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Fast configuration-interaction calculations for nobelium and ytterbium

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We calculate excitation energies for low states of nobelium, including states with an open $5f$ subshell. An efficient version of the many-electron configuration-interaction method for treating the atom as a 16-external-electron system is developed and used. The method is tested on calculations for ytterbium, which has an external electron structure similar to that of nobelium. The results for nobelium are important for prediction of its spectrum and for interpretation of recent measurements. Ytterbium is mostly used to study the features of the method.

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I. INTRODUCTION

The configuration-interaction (CI) method [1,2] is one of a few tools used to calculate the electron structure of open-shell many-electron atoms. However, due to a huge increase of the computational cost with the number of external electrons, practical application is usually limited to systems with only a few (no more than four) external electrons above closed shells. There are no other *ab initio* methods to deal with more complicated polyvalent systems. On the other hand, the use of different semiempirical approaches is questionable when experimental data are poor or absent. Superheavy elements ($Z > 100$) [3,4] and highly charged ions [5] are just two good examples of such systems. Lack of good theoretical approaches is a big obstacle in the use of complicated atomic systems in fundamental research. An important step to address the problem was done in recent work [6]. It was demonstrated that neglecting off-diagonal matrix elements in the CI matrix between highly excited states can be used to reduce the CI problem to a matrix eigenvalue problem with a relatively small matrix with modified (compared to the standard CI approach) matrix elements. Since the corrections to matrix elements were similar to the second-order perturbation theory corrections to the energy, the method was called CI with perturbation theory (CIPT). Similar approaches were later used in a number of works [7–9], while a somewhat different variant of CI plus PT method was developed in [10,11]. This made it possible to perform calculations for complicated atomic systems such as Yb (including states with excitations from the $4f$ subshell) [6,12], W [6], Ta, Db [13], Og [14], etc.

In this work we further develop the method to make it substantially more efficient. We demonstrate that neglecting the difference between energies of the states of the same excited configuration allows one to separate the summation over projections of the total angular momentum of single-electron states from the summation over other quantum numbers. Since the summation over projections is the same for all similar configurations, it can be performed only once and then reused for other similar configurations. This reduces the computational time for Yb more than 20 times while the effect on the accuracy of the calculations is negligible. We use the Yb atom as an example and then apply the method to nobelium. This allows us to predict the No spectrum including states with excitations from the $5f$ subshell. It is also important that we provide a proof of validity of previous calculations used for interpretation of the experimental measurements. The energy, hyperfine structure, and isotope shift for the ${}^1P^o_1$ state of several No isotopes were measured [15] and used together with atomic calculations to extract the nuclear parameters of these isotopes [16]. The nobelium atom was treated in the calculations as a system with two valence electrons above closed shells. It is known that similar treatment of the ${}^1P^o_1$ state of Yb gives very poor results due to the mixing with a close state containing excitation from the $4f$ subshell. This mixing cannot be properly accounted for in the calculations of two valence electrons above closed shells. We demonstrate that the situation in No is different and the corresponding mixing is small. Therefore, interpretation of the measurements based on the two-valence-electron calculations is correct. New energy levels for low states of No including those with an open $5f$ subshell have been calculated.

II. FAST CONFIGURATION-INTERACTION METHOD

Fast configuration-interaction method (FCI) is a modification of the CIPT method introduced in Ref. [6]. We start from its brief description using the ytterbium atom as an example. We consider Yb as a system with 16 electrons above closed shells. The CI Hamiltonian has the form

$$H^{\mathrm{CI}} = \sum_i^{16} h_i + \sum_{i<j}^{16} \frac{e^2}{r_{ij}}, \qquad (1)$$

where h_i is the single-electron part of the Hamiltonian,

$$h_i = c\alpha \cdot \mathbf{p}_i + (\beta - 1)mc^2 + V^{\mathrm{HF}}(r_i). \tag{2}$$

Here $V^{\mathrm{HF}}(r)$ is the self-consistent Hartree-Fock (HF) potential (including the nuclear part) obtained in the V^{N-1} approximation, with one $6s$ electron removed from the HF calculations. The many-electron wave function for 16 external electrons has the form of an expansion over single-determinant basis states:

$$\Psi(r_1, \dots, r_{16}) = \sum_i c_i \Phi_i(r_1, \dots, r_{16}). \tag{3}$$

The basis states $\Phi_i(r_1, \dots, r_{N_e})$ are obtained by distributing 16 electrons over a fixed set of single-electron orbitals. The coefficients of expansion c_i and corresponding energies E are found by solving the CI matrix eigenvalue problem

$$(H^{\mathrm{CI}} - EI)X = 0, \tag{4}$$

where I is the unit matrix, the vector $X = \{c_1, \dots, c_{N_s}\}$, and N_s is the number of many-electron basis states. It is assumed that a few first terms in the expansion (3) represent a good approximation for the state of interest and the rest of the sum is just a small correction. Then one can neglect the off-diagonal matrix elements between the states from the second part of the expansion and reduce the CI problem to one with a small matrix and modified matrix elements (see Ref. [6] for details)

$$\langle i|H^{\mathrm{CI}}|j\rangle \to \langle i|H^{\mathrm{CI}}|j\rangle + \sum_k \frac{\langle i|H^{\mathrm{CI}}|k\rangle\langle k|H^{\mathrm{CI}}|j\rangle}{E - E_k}. \tag{5}$$

Here $|i\rangle \equiv \Phi_i(r_1, \dots, r_{16})$, $E_k = \langle k|H^{\mathrm{CI}}|k\rangle$, and E is the energy of the state of interest [the same as E in (4)]. Since this energy is not known in advance, one needs to perform iterations over it. Iterations are important. They mean the summation of the most important higher-order diagrams.

Starting from this point, we consider further modifications to Eq. (5) which lead to the FCI method. The summation in (5) goes over all states of excited configurations. If we neglect the energy difference between states of the same configuration, the summation in (5) can be divided into two parts

$$\sum_k \frac{\langle i|H^{\mathrm{CI}}|k\rangle\langle k|H^{\mathrm{CI}}|j\rangle}{E - E_k} \approx \sum_c \frac{1}{E - E_c} \sum_{k_c} \langle i|H^{\mathrm{CI}}|k_c\rangle\langle k_c|H^{\mathrm{CI}}|j\rangle. \tag{6}$$

The first summation is over excited configurations and E_c is the average energy of each configuration. These energies can be expressed analytically in terms of the radial integrals of the Hamiltonian (1) [1,17,18] or calculated numerically. The second summation is over many-electron configuration state functions of a given configuration. These functions differ by the values of projections of the total angular momenta of individual electronic states, but have all other quantum numbers fixed. Therefore, the second summation can be rewritten as

$$\sum_{k_c} \langle i|H^{\mathrm{CI}}|k_c\rangle\langle k_c|H^{\mathrm{CI}}|j\rangle = \sum_{\alpha\alpha'} r_{ij}^{\alpha\alpha'} h_\alpha h_{\alpha'} + \sum_{\alpha\beta} s_{ij}^{\alpha\beta} h_\alpha q_\beta + \sum_{\beta\beta'} t_{ij}^{\beta\beta'} q_\beta q_{\beta'}. \tag{7}$$

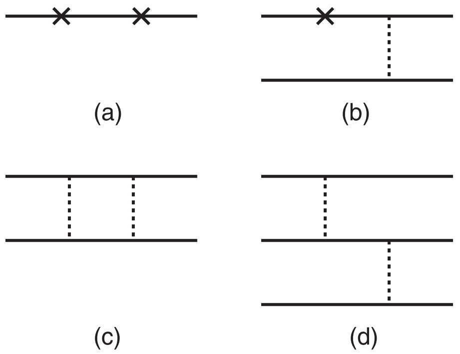

FIG. 1. Four diagrams corresponding to three terms in (7). The last term in (7) corresponds to diagrams (c) and (d).

Here h_α and q_β are the one- and two-electron radial integrals of the CI Hamiltonian (1) and α and β are shorthand for the corresponding sets of electronic quantum numbers, for example, $\alpha = n_1 l_1 j_1$ and $n_2 l_2 j_2$. The three terms on the right-hand side of (7) correspond to the four diagrams in Fig. 1 (there are two diagrams for the last term). The coefficients $r_{ij}^{\alpha\alpha'}$, $s_{ij}^{\alpha\beta}$, and $t_{ij}^{\beta\beta'}$ do not depend on the principal quantum numbers of the one-electron states. They can be calculated only once for a whole set of configurations, which differ by the principle quantum numbers. For example, these coefficients are the same for all configurations of the type $4f^{14}nsn's$ $(6 < n < n' \leqslant n_{\max})$. Since the number of similar configurations can get to over 100, the effect of reuse of the coefficients is substantial.

We do not have explicit expressions for the coefficients r, s, and t in (7) because all summations over projections are done numerically. The procedure is as follows. We calculate terms in (6) separately for each Coulomb integral or single-electron matrix element. The result is the set of numbers which are the coefficients r, s, and t in (7). Substituting appropriate Coulomb integrals and singe-electron matrix elements gives the value of the correction (6) for a relevant configuration.

To make a single-electron basis we use the B-spline technique [19] with 40 splines of order 9 in each partial wave in a box of radius $40a_B$. The basis used in the calculations is limited to 14 states above the core in each partial wave up to a maximum value of the angular momentum $l_{\max} = 4$. In our experience, having 14 states above the core is sufficient to saturate the basis. The contribution of the states with angular momentum $l > 4$ is smaller than the effect of neglecting the off-diagonal CI matrix elements. On the other hand, these contributions can be easily included at the cost of a slightly longer computation time. Note also that there is no formal limitation on the number of external electrons in both the FCI theory and CIPT [6] methods except for the reasonable size of the CI matrix (which is much smaller than in the traditional CI anyway).

Breit and quantum electrodynamic (QED) corrections are included in the calculations via relevant corrections to the Hartree-Fock potential. Breit interaction introduces a correction to the exchange part of the potential, while QED effects are included via semiempirical correction to the direct Hartree-Fock potential (see, e.g., [13] for details).

TABLE I. Comparison of energies (in cm^{-1}) and computational times (in minutes) for low states of ytterbium calculated with the use of the CIPT and FCI methods. Note that all states of the same parity and total angular momentum are calculated in one run of the program. Therefore, computational time is shown only for the lowest state. Here Δ is the difference between experimental and theoretical energies and Δ_{th} is the difference between CIPT and FCI energies. All theoretical energies are presented with respect to the FCI ground state. Gain is the ratio of the CIPT computational time to the FCI computational time.

			CIPT			FCI				
State		Expt. [20]	Energy (cm^{-1})	Δ (cm^{-1})	time (min)	Energy (cm^{-1})	Δ (cm^{-1})	Δ_{th} (cm^{-1})	time (min)	Gain
					Even					
$4f^{14}6s^2$	$^1S_0$	0	73	73	2	0	0	73	<1	~6
$4f^{14}5d6s$	$^3D_1$	24489	27692	−3203	68	27622	−3133	70	3	23
$4f^{14}5d6s$	$^3D_2$	24751	27753	−3002	78	27632	−2881	121	3.3	23
$4f^{14}5d6s$	$^3D_3$	25271	27873	−2602	55	27812	−2541	61	2.5	22
$4f^{14}5d6s$	$^1D_2$	27678	28244	−566		28125	−447	119		
					Odd					
$4f^{14}6s6p$	$^3P^o_0$	17288	17870	−582	215	17820	−532	50	9	24
$4f^{14}6s6p$	$^3P^o_1$	17992	18374	−382	267	18264	−272	110	10	27
$4f^{14}6s6p$	$^3P^o_2$	19710	20076	−366	299	20049	−339	27	13	23
$4f^{13}5d6s^2$	$(7/2,3/2)^o_2$	23188	24904	−1716		24806	−1618	98		
$4f^{13}5d6s^2$	$(7/2,3/2)^o_3$	27445	27261	184	221	27064	381	197	11	20
$4f^{14}6s6p$	$^1P^o_1$	25068	24433	635		24316	752	117		
$4f^{13}5d6s^2$	$(7/2,5/2)^o_1$	28857	29512	−655		29380	−523	132		

The results of calculation for energy levels of Yb are shown in Table I. All results are obtained by the same computer code, which has options to run in either CIPT or FCI mode. Therefore, the difference between the CIPT and FCI results (Δ_{th}) is only due to the neglect of the energy difference between states within the same excited configuration. Some difference between the present and previously published CIPT results [6,12] is due to the differences in the size of the set of configurations. The present code uses a different algorithm to generate excited configurations from the reference configurations. In our CIPT calculations [6], the number of reference calculations used to generate other configurations was often smaller than the number of configurations included in the effective CI matrix. In the present FCI calculations these two numbers are the same. The reference configurations are used to generate all other configurations by exciting one or two electrons in all available basis states. Using all configurations in the effective CI matrix as reference configurations means that we have more states in the perturbative correction (6).

The data in Table I show that switching from the CIPT to FCI approaches results in a substantial gain in efficiency (more than 20 times for Yb) while having only a negligible effect on the energies. Note also that the use of the FCI instead of CIPT method does not affect the calculation of the matrix elements. The form of the calculated wave function is the same in both methods. Calculation of the matrix elements was considered in [12,13].

III. NOBELIUM

Nobelium is the heaviest element ($Z = 102$) for which experimental spectroscopic data are available. The frequency of the strong electric dipole transition from the ground state to a state of opposite parity and the first ionization potential have been recently measured [15,21]. The measurements [15] include the hyperfine structure and isotope shifts for three nobelium isotopes ^{252}No, ^{253}No, and ^{254}No. The data were used to extract nuclear parameters, such as nuclear radii and magnetic dipole and electric quadrupole moments. This procedure relies on the atomic calculations. In particular, an advanced combination of the CI with coupled-cluster method was used [15,16]. The nobelium atom has an electron structure similar to that of ytterbium. Its ground state is $[\mathrm{Ra}]5f^{14}7s^2\ ^1S_0$. The state for which the frequencies of the transitions were measured was $[\mathrm{Ra}]5f^{14}7s7p\ ^1P_1$. The calculations treated nobelium as a system with two valence electrons above closed shells. However, it is not known in advance whether such calculations produce good results for No. Similar calculations for the $4f^{14}6s6p\ ^1P_1$ state of Yb give very poor results for the hyperfine structure [12] and electric dipole transition amplitude from the ground state [22] due to the strong mixing with the close state of the same parity and J but with an excitation from the $4f$ subshell, $4f^{13}5d6s^2(7/2,5/2)^o_1$ (last row of Table I). This mixing cannot be included in the two-valence-electron calculations. However, treating Yb as a 16-electron system with the CIPT method leads to dramatic improvement of the results [12]. The results of the FCI calculations presented in Table II show that the potentially trouble-making state of the $5f^{13}7s^26d$ configuration in No (last row of Table II) is significantly higher on the energy scale of No than a similar state in Yb. The energy interval in No is five times larger and mixing is small. The mixing in the $^1P_1$ state of interest is 98% to 2% in No (2% admixture of the state with excitation from the $5f$ subshell) and 75% to 25% in Yb. This means that the mixing in No can be neglected and the $7s7p\ ^1P_1$ state can be treated as a two-valence-electron state.

TABLE II. Calculated excitation energies (in cm^{-1}) and g factors for the lowest states of nobelium, in comparison with earlier calculations and experiment.

		FCI (this work)		Other [16]	
State		Energy	g factor	Cut CI	CI+all
$5f^{14}7s^2$	${}^1S_0$	0	0	0	
$5f^{14}7s7p$	${}^3P^o_0$	20091	0.0000	16360	19567
	${}^3P^o_1$	21201	1.4581	18138	21042
	${}^3P^o_2$	26177	1.5000	22536	26133
	${}^1P^o_1$	29783[a]	1.0423	30237[a]	30203[a]
$5f^{14}7s6d$	${}^3D_1$	31057	0.5000	31003	28436
	${}^3D_2$	31132	1.1589	31223	28942
	${}^3D_3$	31579	1.3333	31608	30183
	${}^1D_2$	32858	1.0078	37980	33504
$5f^{13}7s^26d$	${}^3P^o_2$	42756	1.4414	45720	
	${}^3H^o_5$	44294	1.0235	49731	
	${}^5F^o_3$	45452	1.2229	52172	
	${}^3H^o_6$	45742	1.1667	52415	
	${}^5K^o_4$	46123	1.1192	53701	
	${}^1D^o_2$	46718	1.0258	54016	
	${}^5K^o_4$	47713	1.1143	56597	
	${}^3F^o_3$	47855	1.0807	56958	
	${}^1P^o_1$	47952	1.1334	55695	

[a] The experimental value is 29 962 cm^{-1} [23].

Note the good agreement of the FCI energies with the only known experimental value and with sophisticated calculations by the CI plus all-order method for the two-valence-electron states above the closed-shell core of No. There are two major sources of uncertainty in the FCI calculations. One is the neglect of core-valence correlations with core states below $5f$. The other is the perturbative treatment of the excited configurations. Both these effects are treated more accurately in the CI plus all-order calculations. Therefore, if the mixing with states containing excitations from the $5f$ subshell can be neglected, the CI plus all-order calculations are preferable and probably more accurate. From these calculations we know that when the No atom is treated as a two-valence-electron system, about 95% of the core-valence correlations come from the $5f$ electrons (this is also true for the $4f$ electrons of Yb). These correlations are included in the FCI calculations. This explains the high accuracy of the results.

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