Exponential increase of energy level density in atoms: Th and Th II

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We present analytical estimates and numerical calculations showing that the energy level density in open-shell atoms increases exponentially with increase of excitation energy. As an example, we use the relativistic Hartree-Fock and configuration interaction methods to calculate the density of states of Th and Th II. The result is used to estimate the effect of electrons on the nuclear transition which is considered for the use in a nuclear clock.

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I. INTRODUCTION

The exponential increase of density of states is well known in nuclear physics (see, e.g. [1]). Similar problem in atomic physics has not been considered so far. It is well-known that the density of the Rydberg levels (with one excited electron) tends to infinity at ionization limit. However, there are also compound states with several excited electrons. As we will see below, the density of such states increases exponentially with the excitation energy.

The concept of the density of states $\rho(E)$ can be especially useful for the cases of the dense and complicated spectrum. This takes place for practically any many-electron atom at sufficiently high excitation energies, in particular at energies close or above the ionization limit. In the latter case we speak about density of Feshbach resonances corresponding to the quasi-stationary compound states with several excited electrons. For atoms with open $d$ or $f$ shells the spectrum is complicated even at low energies. Experimental data for highly excited states are often absent. Accurate calculations using specific atomic states in the area of dense spectrum is very difficult if not impossible. Even identification of such states is often problematic. On the other hand, statistical approaches, which use functions obtained by averaging over large number of states, can be very useful. An interesting case was considered in Ref. [2] where properties of excited states of cerium atom were studied using statistical analysis. It has been demonstrated that the Ce atom is an example of quantum chaotic system in which highly excited states are similar to compound states of heavy nuclei. Density of states $\rho$ is used in the criteria for the chaos to take place: $H_{ij} > D_{ij} \equiv 1/\rho_{ij}$. Here $H_{ij}$ is the off-diagonal matrix element of the effective Hamiltonian between many-electron states $i$ and $j$, and $D_{ij}$ is the energy interval between the states which can be mixed by $H_{ij}$. Statistical theory based on the properties of chaotic eigenstates [2, 3] allows one to calculate average orbital occupation numbers, matrix elements and amplitudes between chaotic states, enhancement of weak interactions and increase of entropy. Another important example is the effect of atomic electrons on nuclear transitions, which will be considered below. The concept of the density of states is also needed to estimate a number of states missed in experimental spectra.

In this paper we present simple analytical estimates explaining exponential increase of density of states containing several excited electrons. Then we perform numerical calculations of density of compound states using thorium as an example due to its importance for the construction of nuclear clock.

The proposed clock [4] utilizes the use of the nuclear transition between a metastable isomeric state and the ground state of $^{229}$Th. The frequency of this transition is unusually low, about 7 eV, and can be accessed by lasers. Additional interest is due to the fact that this transition must be very sensitive to the time-variation of the fine structure constant [5]. The effect of electrons on the nuclear transition in Th II and Th IV ions, also known as electronic bridge process, was considered in Refs. [6, 7] (see also [8]). In this process the nuclear transition is accompanied by an electron transition from the ground state to an exited state followed by emission of the photon. The electronic bridge process may have significant effect on the performance of the nuclear clock in the case of resonance between nuclear and atomic transitions. However, neither nuclear frequency nor electron spectrum are known sufficiently well to make reliable estimations. The measured values for the frequency of the nuclear transition varies form $3.5 \pm 1.0$ eV [9] to $7.6 \pm 0.5$ eV [10]. Electron spectrum of Th II is also not known at energies around 7.6 eV. In this situation instead of calculating the value of the electronic bridge process one can consider estimation of the probability for the result to be within some range of values. This can be done if density of electron states as a function of the energy is known. Knowledge of the electron spectrum density in Th II is also needed for the accurate measurements of the nuclear transition frequency. E. Peik and collaborators [11] plan to use laser excitation of a Th II electron state which may transfer part of the excitation energy to induce the nuclear transition.

II. SIMPLE ANALYTICAL ESTIMATE OF THE NUMBER OF COMPOUND STATES

Let us consider an open ground electron shell containing $n$ electrons and $g_0$ single-electron states; usually
\( g_0 = \sum _l 2(2l+1) \) where \( l \) is the orbital angular momentum of a single-electron state within this shell. A total number of many-body states within this shell is equal to the binomial coefficient,

\[
N_0 = C_n^g = \frac{g_0!}{n!(g_0-n)!} \approx \exp \left[ n \ln \left( \frac{g_0}{n} \right) + 1 \right] \sqrt{\frac{2\pi n}{n!}},
\]

(1)

In the last expression we assumed \( g_0 \gg n \) and used the Stirling formula

\[
n! \approx \sqrt{2\pi n} n^n e^{-n}
\]

(2)

which gives an excellent accuracy even for \( n = 1 \) (the correction is \(-1/(12n))\). Assume for simplicity that all these many-body states have approximately the same energy. Let us now consider next electron shell which is separated from the ground state shell by a single-particle energy interval \( \omega \) and has \( g_1 \) single-electron states. If a total excitation energy of a many-electron state is equal to \( E \), we may transfer \( k = E/\omega \) electrons from the ground shell to the next shell. Now we have a total number of many-electron states

\[
N(E) = C_n^g + C_k^g C_{n-k}^g C_{k}^{g1}.
\]

(3)

Here the first factor \( C_n^g \) gives the number of ways to select \( k \) excited electrons from the available \( n \) electrons, the second factor gives the number of many-body states in the ground shell and the last factor gives the number of many-body states in the next shell. For \( n \gg k \)

\[
N(E) \approx N_0 \left( 1 + \frac{\exp \left[ k \ln \left( \frac{n^2 g_1}{k^2 g_0} \right) + 2k \right]}{2\pi k} \right)
= N_0 + \frac{a}{E} \exp (bE),
\]

(4)

where

\[
a \approx \omega \frac{\exp \left[ n \ln \left( \frac{g_0}{n} \right) + 1 \right]}{2\pi \sqrt{2\pi n}}
\]

(5)

\[
b \approx \ln \left( \frac{n^2 g_1}{k^2 g_0} \right) + \frac{2}{\omega}
\]

(6)

This rough estimate shows that the number of compound states increases exponentially with the number of electrons in the open shell \( n \) and with the number of excited electrons \( k = E/\omega \). Inclusion of the electron excitations to higher shells and the Rydberg spectrum of the single-electron excitations will only make the number of states larger.

The derivation of formula (4) assumes that the number of electrons \( n \) in the open shell is large. We will see below that the exponential increase of the density of states takes place even for \( n \) as small as three.

## Table I: Number of states of even parity and total momentum \( J = 1.5 \) in 10000 cm\(^{-1}\) energy intervals in Th II.

| Interval | Exp.\(^a\) | Full CI\(^b\) | \( H_0 \)\(^c\) | \( H_0 \)\(^d\) |
|----------|------------|----------------|-----------------|----------------|
| 0 - 10000 | 5 | 5 | 1 | 3 |
| 10001 - 20000 | 3 | 3 | 5 | 5 |
| 20001 - 30000 | 4 | 4 | 7 | 7 |
| 30001 - 40000 | 10 | 11 | 7 | 15 |
| 40001 - 50000 | 18 | 10 | 19 | 8 |
| 50001 - 60000 | 8 | 18 | 5 | 26 |
| 60001 - 70000 | 50 | 44 | 90 | |
| 70001 - 80000 | 93 | 94 | 160 | |
| 80001 - 90000 | 161 | 173 | 300 | |
| 90001 - 100000 | 128 | 142 | 168 | |

\(^a\)Experiment [13]
\(^b\)Short basis
\(^c\)No diagonalization, short basis
\(^d\)No diagonalization, long basis

## III. Numerical Calculations

Density of atomic states \( \rho \) can be defined via the relation

\[
N(E) = \int_0^E \rho(\epsilon) d\epsilon,
\]

(7)

where \( N(E) \) is the number of atomic states in the interval from zero energy, which corresponds to the ground state, to the energy \( E \). Total density \( \rho \) is the sum of the partial densities \( \rho_p \) which correspond to the states of definite total momentum \( J \) and parity:

\[
\rho(\epsilon) = \sum_p \rho_p(\epsilon).
\]

(8)

We use relativistic Hartree-Fock (RHF) and configuration interaction (CI) methods to calculate the number of states for given \( J \) and parity. The partial density is calculated by the numerical differentiation

\[
\rho_p(\epsilon) = \frac{N_p(\epsilon + \delta) - N_p(\epsilon - \delta)}{2\delta}.
\]

(9)

The value of \( \delta \) is chosen to have a smooth function for \( \rho_p \). This is achieved when the number of states in the numerator is large. The density function defined this way represents inversed energy interval \( D_p \) averaged over large number of neighboring states, \( \rho_p = 1/D_p \).

We perform the configuration interaction (CI) calculations using the \( V^{N-1} \) basis (see e.g. [12]) calculated in the frozen RHF field of the [Ra]6d\(^2\) configuration for Th II and the [Ra]6d\(^2\)7s configuration for Th I. To test the accuracy of the calculation we use different basis sets for Th II: a short one and a long one. The purpose of using short basis is to show that the non-diagonal matrix elements of the CI matrix can be neglected in the evaluation of the density of states. This allows us to use much larger basis and, consequently, move to higher energies.
In the short basis we include six lowest RHF states above the core in each of the partial waves up to \(l_{\text{max}} = 4\). Two more states in each partial wave are added in the long basis. Apart from that, we allow only single and double excitations from a reference configuration to construct three-electron states for the CI calculations with the use of the short basis. Three-electron excitations are allowed when long basis is used.

For the short basis we perform both the full-scale CI calculations which include matrix diagonalization, and the simplified calculations in which off-diagonal matrix elements of the CI matrix are neglected. This corresponds to an approximation \(E_M \approx \langle M | H^{\text{CI}} | M \rangle\), where \(|M\rangle\) is a three-electron CI state of a definite total momentum \(J\) and parity, \(H^{\text{CI}}\) is the CI Hamiltonian. For the long basis we neglect the off-diagonal matrix elements. The use of this approximation allows us to deal with large number of states (\(\sim 10^5\)). On the other hand, neglecting the non-diagonal CI matrix elements has little effect on the density of states.

Table I shows experimental and calculated number of states in the 10000 cm\(^{-1}\) energy intervals of Th II. We consider even states of total momentum \(J = 1.5\) as an example. These states are important for the electronic bridge process \(^7\). Experimental data ends at about 56000 cm\(^{-1}\). Next two columns correspond to exactly the same CI matrix obtained with the use of the short basis set. It has been diagonalised in the full CI calculations while only diagonal matrix elements are considered in the next column. One can see that neglecting the off-diagonal CI matrix elements does not lead to dramatic changes in the density of states at high energies where the density function is well defined (see eq. (9) and discussion below it).

The last column of Table I shows density of states obtained with the use of long basis without diagonalization. The use of long basis adds more states at large energy and has little effect on the number of states at low energy. Therefore, we use only long basis in the calculations for Th I.

### IV. RESULTS

The results of the calculations for the total density of states are shown on Fig. 1. It is also shown that the calculated data is fitted very well by simple exponential functions. We use two fitting formulae

\[
\rho(\epsilon) = \frac{A}{\epsilon_0} \exp(\epsilon/\epsilon_0) \quad (10)
\]

and

\[
\rho(\epsilon) = \frac{A}{\epsilon} \exp(\epsilon/\epsilon_0), \quad (11)
\]

where \(A\) and \(\epsilon_0\) are fitting parameters. Formula (11) is more consistent with the analytical formula (4) while formula (10) is simpler and behaves better at \(\epsilon \to 0\). The values of the fitting parameters \(A\) and \(\epsilon_0\) for the total density of states of Th II and Th I are presented in Table II. It turns out that \(\epsilon_0\) can be kept the same for all partial densities. The values of parameter \(A_p\) for partial densities are presented in Table III.

The density of states must go to infinity when energy is approaching ionization potential. This is due to the infinite number of Rydberg states which all have about the same energy, close to the ionization potential. In contrast, the number of calculated states goes down at large energies. This is the cut-off effect of the single-electron basis. Adding more highly excited orbitals into the basis increases the number of many-electron states at high energy (see Table I). Ionization potential of Th I is 50867 cm\(^{-1}\) = 0.23 a.u. \(^{14}\) while the one for Th II is about 96000 cm\(^{-1}\) = 0.44 a.u. \(^{15}\). As can be seen from Fig. 1 the fitting works very well for the energies very close to the ionization potentials of Th II and Th I.
higher energies more basis states must be included.

Now we can use the density function to estimate the probability of the electronic bridge process in Th II. According to Ref. [7] the ratio $\beta$ of the electron bridge width to the width of the direct nuclear transition (the electron enhancement factor) is

$$
\beta \approx \left(\frac{\omega}{\omega_N}\right)^3 \frac{R_n}{3(2J_n+1)(2J_n+1)(\omega_{in}+\omega_N)^2},
$$

(12)

where $n$ is the resonance electron state, $\omega$ is the photon frequency, $\omega_N$ is the frequency of the nuclear transition, $J_n$ is the total angular momentum of the resonance state, $J_i$ is the total angular momentum of the ground state ($J_n = J_i = 1.5$ in our case), $R_n$ is the combination of the electron matrix elements for electric dipole and hyperfine transitions between atomic ground state, resonance state $n$ and some odd-parity low lying final atomic state, $\omega_{in}$ is the frequency of the electron transition from the ground to the resonance state, $\omega_N$ is the frequency of the nuclear transition. Resonance corresponds to the condition $\omega_{in} \approx -\omega_N$. As it was discussed in the introduction the exact value for the nuclear frequency is not known and the experimental values range from 3 eV to 8 eV. Estimation of the effect for 3.5 and 5.5 eV were performed in Ref. [7]. The effect for higher $\omega_N$ was not presented since the electron spectra are not known for such energies. Here we perform the estimation for the latest measured value $\omega_N = 7.6$ eV = 0.28 a.u. Using formula (10) and the data from Table III [7] we find that the average energy interval between the relevant electron states is $D_p = 1/\rho_p = 6 \times 10^{-4}$ a.u at this energy. The energy denominator in (12) is at least two times smaller. Therefore, the electron enhancement factor is

$$
\beta \sim 2 \times 10^5 R_n \approx 4 \times 10^3.
$$

(13)

Here we use the root mean square value for $R_n$ which is $R_n \approx 2 \times 10^{-2}$ a.u. for the energies above 7 eV [7].

An interesting effect may take place for neutral thorium if the frequency of the nuclear transition is smaller than the ionization potential of the atom. The density of states of Th I is huge and the resonance situation is highly probable. This can be used to excite the nucleus in a two-step process in which a resonance electron state is excited first, then it gives its energy to excite the nucleus.

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