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Combining configuration interaction with perturbation theory for atoms with a large number of valence electrons

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A version of the configuration interaction (CI) method is developed which treats highly excited many-electron basis states perturbatively, so that their inclusion does not affect the size of the CI matrix. This removes, at least in principle, the main limitation of the CI method in dealing with many-electron atoms or ions. We perform calculations of the spectra of iodine and its ions, tungsten, and ytterbium as examples of atoms with open s, p, d, and f shells. Good agreement of the calculated data with experiment illustrates the power of the method. Its advantages and limitations are discussed.

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I. INTRODUCTION

Many-electron atoms provide a lot of opportunities to study relativistic and many-body effects and to do fundamental research. The spectra of most of the atoms and their ions is very well known and documented, e.g., in the NIST database [1]. However, there are two classes of atomic systems for which experimental data is poor or absent and theoretical data is limited. These are superheavy elements (SHE, $Z > 100$) and highly charged ions (HCI). Both classes are important for fundamental research. The study of the SHE is motivated by the search of the *island of stability*, where the atomic nucleus of a SHE has long lifetime due to its closed-shell structure (see, e.g., [2–4]). The SHE are also interesting objects to study the interplay between correlation and relativistic effects in extreme conditions.

The HCI are used to study relativistic and correlation effects as well, but they are also important for fundamental research. There are many HCI with optical transitions which are sensitive to new physics beyond the standard model, such as variation of the fine-structure constant [5–13], local Lorenz invariance and Einstein equivalence principle violations [14,15], interactions with dark matter [16–19], etc. The HCI can also be used to build atomic clocks of extremely high accuracy [10–13,20–22].

The lack of experimental data can be partly compensated by atomic calculations. However, accurate calculations are possible only for systems with relatively simple electron structure, i.e., systems with few (one to about four) valence electrons above the closed-shell core. There are many good methods which produce very accurate results for such systems. They include configurations interaction [23] (CI), many-body perturbation theory [24] (MBPT), correlation potential (CP) method [25], coupled-cluster [26,27] (CC), multiconfigurational Dirac-Fock (MCDF) method [28], etc., as well as their combinations [29–33]. There are many SHE and HCI which do not fall into this category. For example, transuranium atoms have an open $5f$ subshell and up to 16 valence electrons (for example, the nobelium atom, which has excited states with excitations from the $5f$ and $7s$ subshells); the SHE from Db ($Z = 105$) to Cn ($Z = 112$) have an open $6d$ subshell, and the number of valence electrons ranges from five to 12; the SHE from E115 to E118 have an open $7p$ subshell and from three to eight valence electrons (depending on whether $7s$ electrons are attributed to the core or valence space). Apart from recent measurements of the ionization potential (IP) and the frequency of the strong electric dipole transition ($^1S_0 - ^1P_1^o$) for No [34–36] and IP for Lr [37], the experimental data on the spectra of these elements are practically absent. The number of theoretical studies is limited and accuracy of the analysis is not very high.

The situation with HCI is also complicated. One needs optical transitions for high accuracy of the measurements. Optical transitions in HCI suitable for building very accurate clocks can be found as transitions between states of the same configuration [21]. However, such transitions are usually not sensitive to new physics; one should instead look for optical transitions between states of different configurations [8]. If we limit ourselves to systems with a simple electron structure, then we may come to a situation when there are not many suitable optical transitions near the ground state of HCIs. The need for high measurement accuracy dictates that the optical transition of interest is narrow, i.e., weak. The absence of other strong optical transitions makes it hard to work with these ions. The answer to this problem is to move to systems with more valence electrons, which have more states and transitions. Then we must be able to perform accurate calculations for such systems. Good examples are Ir^{17+} [6,38] and Ho^{14+} [9] ions, which were suggested to search for time variation of the fine-structure constant. The ions have complicated electron structure (the $4f^{13}5s$ configuration in the ground state of Ir^{17+} and the $4f^65s$ configuration in the ground state of Ho^{14+}). While measurements of these spectra are in progress [38,39], interpretation of the results is difficult partly because of poor accuracy of the calculations.

Methods of calculations for many-valence-electron atoms mostly represent versions of the CI approach [23,28,40,41]. They often have many fitting parameters and the accuracy of the results is not very high. There is an interesting approach which considers not only valence electrons but also holes in almost-filled shells [42,43] (see also [33]). For example, the $4f^{13}$ configuration in this approach can be considered as a hole in the fully filled $4f$ subshell. This approach can produce very accurate results but it is also limited to systems with a small number of holes. There is a clear need for further advance in the methods of the calculations for atoms with many valence electrons. In this paper, we consider a version of the CI method in which most of the high-energy many-electron basis states are treated perturbatively rather than being included into the CI matrix diagonalization. This addresses the main problem of the CI method: the huge size of the CI matrix for systems with many valence electrons. As a result, the main limitations of the CI approach are removed and the method can be used practically for any atom. We call this the configuration interaction perturbation theory (CIPT) method and apply it to the iodine atom and its ions, tungsten, and ytterbium atoms as examples of systems with open p, d, and f shells. We demonstrate the strengths and limitations of the approach.

II. REDUCING THE SIZE OF THE CI MATRIX

We begin our discussion of calculations for many-electron atoms with the configuration interaction (CI) technique. There are many versions of the CI method differing in the way the core-valence correlation is included, the basis used, etc. (see, e.g., [29–31]). We shall postpone the discussion of the details of the CI calculations to the consideration of specific examples. In this section, we only consider the very general problem of calculating eigenstates of a Hamiltonian matrix of huge size.

In the CI approach, all atomic electrons are divided into two groups: closed-shell core and remaining valence electrons which occupy the outermost open subshells. The wave function for state number m for valence electrons has the form of expansion over single-determinant basis states,

$$\Psi_m(r_1,\ldots,r_{N_e}) = \sum_i c_{im}\Phi_i(r_1,\ldots,r_{N_e}). \tag{1}$$

The coefficients of expansion c_{im} and corresponding energies E_m are found by solving the CI matrix eigenstate problem,

$$(H^{\mathrm{CI}} - EI)X = 0, \tag{2}$$

where I is the unit matrix, the vector $X = \{c_1,\ldots,c_{N_s}\}$, and N_s is the number of many-electron basis states. The basis states $\Phi_i(r_1,\ldots,r_{N_e})$ are obtained by distributing N_e valence electrons over a fixed set of single-electron orbitals. The number of basis states N_s grows exponentially with the number of electrons N_e (see, e.g., [44]). So does the size of the CI matrix. In practice, the CI matrix reaches an unmanageable size for $N_e \gtrsim 4$. This greatly limits the applicability of the CI method since the number of valence electrons can be as large as 16 (e.g., states of the Yb atom with excitations from the $4f$ subshell). We suggest that under certain conditions, the CI calculations can still be performed for any number of valence electrons at the expense of some small sacrifice of the accuracy of the results. The conditions are as follows:

(i) We are only interested in a few of the lowest eigenstates of the matrix. Note that we construct the CI matrix for atomic states of definite total angular momentum J and parity π, J^π; π is either $+$ or $-$. There is a separate CI matrix for every J^π. Therefore, the few lowest states of every such CI matrix may add up to hundreds of atomic states.

(ii) The many-electron basis states $\Phi_i(r_1,\ldots,r_{N_e})$ are ordered in terms of their energies (i.e., their diagonal matrix element). The state with the lowest energy goes first and the state with the highest energy is the last in the list.

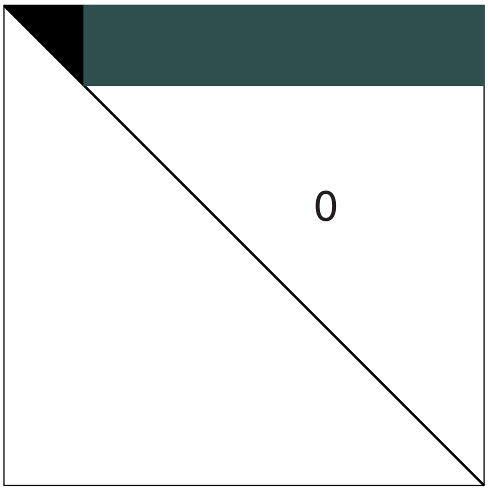

FIG. 1. The structure of the CI matrix. The matrix is real and symmetric, therefore only upper triangular part is shown. The black triangular shape in the top-left corner of the matrix is the *effective* CI matrix. Neglected off-diagonal matrix elements between high-energy states are shown in white.

(iii) The wave-function expansion (1) saturates with a relatively small number of first terms. The rest of the sum is just a small correction.

Note that the current approach is applicable to any matrix, not just the CI matrix. In the general case, the last two conditions can be reformulated in the following way: the matrix has only a relatively small number of large off-diagonal matrix elements, and the matrix can be reorganized in such a way that all important off-diagonal matrix elements are located in the top-left corner of the matrix.

We divide all many-electron basis states Φ_i into two groups. The first group P contains the low-energy states which dominate in the expansion (1). We use the notation N_{eff} for the number of such states ($N_{\mathrm{eff}} \ll N_s$), and we call the corresponding part of the CI matrix the *effective* CI matrix. The second group Q consists of all remaining high-energy states.

We can neglect all off-diagonal matrix elements in the high-energy group Q. Indeed, the contributions of these matrix elements to the energies and wave functions in the low-energy group P are insignificant. These follow from the perturbation theory estimates. The correction to the energy of the low-energy state g from the off-diagonal matrix elements $\langle i|H^{\mathrm{CI}}|j\rangle$ between the high-energy states appears in the third order of the perturbation theory and is suppressed by the two large energy denominators $E_g - E_i$ and $E_g - E_j$:

$$\delta E_g = \sum_{i,j} \frac{\langle g|H^{\mathrm{CI}}|i\rangle\langle i|H^{\mathrm{CI}}|j\rangle\langle j|H^{\mathrm{CI}}|g\rangle}{(E_g - E_i)(E_g - E_j)}. \tag{3}$$

The structure of the full CI matrix is shown in Fig. 1. The matrix is real and symmetric, so that one can consider only the upper (or lower) triangular part of the matrix. The effective CI matrix is in the top-left corner of the full matrix and shown in black. The off-diagonal matrix elements between high-energy states, which are put to zero, are shown in white. The diagonal matrix elements for the high-energy states are not neglected and are shown in black. The off-diagonal matrix elements between low- and high-energy states are shown in gray. The full CI matrix with this structure can be reduced to a much smaller effective CI matrix with modified matrix elements,

$$\langle i|H^{\mathrm{CI}}|j\rangle \rightarrow \langle i|H^{\mathrm{CI}}|j\rangle + \sum_k \frac{\langle i|H^{\mathrm{CI}}|k\rangle\langle k|H^{\mathrm{CI}}|j\rangle}{E^{(0)} - E_k}. \quad (4)$$

Here, $|i\rangle \equiv \Phi_i(r_1,\ldots,r_{N_e})$, $i,j \leqslant N_{\mathrm{eff}}$, $N_{\mathrm{eff}} < k \leqslant N_s$, $E_k = \langle k|H^{\mathrm{CI}}|k\rangle$, and $E^{(0)}$ is an initial approximation to the energy E in (2). In principle, the energies E in (2) and $E^{(0)}$ in (4) should be the same. However, since the energy is not known at the stage of the matrix calculation, one can perform iterations starting from some reasonable approximation for the energy and using the result of (2) for calculating the matrix using (4) at the next iteration. If more than one state of definite J and parity is needed, the iterations should be done separately for each state. This leads to a couple of problems. First, too many runs of the program are needed to calculate several states of the same J and parity: the program becomes very inefficient. Second, different states of the same J^π will correspond to different matrices (4), which makes them nonorthogonal. This may lead to problems when calculating matrix elements between levels.

We propose the following solution to both problems. The energy parameter $E^{(0)}$ in (4) is calculated for each basis state $|i\rangle$ according to its contribution to the states of interest m,

$$E^{(0i)} = \frac{\sum_m c_{im}^2 E_m}{\sum_m c_{im}^2}. \quad (5)$$

The summation goes over all states of interest. Let us consider an example. We are interested in two low-energy states $m = 1,2$, i.e., the sum in Eq. (5) contains only two terms. However, the state i may be any state from the group of the low-energy states P. We will need corresponding energy $E^{(0i)}$ in the calculation of the matrix element in the sum in Eq. (4).

The energy $E^{(0i)}$ is close to those solutions E_m of (2) where the basis state $|i\rangle$ contributes the most. Here we also need iterations over energies E_m. However, only one run of the program is needed and all states come from the same matrix. The results for the energies are very close in both procedures.

Note that the high-energy state corrections to the matrix elements of the effective CI matrix are similar to the second-order perturbation theory (PT) corrections to the energy. Therefore, we will use the corresponding CI and PT notations for the method. We test the assumptions (4) and (5) in Sec. IV by comparing the results of our CIPT method with exact diagonalization of the full CI matrix as shown in Fig. 1.

The calculation of the sum over high-energy states [last term in (4)] takes up most of the computer time. However, the calculation of each term in this sum is independent of the others. This makes the method very convenient for parallel calculations.

In the next sections, we describe in more detail specific calculations for atoms with open s, p, d, and f shells and discuss the advantages and limitations of the suggested approach.

III. IODINE AND ITS IONS: LIMITS OF THE V^{N-M} APPROXIMATION

The iodine atom and its ions are good subjects to study the limitations of the current approach based on reducing the size of the CI matrix and limitations of the V^{N-M} approximation [45]. In the V^{N-M} approximation, the initial Hartree-Fock procedure is done for the N-electron atom with all M valence electrons removed. Then the CI technique is used to build the states of valence electrons. This works well when the overlap between the core and valence states is small. Then the valence electrons have little effect on the core and the core is almost the same in the ion with all M valence electrons removed and in the neutral atom. This can be easily understood by considering the classical analog. If valence atomic electrons are approximated by a charged sphere with a hole inside, and all core electrons are inside this hole, then the charge sphere creates no electrical field inside it and thus has no effect on the internal electrons. This is usually the case when a new shell is started (with new principal quantum number n). In neutral atoms, new shells always start with s and p states. The ground state of neutral I is [Pd]$5s^25p^5$. All core states have $n < 5$. So the overlap between $5s$ and $5p$ states and the core is small. Therefore, it can be considered in the V^{N-7} approximation.

The iodine atom is an extreme case to check both the V^{N-M} approximation and the CIPT method. It is the heaviest atom with an open p shell for which the experimental spectrum is known. The only other heavier atom which has more external p electrons, xenon, has no low-lying excited states. This means that the CIPT method is unlikely to work well for it: the expansion (1) for highly excited states will not be dominated by a small number of terms.

The main advantage of using the V^{N-M} approximation is the relative simplicity of inclusion of the core-valence correlations [45]. They can be included using the lowest, second order of the many-body perturbation theory [30], or single-double (SD) coupled-cluster method [29,31], or all-order correlation potential method [46]. In this work, we use the combination of the SD and CI methods developed in Ref. [31]. We use the V^{Z-7} approximation ($N = Z$ for a neutral atom) and perform the calculations for all ions starting from the I VIII ion which has a closed-shell Pd-like core. The first ion for which we calculate excitation energies, the I VII ion, has only one valence electron. It is clear that the V^{Z-7} approximation is adequate for the I VII ion, but deteriorates with increasing number of valence electrons. This is because the overlap between the core and valence electrons is small but not exactly zero. It is instructive to estimate in advance what kind of uncertainty can be expected in neutral atoms due to the fact that the core is taken from the ion rather that from the neutral atom. For this purpose, we have calculated the energy shift due to the difference of the core potential in the I VII ion and neutral iodine for the $5s$ and $5p$ electrons of I I. The results are $\langle 5s|\delta V_{\mathrm{core}}|5s\rangle = 5055\ \mathrm{cm}^{-1}$, $\langle 5p_{1/2}|\delta V_{\mathrm{core}}|5p_{1/2}\rangle = 3273\ \mathrm{cm}^{-1}$, and $\langle 5p_{3/2}|\delta V_{\mathrm{core}}|5p_{3/2}\rangle = 2891\ \mathrm{cm}^{-1}$. Total shift of the energy of the seven-electron ground state is $\sim$25 000 cm^{-1}, which is about 1% of the total removal energy. The contribution of this shift to the IP of neutral iodine is approximately equal to the energy shift of one $5p_{3/2}$ electron and constitutes about 3.5% of the IP. The effect on the excitation energies is expected to be smaller than 3000 cm^{-1} due to cancelation in energy shifts for lower and upper states. Relative energy shifts for the ions are also small due to larger values of the energies.

TABLE I. Ground-state energies (GSE) and ionization potentials for iodine and its ions from I VII to neutral I and corresponding numerical parameters used in the calculations. NNC is the number of the nonrelativistic configurations included into the effective CI matrix; NRC and $N_{\rm eff}$ are the corresponding numbers of relativistic configurations and configuration state functions (with given total angular momentum and parity); N_s is the total number of CSFs; $N_s - N_{\rm eff}$ is the number of terms in the summation over high-energy states [see Eq. (4)]. The ionization potential is calculated as a difference of the ground-state energies of neighboring ions.

Ion/	Ground state							IP (cm^{-1})		
atom	Conf.	J^π	NNC	NRC	$N_{\rm eff}$	N_s	GSE (a.u.)	CIPT	NIST [1]	Δ
I VII	$5s$	$1/2^+$	14	14	14	14	–3.22403	707590	706600(500)	990
I VI	$5s^2$	0^+	100	276	66	945	–5.96185	600880	599800(3000)	1080
I V	$5s^25p$	$1/2^-$	100	349	228	11092	–7.85009	414419	415510(300)	–1090
I IV	$5s^25p^2$	0^+	100	413	176	18652	–9.33862	326693	325500(200)	1193
I III	$5s^25p^3$	$3/2^-$	100	535	994	106287	–10.42426	238269	238500(200)	–230
I II	$5s^25p^4$	2^+	100	610	1551	168659	–11.11511	151623	154304.0(10)	–2680
I I	$5s^25p^5$	$3/2^-$	100	691	1990	119490	–11.46144	76010	84295.1(2)	–8285

Next we compare the value of the energy shift due to the use of the V^{N-7} potential in neutral iodine with the contribution of the core-valence correlations. The total calculated removal energy for seven valence electrons of neutral iodine is -11.4614 a.u. (see Table I) when core-valence correlations are included. It comes to the value of -11.2225 a.u. when core-valence correlations are neglected. The difference, 0.2389 a.u. or 52 430 cm^{-1}, is about two times larger than the shift due to the use of the V^{N-7} potential ($\sim$25 000 cm^{-1}; see above). This justifies the use of the V^{N-M} approximation for all iodine ions up to the neutral atom. Note that there is an alternative way of taking into account the core-valence correlations which does not require the removal of all valence electrons from the initial approximation because their effect is included via the so-called subtraction diagrams [30].

Table I presents calculated energies of the ground state for all iodine ions from I VII up to neutral I I. Ionization potentials of the ions are calculated as differences of the ground-state energies of the neighboring ions and compared with the data from the NIST database [1]. Relevant computational parameters are also presented. In all cases starting from I VI, we include 100 of the nonrelativistic configurations (NNCs) into the effective CI matrix. NRC and $N_{\rm eff}$ are the corresponding numbers of the relativistic configurations (NRCs) and configuration state functions (CSFs), respectively. All other configurations are included perturbatively as a correction to the effective CI matrix according to formula (4). In the extreme cases of I II and I I, the total number of CSFs (N_s) is larger than the size of the effective CI matrix by about two orders of magnitude. The difference between calculated IPs and those from the NIST databases is smaller than 0.4% for all cases, apart from the extreme cases of I II and I I where its is 1.7% and about 10%, respectively. The deteriorating accuracy with increasing number of valence electrons is expected and most probably caused by insufficient size of the effective CI matrix and incompleteness of the many-electron basis states (e.g., triple and higher excitations are not included).

Table II compares the calculated energy levels of iodine ions with experiment. In general, the accuracy is good, about 1% or better for most of the states. However, we can see one more interesting tendency. The accuracy deteriorates not only with increased number of valence electrons, but also with the increased excitation energy. This is also an expected effect. Highly excited states mix strongly with the high-energy states which are not included into the effective CI matrix and are only treated perturbatively. The accuracy for such states can be improved by increasing the size of the effective CI matrix. On the other hand, the accuracy for low-lying states is significantly better. Note that relatively poor accuracy for the $6s$ and $6p$ states of the I VII ion is due to a different reason which comes from the core-valence correlations. The energy parameter of the Σ_1 operator which is responsible for the core-valence correlations is chosen to get the best results for the lowest states, $5s$ and $5p$ (see, e.g., [30] for details).

IV. TUNGSTEN ATOM

The tungsten atom is a good example of an atom with an open d shell. Its ground-state configuration is [Yb]$5d^46s^2$. It has six valence electrons above the Yb-like closed-shell core. This number is sufficiently large to make the full-scale CI calculations extremely difficult. On the other hand, its spectrum is very well known. Therefore, the atom is good for checking the CIPT technique and demonstrating its use.

The $5d$ valence electrons of W have relatively large overlap with the $5s$ and $5p$ core states, which means that the V^{N-6} approximation would not work well for the atom (see Ref. [45] and the discussion in the previous section). Therefore, we neglect core-valence correlations and use the V^{N-1} initial approximation. Note that choosing a good initial approximation is important for minimizing the size of the effective CI matrix, thus making the calculations more efficient. In full-scale CI calculations, the choice of the initial approximation is less important and the accuracy of the final results vary little from state to state regardless of their configurations. In our present approach, most of the basis states are included perturbatively and only a very limited number of the lowest states are treated accurately via matrix diagonalization. Therefore, it is hardly possible to find an initial approximation which is equally good for states of all configurations. We may choose, for example, that the most important states are those which belong to the $5d^46s^2$ and $5d^46s6p$ configurations to ensure high accuracy for the strong electric dipole transitions from the ground state. Then the V^{N-1} approximation in which one $6s$ electron is removed from the initial self-consistent Hartree-Fock procedure seems to be an adequate choice.

TABLE II. Calculated excitation energies (CIPT, cm^{-1}) of iodine and its ions, compared with experiment.

			Energy			Ion/			Energy		
Ion	State		Expt.	CIPT	Δ	atom	State		Expt.	CIPT	Δ
I VII	$5s$	$^2S_{1/2}$	0	0	0	I IV	$5s^25p^2$	$^3P_0$	0	0	0
	$5p$	$^2P^o_{1/2}$	104960	105161	–201			$^3P_1$	6828	6909	–81
	$5p$	$^2P^o_{3/2}$	119958	120229	–271			$^3P_2$	10982	11167	–185
	$5d$	$^2D_{3/2}$	274019	274559	–540			$^1D_2$	22532	23004	–472
	$5d$	$^2D_{5/2}$	276256	276802	–546			$^1S_0$	37177	37987	–810
	$6s$	$^2S_{1/2}$	335376	337132	–1756		$5s5p^3$	$^5S^o_2$	78084	78495	–411
	$6p$	$^2P^o_{1/2}$	377185	378800	–1615			$^3D^o_1$	99047	99254	–207
	$6p$	$^2P^o_{3/2}$	382985	384596	–1611			$^3D^o_2$	99542	99853	–311
I VI	$5s^2$	$^1S_0$	0	0	0			$^3D^o_3$	102387	102597	–210
	$5s5p$	$^3P^o_0$	85666	86140	–474			$^3P^o_0$	114658	114702	–44
		$^3P^o_1$	89262	89800	–538			$^3P^o_1$	115478	115597	–119
		$^3P^o_2$	99685	100345	–660			$^3P^o_2$	115013	115040	–27
		$^1P^o_1$	127424	126414	1010			$^3S^o_1$	135677	133867	1810
	$5p^2$	$^3P_0$	200085	199827	258	I III	$5s^25p^3$	$^4S^o_{1/2}$	0	0	0
		$^3P_1$	208475	208183	292			$^2D^o_{3/2}$	11711	12149	–438
		$^3P_2$	221984	222252	–268			$^2D^o_{5/2}$	14901	14534	367
		$^1D_2$	209432	209890	–458			$^2P^o_{1/2}$	24299	24640	–341
		$^1S_0$	245659	245657	2			$^2P^o_{3/2}$	29637	30138	–501
	$5s5d$	$^3D_1$	251817	251749	68		$5s5p^4$	$^4P_{5/2}$	85555	88539	–2984
		$^3D_2$	252540	252262	278			$^4P_{3/2}$	90964	93908	–2944
		$^3D_3$	253752	253676	76			$^4P_{1/2}$	92902	95820	–2915
		$^1D_2$	274162	268727	5435			$^2D_{3/2}$	103470	110686	–7216
I V	$5s^25p$	$^2P^o_{1/2}$	0	0	0			$^2D_{5/2}$	106619	112931	–6312
		$^2P^o_{3/2}$	12222	12397	–175	I II	$5s^25p^4$	$^3P_2$	0	0	0
	$5s5p^2$	$^4P_{1/2}$	81018	81417	–399			$^3P_0$	6448	6709	–261
		$^4P_{3/2}$	85556	87337	–1781			$^3P_1$	7087	6910	177
		$^4P_{5/2}$	92558	93108	–550			$^1D_2$	13727	14010	–283
		$^2D_{3/2}$	108780	109274	–494			$^1S_0$	29501	31955	–2454
		$^2D_{5/2}$	111831	112498	–667		$5s^25p^36s$	$^5S^o_0$	81033	88782	–7749
		$^2P_{1/2}$	125704	124835	869		$5s5p^5$	$^3P^o_2$	81908	83765	–1857
		$^2P_{3/2}$	139398	138098	1300			$^3P^o_1$	84222	96489	–12267
		$^2S_{1/2}$	138328	138137	191			$^3P^o_0$	90405	103475	–13070
	$5s^25d$	$^2D_{3/2}$	154050	153666	384		$5s^25p^36s$	$^3S^o_1$	84843	87390	–2547
		$^2D_{5/2}$	155462	155109	353	I I	$5s^25p^5$	$^2P^o_{3/2}$	0	0	0
	$5s^26s$	$^2S_{1/2}$	176814	177614	–802			$^2P^o_{1/2}$	7603	7311	–292
							$5s^25p^46s$	$^2[2]_{5/2}$	54633	64817	–10187
								$^2[2]_{3/2}$	56093	66762	–10669
								$^2[0]_{1/2}$	60896	72829	–11933
								$^2[1]_{3/2}$	61820	72508	–10688
								$^2[1]_{1/2}$	61187	75818	–14625

Indeed, all single-electron s, p, etc. states (including the $6s$ state) are calculated in the field of the frozen $5d^46s$ core, leading to the states of the $5d^46snl$ configurations.

The CIPT results for the W atom are presented in Table III. Calculations for even states were performed when only states of the $5d^46s^2$ and $5d^56s$ were included into the effective CI matrix, while all other states obtained by single and double excitations from these two configurations were included perturbatively. For odd states, we used the $5d^46s6p$, $5d^36s^26p$, and $5d^56p$ configurations as reference configurations to generate states for the effective CI matrix and for the PT expansion.

For the tungsten case, we also ran an exact diagonalization of the CI matrix shown in Fig. 1 using the AMBiT code (see, e.g., [32]); these are presented in the column "Full CI" of Table III. In this calculation, configuration state functions (CSFs) with definite J and parity are formed within each relativistic configuration (i.e., configurations formed in $j-j$ electron coupling) and these are the basis functions for the CI procedure. We keep all matrix elements shown in black and gray in Fig. 1. In addition, we keep all matrix elements between CSFs coming from the same relativistic configuration (these will appear close to the diagonal in the white section). We limit the storage to only the nonzero parts of the matrix and solve using the Davidson method [47] (implemented in [48]), which reduces diagonalization to a series of matrix-vector multiplications. As an example, the $J = 2$ odd-parity matrix size is $N_s \approx 3 \times 10^6$, but $N_{\mathrm{eff}} = 144$ only.

We see in Table III that both the solution of the Full CI and of the CIPT method give good agreement with experiment.

TABLE III. Calculated excitation energies (cm^{-1}) of tungsten in different approximations. Min. CI: only leading configurations included (see text). Full CI: exact diagonalization with all configurations included, but off-diagonal matrix elements between CSFs outside the minimal CI set to zero. CIPT: diagonalization of the effective CI with other configurations included in perturbation theory. Δ is the difference between CIPT and experiment.

Level			Energy (cm^{-1})				
		J	Expt. [1]	Min. CI	Full CI	CIPT	Δ
$5d^46s^2$	^5D	0	0	0	0	0	0
		1	1670	776	1106	1502	168
$5d^56s$	^7S	3	2951	796	2494	2674	277
$5d^46s^2$	^5D	2	3325	1933	2740	2664	661
		3	4830	3287	4272	4506	324
		4	6219	4788	5509	5414	805
$5d^46s^2$	$^3P2$	0	9528	13025	8530	9747	–219
$5d^46s^2$	^3H	4	12161	14994	11730	12963	–802
$5d^46s^2$	$^3P2$	1	13307	16283	12078	13540	–233
$5d^46s^2$	^3G	3	13348	16491	12916	14185	–837
$5d^46s^2$	$^3F2$	2	13777	17411	13030	14648	–871
$5d^46s^2$	^3D	2	14976	18933	14144	15501	–525
		1	18082	21869	17171	18898	–816
$5d^46s6p$	$^7F^o$	0	19389	4750	20303	20920	–1531
		1	20064	5269	20927	21580	–1516
$5d^46s^2$	$^1S2$	0	20174	25063	20255	20916	–742
$5d^56s$	^5P	1	20427	28439	18965	20281	146
		2	20983	25070	17692	22906	–1923
$5d^46s6p$	$^7F^o$	2	21448	6240	22090	22702	–1254
$5d^46s6p$	$^7D^o$	1	21453	7922	22199	23076	–1623

Comparison with diagonalization of the effective CI matrix without PT (the "Min. CI" column) shows that both methods give similar corrections to the level energies. This shows that assumptions (4) and (5) are reasonable.

Note the lower accuracy for the odd states (see Table III). Test calculations show that the accuracy can be further improved if more configurations are moved from the PT expansion to the effective CI matrix. This is a future direction for highly accurate calculations; however, it takes a lot of computer power and is beyond the scope of this work.

V. YTTERBIUM ATOM

The ytterbium atom has the [Ba]$4f^{14}6s^2$ closed-shell configuration in its ground state. However, the excited states of Yb belong to configurations which have excitations from both the $6s$ and $4f$ subshells. This means that a complete description of excited states of Yb is only possible when the atom is treated as a system with 16 valence electrons. There are many successful calculations in which the Yb atom is treated as a two-valence electron system (see, e.g., [49–51]). In these calculations, excitations are allowed only from the $6s^2$ subshell, while the $4f$ electrons are attributed to the core. Good quality of the results indicates that the states with excitations from $6s$ and $4f$ subshells usually do not strongly mix. However, this is not always the case. There is at least one known case when the mixing is important. This is the mixing between the $4f^{14}6s6p\ ^1P^o_1$ state at $E = 25068$ cm^{-1} and the $4f^{13}5d6s^2\ (7/2,5/2)^o_1$ state at $E = 28857$ cm^{-1}. The case is important due to the strong electric dipole transition between the ground and excited $4f^{14}6s6p\ ^1P^o_1$ state. It strongly dominates in the polarizability of Yb [49], it can be used in cooling [52], etc. The experimental value for the electric dipole amplitude is 4.148 a.u., while two-valence-electron calculations give the value of 4.825 a.u.; the difference is due to the mixing of the two odd states [49]. This mixing cannot be accounted for in the two-valence-electron calculations.

Apart from studying the mixing, it might be equally important to be able to get a complete description of the atomic spectrum including states with excitations from the core. This is especially useful when experimental data are incomplete or absent (e.g., superheavy elements and highly charged ions). The Yb atom is a good testing ground for developing appropriate approaches. It represents an extreme case of 16 valence electrons, while its experimental spectrum is very well known.

As in the case of tungsten (see previous section), we start the calculations from the V^{N-1} approximation with one $6s$ electron removed from the self-consistent Hartree-Fock procedure. This leads to adequate treatment of the states of the $4f^{14}6s^2$ and $4f^{14}6s6p$ configurations, while it is less adequate for the states of the $4f^{13}5d6s^2$ configuration. The latter can be compensated at least to some extent be increasing the size of the effective CI matrix.

The results for Yb are presented in Table IV. Calculations for the ground state were performed with the inclusion of only two configurations to the effective CI matrix, the $4f^{14}6s^2$ and the $4f^{14}6s7s$ configurations. Even states with the total angular momentum $J > 0$ were calculated starting from the $4f^{14}6s7s$ and the $4f^{14}6s5d$ configurations. Odd states were calculated starting from the $4f^{14}6s6p$ and the $4f^{13}5d6s^2$ configurations. Accuracy of the results varies from state to state, which should probably be expected for a small-size CI matrix due to different convergence for states with different values of the total angular momentum J. We have seen similar features in the tungsten calculations (see previous section); however, for ytterbium, it is more prominent. As in the case of tungsten, further significant improvement in accuracy can be achieved with an increase of the size of the effective CI matrix. This would take greater computer power.

Table V shows electric dipole (E1) transition amplitudes from the ground state of ytterbium to the first four excited states that satisfy E1 selection rules. The calculations of the present work are done with the use of the random phase approximation (RPA) and CI wave functions as has been described in Ref. [49]. The CI wave function is taken from the calculations of the energies described above, i.e., it has 16 valence electrons and includes excitations from the $4f$ subshell. The result for the $\langle 4f^{14}6s6p\ ^1P^o_1 || E1 || 4f^{14}6s^2\ ^1S_0\rangle$ amplitude is in better agreement with the experiment than any other calculations. This is because the present calculations include the mixing of the $4f^{14}6s6p\ ^1P^o_1$ and $4f^{13}5d6s^2\ ^1P^o_1$ states, while the other calculations treat the ytterbium atom as a two-valence-electron system and cannot include this mixing.

It was noted in Ref. [49] that the calculation of the static dipole polarizability of Yb does not depend on the mixing of the $4f^{14}6s6p\ ^1P^o_1$ and $4f^{13}5d6s^2\ (7/2,5/2)^o_1$

TABLE IV. Calculated excitation energies (CIPT, cm^{-1}) of ytterbium, compared with experiment.

State		J	Energy Expt. [1]	CIPT	Δ
$4f^{14}6s^2$	^1S	0	0	0	0
$4f^{14}6s6p$	$^3P^o$	0	17288	17670	–382
		1	17992	18305	–331
		2	19710	19886	–176
$4f^{13}5d6s^2$	$(7/2,3/2)^o$	2	23188	25028	–1840
$4f^{14}5d6s$	^3D	1	24489	27568	–3079
		2	24751	27217	–2466
$4f^{14}6s6p$	$^1P^o$	1	25068	25597	–529
$4f^{14}5d6s$	^3D	3	25270	27747	–2477
$4f^{13}5d6s^2$	$(7/2,3/2)^o$	5	25859	26343	–484
$4f^{13}5d6s^2$	$(7/2,5/2)^o$	6	27314	27205	109
$4f^{13}5d6s^2$	$(7/2,3/2)^o$	3	27445	27431	14
$4f^{14}5d6s$	^1D	2	27677	28071	–394
$4f^{13}5d6s^2$	$(7/2,3/2)^o$	4	28184	28013	171
$4f^{13}5d6s^2$	$(7/2,5/2)^o$	2	28195	27354	841
		1	28857	30071	–1214
		4	29774	28975	799
		3	30207	29133	1074
		5	30524	29172	1352

states if the energy interval between them is neglected. This is because the sum of squares of the electric dipole matrix elements $\langle 4f^{14}6s6p\ ^1P^o_1||E1||4f^{14}6s^2\ ^1S_0\rangle^2 + \langle 4f^{13}5d6s^2\ (7/2,5/2)^o_1||E1||4f^{14}6s^2\ ^1S_0\rangle^2$ does not depend on mixing. Therefore, it is instructive to compare the sum calculated in two different approximations. The sum is equal to 24.83 a.u. if the amplitudes calculated in the present work are used ($4.31^2 + 2.50^2 = 24.83$; see Table V). The first amplitude calculated in the two-valence-electron approximation is equal to 4.825 a.u. [49]. The contribution of the second state ($4f^{13}5d6s^2\ (7/2,5/2)^o_1$) to the polarizability is simulated by the contribution of the $\langle 4f_{7/2}||E1||5d_{5/2}\rangle$ matrix element into polarizability of the atomic core. The value of this matrix element in the RPA approximation is equal to 1.40 a.u. The sum of squares of the two amplitudes is equal to 25.24 a.u. ($4.825^2 + 1.40^2 = 25.24$). The two numbers (24.83 and 25.84) differ by only 1.6%. This illustrates the fact that the sum of the squares of the two amplitudes does not depend on mixing.

In the present work, we include into the effective CI matrix mixing of the states with excitations from the $4f$ subshell, but we do not include mixing of the states with excitations from the $6s$ or $6p$ states. Therefore, we have good accuracy where the first mixing is more important and poor accuracy where the second mixing is more important. An example of the latter is the triplet state $4f^{14}6s6p\ ^3P^o_1$; the corresponding electric dipole matrix element is given to better accuracy by the two-valence-electron calculations (see Table V).

VI. DISCUSSION

The calculations for representative atoms with open p, d, and f shells discussed above allow one to come to some conclusions about the advantages and limitations of this approach. The most obvious and important advantage is the ability to perform the calculations for any atom or ion regardless of the number of valence electrons. The calculations are totally *ab initio* with absolutely no fitting parameters. The same single-electron basis can be used for many-valence-electron atoms as has been used for few-valence-electron atoms (e.g., B splines in a box [61]) in a number of calculations and has been proved to be complete.

Another important advantage is the huge gain in the efficiency compared with the full-scale CI calculations which can be achieved at the expense of little loss in accuracy by treating most of the high-energy configurations perturbatively.

The method is practically equivalent to the full-scale CI calculations for atoms or ions with few valence electrons (up to four or five). However, in contrast to the full-scale CI, it can be used for systems with any number of valence electrons, but with some limitations. For example, the calculations are sensitive to the choice of initial approximation. Since only a limited number of states are included into the effective CI matrix and most of the states are treated perturbatively, it is important that the low-energy states are sufficiently close to the real physical states of interest and the contribution of the high-energy states is small. It is not always possible to find an approximation which is equally good for states of all low-lying configurations. For example, the V^{N-1} approximation for tungsten discussed above is good for the states of the $5d^46s^2$ and $5d^46snl$ configurations, but it is less appropriate for the

TABLE V. Electric dipole transition amplitudes (reduced matrix elements) between ground and low excited states of Yb (a.u.). Experimental uncertainties are shown in parentheses.

Upper state	Energy (cm^{-1}) Expt. [1]	CIPT	Amplitude CIPT	Expt.	Other theory
$4f^{14}6s6p\ ^3P^o_1$	17992	18305	0.763	0.542(2) [53]	0.54(8) [54]
				0.547(16) [55]	0.587 [49]
					0.41(1) [56]
$4f^{14}6s6p\ ^1P^o_1$	25068	25597	4.31	4.148(2) [57]	4.825 [49]
				4.13(10) [58]	4.40(80) [54]
					4.44 [59]
					4.89 [60]
$4f^{13}5d6s^2\ (7/2,5/2)^o_1$	28857	30071	2.50		
$4f^{13}5d6s^2\ ^1P^o_1$	37415	37529	0.584		

states of the $5d^56s$ configuration. This may lead to a different accuracy of the results for different states even when they belong to the same configuration. This is due to inaccurate treatment of the mixing with other configurations. The situation can be improved at the expense of using more computer power by increasing the size of the effective CI matrix.

Another limitation comes from the fact that at the present stage, we cannot include core-valence correlations for systems with a large number of valence electrons. This is not directly relevant to the approach considered in this work; however, we mention it here because the ways of inclusion of the core-valence correlations for atoms with many valence electrons remains an open problem. The inclusion of the core-valence correlations is usually reduced to modification of the matrix element of the CI matrix [30], similar to what is done here for inclusion of high-energy states [see Eq. (4)]. However, our current approach presents a way of reducing the size of the CI matrix regardless of the origin of its matrix elements, i.e., regardless of whether or not core-valence correlations are included, what kind of basis is used, etc. In Sec. III, we considered an extreme case of the seven-valence-electron atom, iodine. The core-valence correlations were included and the V^{N-7} approximation was used for this purpose. This approach would not work for tungsten or ytterbium or any other atom with a large number of valence electrons. Finding more suitable approaches is a subject for further study.

VII. CONCLUSION

We present a version of the CI method which treats high-energy many-electron basis states perturbatively, hugely reducing the size of the CI matrix. In principle, the method can work for systems with any number of valence electrons. Calculations for iodine and its ions, tungsten, and ytterbium (atoms with open p, d, and f shells) show that good accuracy for the energies can be achieved for a wide range of atomic systems. The method is equivalent to the full-scale CI method for systems with few valence electrons (up to four or five). The accuracy for the energies for such systems is on the level of 1% in both approaches. However, this approach is much more efficient for systems where full-scale CI calculations are difficult (four or five valence electrons). The accuracy for the energies of atoms or ions with a large number of valence electrons (up to 16) is on the level of a few percent and can be controlled by varying the size of the effective CI matrix.

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