A test of the spin-orbit sum rule for actinides using an \textit{ab-initio} calculation

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The expectation value of the angular part of the spin-orbit-coupling (SOC) operator $\langle l \cdot s \rangle$ and the branching ratio for the $N_{4s}$ X-ray-absorption spectroscopy in $\delta$-Pu, $\alpha$-U and face-centered-cubic (fcc) Th are calculated within the framework of the density-functional theory in combination with the local-spin-density approximation (LSDA), the generalized-gradient approximation (GGA) and the LDA+U method. The SOC contribution is calculated in terms of the first- and the second-variations schemes. A strong variation in the magnitudes of the calculated $\langle l \cdot s \rangle$ operator along the actinide series is found. The results show that the SOC sum rule for $\delta$-Pu and $\alpha$-U is reasonably valid, whereas there is a sign mismatch for the case of fcc Th. The calculated branching ratios for the case without SOC in the valence shell strongly deviate from the statistical value.

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The field of actinides attracts considerable interest in terms of experiments and theoretical investigations. Recently, many unique phenomena of the actinide series were discovered, for example, the Pu-based superconductivity\cite{1}, or the phonon dispersion in $\delta$-Pu\cite{2,3,4}, which were ascribed to the nature of the $5f$ electronic states. In order to explain these interesting properties, it is necessary to understand the electronic structure. It was demonstrated experimentally that the spin-orbit coupling (SOC) could not be neglected in the Hamiltonian for the $5f$ states of the actinides.

Van der Laan and Thole\cite{8} proposed a probe for the SOC interaction, which is based on the branching ratio of the core-valence transition in X-ray absorption spectroscopy (XAS). The corresponding sum rule for the $4d \rightarrow 5f$ transition, which is relevant for actinides, reads as:

$$\frac{\langle l \cdot s \rangle}{N_h} = -\frac{15}{4} (B - B_0).$$

(1)

Here, $\langle l \cdot s \rangle$ denotes the angular part of the SOC operator for a particular valence shell with $N_h$ holes. The branching ratio $B$ for an electron transition from a $d$ core shell is defined as:

$$B = \frac{I_{5/2}}{I_{5/2} + I_{3/2}},$$

(2)

where $I_{5/2}$ and $I_{3/2}$ are the total absorptions for the $d_{5/2}$ and $d_{3/2}$ levels, respectively. The quantity $B_0$ is the corresponding branching ratio if there was no SOC in the valence shell. In the case of a negligible core-valence interaction the statistical value of $B_0$ for a $d$ core shell is $3/5$. There are several problems related to the application of the sum rule (1) on experimental data. The number of holes $N_h$ for a particular shell is not exactly known, while the quantity $B_0$ is not measurable, therefore it is necessary to rely on some estimates or hints from calculations. Furthermore, the validity of Eq. (1) is not guaranteed since it is based on a free-atom model. For example, it was demonstrated\cite{9} that the SOC sum rule held well for the $4d$ and $5d$ metals but that it was violated for the $3d$ and $4f$ metals due to the core-valence interactions. The aim of the present paper is to test the validity of the SOC sum rule for actinides by comparing the SOC expectation value $\langle l \cdot s \rangle$ calculated directly from the electronic structure with the value obtained from the calculated branching ratio via Eq. (1). A theoretical approach has several advantages over an experiment, because such a test cannot be performed on measured data, and both the experimentally uncertain quantities, $N_h$ and $B_0$ can be easily determined with a calculation.

The calculations for $\delta$-Pu, $\alpha$-U and the face-centered-cubic (fcc) phase of Th were performed within the framework of the density functional theory by applying the Wien97 code\cite{10}, which adopts the full-potential linearized-augmented-plane-wave (FLAPW) method.\cite{11} The experimental values of the lattice parameters were used. The convergency tests implied that 1000 ($\delta$-Pu and fcc Th) and 864 ($\alpha$-U) $k$ points in the full Brillouin zone (BZ) were enough for a calculation of the corresponding quantities with the desired accuracy when the modified tetrahedron method\cite{12} was used for the BZ integration. The plane-wave cut-off parameters were 6.7 Ry ($\delta$-Pu), 9.8 Ry ($\alpha$-U) and 5.6 Ry (fcc Th).

Since the correlation effects are important for actinides\cite{13,14,15}, the influence of the local-spin-density approximation (LSDA)\cite{16}, the generalized-gradient approximation (GGA)\cite{17} and the LDA+U method\cite{18,19} was investigated. The parameters $U$ and $J$, which appear in the LDA+U scheme, were set to $U = 2$eV and $J = 0.5$eV for all three systems. This universal choice was based on values found in the literature for plutonium (Ref. 15) and uranium (Ref. 20), and it was simply generalized to the case of thorium. The density-functional theory can yield a magnetic solution for actinides\cite{21}, hence the up and down spin states were distinguished. However, for all three systems the resulting magnetic moments were zero within the prescribed accuracy. The criterion for the self-consistency was the difference in the charge densities after the last two iterations being less than $10^{-4}$e/(a.u.)$^3$.

Special attention was paid to the calculation of the
SOC contribution. The standard approach within the FLAPW method is to apply the second variational scheme. In this method the eigenvalues and the eigenvectors are calculated in two steps within each iteration. First, a scalar relativistic Hamiltonian (without the SOC term) is diagonalized. Then, the lowest of the resulting scalar-relativistic eigenvalues and eigenvectors are used as a restricted basis set for diagonalizing the full Hamiltonian with the included SOC term. While the second-variational method is sufficiently accurate, for example, for the 3d transition metals, it might break down for heavy elements like the actinides, as discussed in Refs. 22, 23. A possible way to improve the results is to extend the basis of the second-variational step by including relativistic $p_{1/2}$ local orbitals. An alternative, more straightforward, albeit less time-effective way, is to perform the calculations in terms of the so-called first-variational scheme, where the full Hamiltonian, including the SOC term, is diagonalized in a single step, using the full basis set of the linearized-augmented plane waves. In the present paper, the first- and the second-variational schemes were applied. The SOC term was simply set to zero for the calculation of the branching ratio $B_0$.

The XAS spectra $\mu_{5/2}(\epsilon)$ and $\mu_{3/2}(\epsilon)$ as a function of the photon energy $\epsilon$ were calculated using Fermi’s golden rule in a nonrelativistic dipole approximation that is based on the evaluation of the matrix element for the operator $\mathbf{p} \cdot \mathbf{e}$ with $\mathbf{e}$ denoting the polarization vector of the light. The total absorptions $n_{5/2}$ and $n_{3/2}$, which are required for the calculation of the branching ratios $B$ and $B_0$ (2), were obtained from the integrals:

$$n_j = \int_{E_F}^{E_C} \mu_j(\epsilon) \, d\epsilon,$$

where $E_F$ and $E_C$ denote the Fermi energy and the upper edge of the 5f valence band, respectively. The latter quantity is defined with the number of holes $N_h$ and the corresponding density of states: $n_{5f}(\epsilon)$ as:

$$N_h = \int_{E_F}^{E_C} n_{5f}(\epsilon) \, d\epsilon.$$

The results are presented in Table 1. Common to all the considered systems is a strong deviation of $B_0$ from the statistical value of 3/5 ascribed to a non-negligible coupling between the core and valence electrons. The calculated $B_0$ is almost a constant for $\delta$-Pu, $\alpha$-U and fcc Th, regardless of the method applied for the calculation of the exchange-correlation potential, although there is a slight increasing trend from plutonium to thorium. This might be due to the mixing of the 4d5/2 and 4d3/2 core states, because the splitting between the two core levels grows along the actinide series, as demonstrated in Fig. 1. The magnitudes of the expectation values of the SOC operator $\langle l \cdot s \rangle$ obtained from the calculated branching ratios $B$ and $B_0$ via Eq. (1) in general overestimate the corresponding quantities calculated directly from the electronic structure. The agreement is the best in the case of $\delta$-Pu, within ~4% to ~27%, depending on the calculational details. While there is almost no difference between the results obtained using the LSDA or GGA, and the second-variational scheme yields almost identical results as the diagonalization of the full Hamiltonian with the included SOC term, the LDA+$U$ values differ considerably. The magnitudes of the $\langle l \cdot s \rangle$ operator obtained by applying the first-variational method are larger than the LSDA or GGA values. This is the only case where the magnitude of the directly calculated $\langle l \cdot s \rangle$ operator is smaller than the branching-ratio value, but the agreement is very good, within 4%. However, the situation is the opposite for the case where the second-variational scheme was used for the calculation of the SOC term. The magnitudes are smaller than those obtained using the LSDA or GGA, and the magnitude of the branching-ratio SOC expectation value exceeds the directly calculated quantity by about 27%.

The expectation values of the SOC operator for $\alpha$-U are one order of magnitude larger than the corresponding quantities for $\delta$-Pu, as it would be expected on the basis of the XAS-spectra plot in Fig. 1, where the difference between the $B$ and $B_0$ curves is substantially less pronounced when compared to the case of $\delta$-Pu. The magnitudes of the branching-ratio values are about two times as large as those of the directly calculated quantities. The difference in the results obtained using the LSDA, GGA or the LDA+$U$ method is subtle, as is the influence of choice of the method for including the SOC term.

The expectation value of $\langle l \cdot s \rangle$ for fcc Th is reduced by another order of magnitude in comparison with $\delta$-Pu and $\alpha$-U. While the directly calculated quantity remains negative, the values obtained by applying Eq. (1) are
TABLE I: A comparison between the directly calculated expectation value of the SOC operator $\langle w^{110} \rangle$ per number of holes $N_h$ in the $5f$ shell and the quantity $\frac{12}{N_h} (B - B_0)$, obtained from the calculated XAS spectra. The quantities $B$ and $B_0$ represent the branching ratios for the cases with and without SOC in the $5f$ valence shell, respectively. The values in brackets were obtained by applying the second-variational scheme, while the rest of the values resulted from the first-variational treatment of the SOC term.

| System | Calculation | $\frac{12}{N_h} (B - B_0)$ | $N_h$ | $B_0$ |
|--------|-------------|-----------------------------|-------|-------|
| $\delta$-Pu | LSDA | -0.548 (-0.555) | -0.606 (-0.660) | 8.785 (8.802) | 0.698 |
| | GGA | -0.547 (-0.554) | -0.605 (-0.599) | 8.778 (8.796) | 0.698 |
| | LDA+U | -0.672 (-0.310) | -0.645 (-0.393) | 8.729 (8.853) | 0.699 |
| $\alpha$-U | LSDA | -0.035 (-0.035) | -0.066 (-0.059) | 11.430 (11.514) | 0.701 |
| | GGA | -0.034 (-0.035) | -0.068 (-0.066) | 11.518 (11.496) | 0.700 |
| | LDA+U | -0.033 (-0.038) | -0.066 (-0.066) | 11.537 (11.619) | 0.699 |
| fcc Th | LSDA | -0.002 (-0.002) | 0.006 (0.008) | 13.512 (13.524) | 0.702 |
| | GGA | -0.002 (-0.002) | 0.005 (0.008) | 13.516 (13.528) | 0.702 |
| | LDA+U | -0.001 (-0.001) | 0.006 (0.009) | 13.612 (13.622) | 0.702 |

In conclusion, the applicability of the SOC sum rule for actinides was investigated theoretically by comparing the quantities obtained from the calculated branching ratios with the mixed, spin-up and spin-down, matrix elements of the orbital-dependent potential, which are supposedly too large to be taken into account by means of the second-variational scheme. The experimentalists should bear in mind that the branching ratio $B_0$ for the case where the SOC interaction in the valence band is switched off strongly deviates from the statistical value.

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