Calculated gadolinium atomic electron energy levels and Auger electron emission probability as a function of atomic number $Z$

G.V. Miloshevsky $^a$, V.I. Tolkach $^a$, Gad Shani $^b$,* Semion Rozin $^b$

$^a$ The Academic Scientific Complex ‘A.V. Luikov Institute of Heat and Mass Transfer’ of the National Academy of Sciences of Belarus, 15 P. Brouki, Minsk BY-220072, Belarus

$^b$ Department of Nuclear Engineering, Ben Gurion University, P.O. Box 653, Beer Sheva 84105, Israel

Received 25 October 2001; received in revised form 20 December 2001

Abstract

Auger electron interaction with matter is gaining importance in particular in medical application of radiation. The production probability and energy spectrum is therefore of great importance. A good source of Auger electrons is the $^{157}$Gd(n,$\gamma$)$^{158}$Gd reaction. The present article describes calculations of electron levels in Gd atoms and provides missing data of outer electron energy levels. The energy of these electron levels missing in published tables, was found to be in the 23–24 and 6–7 eV energy ranges respectively. The probability of Auger emission was calculated as an interaction of wave function of the initial and final electron states. The wave functions were calculated using the Hartree–Fock–Slater approximation with relativistic correction. The equations were solved using a spherical symmetry potential. The error for inner shell level is less than 10%, it is increased to the order of 10–15% for the outer shells. The width of the Auger process changes from 0.1 to 1.2 eV for atomic number $Z$ from 5 to 70. The fluorescence yield width changes five orders of magnitude in this range. Auger electron emission width from the K shell changes from $10^{-2}$ to $\sim 1$ eV with $Z$ changing from 10 to 64, depending on the final state. For the L shell it changes from 0 to 0.25 when it $Z$ changes from 20 to 64. © 2002 Published by Elsevier Science B.V.

Keywords: Auger electrons; Gadolinium; Hartree–Fock–Slater approximation; Transition probability; Electrons energy levels; Fluorescence yield

1. Introduction

Auger electrons are found to be a very useful tool in radiation therapy. Due to their short range, Auger electrons can damage organic molecules within 20 nm (DNA size) from their origin. Gadolinium is a good potential source of Auger electrons for such a purpose if introduced into the cell and linked to the DNA [1]. A large number of Auger electrons are emitted following the reaction $^{157}$Gd(n,$\gamma$)$^{158}$Gd. The reaction has a very high cross-section, $\sim 250 000$ b for thermal neutrons, therefore a lower neutron beam intensity will be needed compared to other methods of neutron...
capture therapy. A problem arose in trying to calculate the number of Auger electrons emitted from that reaction and their energy, due to the lack of accurate data regarding electron energy levels, in particular in the outer shells, of gadolinium atoms. The present paper provides new, accurate energy levels, calculated using the Hartree–Fock–Slater (HFS) approximation. The probability of Auger electron emission and fluorescence from some shells was also calculated as a function of atomic number.

2. Auger process probability

Several processes are capable of initiating an Auger cascade in atoms. The probability of the Auger process [2] is a function of the matrix element of the interaction of falling into a vacancy in another shell. This probability can be expressed as the probability of the Auger transitions that the transitions probability for separate K–XY or L–XY channels can differ by a few orders of magnitude. The integral describing the probability will be maximum if the main maxima of the wave functions in the initial and final states are close. The greatest overlap of the wave functions occurs for the same shell (Coster–Kronig transitions). The probability is rather great for electrons with the same orbital number, for example K–L₁L₂. In this case, the 2s-1s transition takes place and the wave functions are strongly overlapped (the similar radiative transitions are forbidden by selection rules). In contrast, the transitions with strongly distinguished orbital numbers are highly suppressed. For example, the probability of the K–M₄X transition is very small as the 1s and 3d wave functions overlap insignificantly. The probability of the K–XY transitions is low, if the X and Y states are strongly distinguished in energy. In this case, the distance between the electrons is large and the integral is small.

To evaluate the kinetic energy of an Auger electron the value $E_{\lambda} = \Delta E - E_n$ is often used,
where \( E_n \) is its binding energy. This approximation is not accurate. The value \( E_n \) is a one-electron eigenvalue found by the solution of the HFS equations. To determine the Auger-electron kinetic energy accurately, it is necessary to calculate the total energy of an atom and then to determine the transition energy \( \Delta E \) as the difference of two total energies of an atom in different states. The total energy may be evaluated as

\[
E'_{\text{tot}} = \int \Psi_1 H_1 \Psi_1 \, dr,
\]

where \( H_1 \) is the system Hamiltonian which includes the operators of kinetic and potential energy of all atomic electrons. The wave function \( \Psi_1 = P_1(r_1)P_2(r_2)\cdots \) is a product of one-electron orbitals. For example, consider the K–L1L2 transition. In the initial state, there is the vacancy in the K-shell that corresponds to the following distribution of the electrons over shells 1s2s2p6. In the final state 1s2s2p5 the relaxation of the atomic electrons occurs and the total energy is changed as follows:

\[
E''_{\text{tot}} = \int \Psi_2 H_2 \Psi_2 \, dr.
\]

The kinetic Auger-electron energy is expressed by \( E_A = E'_{\text{tot}} - E''_{\text{tot}} \). This improvement is more essential for the outer atomic shells and the Coster–Kronig transitions as in this case the transition takes place between the subshells with close energies.

In practical applications the fluorescence yield is used instead of the probability for Auger process. This value is determined as \( \delta = \frac{W_r}{(W_r + W_a)} \), where \( W_r \) is the probability of radiation emission. The latter is determined using the oscillator strengths of transitions in accordance with the expression

\[
W_r = \frac{2\hbar^2 \Delta \varepsilon^2}{m_e c^2 |f|},
\]

where \( \Delta \varepsilon \) is the energy of transition, \( f \) is the oscillator strength. The oscillator strength is calculated using the HFS wave functions

\[
f = \frac{2m_e \Delta E}{3\eta} \frac{l_{\text{max}}}{2l + 1} r^2, \quad R = \int P_i(r) r P_f(r) \, dr.
\]

Here \( l \) is the orbital number of the shell from which the radiative transition occurred, \( l_{\text{max}} \) is the maximum of the two orbital numbers considered. The matrix element \( R \) is determined by the integral from the wave functions of initial and final states.

The total probability of the Auger-electron yield from an atom is slightly dependent on the atomic number \( Z \). The probability of X-ray emission is proportional to the fourth power of the atomic number. For this reason the probability of the Auger process for heavy elements is significantly lower than that for radiative emission. For example, the fluorescence yield from the transition K–L1L2 for carbon is 0.26\%, for nitrogen 0.6\%, for oxygen 0.92\% and it is about 93.4\% for gadolinium, i.e. the probability of the Auger process for gadolinium is low. The probability of radiative transitions drops with decreasing energy. For this reason, the fluorescence yield decreases significantly with increasing the shell number. For gadolinium, the fluorescence yield from the L shell is less than 20\% and from the M shell it is less than 1\%.

3. Results

Using the theory above we have performed energy level calculations for gadolinium. A comparison of our results with the experimental data [5] is presented in Table 1. It is evident that for inner electrons shells (1s\(^2\), 2s\(^2\), 2p\(^6\), 3s\(^2\) and 3p\(^6\)) the error is not higher than 1\%. The accuracy of energy level for the 3d\(^{10}\) shell is slightly lower. The error is increased for the 4d\(^{10}\), 5p\(^6\), 5d shells which are close to the 4f\(^7\) shell. For these shells, the error is 10–15\%. The reason for the accuracy decrease is the following. The HFS equations were solved using the spherically symmetrical potential. However, for the unfilled 4f\(^7\) shell the deviation from the symmetrical potential is essential. The electrostatic interaction of electrons in the unfilled shell leads to splitting of the average shell energy into the numerous terms \(^5L\). Their number is maximum for the 4f\(^7\) shell. There is a problem in determining the type of bond correctly between the electrons of these terms as the approximation of LS coupling for the rare-earth elements is not
accurate. It should be noted that more complex methods such as the Hartree–Fock and Multi-configuration Hartree–Fock do not allow the improvement of the calculations accuracy. Thus, the energy of inner shell electrons is determined with a sufficient accuracy using the HFS approximation.

4. Discussion

Comparisons with other theoretical result were also carried out. It is of interest to compare our computations for gadolinium with other calculated data. In [6–10] the data for gadolinium are not presented, but there are data for neodymium ($Z = 60$) and terbium ($Z = 64$). For these elements, the probability of the Auger process is insignificantly distinguished from that for gadolinium. Therefore, it is possible to compare these probabilities. In Fig. 1, the probabilities of Auger transitions as a function of atomic number $Z$ are shown. The average values of the K–XY transitions are compared. Our results are in satisfactory agreement with data from [7–10]. In Fig. 2, the probabilities of X-ray emission are presented, which are compared to data from [7,8,10]. It is of interest to compare not only integrated quantities, but also the probability of transitions in separate channels. In Fig. 3 the comparison of our results with data from [9] is presented for the K–LL, K–LM, K–LN transitions. It is evident that accuracy of our calculations is 15–20%. With increasing the shell principal quantum number from which the ionization takes place, the probability of Auger process decreases. It is evident that the maximum probability occurs for the K–LL transition. The probabilities of the K–LM and K–LN transitions

<table>
<thead>
<tr>
<th>Level</th>
<th>Theory</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s_{1/2}</td>
<td>K</td>
<td>50182.9</td>
</tr>
<tr>
<td>2s_{1/2}</td>
<td>L_{1}</td>
<td>8351.2</td>
</tr>
<tr>
<td>2p_{1/2}</td>
<td>L_{2}</td>
<td>7980.6</td>
</tr>
<tr>
<td>2p_{3/2}</td>
<td>L_{3}</td>
<td>7369.2</td>
</tr>
<tr>
<td>3s_{1/2}</td>
<td>M_{1}</td>
<td>1876.7</td>
</tr>
<tr>
<td>3p_{1/2}</td>
<td>M_{2}</td>
<td>1706.0</td>
</tr>
<tr>
<td>3p_{3/2}</td>
<td>M_{3}</td>
<td>1581.0</td>
</tr>
<tr>
<td>3d_{2/2}</td>
<td>M_{4}</td>
<td>1727.2</td>
</tr>
<tr>
<td>3d_{3/2}</td>
<td>M_{5}</td>
<td>1240.9</td>
</tr>
<tr>
<td>4s_{1/2}</td>
<td>N_{1}</td>
<td>387.3</td>
</tr>
<tr>
<td>4p_{1/2}</td>
<td>N_{2}</td>
<td>318.5</td>
</tr>
<tr>
<td>4p_{3/2}</td>
<td>N_{3}</td>
<td>290.8</td>
</tr>
<tr>
<td>4d_{2/2}</td>
<td>N_{4}</td>
<td>173.0</td>
</tr>
<tr>
<td>4d_{3/2}</td>
<td>N_{5}</td>
<td>167.1</td>
</tr>
<tr>
<td>5s_{1/2}</td>
<td>O_{1}</td>
<td>57.6</td>
</tr>
<tr>
<td>5p_{1/2}</td>
<td>O_{2}</td>
<td>37.7</td>
</tr>
<tr>
<td>5p_{3/2}</td>
<td>O_{3}</td>
<td>33.8</td>
</tr>
<tr>
<td>4f_{5/2}</td>
<td>O_{5}</td>
<td>24.0</td>
</tr>
<tr>
<td>4f_{7/2}</td>
<td>O_{7}</td>
<td>23.1</td>
</tr>
<tr>
<td>5d_{1/2}</td>
<td>O_{8}</td>
<td>7.5</td>
</tr>
<tr>
<td>6s_{1/2}</td>
<td>P_{1}</td>
<td>6.16</td>
</tr>
</tbody>
</table>

Fig. 1. Total Auger width as a function of atomic number.

Fig. 2. Radiative width of fluorescence yield as a function of atomic number.
are significantly lower. In Fig. 4 a comparison of [11] data with the results of our calculations for the L–XY transitions is shown. It was unexpected that there is a non-monotonicity in the dependence of the probability of Auger transitions on the atomic number \( Z \). We can assume that the transitions for the given channel are more sensitive to the accuracy of approach used. The analysis of the separate channels contribution to the L–XY transitions shows that the maximum contribution occurred from the \( L_2,3-M_{4,5}X \) transitions. The \( M_{4,5} \) term in spectroscopic notation corresponds to 3d level. As it was mentioned above, the \( nd \) levels have the greatest error in energy. The error of the wave functions is also maximum. It is due to the fact that d-electron has a large centrifugal barrier and the maxima of the wave function are located on the periphery. The calculation accuracy of the self-consistent field is low at this distance from the nucleus (it is not an asymptotic). In general, the accuracy in comparison with [11] is about 30–50%.

Calculations of Auger-electron and X-ray probabilities, and fluorescence yields were performed for carbon, nitrogen, oxygen and gadolinium. The calculations were carried out with maximum detail of various Auger transition schemes. For gadolinium, 780 different channels for all the shells were taken into consideration. For the atoms mentioned above, the special data banks containing the probabilities of Auger-electron and fluorescence yields and its energies were created. Test calculations for calcium, zinc, tin and some other elements were also carried out. The probabilities of optical transitions computed using the HFS method were compared to those calculated using the experimental oscillator strengths [12]. For all the cases, the error was not higher than 15–20%. The calculated probabilities of Auger transitions were averaged over different components and were compared with experimental values presented in handbook [13].

References