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Relativistic configuration-interaction calculations for atoms with one valence electron based on altering hydrogenlike or Dirac-Fock spin orbitals

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Relativistic configuration-interaction calculations using hydrogenlike or Dirac-Fock spin orbitals of the transition from the ground state to some $np_{1/2}$, $np_{3/2}$ low-lying excited states for the alkali metals are presented. In these calculations each virtual spin orbital corresponds to a unique noninteger atomic number determined iteratively using the virtual-particle model. The virtual-particle model based on "condensed-space" idea is here adopted to many electron systems consisting of a single valence electron and the core. The transition energy and the oscillator strength values were computed for sodium, potassium, rubidium, cesium, and francium. Both hydrogenlike and Dirac-Fock basis functions have been used in the computations for comparison.

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I. INTRODUCTION

One of the most important and widespread approaches to the calculation of atomic properties remains the relativistic configuration-interaction (RCI) scheme. The high-precision RCI calculations use very large scale basis-set expansion and can be run on powerful computers. The choice of basis functions is very important as it can largely improve the efficiency of RCI calculations. In addition the relativistic calculations use the Dirac Hamiltonian, which is nonlimited from below; thus, additional constraints must be imposed on basis functions. In our recent study we proposed hydrogenlike basis functions which proved to be very efficient in RCI calculations for heliumlike or lithiumlike systems. The hydrogenlike wave functions can be easily determined numerically or represented analytically. We applied them to the Dirac-Coulomb and Dirac-Coulomb-Breit Hamiltonians, where the projection onto the no-pair Hamiltonian was done only through the choice of the one-electron hydrogenlike energy states. None of the spurious eigenstates have been observed so far. In the present work we continue the study of hydrogenlike basis functions and their possible application to the calculations of many-electron atoms as well as of heavy atoms. It is our aim to set up virtual states of the "condensed-space" formalism developed in our recent work [1] for use in each atomic system.

In our last paper [1] we considered the space (denoted as E) for charged particles in hydrogenlike states. Furthermore, we have introduced the $\hat{Z}$ operator and the eigenstates

$$\hat{Z}|q\rangle = Z_q|q\rangle, \tag{1}$$

which belong to the E space. We can write the one-electron Dirac-Coulomb eigenequations with the aid of the $\hat{Z}$ operator,

$$\left(\hat{h}_D - \frac{\hat{Z}}{r}\right)\phi_q = \epsilon\phi_q, \tag{2}$$

where $\hat{h}_D$ is the Dirac kinetic-energy operator and ϕ_q is the wave function of the particle in the $|q\rangle$ state of the E space. Since the E space is spanned by spectroscopic states, the eigenvalues Z_q are the integer values. Moreover, all Z_q eigenvalues of a given particle are degenerate. For example, the electron in a hydrogen atom has Z_q equal to 1 in all its spectroscopic states. Following the concept of the condensed space of energy levels discussed in [1], a condensed-space transformation was defined which, applied to the E space, generates the so-called condensed $E^{(s)}$ space. The possible Z_q eigenvalues depend on integer parameter s and are determined by the relation

$$\frac{A(s+1)}{(s+1)\sqrt{\left(\frac{|\kappa|+s}{1+s}\right)^2-(\alpha A)^2}+n-|\kappa|+s(b-1)} = \frac{Z_{n\kappa}}{\sqrt{\kappa^2-(\alpha Z_{n\kappa})^2}+n-|\kappa|}, \tag{3}$$

where A is the atomic number, α is the fine-structure constant, and the integers $n \geqslant b, |\kappa| \leqslant n$ are quantum numbers. The b parameter refers to the quantum number of the lowest state from the $E^{(s)}$ space. One can note that the degeneration of the Z_q eigenvalues is removed in the $E^{(s)}$ space. Since all Z_q values are not integers, all states in the $E^{(s)}$ space are virtual. By definition both the E and $E^{(s)}$ spaces have a common ground energy state. One could interpret these two spaces as two different potentials. However, it is known from theory that different potentials cannot have the same ground state. We think that a possible interpretation is that the condense-space transformation creates new virtual particles, where each particle corresponds to a different Z_q eigenvalue. Thus, we might possibly interpret the $E^{(s)}$ space as representing the interacting virtual-particle system in the Coulomb field. The parameter s should refer to the number of created virtual particles. The E space would refer here to a single charged particle in the Coulomb potential, which would be the so-called background potential for the interacting virtual particles.

The possible application of the condensed-space concept to the atomic structure calculation was discussed in [1]. One chooses the E space as a set of spectroscopic states of the studied atomic system. Next, the condensed-space transformation is used to construct the $E^{(s)}$ space of virtual states. The integer s parameter discussed in detail in [1] should be chosen to be as large as possible. Each virtual state is designated by two quantum numbers n, κ, and the

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corresponding $\hat{Z}$ eigenvalues are evaluated from relation (3). The wave functions $\phi_{n,k}$ are determined by solving Eq. (2).

The energy structure calculations of He-like and Li-like systems were performed in our last paper [1] within the framework of the $E^{(s)}$ space concept as a virtual-particle model. In this paper we propose to extend this concept to many-electron systems with a single electron outside the closed-shell core. We present here calculations of the transition energy and of oscillator strengths for the low exited states $ns_{1/2}$-$np_{1/2}$ and $ns_{1/2}$-$np_{3/2}$ in the alkali atoms.

II. CALCULATIONS

The application of our virtual-particle model is not limited to only two- or three-electron systems. However, one can remember that it treats a many-electron system as a number of virtual particles in the Coulomb field which have to reproduce the Coulomb repulse interaction between the electrons. For a many-electron atom it would require a large number of virtual particles and, consequently, a huge CI space. For example, in the case of three -electron systems the basis-set expansion sometimes included hundreds of thousands of configuration state functions (CSFs) and over a hundred spin orbitals.

In many-electron systems some electrons can be treated as the core, and others can be treated as the valence electrons, which is a common approach. Among electron correlation effects, the most important are usually intravalence correlations and core-valence correlations which represent polarization of the core. The natural approach would be to treat the only valence electrons within the framework of the virtual-particle model with the Hartree-Fock (HF) or Dirac-Fock (DF) orbitals describing the core electrons. The main problem concerns the condensed-space transformation [1], which operates only on hydrogenlike energy levels. It requires us to choose the spectroscopic space E of the hydrogenlike states, which would represent the background potential for interacting electrons. For the few-electron atoms where all electrons are to be treated within the framework of the virtual-particle model, the nucleus potential should obviously be chosen as the background potential. However, in the case of the existing core electrons the valence electrons do not affect the pure Coulomb attraction by the nucleus. The Coulomb approximation may be valid only at a long distance from the core. Thus, if we neglect the core electrons in the process of generation of the virtual particles, as a consequence, they cannot properly represent the core-valence as well as the intravalence-electron interactions. In fact, we cannot introduce the influence of the core electrons or another distribution of the electronic charge into the process of generation of the $E^{(s)}$ condensed energy-level space. However, it is possible to include the screening effect of the core electrons in the $\hat{Z}$ operator.

We start by choosing the background potential as the sum of the nucleus potential and the HF potential of the core-electrons at large r,

$$-\frac{A-N}{r}, \tag{4}$$

where N is the number of core electrons and A is the atomic number. The energy levels for the $E^{(s)}$ space may be determined from the relations

$$\epsilon_{n,\kappa} = \frac{c^2}{\sqrt{1+\frac{\alpha^2(A-N)^2(s+1)^2}{\gamma+n-\kappa+s(b-1)}}},$$
$$\gamma = \sqrt{(\kappa+s)^2-\alpha^2(A-N)^2(s+1)^2}. \tag{5}$$

It should be noted that $\epsilon_{n,\kappa}$ is the energy eigenvalue of Eq. (2) for the corresponding $Z_{n\kappa}$ parameter satisfying Eq. (3) in the case where A is replaced by $A-N$. Thus, with the energy levels of the $E^{(s)}$ space, one can use Eq. (2) to determine the $\hat{Z}$ eigenvalues.

Let us consider now the corresponding single-particle Dirac equation with the screening-potential term in the DF approximation,

$$\left(\hat{h}_D - \frac{\hat{Z}}{r} + V_{DF}(r)\right)\phi_q = \epsilon\phi_q. \tag{6}$$

There are now two possible approaches to the virtual-particle model. In the first one, we rewrite Eq. (6) for the particular atomic system as

$$\left(\hat{h}_D - \frac{A}{r} - \frac{Z_{n\kappa}}{r} + V_{DF}(r)\right)\phi_{n\kappa} = \epsilon\phi_{n\kappa}, \tag{7}$$

where A is the atomic number. This equation may be used to generate the virtual wave functions. The $Z_{n\kappa}$ parameters should be determined from Eq. (3) within the ionic potential (4). In this method the core electrons influence the wave function of the virtual particles rather than the $\hat{Z}$ operator. The proper CI calculations with the Dirac-Fock spin orbitals were considered.

In the other approach one can use the hydrogenlike spin orbitals, but it is necessary to find a new equation for $Z_{n\kappa}$ rather than using Eq. (3), where the screening by the core electrons is included. We start with Eq. (6) in terms of radial functions and integrate it from a certain point r_0 to infinity, which results in

$$\begin{aligned}\int_{r_0}^{\infty}\Bigg[cP_{n\kappa}\left(\frac{d}{dr}-\frac{\kappa}{r}\right)Q_{n\kappa}\\ - cQ_{n\kappa}\left(\frac{d}{dr}+\frac{\kappa}{r}\right)P_{n\kappa} + 2c^2Q_{n\kappa}^2\Bigg]dr\\ = \int_{r_0}^{\infty}\left(\epsilon_{n,\kappa}+\frac{Z_{n\kappa}}{r}-V_s\right)(P_{n\kappa}^2+Q_{n\kappa}^2)dr.\end{aligned} \tag{8}$$

This equation can be used to evaluate the Z_{nk} eigenvalues of the $\hat{Z}$ operator in the presence of the screening potential. The screening potential V_s includes only the part of the Dirac-Fock direct potential,

$$V_s = \frac{1}{r}\int_0^r \rho(r')dr', \tag{9}$$

where $\rho(r)$ is the radial probability density of the core electrons. The $\epsilon_{n,\kappa}$ parameters are the energies obtained from Eq. (5). $P_{n\kappa}, Q_{n\kappa}$ are the radial parts of the hydrogenlike wave functions determined by solving single-particle Dirac equation (2). It should be noted that relation (3) provides the $Z_{n\kappa}$ parameters satisfy Eq. (8) unless the screening term V_s does not vanish. In general, we solve Eq. (8) by splitting it into two identities. We chose the r_0 parameter as the classical turning point obtained from the identity

$$\int_{r_0}^{\infty}\left[cP_{n\kappa}\left(\frac{d}{dr}-\frac{\kappa}{r}\right)Q_{n\kappa} -cQ_{n\kappa}\left(\frac{d}{dr}+\frac{\kappa}{r}\right)P_{n\kappa}+2c^2Q_{n\kappa}^2\right]dr=0. \quad (10)$$

This brings the right-hand side of Eq. (8) to another identity,

$$0=\int_{r_0}^{\infty}\left(\epsilon_{n,\kappa}+\frac{Z_{n\kappa}}{r}-V_s\right)\left(P_{n\kappa}^2+Q_{n\kappa}^2\right)dr. \quad (11)$$

The $Z_{n\kappa}$ quantities may be determined iteratively. In this case we need to evaluate the $P_{n\kappa},Q_{n\kappa}$ eigenfunctions of Eq. (2) for an approximate value of $Z_{n\kappa}$ at a particular step of the iteration procedure. The iteration procedure is continued until the identity (11) is fulfilled with accuracy better than 10^{-6}, which requires a few or more iteration steps. In our calculations we used identities (10) and (11) to generate the hydrogenlike spin orbitals together with $Z_{n\kappa}$ in the iteration procedure. Once the $Z_{n\kappa}$ parameters have been determined for the system studied, the hydrogenlike spin orbitals are evaluated from Eq. (2) and then are used in the CI scheme.

The virtual-particle model where the eigenvalues of operator $\hat{Z}$ are defined by the identities (10) and (11) is the generalization of the virtual-particle model based on Eq. (3). It provides a suitable framework for the calculations of a two- or three-electron system, as shown in our previous study [1]. We think that the correlation between two or three valence electrons may also be treated by this method. The second important effect is the correlations between valence and core electrons, especially in the alkali atoms which are the subject of this study. The core-valence interactions can be treated within the framework of the virtual-particle model, but this requires extra information about the core-electron system. It is known that core-valence correlations are responsible for the polarization of the core. In many approaches the additional term including the polarization of the core is considered in the effective potential. For example, Migdalek and Baylis [2] have introduced the polarization model potential based on the static dipole polarizability in the relativistic calculations. The configuration-interaction scheme accounts for the polarization effects of the core through the inclusion of the $|aq\rangle$ states in the basis set, where a designates the core electron and q designates the valence electron allowing for single excitation from the core. Within the framework of the virtual-particle model the core electron and the valence electron are represented by the number of virtual particles corresponding to the $|a_i\rangle$ and $|q_j\rangle$ one-electron states, respectively. On the other hand, if we considered the $|vw\rangle$ states which represent two valence electrons, they would be treated within the virtual-particle model exactly in the same way as the pair of core and valence electrons. Such equivalence seems to be incorrect. In fact, our calculations yielded in such a case overestimated ionization energies in alkali atoms. The problem disappears if we suppose that core electrons can fill only a finite number of virtual states, which means that the virtual particles which represent the core electrons should not be excited beyond the upper bound of the E_I energy level unless they would behave as the valence electrons in the virtual-particle model. This condition was fulfilled through the construction of the basis set where the $|a_i q\rangle$ states were excluded from the basis unless the energies of the $|a_i\rangle$ states were lower than E_I. The value of the E_I parameter was fitted to reproduce the best theoretical approximation of the experimental ionization energy of the ground state of the system studied. If the ionization energy is unknown, then it must be determined from the calculations. However, the basis-set expansion should be complete in view of single and double excitations from the core. In this case the parameter s appearing in formula (5) should refer to the number of excited electrons, i.e., $s=1,2$ when two and three electrons are excited, respectively. The maximization of the value of s results in faster convergence of the CI. But this may be used only if all electrons can be excited (two- or three-electron systems) or if one can control convergence of the CI scheme with the aid of an extra parameter like ionization energy.

The virtual-particle model based on the identities (10) and (11) has been applied in the relativistic CI calculations for systems with one electron outside the closed-shell core, such as sodium, potassium, rubidium, cesium, and francium. In the case of a francium atom we encountered the drastic problem of the appearance of spurious eigenstates. We suppose that the V_s screening potential (9), which includes only the monopole contribution of the Coulomb interaction, is not valid here due to the strong polarization of the inner-shell electrons in francium. The motion of the valence electron inside the region of the inner shells, which is familiar from quantum mechanics, results in the polarization of each core electron. The configuration-interaction approach, in general, properly treats the electron correlation effects rather than polarization of the core, which arises as a dipole moment in the core that is induced by the valence electron. Since most configuration-interaction approaches include the electrons from the outermost core shell in the core-valence correlations, the polarization of the inner-shell electrons may be included as an additional screening effect in the potential. This should be a very small effect for light systems and would grow larger with increasing the number of core electrons. It also depends on the types of spin orbitals. For example, using the wave functions in the frozen-core DF approximation, one would not observe that effect at all. But the hydrogenlike spin orbitals, due to their great penetration ability, would induce the polarization of the inner-shell electrons.

A. Core-polarization operator

In order to include polarization effects we expand the screening potential in terms of multipole potentials as

$$V_s=\frac{1}{r}\int_0^r\rho(r')dr'+\sum_{k>0}\frac{C^{(k)}}{r^{k+1}}\int_0^r r'^k\rho_a(r')dr'. \quad (12)$$

We assume that the magnetic interaction between the orbital or total angular momenta of the core electron and the virtual particle results in nonvanishing terms in the multipole expansion. Under this assumption we have introduced polarization operator $\hat{P}$, which is defined as

$$\hat{P}_j(n_a l_a j_a)\equiv r'\frac{j_a+\frac{1}{2}}{4}\left(\hat{j}+\frac{1}{2}\right), \quad (13a)$$

$$\hat{P}_l(n_a l_a)\equiv r'\frac{l_a\hat{l}}{4}, \quad (13b)$$

where the $\hat{P}_j$ and $\hat{P}_l$ operators correspond to average magnetic interactions $\overline{m_{j_a} m_j}$ and $\overline{m_{l_a} m_l}$, respectively. We use the notation $\hat{P}_j(n_a l_a j_a)$, which designates that such an operator is associated with the core spin orbital denoted by the $n_a l_a j_a$ quantum numbers. The operator is acting in the space of the angular momentum. We found that $\hat{P}_l$ is valid for the light systems like sodium or potassium, whereas $\hat{P}_j$ is valid for rubidium, cesium, and francium systems. With the aid of definition (13a) we can write a first-order correction to the screening potential due to the particular core spin orbital as

$$V_a^{(1)} = -\frac{\left(j_a + \frac{1}{2}\right)\left(j + \frac{1}{2}\right)}{2r^2} N_a \int_0^r r' \rho_a(r') dr', \tag{14}$$

where we use a to designate the core spin orbital and N_a to designate its occupation. The above expression represents the dipole interaction in the expansion (12).

Let us consider now the screened potential with respect to the infinitesimal change in the charge density. For this purpose we write

$$V_s = \frac{1}{r} \int_0^r \rho(r') dr' - \frac{1}{r} \int_0^r \delta\rho(r') dr', \tag{15}$$

where $\delta\rho$ is the change of the core charge density induced by virtual particles. The second term of the above expression corresponds to the dipole part of Eq. (12). Combining these equations, we obtain the equation for the change of the charge density as

$$\delta\rho = -\hat{\alpha} \frac{\delta r'}{r} \rho. \tag{16}$$

The quantity $\hat{\alpha}\delta r'$ is the infinitesimal polarization operator. Making use of the solution to Eq. (16), we write the expression for the screened potential with the aid of the polarization operator,

$$V_s = \frac{1}{r} \int_0^r \left(\mu e^{-\frac{\hat{P}}{r}} - \mu + 1\right) \rho(r') dr', \tag{17}$$

with $\mu = 1,2$ for $\hat{P}_l$ and $\hat{P}_j$, respectively. Expanding the exponential part of the screening potential, one can obtain the relations for the higher-order polarization operators. The zero-order operator is here defined as

$$\hat{P}_j^{(0)} \equiv 1, \tag{18}$$

and the corresponding higher-order polarization operators have to satisfy the following relations:

$$\hat{P}_j^{(2)}(nl) = \hat{P}_j^{(1)}(nlj_a) \hat{P}_j^{(1)}(nlj_b), \tag{19a}$$

$$\hat{P}_j^{(3)}(nl_b l_a j_a) = \hat{P}_j^{(2)}(nl_b) \hat{P}_j^{(1)}(nl_a j_a), \tag{19b}$$

$$\hat{P}_l^{(2)}(nl_a l_b) = \hat{P}_l^{(1)}(nl_a) \hat{P}_l^{(1)}(nl_b), \tag{19c}$$

$$\hat{P}_j^{(k_1+k_2)}(n) = \hat{P}_j^{(k_1)}(n) \hat{P}_j^{(k_2)}(n). \tag{19d}$$

These relations, together with expressions (13), may be regarded as the definition of the first-, second-, and the higher-order polarization operators. Note that the second-order operator is associated with all orbitals in the nl subshell, but the third-order one is associated with the orbitals in the coupled subshells. The second-order operators involve a pair of spin orbitals from the common subshell which satisfy $|j_a - j_b| = 1$. For example, $(p_{1/2}, p_{3/2})$, $(d_{3/2}, d_{5/2})$, etc. The third-order operator must involve the pair of the subshells, i.e., (sp). Using the above definitions, one can obtain the following expression for the second-order operator:

$$\hat{P}_j^{(2)}(n_a l_a) = r'^2 \frac{l_a(l_a+1)}{16} \left(\hat{j} + \frac{1}{2}\right)^2. \tag{20}$$

In general, we may write

$$\hat{P}_j^{(k)} = r'^k C_a^{(k)} \left(\hat{j} + \frac{1}{2}\right)^k, \tag{21}$$

where the coefficients $C_a^{(k)}$ may be evaluated from relations (19). Finally, we may write the expression for the first- and second-order core-polarization corrections to the screening potential as

$$\delta V_s = \sum_a 2N_a \int_0^r \rho_a(r') dr' \left(-\frac{\hat{P}_j^{(1)}}{r^2} + \frac{\hat{P}_j^{(2)}}{2! \cdot r^3}\right), \tag{22}$$

where the sum extends over all inner (i.e., fully occupied) core spin orbitals. We have made an assumption that the only closed subshells may be polarized by the virtual particles.

The potential term V_s in Eq. (11) must be supplemented by the polarization correction. This allowed us to achieve the proper screening effect for the virtual particles. As mentioned earlier, the polarization correction for light systems like potassium included only the first-order operator $\hat{P}_l^{(1)}$. In the case of sodium, since the core consists only of $1s$ and $2s$ subshells, the core-polarization correction vanishes. We found that expression (22) for polarization correction is valid for systems where the jj-coupling scheme becomes important, such as rubidium, cesium, and francium.

In our study we present the relativistic calculation of the energy levels and oscillator strengths for some low-lying states in atoms with one electron outside the closed shells, such as alkali metals. We performed CI calculations employing both Dirac-Fock spin orbitals and hydrogenlike spin orbitals for comparison. Here, we use a modified version of Desclaux's [3] code for the solving one-electron Dirac equations. The numerical wave functions were determined with a value of 0.0105 for the exponential mesh step. The values of the oscillator strength were obtained using the adopted Desclaux program.

B. RCI calculations of transitions and oscillator strengths based on Dirac-Fock spin orbitals

In order to calculate the virtual basis functions we employed Eq. (7) with a frozen-core DF potential as the V_{DF} screened potential. The spin orbitals for the closed shells have been determined from the SC-DF (single configuration Dirac-Fock) calculation for the ground state of the atom. Next, the virtual basis function was determined from Eq. (7) in the frozen-core approximation with the corrected term $Z_{n\kappa}/r$ to the nuclear potential. However, solving the eigenequation (7), one can encounter the problem of convergence while calculating some of the excited states. This problem may be omitted if the term $Z_{n\kappa}/r$ is substituted by the corresponding correction to the effective electron occupations of the outermost core shells. The value of $Z_{n\kappa}$ should be subtracted from the total electronic

TABLE I. Results of the ionization energies (in eV) for the ground states of atoms in alkali metals obtained by the RCI calculations based on hydrogenlike (SH) and Dirac-Fock (DF) basis functions.

	SH	DF	Expt.[a]
Na	5.13947	5.13942	5.1391
K	4.34097	4.34083	4.34066
Rb	4.17747	4.17759	4.17713
Cs	3.89092	3.89452	3.89391
Fr	4.06577	4.07310	4.07274

[a] Reference [4].

charge of the closed core shells proportionally to their electron occupation numbers.

The construction of the basis-set expansion was performed in a way that allowed us to obtain the best theoretical approximation of the ground ionization energy of the system studied. Trial CI calculations of the ground-state ionization energy allowed us to determine the range of excitations for the correlated orbitals and build the proper CSF space.

Basically, the configuration state functions corresponded to the single excitation from the outermost core shell. The CSF space included the doubly excited states $|n_c l_c j_c nlj\rangle$, where the range of excitations for the orbitals $\{n_c l_c, nl\}$ were given by $\{11p, 38s\}$ in sodium, $\{8p, 40s\}$ in potassium, $\{12p, 45s\}$ in rubidium, $\{15p, 50s\}$ in cesium, and $\{21p, 57s\}$ in the francium atom, respectively. In order to account for the relaxation of the core we also included some configuration state functions with doubly excited states from the core. They were the $|3s^2; nlj\rangle$, $|4s^2; nlj\rangle$, $|5s^2; nlj\rangle$, $|6s^2; nlj\rangle$, and $|7s^2; nlj\rangle$ states for sodium, potassium, rubidium, cesium, and francium, respectively. The number of configurations used in the CI calculation varied from 16 000 to 70 000 CSFs depending on the system. The obtained results for the ground-state ionization energies for alkali metals are presented in Table I.

TABLE II. Energies (in cm^{-1}) for the $3s_{1/2}$-$np_{1/2}$ and $3s_{1/2}$-$np_{3/2}$ transitions in neutral sodium as calculated with hydrogenlike (SH) and Dirac-Fock (DF) basis functions.

Level	SH	DF	ΔE_{nlj}(SH)[a]
$3p\ ^2P_{1/2}$	16954.4	16961.2	1.8
$^2P_{3/2}$	16971.8	16979.2	1.6
$4p\ ^2P_{1/2}$	30262.6	30270.2	4.4
$^2P_{3/2}$	30268.3	30276.1	4.3
$5p\ ^2P_{1/2}$	35039.1	35042.7	1.3
$^2P_{3/2}$	35041.7	35045.3	1.2
$6p\ ^2P_{1/2}$	37296.6	37298.2	−0.3
$^2P_{3/2}$	37297.9	37299.6	−0.3
$7p\ ^2P_{1/2}$	38541.2	38542.1	−1.0
$^2P_{3/2}$	38542.0	38542.9	−1.1
$8p\ ^2P_{1/2}$	39299.7	39300.2	−1.4
$^2P_{3/2}$	39300.3	39300.7	−1.4
$9p\ ^2P_{1/2}$	39795.9	39796.3	−1.4
$^2P_{3/2}$	39796.2	39796.6	−1.4
$10p\ ^2P_{1/2}$	40136.9	40138.8	−0.1
$^2P_{3/2}$	40137.2	40139.1	−0.2

[a] Difference between the experimental [4] and SH values.

TABLE III. Comparison of oscillator strengths (f value) in sodium calculated in length gauge.

Transition	SH	DF	Other
$3s_{1/2}$-$3p_{1/2}$	3.210^{-1}	3.220^{-1}	3.201^{-1}[a]
$3s_{1/2}$-$3p_{3/2}$	6.426^{-1}	6.445^{-1}	6.407^{-1}[a]
$3s_{1/2}$-$4p_{1/2}$	4.278^{-3}	4.211^{-3}	4.035^{-3}[b]
$3s_{1/2}$-$4p_{3/2}$	8.701^{-3}	8.570^{-3}	8.208^{-3}[b]
$3s_{1/2}$-$5p_{1/2}$	6.081^{-4}	5.953^{-4}	5.562^{-4}[b]
$3s_{1/2}$-$5p_{3/2}$	1.250^{-3}	1.225^{-3}	1.144^{-3}[b]
$3s_{1/2}$-$6p_{1/2}$	1.775^{-4}	1.742^{-4}	
$3s_{1/2}$-$6p_{3/2}$	3.678^{-4}	3.614^{-4}	
$3s_{1/2}$-$7p_{1/2}$	7.423^{-5}	6.950^{-5}	
$3s_{1/2}$-$7p_{3/2}$	1.547^{-4}	1.451^{-4}	
$3s_{1/2}$-$8p_{1/2}$	3.780^{-5}	3.662^{-5}	
$3s_{1/2}$-$8p_{3/2}$	7.909^{-5}	7.676^{-5}	
$3s_{1/2}$-$9p_{1/2}$	2.179^{-5}	2.154^{-5}	
$3s_{1/2}$-$9p_{3/2}$	4.574^{-5}	4.528^{-5}	
$3s_{1/2}$-$10p_{1/2}$	1.393^{-5}	1.422^{-5}	
$3s_{1/2}$-$10p_{3/2}$	2.932^{-5}	2.995^{-5}	

[a] Reference [5].

[b] Reference [6].

Further, we carried out the calculations in Dirac-Coulomb approximation for the transitions $ns_{1/2}$-$np_{1/2}$ and $ns_{1/2}$-$np_{3/2}$ for some low-lying excited states. The obtained results for all alkali metals of the transition energies as well as oscillator strengths are presented in Tables II–XI.

C. RCI calculations of transitions and oscillator strengths based on hydrogenlike spin orbitals

In the second approach we chose hydrogenlike basis functions as the virtual one-electron states. The core spin orbitals were still determined in the single-configuration Dirac-Fock calculations for the ground state of the system

TABLE IV. Energies (in cm^{-1}) for the $4s_{1/2}$-$np_{1/2}$ and $4s_{1/2}$-$np_{3/2}$ transitions in neutral potassium as calculated with hydrogenlike (SH) and Dirac-Fock (DF) basis functions.

Level	SH	DF	ΔE_{nlj}(SH)[a]
$4p\ ^2P_{1/2}$	12985.5	12995.6	–0.3
$^2P_{3/2}$	13042.6	13053.5	0.3
$5p\ ^2P_{1/2}$	24699.3	24709.7	2.1
$^2P_{3/2}$	24718.0	24728.5	2.1
$6p\ ^2P_{1/2}$	28999.1	29000.0	0.2
$^2P_{3/2}$	29007.5	29008.4	0.2
$7p\ ^2P_{1/2}$	31070.6	31069.0	–0.7
$^2P_{3/2}$	31075.1	31073.6	–0.7
$8p\ ^2P_{1/2}$	32228.6	32229.8	–1.1
$^2P_{3/2}$	32231.3	32232.5	–1.1
$9p\ ^2P_{1/2}$	32941.1	32942.5	–0.9
$^2P_{3/2}$	32942.8	32944.2	–0.9
$10p\ ^2P_{1/2}$	33409.8	33412.2	0.4
$^2P_{3/2}$	33411.0	33413.4	0.4
$11p\ ^2P_{1/2}$	33745.1	33738.2	8.6
$^2P_{3/2}$	33746.0	33739.0	8.7

[a] Difference between the experimental [4] and SH values.

TABLE V. Comparison of oscillator strengths (f value) in potassium calculated in length gauge.

Transition	SH	DF	Other[a]	Expt.[b]
$4s_{1/2}$-$4p_{1/2}$	3.33^{-1}	3.32^{-1}	3.33^{-1}	3.24^{-1}
$4s_{1/2}$-$4p_{3/2}$	6.69^{-1}	6.67^{-1}	6.69^{-1}	6.52^{-1}
$4s_{1/2}$-$5p_{1/2}$	2.68^{-3}	2.46^{-3}	$2.59-3$	2.58^{-3}
$4s_{1/2}$-$5p_{3/2}$	5.82^{-3}	5.36^{-3}	5.63^{-3}	5.54^{-3}
$4s_{1/2}$-$6p_{1/2}$	2.67^{-4}	2.17^{-4}	2.45^{-4}	2.53^{-4}
$4s_{1/2}$-$6p_{3/2}$	6.24^{-4}	5.16^{-4}	5.75^{-4}	5.76^{-4}
$4s_{1/2}$-$7p_{1/2}$	5.59^{-5}	5.96^{-5}	4.92^{-5}	6.08^{-5}
$4s_{1/2}$-$7p_{3/2}$	1.41^{-4}	1.50^{-4}	1.26^{-4}	1.52^{-4}
$4s_{1/2}$-$8p_{1/2}$	1.80^{-5}	1.41^{-5}	1.46^{-5}	1.72^{-5}
$4s_{1/2}$-$8p_{3/2}$	4.87^{-5}	3.97^{-5}	4.05^{-5}	4.56^{-5}
$4s_{1/2}$-$9p_{1/2}$	7.19^{-6}	4.43^{-6}	5.56^{-6}	6.45^{-6}
$4s_{1/2}$-$9p_{3/2}$	2.08^{-5}	1.41^{-5}	1.67^{-5}	1.82^{-5}
$4s_{1/2}$-$10p_{1/2}$	3.46^{-6}	1.72^{-6}	2.51^{-6}	
$4s_{1/2}$-$10p_{3/2}$	1.06^{-5}	6.18^{-6}	8.14^{-6}	
$4s_{1/2}$-$11p_{1/2}$	1.38^{-6}	7.40^{-7}	1.28^{-6}	
$4s_{1/2}$-$11p_{3/2}$	4.93^{-6}	3.04^{-6}	4.47^{-6}	

[a] Reference [7].
[b] Reference [8].

under consideration. The wave functions of the core spin orbitals were later used to evaluate the radial density of the electronic charge in expression (12) for the screened potential. Further, we used relations (10) and (11) and the single-particle Dirac equation (2) iteratively to determine the parameters Z_{nk} and the corresponding hydrogenlike spin orbitals, which were later used as basis functions in the relativistic configuration-interaction scheme.

The construction of the basis set was performed in a way analogous to the case where the Dirac-Fock basis functions were used. Here, the range of the excitations for the correlated orbitals was given by $\{4p,52s\}$ in sodium, $\{5d,49s\}$ in potassium, $\{8p,70s\}$ in rubidium, $\{10f,70s\}$ in cesium, and $\{14p,70s\}$ in francium, respectively. The basis-set expansions were given by $52s50p49d49f$ for sodium, $49s48p47d48f$ for potassium, $70s68p66d65f$ for rubidium, $70s68p66d64f$ for cesium, and $70s68p66d64f$ for francium. The resulting total number of configurations varies from 3800 to 40 000 depending on the system. The obtained results for all alkali metals of the transition energies and of oscillator strengths are presented in Tables II–XI.

TABLE VI. Energies (in cm^{-1}) for the $5s_{1/2}$-$np_{1/2}$ and $5s_{1/2}$-$np_{3/2}$ transitions in neutral rubidium as calculated with hydrogenlike (SH) and Dirac-Fock (DF) basis functions.

Level	SH	DF	ΔE_{nlj}(SH)[a]
$5p\ {}^2P_{1/2}$	12581.7	12566.4	−2.7
${}^2P_{3/2}$	12819.9	12800.5	−3.4
$6p\ {}^2P_{1/2}$	23714.4	23721.7	0.6
${}^2P_{3/2}$	23792.7	23797.8	−0.1
$7p\ {}^2P_{1/2}$	27835.8	27838.3	−0.8
${}^2P_{3/2}$	27871.5	27872.8	−1.4
$8p\ {}^2P_{1/2}$	29835.3	29835.8	−0.4
${}^2P_{3/2}$	29854.4	29854.3	−0.6
$9p\ {}^2P_{1/2}$	30954.9	30958.6	4.0
${}^2P_{3/2}$	30966.5	30969.7	3.7
$10p\ {}^2P_{1/2}$	31630.0	31656.6	23.8
${}^2P_{3/2}$	31639.1	31663.8	22.1

[a] Difference between the experimental [4] and SH values.

TABLE VII. Comparison of oscillator strengths (f value) in rubidium calculated in length gauge.

Transition	SH	DF	Other[a]	Expt.[b]
$5s_{1/2}$-$5p_{1/2}$	3.42^{-1}	3.40^{-1}	3.43^{-1}	3.24^{-1}
$5s_{1/2}$-$5p_{3/2}$	6.94^{-1}	6.90^{-1}	6.96^{-1}	6.68^{-1}
$5s_{1/2}$-$6p_{1/2}$	3.67^{-3}	3.28^{-3}	3.65^{-3}	3.73^{-3}
$5s_{1/2}$-$6p_{3/2}$	9.76^{-2}	8.83^{-3}	9.68^{-3}	9.54^{-3}
$5s_{1/2}$-$7p_{1/2}$	4.60^{-4}	3.80^{-4}	4.59^{-4}	4.87^{-4}
$5s_{1/2}$-$7p_{3/2}$	1.48^{-3}	1.26^{-3}	1.46^{-3}	1.48^{-3}
$5s_{1/2}$-$8p_{1/2}$	1.18^{-4}	9.22^{-5}	1.21^{-4}	1.38^{-4}
$5s_{1/2}$-$8p_{3/2}$	4.45^{-4}	3.66^{-4}	4.43^{-4}	4.68^{-4}
$5s_{1/2}$-$9p_{1/2}$	4.60^{-5}	4.00^{-5}	4.59^{-5}	5.22^{-5}
$5s_{1/2}$-$9p_{3/2}$	1.92^{-4}	1.73^{-4}	1.88^{-4}	1.97^{-4}
$5s_{1/2}$-$10p_{1/2}$	2.13^{-5}	9.83^{-6}	2.18^{-5}	2.61^{-5}
$5s_{1/2}$-$10p_{3/2}$	9.58^{-5}	6.01^{-5}	9.74^{-5}	1.08^{-4}

[a] Reference [7].
[b] Reference [9].

III. DISCUSSION OF RESULTS

The present calculations were carried out with the aid of the ground-state ionization energies of the systems studied. In fully *ab initio* calculations the ionization energy of the ground state should be determined first. This is the most tedious calculation because the large basis-set expansion which includes double excitations from the core has to be used. The results of the calculated ionization energies of the ground state in sodium obtained with the RCI calculations based on hydrogenlike (SH) basis functions are presented in Table XII, which also shows the convergence of the CI calculations.

Table I contains the values of ionization energies of the ground state of atoms which were achieved during the establishing of the CSF basis-set expansions by two (SH and DF) methods. The ground-state ionization energies were regarded here as the parameters which helped us to set the upper bound on the excitations of spin orbitals.

Our results for light alkali metals such as sodium and potassium are presented in Tables II–V. Tables II and IV present the

TABLE VIII. Energies (in cm^{-1}) for the $6s_{1/2}$-$np_{1/2}$ and $6s_{1/2}$-$np_{3/2}$ transitions in neutral cesium as calculated with hydrogenlike (SH) and Dirac-Fock (DF) basis functions.

Level	SH	DF	ΔE_{nlj}(SH)[a]
$6p\ {}^2P_{1/2}$	11161.7	11157.1	16.6
${}^2P_{3/2}$	11712.7	11700.1	19.6
$7p\ {}^2P_{1/2}$	21741.1	21773.4	24.2
${}^2P_{3/2}$	21920.3	21950.2	26.1
$8p\ {}^2P_{1/2}$	25682.7	25714.6	26.1
${}^2P_{3/2}$	25764.0	25795.3	27.5

[a] Difference between the experimental [4] and SH values.

TABLE IX. Comparison of oscillator strengths (f value) in cesium calculated in length gauge.

Transition	SH	DF	Other[a]	Expt.[b]
$6s_{1/2}$-$6p_{1/2}$	3.43^{-1}	3.40^{-1}	3.47^{-1}	3.47 ± 0.02^{-1}
$6s_{1/2}$-$6p_{3/2}$	7.13^{-1}	7.07^{-1}	7.20^{-1}	7.21 ± 0.02^{-1}
$6s_{1/2}$-$7p_{1/2}$	2.43^{-3}	2.01^{-3}	2.55^{-3}	2.67 ± 0.04^{-3}
$6s_{1/2}$-$7p_{3/2}$	1.06^{-2}	9.28^{-3}	1.08^{-2}	1.13 ± 0.04^{-2}
$6s_{1/2}$-$8p_{1/2}$	2.07^{-4}	1.37^{-4}	2.33^{-4}	2.54 ± 0.1^{-4}
$6s_{1/2}$-$8p_{3/2}$	1.66^{-3}	1.35^{-3}	1.73^{-3}	1.85 ± 0.09^{-3}

[a] Reference [7].
[b] Reference [10].

energy levels $np_{1/2}$, $np_{3/2}$ of the low excited states, which were calculated using both hydrogenlike (SH) and Dirac-Fock (DF) basis functions. Note that good agreement of the ionization energies corresponds to the excellent results of the transition energies, where, in most cases, the agreement with experimental data is better than 0.01%. As can be seen from Tables II and IV, both methods (SH and DF) yielded energy-level values that were comparable in accuracy, although the method employing Dirac-Fock spin orbitals required the use of longer basis-set expansions (see Secs. IIB and IIC). This probably follows from the fact that DF basis functions have a small overlap with the core orbitals, and as a consequence, they poorly account for the core-valence correlations.

The corresponding results for rubidium, cesium, and francium are presented in Tables VI, VIII, and X. As can be seen, the number of excited states determined with high accuracy successively decreased with the increasing number of core electrons. One can note the advantage of the Dirac-Fock over the hydrogenlike basis functions where the most excited states are concern. In cesium and francium the DF results of the transition energies agree much better with experimental data than the corresponding results obtained by the SH calculations. The method employing Dirac-Fock spin orbitals allowed us to obtain even more higher excited states for cesium and francium systems (not presented in this study) with high accuracy.

The reason is that the DF calculations better account for the relaxation of the core than the corresponding SH calculations. Our calculations were performed in the frozen-core approximation, which guarantees the orthogonality of the spin orbitals. The core orbitals were optimized during SCF calculations of the ground state of the system. However, such an approach neglects the relaxation of the core. The relaxation increases as the number of core electron increases. Thus, it is considerably more important if the heavy alkali metals are computed. Obviously, Dirac-Fock spin orbitals account better for the relaxation than hydrogenlike spin orbitals. The effect of the relaxation may be treated simultaneously with the correlation effects in the configuration-interaction scheme. However, when heavy systems like cesium or francium are considered, the basis-set expansion should probably be considerably extended to include the triple excitations.

The results of the oscillator strength for the $ns_{1/2}$-$np_{1/2}$ and $ns_{1/2}$-$np_{3/2}$ transitions are presented in Tables III, V, VII, IX, and XI. By comparing SH and DF results one can see deviations obtained in f values, particularly for the transitions to the high excited states. These deviations increase with an increasing nuclear number of alkali metals and with an increasing principle quantum number of the upper states. The results obtained using Dirac-Fock basis functions (DF) are too low in comparison with other [7] calculations presented here, whereas SH results are in reasonable agreement. We may conclude that Dirac-Fock basis functions generated in the frozen-core approximation probably do not properly account for polarization of the core. Since the polarization of the core diminishes the values of the oscillator strengths, the method based on Dirac-Fock basis functions has a tendency to overestimate the core-polarization effects. It is worth noticing that the electron correlation effects, relaxation as well as the electron-electron interaction, are treated uniformly within the virtual-particle model where the virtual particles are represented by the hydrogenlike wave functions. If the virtual particles are represented by the Dirac-Fock basis functions, correlation and relaxation should be included separately since the wave functions are generated in the self-consistent electronic field. However, this would lead us to use the unique basis functions for the individual atomic state.

TABLE X. Energies (in cm^{-1}) for the $7s_{1/2}$-$np_{1/2}$ and $7s_{1/2}$-$np_{3/2}$ transitions in neutral francium as calculated with hydrogenlike (SH) and Dirac-Fock (DF) basis functions.

Level	SH	DF	MBPT[a]	ΔE_{nlj}(SH)[b]
$7p\ ^2P_{1/2}$	12266.2	12205.2	12167.0	− 28.8
$^2P_{3/2}$	13896.4	13878.6	13896.7	27.4
$8p\ ^2P_{1/2}$	23056.1	23116.9		56.9
$^2P_{3/2}$	23602.2	23656.0		56.1

[a] Many-body perturbation theory (Refs. [11,12]).
[b] Difference between the experimental [4] and SH values.

TABLE XI. Comparison of oscillator strengths (f value) in francium calculated in length gauge.

Transition	SH	DF	MBPT[a]	Expt.[b]
$7s_{1/2}$-$7p_{1/2}$	3.40^{-1}	3.37^{-1}	3.40^{-1}	3.40^{-1}
$7s_{1/2}$-$7p_{3/2}$	7.31^{-1}	7.32^{-1}	7.35^{-1}	7.36^{-1}
$7s_{1/2}$-$8p_{1/2}$	3.97^{-3}	2.42^{-3}		
$7s_{1/2}$-$8p_{3/2}$	3.24^{-2}	2.61^{-2}		

[a] Reference [11].
[b] For references to experimental works see [12].

TABLE XII. Computed ionization energy (in eV) for the ground state of sodium as a function of the size of CI basis set.

CSF	Excitations from the core	RCI (SH)
709	S	5.13133
1372	S	5.13742
7874	S	5.13812
18442	S	5.13825
120813	SD	5.13895
216178	SD	5.139085
Expt.		5.1391[a]

[a] Reference [4].

IV. SUMMARY

This study demonstrates two approaches to the generation of the basis functions used in the relativistic configuration-interaction calculations. Dirac-Fock basis functions and hydrogenlike basis functions were considered. The method based on the virtual-particle model which was developed in our previous study [1] has been generalized to the heavier systems consisting of the valence electron and the core. The virtual particles are represented by the parametric wave functions. Each of the wave functions in this model corresponds to the Z_{nk} parameter, which is the noninteger nucleus number. We found the general equation for these quantities which is valid in the presence of the screened potential. Such potentials must appear when the core electrons are considered.

In order to obtain accurate values of noninteger nuclear numbers the wave function should have the correct asymptotic behavior. It is essential for hydrogenlike wave functions evaluated numerically. In our calculations the hydrogenlike wave functions were determined numerically with a very dense computational mesh. The method also uses very high excited spin orbitals that may be difficult to determine with the desired accuracy. This inconvenience may be easily overcome by using an analytical representation of hydrogenlike spin orbitals.

Our calculations took advantage of extra parameters, which were the ground-state ionization energies taken from the experimental data. These parameters were helpful in establishing the basis sets. Therefore, we might be able to obtain highly accurate results by using not very large CI expansions. However, the ionization energies could be determined theoretically from the large-scale RCI calculations. Thus, this method can still be considered an *ab initio* approach.

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