band-like f electrons in the trivalent state exceeds 0.6 or so, then the divalent state is energetically more favourable. When this number is reduced to around 0.5, then we find a small energy difference of 20 mRyd or less between the trivalent and divalent configurations. In this category we find all the systems which are commonly known as intermediate-valence systems such as YbBiPt. We also find that the correlations in these systems, with approximately 0.5 of band-like f electrons concentrated in a narrow peak, are not adequately described in the SIC-LSD formalism, and improved treatment of the correlations such as is provided by the dynamical mean-field theories (DMFT) is needed [37]. However, for those systems which have a well defined valency, such as the Yb pnictides which are trivalent or the Yb chalcogenides which are divalent, the SIC-LSD provides an excellent description. In fact, the findings of the SIC-LSD approach are in excellent agreement with the results of a semi-phenomenological scheme for calculating valencies, in which the atomic f-f interactions are treated exactly and band theory is used only to calculate the conduction electrons in the presence of the localized f states [29].

4. Valency of the actinides

The 5f electrons of the actinides are less localized than the 4f electrons in the rare earths, which is reflected in a broader spectrum of valencies. The early actinides, Th, Pa, U and Np, are characterized by itinerant f electrons, and the observed lattice constants and crystal structures can be explained by band-structure calculations based upon the LSD approximation, with all f electrons treated as normal band electrons [38]. From Am onwards, the f electrons start to localize due to the large on-site Coulomb interaction, and the electronic structure resembles that of the rare earths. Pu lies at the borderline of this delocalization-localization transition, with a correspondingly complex phase diagram.

We have applied the SIC-LSD approach to the calculation of the total energies, as a function of atomic volumes, for the actinides from U to Fm. For each case several valency configurations have been investigated. The overview of the valency change across the whole actinide series, in comparison with the results for the rare earths, is presented in figure 3. The trends of the energy difference between the divalent and trivalent configurations are qualitatively the same in the actinides and lanthanides. For the rare earths however, Eu, the system isoelectronic with Am, has already become divalent, while Am dips towards the divalent configuration, but remains trivalent. More specifically, the overall total-energy minima have been found to occur for the trivalent configuration in the case of Pu, Am, Cm, Bk and Cf. For Es and Fm the divalent

configuration gives the lowest ground-state energy. For Es the divalent equilibrium volume is close to the experimental result. Fm has never been prepared in the solid state. In general, the predicted gradual transition [8] from trivalent Cm, Bk, Cf towards divalent Es and Fm has been well reproduced in the parameter-free SIC-LSD approach. In the trivalent configuration, a narrow f band hybridizes with a broad s-d band, as is the case with the lanthanides. The position of the Fermi level with respect to the f peak determines the number of band f electrons, and as the f peak becomes increasingly filled, correlations become important. At Es, the degree of filling is such that the divalent ground-state configuration, which takes into account these correlations, is preferred. U and Np have the lowest energy when the f electrons are fully delocalized, thus confirming the itinerant character of f electrons in the early actinides.

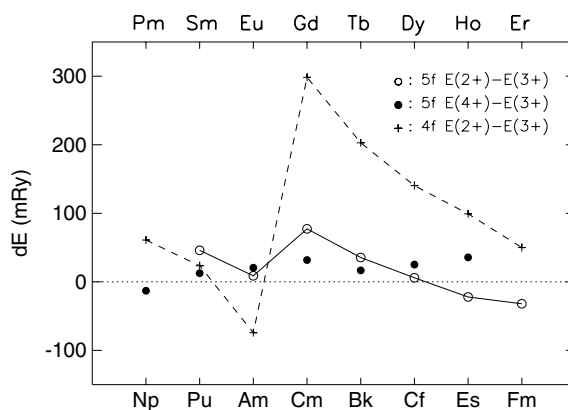


Figure 3. Trends in the energy differences between the divalent and trivalent atomic configurations (open circles) and between the tetravalent and trivalent configurations (filled circles) of the actinides. The crosses are the energy differences between the divalent and trivalent rare earths. (After [39].)

As a detailed example of the SIC-LSD formalism at work, in figure 4 the total energy, as a function of volume, is shown for respectively the divalent (f^8), trivalent (f^7) and tetravalent (f^6) configurations of Cm. The energy minimum in the trivalent configuration is more than 30 mRyd lower than those of the divalent and tetravalent configurations, which is an indication for the relative stability of the half-filled f shell. The calculated equilibrium volume of Cm has turned out to be in good agreement with the corresponding experimental equilibrium value [10].

As mentioned before, the SIC-LSD approach is not a cure for all the problems of the LSD approximation. An example of this is provided by elemental Pu. In figure 5 one can see that for Pu, four different localized configurations lie within a range of 80 mRyd from the trivalent ground state: they correspond to the tetravalent, pentavalent, hexavalent and septavalent valencies. Of these, the hexavalent and septavalent ones have equilibrium volumes close to 168 au, the experimental δ -phase of Pu. These involve respectively two and one localized f states. The energy minima of the LSD calculation and the septavalent configuration differ only by 3 mRyd and their equilibrium volumes differ by 27%. These results are similar to the differences calculated between the α - and γ -phases of Ce [17, 18]. This is not that surprising since the metals in the periodic system to the left of Pu are systems where the f electrons are delocalized. In this sense Pu is the 5f equivalent of the 4f Ce metal. Unfortunately, for Pu, the calculated SIC-LSD equilibrium volume, which occurs in the trivalent state, is approximately 30% too large compared to the experimental volume of δ -Pu. This implies that the appropriate ground state is intermediate between the fully localized and the fully delocalized pictures offered by the SIC-LSD and LSD approximations, respectively [39]. This view is supported

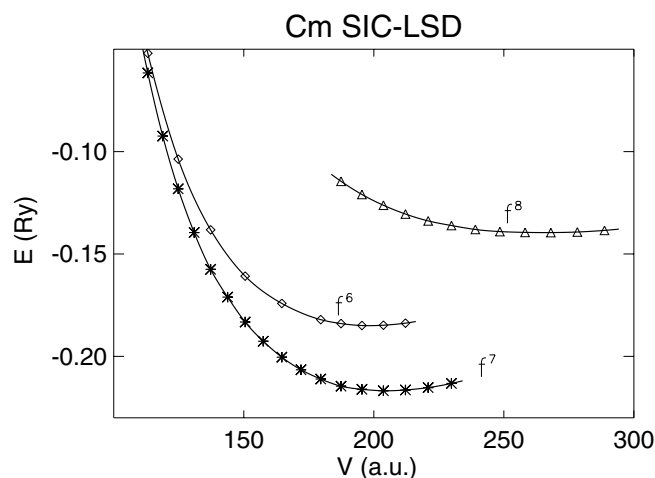


Figure 4. Pressure–volume curves for Cm for the trivalent f^7 configuration (crosses), the divalent f^8 configuration (diamonds) and the tetravalent f^6 configuration. The experimental volume is 202 au.

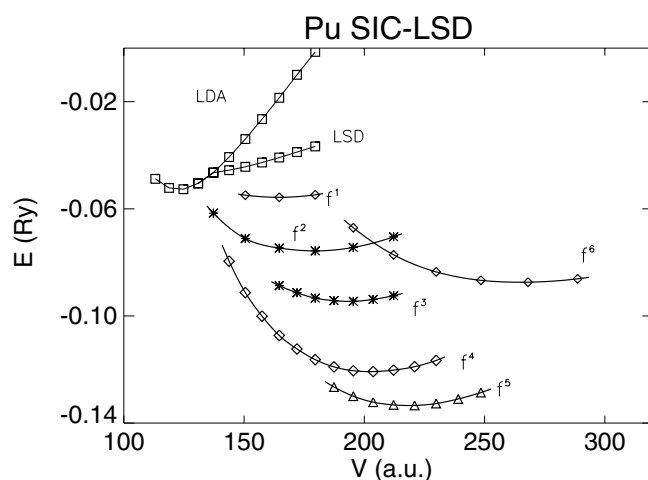


Figure 5. Pressure–volume curves for Pu for eight different possible configurations. (See the text for a full description; f^5 corresponds to the trivalent configuration.) (After [39].)

by large discrepancies among different theories and calculations [37, 40, 41], indicating that δ -Pu might need to be described by more accurate theories [37].

5. Summary

Figure 6 summarizes our simple rule for determining the valencies of the rare earths and actinides. When the number of band-like f electrons exceeds a value of approximately 0.6, then it becomes more advantageous for this electron to localize and for the system to reduce valency. All rare earths, rare-earth sulphides and actinides follow this rule. This describes the gradual transition from trivalent towards divalent actinide in the series Cm, Bk, Cf, resulting in divalent Es and Fm, according to expectations [8]. In addition, it describes the different

behaviour in the elemental rare earths where the corresponding sequence is delocalized to trivalent (Pr–Sm) to divalent (Eu) to trivalent (Gd–Tm), and finally divalent (Yb) [2]. The 5f system isoelectronic with Eu is Am and our calculations give Am as trivalent. The reason for the difference in valency between Eu and Am is presumably the stronger exchange splitting in the 4f states which causes Eu to behave as a system with a nearly filled f shell in the majority band and an unoccupied minority f band. For the 5f states the spin–orbit coupling is much stronger, so there is no longer a clear separation between minority and majority bands, these bands hybridize strongly and Am does not look like a system with a nearly filled f shell. As regards the other actinides, the SIC-LSD provides an accurate description of the heavier actinide elements, which are characterized by localized 5f behaviour. The localization energy is given by the 5f self-interaction correction. This energy is about half of what was found for the 4f states in the rare earths (figure 3). From comparing our results on the actinides with the corresponding calculations for the rare earths, we are confident that the SIC-LSD approximation describes the valency trends through the rare-earth and actinide series. Only for δ -Pu do we conclude that a complete description seems to be beyond this simple SIC-LSD approach. In this case, our calculations indicate the importance of all configurations from divalent to septavalent and the necessity of considering them in a more complete theory.

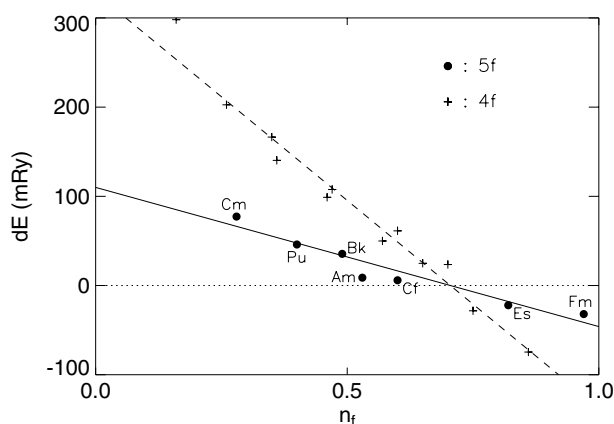


Figure 6. The correlation between the number of band f electrons in the trivalent configuration and the energy difference between the divalent and trivalent atomic configurations.

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