Theoretical study of electron structure of fermium ($Z = 100$): energy levels and transition rates

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Calculation of the excited states and electromagnetic transition probabilities in atoms with open f-shell, like erbium and fermium, is a challenging problem due to a very large number of mixed configurations. We use recently developed version of the configuration interaction method for open shells to study electron structure of fermium atom. We calculate excitation energies of odd states connected to the ground state by the electric dipole transition and corresponding transition rates. The results are in good agreement with experiment and earlier calculations for seven previously studied states. Twenty eight new states are reported. We use similar calculations for erbium, which is lighter analog of fermium, to validate the method and estimate the accuracy of the calculations.

I. INTRODUCTION

Fermium is one of two heaviest atoms for which experimental spectroscopic data are available. It was intensively studied in last two decades both theoretically and experimentally.1,3 Frequencies of seven electric dipole transitions from the ground state to excited odd states have been measured2,6 and first ionization potential have been obtained7,8. The measurements were led by theoretical predictions made with the use of the multi-configurational Dirac-Fock method (MCDF)2,6. It is clear from comparing these data to the spectrum of the erbium atom, which is lighter analog of Fm, that large number of Fm states still escaped experimental detection and theoretical determination. Further study of Fm is needed to understand its electron structure and its difference from Er caused by interplay between correlation and relativistic effects.

The only other atom, which is heavier than Fm and for which spectroscopic data are available is nobelium. Frequency of just one electric dipole transition between ground state singlet 7s2 1S0 and excited odd-parity singlet 7s7p 1P0 have been measured for three isotopes, 252,253,254 No10,11. These measurements lead to determination of the isotope shift (IS) between these isotopes and to the hyperfine structure (hfs) of the 253 No isotope. The study of hfs combined with atomic calculations10 lead to extraction of the values of nuclear dipole magnetic and quadrupole electric moments.

The ground state of Fm is 5f127s2 3H6. The seven odd states for which the measurements were done all belong to one odd configuration 5f127s7p 3P0. However, it is very well known that erbium, which is lighter analog of Fm, has very rich spectrum, with odd states of mostly two configurations, 4f116s6p and 4f116s25d13. It is natural to expect similar features in Fm. In this work we perform calculations for both atoms using the same approach. Calculations for Er mostly serve as a guide for the accuracy of calculations. Calculations for Fm demonstrate that the two atoms have much in common. Some differences in the spectra can be explained by stronger relativistic effects in Fm. We calculate odd excited states which are connected to the ground state by the electric dipole transition. We calculate the transition rates to identify stronger transitions which would be easier to detect. We compare our calculations to the experiment and previous MCDF calculations.

II. METHOD OF CALCULATION

We use recently developed CIPT (configuration interaction with perturbation theory) method12 to perform the calculations. The method was especially developed for atoms with open shells which have large number of electrons in valence space. It was successfully used for atoms with open f17, d14, and p13 shells. The maximum number of electrons in valence space was sixteen (Yb and No11,12,17). The main idea of the method is neglecting off-diagonal matrix elements between high states in the CI matrix. The idea is used in several similar approaches20,22. However, in the CIPT method one more step is made, the whole CI matrix is reduced to the matrix of much smaller size, in which matrix elements between low-lying states are corrected by expression similar to the second-order perturbative correction to the energy

$$
\langle i|H^{\text{CI}}|j \rangle \rightarrow \langle i|H^{\text{CI}}|j \rangle + \sum_k \frac{\langle i|H^{\text{CI}}|k \rangle \langle k|H^{\text{CI}}|j \rangle}{E_k - E_i}.
$$

Summation in (1) goes over all high states. The energies and wave functions are found by solving matrix eigenvalue problem

$$
(H^{\text{CI}} - EI) X = 0,
$$

with $H^{\text{CI}}$ matrix given by (1). Reducing the matrix size by (1) does not affect the resulting energies as long as the energy $E$ is the same in (1) and (2). Since the energy is not known in advance, the iterations over energy are
needed. Usually five to ten iterations is enough for full convergence.

We use the B-spline technique to build a single-electron basis set. These states are constructed as linear combinations of B-splines which are eigenstates of the relativistic Dirac-Hartree-Fock Hamiltonian (DHF) with the $V^{N-1}$ potential. The self-consistent DHF procedure is first done for an atom with one electron removed. For example, the ground states of Er belongs to the $[\text{Xe}]4f^{12}6s^2$ configuration. The DHF procedure is done for the $[\text{Xe}]4f^{12}6s$ configuration and basis states for valence electrons are calculated in resulting $V^{N-1}$ potential. Similarly, the $[\text{Rn}]5f^{12}7s$ configuration is used in the DHF calculations for Fm. Many-electron basis states for the CI calculations are constructed by exciting one or two electrons from initial reference valence configurations. For example, to calculate even states of Er, we use the time-dependent Hartree-Fock method [24] (equivalent to the random-phase approximation (RPA)) to do this. The RPA equations are first solved for the CI matrix while all states obtained by exciting electrons from these configurations go to the effective CI matrix. All states, obtained by single and double excitations are used in the perturbative term (last term in (1)). For odd states we use four reference configurations $4f^{12}6sp$, $4f^{12}6s^2p$, $4f^{11}6s^2d$ and $4f^{12}6s^5f$. All states from these four configurations go to the effective CI matrix while all states obtained by exciting electrons from these configurations go to the perturbative term. Similarly for Fm, the configurations are $5f^{12}7s^2$ for even states and $5f^{12}7s7p$, $5f^{12}7s8p$, $5f^{11}7s^26d$ and $5f^{12}7s6f$ for odd states.

The calculations are fully relativistic. Our single-electron operator in the DHF and CI Hamiltonians comes from Dirac equation. Furthermore, Breit and quantum electromagnetic corrections are included similar to what was done in our previous works [17].

To calculate amplitudes of electric dipole transitions we need to include external electric field in the equations. We use the time-dependent Hartree-Fock method [24] (equivalent to the random-phase approximation (RPA)) to do this. The RPA equations are first solved for the atom in the same $V^{N-1}$ approximation as in the DHF calculations. The RPA equations

$$(H^{\text{DHF}} - \epsilon_i) \delta \psi_i = - (\hat{d} + \delta V^{N-1}) \psi_i$$

are iterated for all atomic states $i$ to find the correction to the atomic potential $\delta V^{N-1}$ caused by the effect of external field. Transition amplitudes are calculated as

$$A_{ab} = \langle a | \hat{d} + \delta V^{N-1} | b \rangle,$$

where $|a\rangle$ and $|b\rangle$ are many-electron states obtained in the CI calculations. $\hat{d}$ is the electric dipole operator (we use length form, $\hat{d} = -e \sum_n r_n$). The rate of spontaneous emission from state $b$ to state $a$ is given by (atomic units)

$$T_{ab} = \frac{4}{3} (\alpha \omega_{ab})^3 \frac{A_{ab}}{2J_b + 1},$$

where $\alpha$ is the fine structure constant, $\omega_{ab}$ is the frequency of the transition.

The results for energy levels and transition rates for Er are presented in Table 11 and compared to experiment. We see that the difference between theory and experiment for the energies is usually just few hundred cm$^{-1}$. Similar accuracy should be expected for Fm.

Table 11 also presents the values of calculated and experimental Landé $g$-factors. The $g$-factors are useful for identification of states. In some cases (e.g., when no experimental values are available) it is useful to compare calculated $g$-factors to a non-relativistic expression

$$g_{NR} = 1 + \frac{J(J + 1) - L(L + 1) + S(S + 1)}{2J(J + 1)},$$

where $J$ is the total angular momentum, $L$ and $S$ are total orbital and spin angular momenta, respectively.

III. RESULTS

The results for Fm are presented in Table III. As it is expected the spectrum of Fm is very similar to those of Er. There are some differences too mostly caused by relativistic effects which are expected to be about two times larger in Fm than in Er. To understand the difference we compare uppermost single-electron $7s$, $7p$ and $6d$ orbitals of Fm to the $6s$, $6p$ and $5d$ orbitals of Er. Fig. 11 shows upper components of the Er and Fm orbitals. Stronger relativistic effects of Fm move the $7s_{1/2}$ and $7p_{1/2}$ orbitals closer to the nucleus than similar $6s_{1/2}$ and $6p_{1/2}$ orbitals in Er. This is because relativistic effects are stronger on short distances where $s$ and $p_{1/2}$ orbitals are not small. Direct relativistic effects act as attraction to the nucleus. In contrast, the $p_{3/2}$, $d_{3/2}$ and $d_{5/2}$ are small on short distances and relativistic effects in them dominate by exchange interaction with $s_{1/2}$ and $p_{1/2}$ orbitals of atomic core. Therefore, the $7p_{3/2}$, $6d_{3/2}$ and $6d_{5/2}$ orbitals of Fm are father from the nucleus than corresponding orbitals of Er. The trend is further illustrated by the data in Table 11 which presents single-electron DHF energies of the considered states. Note that both, Fig. 11 and Table 11 show that the difference between Er and Fm is relatively small. This means that the spectra of two atoms should be similar and that numerical uncertainty in calculated data for Fm is similar to those of Er.

Table 11 shows calculated odd-parity states of Fm, which are connected to the ground state via the electric dipole transition. Corresponding transition rates are also presented to indicate which transitions might be easier to observe. There is good agreement with available experimental data and MCDF calculations. However, it is clear that large number of states were missed in previous studies.

Table 11 also presents calculated values of the Landé $g$-factors. They are used to generate state names by comparing calculated $g$-factors to the non-relativistic expression (see explanation below formula (4)).
Comparing the data in Tables II and III indicate that the spectra of two atoms are very similar indeed. There are some differences which should be attributed to relativistic effects. E.g., the gap between ground and first excited states is larger in Fm than in Er. The later is most probably due to larger fine structure of p and d states.

First ionisation potential (IP) of an atom is calculated as a difference between the ground state energy of the
FIG. 1: Upper components of lowest valence 6s_{1/2}, 6p_{1/2}, 6p_{3/2}, 5d_{3/2}, 5d_{5/2} orbitals of Er (solid lines) and 7s_{1/2}, 7p_{1/2}, 7p_{3/2}, 6d_{3/2}, 6d_{5/2} orbitals of Fm (dot lines).

TABLE II: Single-electron energies (in a.u.) of the lowest valence orbitals of Er and Fm.

| State | Energy (Er) | State | Energy (Fm) |
|-------|------------|-------|-------------|
| 6s_{1/2} | -0.4065 | 7s_{1/2} | -0.4269 |
| 6p_{1/2} | -0.1210 | 7p_{1/2} | -0.1240 |
| 6p_{3/2} | -0.1140 | 7p_{3/2} | -0.1057 |
| 5d_{3/2} | -0.0837 | 6d_{3/2} | -0.0819 |
| 5d_{5/2} | -0.0832 | 6d_{5/2} | -0.0809 |

neutral atom and that of the single-ionised ion. The calculations are the same as ones for the transition energies. Our value for IP of Er is 6.102 eV, which is in excellent agreement with the experimental value 6.1077 eV [14]. Similarly, the calculated IP of Fm, 6.559 eV, is in very good agreement with experimental value 6.52(13) eV [9]. In contrast to calculation of transition energies, where very little published data can be found, the calculation of IP of Fm have been performed by many authors. A detailed review of the results can be found in Ref. [9]. Our result is the closest to the experimental value. Another very accurate result has been obtained by the CCSD(T) calculations of Ref. [9]. Its value is 6.469 eV. Our value is only about 1% larger.

IV. CONCLUSIONS

All odd energy levels of Fm within optical range (E < 40000 cm^{-1}) which are connected to the ground state via the electric dipole transition are calculated with uncertainty of few hundred cm^{-1}. The results are in good agreement with previous theoretical and experimental studies where the data are available. Twenty eight new levels are reported. The transition rates are also calculated. These transition rates might be useful for planning further experimental study.

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TABLE III: Excitation energies ($E$, cm$^{-1}$), electric dipole transition rates to the ground state ($A_{ki}$, s$^{-1}$), and $g$-factors for some low odd states of Fm atom with $J=5,6,7$.

| N     | Conf. | LSJ | Present | Exp. | $A_{ki}$ | Present | Exp. | $g$ |
|-------|-------|-----|---------|------|--------|---------|------|----|
| 1     | $5f^{12}7s^2$ | $I_6^2$ | 18915 | >13000$^b$ | 0.00 | 1.0383·10$^5$ | 0.00 | 1.1619 |
| 2     | $5f^{11}7s^26d$ | $I_6^1$ | 19012 | 0.00 | 1.9756·10$^6$ | 0.00 | 1.2880 |
| 3     | $5f^{11}7s^27p$ | $I_6^0$ | 19080 | 0.00 | 1.5304·10$^5$ | 0.00 | 1.2594 |
| 4     | $5f^{11}7s^26d$ | $I_6^0$ | 20077 | 0.00 | 1.1638·10$^7$ | 0.00 | 1.2378 |
| 5     | $5f^{11}7s^27p$ | $I_6^0$ | 20399 | 0.00 | 1.6751·10$^7$ | 0.00 | 1.0843 |
| 6     | $5f^{11}7s^27p$ | $I_6^0$ | 20711 | 0.00 | 1.9571·10$^7$ | 0.00 | 1.1921 |
| 7     | $5f^{11}7s^26d$ | $I_6^0$ | 31175 | 0.00 | 7.6499·10$^4$ | 0.00 | 1.1527 |
| 8     | $5f^{11}7s^26d$ | $I_6^0$ | 33761 | 0.00 | 2.7206·10$^6$ | 0.00 | 1.1574 |
| 9     | $5f^{11}7s^26d$ | $I_6^0$ | 33758 | 0.00 | 2.0954·10$^6$ | 0.00 | 1.1527 |
| 10    | $5f^{11}7s^26d$ | $I_6^0$ | 24294 | 0.00 | 2.3928·10$^6$ | 0.00 | 1.2003 |
| 11    | $5f^{11}7s^27p$ | $I_6^0$ | 25392 | 0.00 | 1.3486·10$^7$ | 0.00 | 1.2351 |
| 12    | $5f^{11}7s^27p$ | $I_6^0$ | 25442 | 252426 | 25099.8±0.2 | 4.6168·10$^6$ | 1.89·10$^6$ | (3.4±0.8)·10$^6$ | 1.1861 |
| 13    | $5f^{11}7s^27p$ | $I_6^0$ | 25494 | 25471 | 25111.8±0.2 | 2.5808·10$^6$ | 1.28·10$^6$ | (3.5±0.7)·10$^6$ | 1.1204 |
| 14    | $5f^{11}7s^27p$ | $I_6^0$ | 28520 | 27633 | 27389±1.5 | 1.1451·10$^8$ | 1.98·10$^8$ | 1.2120 |
| 15    | $5f^{11}7s^27p$ | $I_6^0$ | 28662 | 27934 | 27466±1.5 | 3.3511·10$^7$ | 2.43·10$^7$ | ≥2.9·10$^6$ | 1.2485 |
| 16    | $5f^{11}7s^27p$ | $I_6^0$ | 28690 | 28540 | 28185±1.5 | 1.6097·10$^8$ | 2.82·10$^7$ | 1.2029 |
| 17    | $5f^{11}7s^27p$ | $I_6^0$ | 28995 | 28377±1.5 | 2.3251·10$^8$ | 1.7444 |
| 18    | $5f^{11}7s^27p$ | $I_6^0$ | 29348 | 27802 | 28391±1.5 | 3.2227·10$^8$ | 3.67·10$^8$ | ≥1.1·10$^7$ | 1.1455 |
| 19    | $5f^{11}7s^27p$ | $I_6^0$ | 30236 | 29359 | 1.8429·10$^4$ | 3.58·10$^7$ | 1.1338 |
| 20    | $5f^{11}7s^26d$ | $I_6^0$ | 30519 | 30494 | 3.8572·10$^6$ | 1.0814 |
| 21    | $5f^{11}7s^26d$ | $I_6^0$ | 31953 | 31993 | 3.4736·10$^5$ | 1.1369 |
| 22    | $5f^{11}7s^26d$ | $I_6^0$ | 32200 | 32220 | 1.1719·10$^6$ | 1.1124 |
| 23    | $5f^{11}7s^27p$ | $I_6^0$ | 32295 | 32329 | 8.6814·10$^4$ | 1.0373 |
| 24    | $5f^{11}7s^27p$ | $I_6^0$ | 32583 | 32583 | 1.1635·10$^6$ | 1.1403 |
| 25    | $5f^{11}7s^27p$ | $I_6^0$ | 32693 | 32693 | 4.3436·10$^6$ | 1.0969 |
| 26    | $5f^{11}7s^27p$ | $I_6^0$ | 33093 | 33093 | 5.9416·10$^4$ | 1.0494 |
| 27    | $5f^{11}7s^27p$ | $I_6^0$ | 33328 | 33328 | 2.5223·10$^6$ | 1.0942 |
| 28    | $5f^{11}7s^27p$ | $I_6^0$ | 33575 | 33575 | 1.1680·10$^4$ | 1.1448 |
| 29    | $5f^{11}7s^27p$ | $I_6^0$ | 33656 | 33656 | 8.9755·10$^5$ | 1.0886 |
| 30    | $5f^{11}7s^27p$ | $I_6^0$ | 33750 | 33750 | 4.0337·10$^5$ | 1.0760 |
| 31    | $5f^{11}7s^27p$ | $I_6^0$ | 35020 | 35020 | 1.6194·10$^7$ | 1.0968 |
| 32    | $5f^{11}7s^27p$ | $I_6^0$ | 35106 | 35106 | 1.7174·10$^7$ | 1.0834 |
| 33    | $5f^{11}7s^27p$ | $I_6^0$ | 35442 | 35442 | 5.2698·10$^6$ | 1.0987 |
| 34    | $5f^{11}7s^27p$ | $I_6^0$ | 36587 | 36587 | 4.5135·10$^7$ | 1.1463 |

$^a$Refs. [16, 17]
$^b$Ref. [7]