Development of a configuration-interaction plus all-order method for atomic calculations

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We develop a theoretical method within the framework of relativistic many-body theory to accurately treat correlation corrections in atoms with few valence electrons. This method combines the all-order approach currently used in precision calculations of properties of monovalent atoms with the configuration-interaction approach that is applicable for many-electron systems. The method is applied to Mg, Ca, Sr, Zn, Cd, Ba, and Hg to evaluate ionization energies and low-lying energy levels.

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I. INTRODUCTION

The development of the relativistic all-order method, where all single and double excitations of the Dirac-Hartree-Fock wave function are included to all orders of perturbation theory, led to accurate predictions for energies, transition amplitudes, hyperfine constants, polarizabilities, C_3 and C_6 coefficients, isotope shifts, and other properties of monovalent atoms, as well as the calculation of parity-violating amplitudes in Cs, Fr, and Ra^+ [1–6]. This method was also used to calculate magic wavelengths [7] as well as black-body radiation shifts [8] and quadrupole moments [9] that are of interest to atomic-clock research. The all-order method is designed to treat core-core and core-valence correlations with high accuracy. It is one of the most accurate methods currently being used in the atomic structure calculation. However, its applications so far have been limited to monovalent systems. Readers are referred to Ref. [3] and references therein for a review of this method and its applications.

Precision calculations for atoms with several valence electrons require an accurate treatment of the very strong valence-valence correlation; a perturbative approach leads to significant difficulties. The complexity of the all-order formalism for matrix elements also increases drastically as the number of valence electrons increases; for example, the expression for all-order matrix elements in divalent systems contains several hundred terms instead of the 20 terms in the corresponding monovalent expression. Therefore, we found it impractical to develop a direct extension of the all-order approach to more complex systems, both due to the large valence-valence correlation corrections and the very large number of terms noted above in the matrix element formulas.

A more promising method for the study of atomic properties of more complicated systems that combined configuration-interaction (CI) and many-body perturbation theory (MBPT) was developed in Ref. [10]. The CI +MBPT method was applied to the calculation of atomic properties of various systems in a number of works (see [11–20] and references therein) and to the calculation of parity-violating amplitudes in Tl and Yb [21,22]. The strengths of the configuration-interaction method are broad applicability and all-order treatment of the valence-valence correlation corrections. However, the precision of the CI method is generally drastically limited for large systems by the number of the configurations that can be included. As a result, core excitations are neglected or only a small number of them is included, leading to a significant loss of accuracy for heavier systems. The CI+MBPT approach allows one to incorporate core excitations in the CI method by constructing an effective Hamiltonian H^{eff} that incorporates certain perturbation-theory terms. The CI method is then applied to the modified H^{eff} to obtain improved energies and wave functions.

Because of the rapid increase in the number of terms of the MBPT expansion, the CI+MBPT approach becomes impractical already in the third order of MBPT. For that reason, the CI+MBPT approach is usually restricted to the second order. Some higher-order corrections can be accounted for by introducing screening coefficients to second-order diagrams. These screening coefficients can be found either by averaging two-electron second-order diagrams or by semiempirical fitting of experimental energies. The second-order expression for one-body correction to the Hamiltonian is corrected by the all-order chains of such terms in some works (see, for example, Ref. [23]). In 2004, a modification of the effective Hamiltonian using the all-order pair equations was proposed and tested on a "toy" four-electron model [24]. An efficient method of including core-valence correlations into the CI calculations was presented by Dzuba and Flambaum in [14]. The CI Hamiltonian for N valence electrons was calculated using orbitals in the complete V^N potential (the mean field

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produced by all electrons); the one- and two-body corrections to the effective Hamiltonian were obtained by using the many-body perturbation theory with dominating classes of diagrams included to all orders.

In the present work, we combine the all-order method, currently used in precision calculations of properties of monovalent atoms, with the CI approach. In the CI + all-order approach, core excitations are incorporated in the CI method by constructing an effective Hamiltonian using fully converged all-order excitation coefficients. Therefore, the core-core and core-valence sectors of the correlation corrections for systems with few valence electrons will be treated with the same accuracy as in the all-order approach for monovalent atoms. Then, the CI method is used to treat valence-valence correlations. This method is expected to yield accurate wave functions for subsequent calculations of atomic properties such as lifetimes, polarizabilities, hyperfine constants, parity-violating amplitudes, etc. The present work is motivated by the urgent need for precision calculations of atomic properties of heavy atoms with few valence electrons for applications such as atomic-clock research, quantum information, study of fundamental symmetries, searches for variation of the fundamental constants, and tests of high-precision experimental methods. The development of the CI + all-order method is also aimed at filling the long-standing gap between the accuracy of theoretical and experimental parity-violation studies in systems with few valence electrons. Atomic properties of various atoms and ions are also of interest for astrophysics applications.

Our method is generally applicable, i.e., not restricted to the specific type of the system. We test the present approach on the calculation of the energy levels of Mg, Ca, Sr, Cd, Zn, Ba, and Hg to demonstrate a significant improvement in comparison with CI + second-order MBPT values. We also discuss calculations of transition matrix elements and polarizabilities.

We provide a brief description of the all-order and CI +MBPT formalisms in Secs. II and III, respectively. The CI + all-order approach is described in Sec. IV. Finally, we present results for removal energies in divalent systems calculated using the CI + all-order approach and discuss perspectives for further applications and development.

II. RELATIVISTIC ALL-ORDER METHOD FOR MONOVALENT SYSTEMS

Our point of departure is the relativistic no-pair Hamiltonian $H = H_0 + V_I$ obtained from QED by [25]

$$H_0 = \sum_i \epsilon_i : a_i^\dagger a_i :, \tag{1}$$

$$V_I = \frac{1}{2}\sum_{ijkl} v_{ijkl} : a_i^\dagger a_j^\dagger a_l a_k : + \sum_{ij}(V_{HF} - U)_{ij} : a_i^\dagger a_j :. \tag{2}$$

Here, v_{ijkl} are two-particle matrix elements of the Coulomb interaction g_{ijkl}, or Coulomb + Breit interaction $g_{ijkl} + b_{ijkl}$, and $V_{HF} = \Sigma_a(v_{iaja} - v_{iaaj})$ is the *frozen-core* Dirac-Fock potential. The summation index a in V_{HF} ranges over states in

the closed core. The quantity ϵ_i in Eq. (1) is the eigenvalue of the Dirac equation $h(\mathbf{r})\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$, where

$$h(\mathbf{r}) = c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2 - \frac{Z}{r} + U(r). \tag{3}$$

In our previous all-order calculations of monovalent atoms, we took U to be frozen-core V^{N-1} potential $U = V_{HF}$. Such a choice greatly simplifies the calculations since the second term in Eq. (2) vanishes in this case. In this work, we use the same type of potential (V^{N-2} for divalent systems), but different potentials may be used in the future.

In the coupled-cluster method, the exact many-body wave function is represented in the form [26]

$$|\Psi\rangle = \exp(S)|\Psi^{(0)}\rangle, \tag{4}$$

where $|\Psi^{(0)}\rangle$ is the lowest-order atomic state vector. The operator S for an N-electron atom consists of "cluster" contributions from one-electron, two-electron, ..., N-electron excitations of the lowest-order state vector $|\Psi^{(0)}\rangle$: $S = S_1 + S_2 + \cdots + S_N$.

The all-order method described in detail in Refs. [1,2] is a linearized version of the coupled-cluster method, where all nonlinear terms in the expansion of the exponential are omitted; the all-order wave function takes the form

$$|\Psi\rangle = \{1 + S_1 + S_2 + S_3 + \cdots + S_N\}|\Psi^{(0)}\rangle. \tag{5}$$

Restricting the sum in Eq. (5) to single, double, and valence triple excitations yields the following expansion for the state vector of a monovalent atom in state v:

$$
\begin{aligned}
|\Psi_v\rangle = \Bigg[&1 + \sum_{ma}\rho_{ma}a_m^\dagger a_a + \frac{1}{2}\sum_{mnab}\rho_{mnab}a_m^\dagger a_n^\dagger a_b a_a + \\
&+ \sum_{m\neq v}\rho_{mv}a_m^\dagger a_v + \sum_{mna}\rho_{mnva}a_m^\dagger a_n^\dagger a_a a_v \\
&+ \frac{1}{6}\sum_{mnrab}\rho_{mnrvab}a_m^\dagger a_n^\dagger a_r^\dagger a_b a_a a_v \Bigg]|\Psi_v^{(0)}\rangle,
\end{aligned}
\tag{6}
$$

where the indices m, n, and r range over all possible virtual states while indices a and b range over all occupied core states. The lowest-order wave function $|\Psi_v^{(0)}\rangle$ is

$$|\Psi_v^{(0)}\rangle = a_v^\dagger|\Psi_C\rangle, \tag{7}$$

where $|\Psi_C\rangle$ is the lowest-order frozen-core wave function. The quantities ρ_{ma} and ρ_{mv} are single-excitation coefficients for core and valence electrons; ρ_{mnab} and ρ_{mnva} are core and valence double-excitation coefficients, respectively; ρ_{mnrvab} are the valence triple excitation coefficients. In the single-double (SD) implementation of the all-order method, only single and double excitations are included. In the (single, double, and partial triple) SDpT variant of the all-order method, valence triple excitations are included perturbatively, as described in Ref. [2].

To derive equations for the excitation coefficients, the state vector $|\Psi_v\rangle$ is substituted into the many-body Schrödinger equation $H|\Psi_v\rangle = E|\Psi_v\rangle$ and terms on the left-

and right-hand sides are matched based on the number and type of operators they contain, leading to the equations for the excitation coefficients given in [2].

We note that all nonlinear terms at the single-double level have been added in the formulation of the all-order method in Ref. [27]. This version of the all-order method is equivalent to the coupled-cluster single-double method for a finite basis set. It was shown in Refs. [28,29] that both nonlinear terms and complete valence triple excitations must be included to improve the accuracy of the linearized coupled-cluster SD method. In the present work, we use linearized SD variant of the all-order method since the SD method already leads to excellent results for a large number of the atomic properties and is computationally efficient.

The resulting SD all-order equations for valence excitation coefficients are

$$(\epsilon_v - \epsilon_m + \delta E_v)\rho_{mv} = \sum_{bn} \widetilde{g}_{mbvn}\rho_{nb} + \sum_{bnr} g_{mbnr}\widetilde{\rho}_{nrvb}$$
$$- \sum_{bcn} g_{bcvn}\widetilde{\rho}_{mnbc}, \tag{8}$$

$$(\epsilon_{vb} - \epsilon_{mn} + \delta E_v)\rho_{mnvb}$$
$$= g_{mnvb} + \sum_{cd} g_{cdvb}\rho_{mncd} + \sum_{rs} g_{mnrs}\rho_{rsvb}$$
$$+ \left[\sum_r g_{mnrb}\rho_{rv} - \sum_c g_{cnvb}\rho_{mc} + \sum_{rc} \widetilde{g}_{cnrb}\widetilde{\rho}_{mrvc} \right] + \begin{bmatrix} v \leftrightarrow b \\ m \leftrightarrow n \end{bmatrix}, \tag{9}$$

where δE_v is the valence correlation energy $\delta E_v = E_v - \epsilon_v$, $\epsilon_{ij} = \epsilon_i + \epsilon_j$, and $\widetilde{\rho}_{mnvb} = \rho_{mnvb} - \rho_{nmvb}$. The correlation correction to the energy of the state v is given in terms of the excitation coefficients by

$$\delta E_v = \sum_{ma} \widetilde{g}_{vavm}\rho_{ma} + \sum_{mab} g_{abvm}\widetilde{\rho}_{mvab} + \sum_{mna} g_{vbmn}\widetilde{\rho}_{mnvb}. \tag{10}$$

Equations for core excitation coefficients ρ_{ma} and ρ_{mnab} are obtained from the above equations by replacing the valence index v by a core index a and removing δE_v from the left-hand side of the equations. We note that the right-hand side of the valence energy equation is identical to the right-hand side of the equation for ρ_{mv} with $m = v$. Equations for the correlation energy and all excitation coefficients are solved iteratively. Every iteration picks up correlation terms corresponding to the next-higher order of perturbation theory until the correlation energy converges to sufficient numerical accuracy. Therefore, the all-order approach includes dominant MBPT terms to all orders.

Matrix elements for any one-body operator $Z = \sum_{ij} z_{ij} a_i^\dagger a_j$ are obtained within the framework of the all-order method as

$$Z_{wv} = \frac{\langle \Psi_w | Z | \Psi_v \rangle}{\sqrt{\langle \Psi_v | \Psi_v \rangle \langle \Psi_w | \Psi_w \rangle}}, \tag{11}$$

where $|\Psi_v\rangle$ and $|\Psi_w\rangle$ are given by the expansion (6). In the SD approximation, the resulting expression for the numerator of Eq. (11) consists of the sum of the Dirac-Fock (DF) matrix element z_{wv} and 20 other terms that are linear or qua-

dratic functions of the excitation coefficients. The advantage of this approach is that the expression in Eq. (11) does not depend on the nature of the operator Z, only on its rank and parity. Therefore, matrix elements of any one-body operator may be calculated with the same general code.

The complexity of the all-order formalism for matrix elements increases drastically with the number of valence electrons. We have derived the expression for all-order matrix elements in divalent systems; it contains several hundred terms instead of the 20 terms in the corresponding monovalent expression. Therefore, it is impractical to extend the all-order method to the case of more complicated atoms in its present implementation directly, i.e., to start a single-double expansion from the divalent lowest-order wave function containing $a_w^\dagger a_v^\dagger | \Psi_C \rangle$. Such an approach also leads to "intruder state" problems well known in the perturbation expansions based on the Rayleigh-Schrödinger implementation of the MBPT.

We note that the relativistic couple-cluster method has been successfully applied to the calculation of the energies and electron affinities in systems with few electrons (see Refs. [30–34] and references therein). It is rather difficult to apply this method for calculation of other atomic properties such as transition matrix elements. However, using the *finite field* technique one can use this method, for example, to calculate quadrupole hyperfine constants in such a heavy atoms as Au [35].

III. CI+MBPT METHOD

A combination of the CI method and perturbation theory was developed in Ref. [10]. It was based on the Dirac-Fock code [36] and CI code [37]. This approach has been later applied to the calculation of atomic properties of various systems in a number of works (see [11–18] and references therein). In Refs. [21,22], the CI+MBPT method was used to calculate PNC amplitudes in Tl and Yb, respectively (in the latter case, the nuclear-spin-dependent amplitude was calculated).

In the CI method, the many-electron wave function is obtained as a linear combination of all distinct states of a given angular momentum J and parity [16],

$$\Psi_J = \sum_i c_i \Phi_i, \tag{12}$$

in other words, a linear combination of Slater determinants of proper symmetry from a model subspace [10].

Energies and wave functions of low-lying states are determined by diagonalizing an effective Hamiltonian,

$$H^{\text{eff}} = H_1 + H_2, \tag{13}$$

where H_1 represents the one-body part of the Hamiltonian, and H_2 represents the two-body part (Coulomb or Coulomb + Breit matrix elements v_{ijkl}). We use Coulomb matrix elements g_{ijkl} in the present work. The resulting wave functions are used to calculate matrix elements and other properties such as polarizabilities, parity-violating amplitude, etc. The precision of the configuration-interaction method is drastically limited for large systems by the number of the configu-

rations that can be included. Consequently, core excitations are entirely omitted or only a small number is included, leading to a significant loss of accuracy for heavy atoms.

The CI+MBPT approach allows one to incorporate core excitations in the CI method by including certain higher-order terms in an effective Hamiltonian (13). The CI method is then applied as usual with the modified H^{eff} to obtain improved energies and wave functions. Somewhat different versions of the CI+MBPT method exist; here, we describe the approach used in the present work and follow the designations of Ref. [23].

In the CI+MBPT approach, the one-body part H_1 is modified to include the correlation potential Σ_1 that accounts for part of the core-valence correlations,

$$H_1 \rightarrow H_1 + \Sigma_1. \tag{14}$$

Either the second-order expression $\Sigma_1^{(2)}$ or all-order chains of such terms can be used (see, for example, Ref. [23]). The latter approach corresponds to replacing Dirac-Fock orbitals by Brueckner orbitals. The second-order matrix elements $(\Sigma_1^{(2)})_{yx}$ are given by

$$(\Sigma_1^{(2)})_{yx} = \sum_{mab} \frac{g_{myab}\widetilde{g}_{mxab}}{\epsilon_{ab} - \epsilon_{xm} + \widetilde{\epsilon}_y - \epsilon_y} + \sum_{mna} \frac{g_{mnxa}\widetilde{g}_{mnya}}{\widetilde{\epsilon}_y + \epsilon_a - \epsilon_{mn}}. \tag{15}$$

We use the same designations as in Sec. II; indices from the middle of the alphabet m and n range over all possible virtual states while indices a and b range over all occupied core states. The one-particle energies ϵ_i are written together as $\epsilon_{ij} = \epsilon_i + \epsilon_j$ for brevity. The summation over index i implies the sum over the quantum numbers $n_i \kappa_i m_i$.

The CI+MBPT approach is based on the Brillouin-Wigner variant of MBPT rather than the Rayleigh-Schrödinger variant. Use of the Rayleigh-Schrödinger MBPT for systems with more than one valence electron leads to a nonsymmetric effective Hamiltonian and to the problem of intruder states. In the Brillouin-Wigner variant, the effective Hamiltonian is symmetric and accidentally small denominators do not arise; however, Σ_1 and Σ_2 became energy dependent. Specifically, the one-body correction Σ_1 depends on the energy $\widetilde{\epsilon}_y$ [see Eq. (15)]. Ideally, the energy $\widetilde{\epsilon}_y$ should be calculated from the particular eigenvalue of the effective Hamiltonian (13). In practice, we use several approaches. The simplest and the most practical one is to set the energy $\widetilde{\epsilon}_y$ to the Dirac-Fock energy of the lowest orbital for the particular partial wave. For example, we use $\widetilde{\epsilon}_{ns} = \epsilon_{3s}$ for all ns orbitals of Mg system. This approximation usually works reasonably well for atomic states belonging to the lowest configurations of a given symmetry. Another approach is to set the energy of all orbitals for a particular partial wave to a certain value; one value is specified for each partial wave. This approach allows one to generate better atomic wave functions for subsequent evaluation of the atomic properties by selecting the values of $\widetilde{\epsilon}$ so final energy eigenstates are tuned to the experimental values. We have also developed a more elaborate method that involves calculating derivatives of the Σ_1 and Σ_2 with respect to $\widetilde{\epsilon}$ that allows to adjust the effective Hamiltonian as suggested in [10]. Our implementa-

tion of the CI + all-order method permits us to use any of these strategies.

Performing analytical sums over all magnetic quantum numbers yields the expression

$$(\Sigma_1^{(2)})_{yx} = -\sum_{mab} \sum_K \frac{1}{[K][j_y]} \frac{X_K(myab)Z_K(mxab)}{\epsilon_{ab} - \epsilon_{xm} + \widetilde{\epsilon}_y - \epsilon_y}$$
$$+ \sum_{mna} \sum_K \frac{1}{[K][j_y]} \frac{X_K(mnxa)Z_K(mnya)}{\widetilde{\epsilon}_y + \epsilon_a - \epsilon_{mn}}, \tag{16}$$

where K is multipolarity restricted by conventional triangular rules, $[K] = 2K+1$, and the summations over all lower-case indexes i now designate sums over n_i and κ_i. We use similar designations for the sums listed below to avoid explicitly writing out all quantum numbers in all sums. The quantity $X_K(mnab)$ is

$$X_K(mnab) = (-1)^K \langle \kappa_m \| C^K \| \kappa_a \rangle \langle \kappa_n \| C^K \| \kappa_b \rangle R_K(mnab), \tag{17}$$

where $R_K(mnab)$ are (relativistic) Slater integrals and $\langle \kappa_m \| C^K \| \kappa_a \rangle$ are reduced matrix elements of a normalized spherical harmonics. $Z_K(mnab)$ is given by

$$Z_K(mnab) = X_K(mnab) + \sum_{K'} [K] \begin{Bmatrix} j_m & j_a & K \\ j_n & j_b & K' \end{Bmatrix} X_{K'}(mnba). \tag{18}$$

The two-body Coulomb interaction term H_2 is modified by including the two-body part of the core-valence interaction that represents screening of the Coulomb interaction by valence electrons,

$$H_2 \rightarrow H_2 + \Sigma_2, \tag{19}$$

where Σ_2 is calculated in the second-order MBPT in CI +MBPT approach. The second-order matrix elements $(\Sigma_2^{(2)})_{mnvw}$ are given by

$$(\Sigma_2^{(2)})_{mnvw} = \sum_{cd} \frac{g_{vwcd}g_{mncd}}{\epsilon_{cd} - \epsilon_{mn} + \widetilde{\epsilon}_v - \epsilon_v + \widetilde{\epsilon}_w - \epsilon_w}$$
$$+ \left[\sum_{rc} \frac{\widetilde{g}_{wrnc}\widetilde{g}_{mrvc}}{\widetilde{\epsilon}_v + \epsilon_c - \epsilon_{mr} + \widetilde{\epsilon}_w - \epsilon_w} + \begin{pmatrix} m & \Leftrightarrow & n \\ v & \Leftrightarrow & w \end{pmatrix} \right]. \tag{20}$$

Performing an angular reduction leads to

$$(\Sigma_2^{(2)})_K(mnvw)$$
$$= \sum_{cd} \sum_{LK'} [K] \begin{Bmatrix} j_m & j_v & K \\ L & K' & j_c \end{Bmatrix} \begin{Bmatrix} j_n & j_w & K \\ L & K' & j_d \end{Bmatrix}$$
$$\times \frac{X_L(vwcd)X_{K'}(cdmn)}{\epsilon_{cd} - \epsilon_{mn} + \widetilde{\epsilon}_v - \epsilon_v + \widetilde{\epsilon}_w - \epsilon_w}$$
$$- \sum_{rc} \frac{(-1)^{j_w+j_n+K}}{[K]} \frac{Z_K(wrnc)Z_K(mrvc)}{\widetilde{\epsilon}_v + \epsilon_c - \epsilon_{mr} + \widetilde{\epsilon}_w - \epsilon_w}$$
$$- \sum_{rc} \frac{(-1)^{j_v+j_m+K}}{[K]} \frac{Z_K(vrmc)Z_K(nrwc)}{\widetilde{\epsilon}_w + \epsilon_c - \epsilon_{nr} + \widetilde{\epsilon}_v - \epsilon_v}. \tag{21}$$

MBPT corrections associated with terms Σ_1 in Eq. (14) and Σ_2 in Eq. (19) typically grow with nuclear charge Z leading to a deterioration of the accuracy of the CI + second-order MBPT results for heavier more complicated systems. The order-by-order extension of this method does not look promising for two reasons. First, the complexity of the MBPT expansion for systems with more than one valence electron already makes third-order calculations impractical. Second, the convergence of the MBPT series is not well studied, but it is known that the third order is often less accurate than the second order. This is why it was so important to develop an all-order extension of the MBPT method for monovalent systems.

IV. CI + ALL-ORDER METHOD

In the CI + all-order approach, corrections to the effective Hamiltonian Σ_1 and Σ_2 are calculated using the all-order method, in which the effective Hamiltonian contains dominant core and core-valence correlation corrections to all orders, as discussed in Sec. II. The core-core and core-valence sectors of the correlation corrections for systems with few valence electrons are treated in the all-order method with the same accuracy as in the all-order approach for the monovalent systems. The CI method is then used to evaluate valence-valence correlations.

First, we express the all-order equations (8)–(10) in terms of matrix elements of Σ_1 and Σ_2 and explicitly include the

energy dependence. We also need to add an all-order equation for the excitation coefficients ρ_{mnvw} to obtain Σ_2. This equation is equivalent to Eq. (9) with core index b replaced by valence index w.

Σ_1 and Σ_2 are essentially the all-order excitation coefficients ρ_{mv} and ρ_{mnvw},

$$\Sigma_{ma} = \rho_{ma}(\epsilon_a - \epsilon_m),$$

$$\Sigma_{mnab} = \rho_{mnab}(\epsilon_{ab} - \epsilon_{mn}),$$

$$\Sigma_{mnva} = \rho_{mnva}(\widetilde{\epsilon}_v + \epsilon_a - \epsilon_{mn}),$$

$$\Sigma_{mv} \equiv (\Sigma_1)_{mv} = \rho_{mv}(\widetilde{\epsilon}_v - \epsilon_m),$$

$$\Sigma_{mnvw} \equiv (\Sigma_2)_{mnvw} = \rho_{mnvw}(\widetilde{\epsilon}_v + \widetilde{\epsilon}_w - \epsilon_{mn}).$$

The quantities Σ_{ma}, Σ_{mnab}, and Σ_{mnva} are used in the all-order iteration procedure but do not explicitly appear in the effective Hamiltonian. The core equations for ρ_{ma} and ρ_{mnab} are not modified from the original all-order monovalent code. The excitation coefficients ρ_{ma} and ρ_{mnab} are simply multiplied by the appropriate energy differences to obtain the terms Σ_{ma} and Σ_{mnab} needed by other programs. Rewriting the other all-order equations in terms of Σ and removing terms that will be otherwise double counted by the CI part of the calculations, we obtain the following set of equations:

$$\Sigma_{mv} \equiv (\Sigma_1)_{mv} = \sum_{nb} \frac{\widetilde{g}_{mbvn}\Sigma_{nb}}{\epsilon_{bn} + \widetilde{\epsilon}_v - \epsilon_v} - \sum_{bcn} \frac{\widetilde{g}_{bcvn}\Sigma_{mnbc}}{\epsilon_{bc} - \epsilon_{mn} + \widetilde{\epsilon}_v - \epsilon_v} + \sum_{bnr} \frac{\widetilde{g}_{mbnr}\Sigma_{nrvb}}{\widetilde{\epsilon}_v + \epsilon_b - \epsilon_{nr}}, \tag{22}$$

$$\Sigma_{mnvb} = g_{mnvb} + \sum_{cd} \frac{g_{cdvb}\Sigma_{mncd}}{\epsilon_{cd} - \epsilon_{mn} + \widetilde{\epsilon}_v - \epsilon_v} + \sum_{rs} \frac{g_{mnrs}\Sigma_{rsvb}}{\widetilde{\epsilon}_v + \epsilon_b - \epsilon_{rs}} - \sum_c \frac{g_{cnvb}\Sigma_{mc}}{\epsilon_c - \epsilon_m + \widetilde{\epsilon}_v - \epsilon_v} + \sum_r \frac{g_{mnvr}\Sigma_{rb}}{\epsilon_b - \epsilon_r + \widetilde{\epsilon}_v - \epsilon_v}$$

$$- \sum_c \frac{g_{mcvb}\Sigma_{nc}}{\epsilon_c - \epsilon_n + \widetilde{\epsilon}_v - \epsilon_v} + \sum_{cr} \frac{\widetilde{g}_{cnrb}\Sigma_{mrvc}}{\widetilde{\epsilon}_v + \epsilon_c - \epsilon_{mr}} - \sum_{cr} \frac{g_{cnrb}\Sigma_{rmvc}}{\widetilde{\epsilon}_v + \epsilon_c - \epsilon_{mr}} - \sum_{cr} \frac{g_{mcrb}\Sigma_{rnvc}}{\widetilde{\epsilon}_v + \epsilon_c - \epsilon_{nr}}$$

$$+ \sum_{cr} \frac{\widetilde{g}_{mcvr}\Sigma_{rncb}}{\epsilon_{cb} - \epsilon_{nr} + \widetilde{\epsilon}_v - \epsilon_v} - \sum_{cr} \frac{g_{mcvr}\Sigma_{nrcb}}{\epsilon_{cb} - \epsilon_{nr} + \widetilde{\epsilon}_v - \epsilon_v} - \sum_{cr} \frac{g_{cnvr}\Sigma_{mrcb}}{\epsilon_{cb} - \epsilon_{mr} + \widetilde{\epsilon}_v - \epsilon_v}, \tag{23}$$

$$\Sigma_{mnvw} \equiv (\Sigma_2)_{mnvw} = \sum_{cd} \frac{g_{cdvw}\Sigma_{mncd}}{\epsilon_{cd} - \epsilon_{mn} + \widetilde{\epsilon}_v - \epsilon_v + \widetilde{\epsilon}_w - \epsilon_w} - \sum_c \frac{g_{cnvw}\Sigma_{mc}}{\epsilon_c - \epsilon_m + \widetilde{\epsilon}_v - \epsilon_v + \widetilde{\epsilon}_w - \epsilon_w} - \sum_c \frac{g_{mcvw}\Sigma_{nc}}{\epsilon_c - \epsilon_n + \widetilde{\epsilon}_v - \epsilon_v + \widetilde{\epsilon}_w - \epsilon_w}$$

$$+ \sum_{cr} \frac{\widetilde{g}_{cnrw}\Sigma_{mrvc}}{\widetilde{\epsilon}_v + \epsilon_c - \epsilon_{mr} + \widetilde{\epsilon}_w - \epsilon_w} - \sum_{cr} \frac{g_{cnrw}\Sigma_{rmvc}}{\widetilde{\epsilon}_v + \epsilon_c - \epsilon_{mr} + \widetilde{\epsilon}_w - \epsilon_w} - \sum_{cr} \frac{g_{mcrw}\Sigma_{rnvc}}{\widetilde{\epsilon}_v + \epsilon_c - \epsilon_{nr} + \widetilde{\epsilon}_w - \epsilon_w}$$

$$+ \sum_{cr} \frac{\widetilde{g}_{mcvr}\Sigma_{rncw}}{\epsilon_c + \widetilde{\epsilon}_w - \epsilon_{nr} + \widetilde{\epsilon}_v - \epsilon_v} - \sum_{cr} \frac{g_{mcvr}\Sigma_{rnwc}}{\epsilon_c + \widetilde{\epsilon}_w - \epsilon_{nr} + \widetilde{\epsilon}_v - \epsilon_v} - \sum_{cr} \frac{g_{cnvr}\Sigma_{rmwc}}{\epsilon_c + \widetilde{\epsilon}_w - \epsilon_{mr} + \widetilde{\epsilon}_v - \epsilon_v}. \tag{24}$$

The energy denominators are now explicitly written out and the energy dependence is introduced following the prescription of the CI + second-order MBPT approach. Putting $\tilde{\epsilon}_v = \epsilon_v$ yields the original all-order equations (8) and (9) for monovalent systems up to δE_v terms on the left-hand side. The term containing ρ_{rv} is removed from Eq. (23) since it is included in the CI calculation. Equation (24) for Σ_{mnvw} does not have terms that would corresponds to the first, third, and fifth terms of Eq. (23) for Σ_{mnva} since these terms are accounted for by the CI as well. Therefore, no iteration is required in the last equation since Σ_{mnvw} does not appear on its right-hand side; the last equation needs to be evaluated only once after all other equations have converged. The last equation is also significantly faster to evaluate than similar equations for Σ_{mnab} and Σ_{mnva} since it does not contain the term with four indexes over the virtual orbitals [term 3 in Eq. (23)]. We note that this is the only equation that is not present in any form in the all-order code for monovalent systems.

Below, we outline a step-by-step application of the CI + all-order method.

Step 1: a finite basis set is generated in a spherical cavity of radius R. All calculations are carried out with same basis set. The second-order MBPT is used to generate $(\Sigma_1^{(2)})_{vw}$ and $(\Sigma_2^{(2)})_{mnvw}$, where m,n,v,w are any basis set functions. Highly excited orbitals can be omitted without loss of accuracy. A subset of the basis set orbitals is selected for which all-order values of $(\Sigma_1)_{vw}$ and $(\Sigma_2)_{mnvw}$ are to be obtained. In our calculation, this set includes the first three ns, $np_{1/2}$, $np_{3/2}$, $nd_{3/2}$, and $nd_{5/2}$ states for each system. We found that the inclusion of the additional orbitals did not significantly change the results and treating the remaining corrections to the effective Hamiltonian in the second order should be sufficiently accurate. This issue is addressed in more detail in the next section.

Step 2: the all-order core ρ_{ma} and ρ_{mnab} excitation coefficients are obtained by the iterative solution of the corresponding equations in the appropriate potential (for example, V^{N-2} for divalent systems) in the same way as for monovalent systems. The core correlation energy is used as a convergence parameter and is generally required to converge to 10^{-5} relative accuracy. The core excitation coefficients are multiplied by the appropriate denominators as described above to obtain Σ_{ma} and Σ_{mnab} after the iterations are complete.

Step 3: the core quantities Σ_{ma} and Σ_{mnab} are used to obtain Σ_{mv} and Σ_{mnva}, again by an iteration procedure, for a large number of excited m,n, and v orbitals. The valence correlation energy for the state v is used as a convergence parameter. These steps are carried out in exactly the same way as our present monovalent all-order calculations with the omission of the valence-valence diagrams as described above. The iterations of excitation coefficients result in the summation of the relevant classes of MBPT terms to all orders. We note that the term Σ_{mv} gives the all-order correction to the one-body part of the effective Hamiltonian.

Step 4: the all-order expression for $(\Sigma_2)_{mnvw}$ corrections to the effective Hamiltonian is calculated using Eq. (24) with previously stored fully converged values of Σ_{ma}, Σ_{mnab}, and Σ_{mnvb}.

Step 5: CI calculations are carried out to generate accurate wave functions with the effective Hamiltonian constructed using Σ_1 and Σ_2 obtained in the previous steps.

Step 6: the resulting wave functions are used to obtain various matrix elements and derived quantities such as PNC amplitudes. In the current CI+MBPT approach [16], matrix elements are calculated by replacing "bare" matrix elements by the "dressed" matrix elements using the random-phase approximations (RPA). In this work, we use the same approach. This issue will be further discussed in the next section.

The method described above treats electronic correlation in systems with several valence electrons in a significantly more complete way than the CI+MBPT approach owing to the inclusion of the additional classes of MBPT terms in Σ_1 and addition of all-order (rather than second-order) correction in Σ_2. We note that our present all-order code is capable of efficiently evaluating the large number of the core-valence all-order excitation coefficients needed for the implementation of the CI + all-order approach.

V. RESULTS AND DISCUSSIONS

We compare the results of our CI, CI+MBPT, and CI + all-order *ab initio* calculations for the two-electron binding energies of Mg, Ca, Zn, Sr, Cd, Ba, and Hg with experiment in Table I. Results for the energies of Mg, Ca, Cd, and Ba counted from the ground state are compared with experiment in Table II. The same designations are used in both tables. The energy values are given in cm^{-1}. Relative differences of our results with experiment are given in the last three columns of Tables I and II to illustrate the accuracy of each approach.

The same parameters and basis set are used in all three calculations for each system. The finite basis set of 245 orbitals that include $l = 0, \ldots, 5$ partial waves is formed in the spherical cavity with a 50 a.u. radius. The CI calculation includes only valence shell excitations as described above, i.e., CI calculation is carried out in the same way for all three cases. All summations over the excited states in the second-order and the all-order calculations are always carried out over the entire basis set.

A sufficiently large number of the effective Hamiltonian matrix elements is modified in the CI + second-order MBPT calculation. There is no need to include corrections to the entire Hamiltonian as the corrections from the remaining terms are negligible as described below. The CI + all-order calculations include the replacement of the most important Σ_1 and Σ_2 terms by their all-order values. The remaining corrections from the effective Hamiltonian retain their second-order values as described above. We find that it is sufficient to carry out all-order calculations for the first three ns, $np_{1/2}$, $np_{3/2}$, $nd_{3/2}$, and $nd_{5/2}$ states and modify the corresponding Σ_1 and Σ_2. For example, indexes m,n,v,w in $(\Sigma_1)_{mv}$ and $(\Sigma_2)_{mnvw}$ in Ca calculation include $4s$, $5s$, $6s$, $4p_{1/2}$, $5p_{1/2}$, $6p_{1/2}$, $4p_{3/2}$, $5p_{3/2}$, $6p_{3/2}$, $3d_{3/2}$, $4d_{3/2}$, $5d_{3/2}$, $3d_{5/2}$, $4d_{5/2}$, and $5d_{5/2}$ states. To test that the above number of the corrected Hamiltonian matrix elements is sufficient, we have carried out the following test in Ca:

TABLE I. Comparison of the CI, CI+MBPT, and CI + all-order *ab initio* results for the two-electron binding energies of Mg, Ca, Zn, Sr, Cd, Ba, and Hg with experiment. The energies are given in cm^{-1}. The relative difference with experimental values is given in the last three columns in %.

Element	State	Energies				Differences with experiment (%)		
		Expt.	CI	CI+MBPT	CI + all-order	CI	CI+MBPT	CI + all-order
Mg	$3s^2\ ^1S_0$	182939	179537	182717	182877	1.86	0.12	0.03
Ca	$4s^2\ ^1S_0$	145058	139068	145985	145517	4.13	−0.64	−0.32
Zn	$4s^2\ ^1S_0$	220662	204083	218521	219442	7.51	0.97	0.55
Sr	$5s^2\ ^1S_0$	134896	127858	136082	135322	5.22	−0.88	−0.32
Cd	$5s^2\ ^1S_0$	208915	188884	210716	208620	9.59	−0.86	0.14
Ba	$6s^2\ ^1S_0$	122721	114898	124956	123363	6.37	−1.82	−0.52
Hg	$6s^2\ ^1S_0$	235469	207652	241152	236626	11.81	−2.41	−0.49

(1) the number of second-order Σ_1 and Σ_2 matrix elements included was increased from 535 to 878 and from 4 879 832 to 19 236 743, respectively;

(2) the number of second-order Σ_1 and Σ_2 matrix elements replaced by all-order values was increased from 168 to 305 and from 592 634 to 2 898 122, respectively, by including the $7s$, $7p_{1/2}$, $7p_{3/2}$, $6d_{3/2}$, $6d_{5/2}$, $4f_{5/2}$, $4f_{7/2}$, $5f_{5/2}$, and $5f_{7/2}$ states into the m, n, v, w index set.

The ionization potential and most of the Ca levels that we considered shifted by less than 1 cm^{-1}. The largest changes observed for the $4s3d$ levels were still very small, 0.1%. This was expected since the nd levels are known to be the most affected by the partial-wave restrictions. We note that the energies $\tilde{\epsilon}_v$ and $\tilde{\epsilon}_w$ in Eqs. (22)–(24) were set in the present calculation to the corresponding Dirac-Fock values for the lowest state for each partial wave. The second-order calculations were carried out in the same way. Therefore, the results listed in Tables I and II are completely *ab initio*.

We find that the all-order ionization potential results are in significantly better agreement with experiment in comparison with the CI+MBPT values even in the case of Mg, where the agreement with experiment is already excellent in the CI+MBPT approach. We also find almost no deterioration in the accuracy of the two-electron binding energies from Ca to Hg; the all-order method reduces the differences with experiment by about a factor of 3 in comparison with the second-order data. Similar improvements are observed for most of the excited states listed in Table II with the exception of $5d6s$ states of Ba. The accuracy of the SD all-order approach is expected to be lower for Ba since the SD method omits certain parts of the third-order energy correction associated with valence triple excitations [last term in Eq. (6)]. This contribution was found to increase significantly for heavier alkalis [2]. The problem is corrected in the SD all-order method by explicitly adding the missing part of the third-order correction. Within our approach, this issue may be treated in an *ab initio* way by adding the valence triple excitation terms perturbatively to the all-order as was done for the monovalent systems in Ref. [2] and removing terms that are accounted for by the CI. We note that a factor of 3 improvement in the relative differences with experiment is still observed for the $6s\,6p$ energies calculated with the all-order method.

We observe that essentially all of the states in Ba listed in Table II are shifted by the same relative amount in the all-order approach, unlike the case of CI+MBPT. In this case, it is possible to carry out another calculation with different $\tilde{\epsilon}_v$ and $\tilde{\epsilon}_w$ resulting in final energies in very close agreement with experiment in order to get an improved representation of the wave functions for subsequent evaluation of atomic properties. The results of such a calculation for Ba are given in Table III. The one-particle $\tilde{\epsilon}$ energies for ns and np orbitals in this calculation are set to $\tilde{\epsilon}_{ns} = -0.48$ a.u. and $\tilde{\epsilon}_{np_{1/2,3/2}} = -0.40$ a.u., the energies for the other partial waves are set to the Dirac-Fock values for the lowest orbital just as in the previous calculation. The results of this calculation are in excellent agreement with experiment. Moreover, the $\Delta(^3D_1 - {}^3P_0)$ energy difference, which is very difficult to accurately calculate agrees with experiment to 11 cm^{-1}.

Our calculations have yielded accurate wave functions for subsequent evaluation of the atomic properties. Matrix elements of one-body operators such as E1, E2, hyperfine, parity violation, etc., are evaluated in the framework of the CI+MBPT approach in the RPA approximation [10] (as described in step 6 of the previous section), sometimes with subsequent addition of the dominant normalization and structure radiation terms. In the CI + all-order method, we can use exactly the same method to evaluate matrix elements. Our preliminary calculations of the $^3P_0$ polarizability values for Ca and Sr indicate better agreement of the CI + all-order *ab initio* results with recommended values from Ref. [38] in comparison with the CI+MBPT approach. The complete implementation of the all-order approach would require an addition of the all-order corrections to the matrix elements beyond the modification of the wave function that is the subject of the present paper. This approach will implicitly include dominant normalization, structure radiation, and other corrections to all orders. In further work, we plan to replace the RPA matrix elements by all-order counterparts that are linear or quadratic functions of the excitation coefficients [2]. The terms that are accounted by the CI will have to be removed to avoid double counting. The ability to conduct calculations in various approximations will also allow one to carry out the evaluation of uncertainties of atomic properties needed for many applications such as the calcula-

TABLE II. Comparison of the CI, CI+MBPT, and CI + all-order *ab initio* results for the energy levels of Mg, Ca, Cd, and Ba with experiment. Two-electron binding energies are given in the first row for each element; the other values are counted from the ground-state energy. The energies are given in cm^{-1}. The relative difference with experimental values is given in the last three columns in %.

Element	State	Energies				Differences with experiment (%)		
		Expt.	CI	CI+MBPT	CI + all-order	CI	CI+MBPT	CI + all-order
Mg	$3s^2\ ^1S_0$	182939	179537	182717	182877	1.86	0.12	0.03
	$3s4s\ ^3S_1$	41197	40409	41132	41175	1.91	0.16	0.05
	$3s4s\ ^1S_0$	43503	42689	43459	43502	1.87	0.10	0.00
	$3s3d\ ^1D_2$	46403	45119	46318	46384	2.77	0.18	0.04
	$3s3d\ ^3D_1$	47957	46972	47892	47936	2.05	0.14	0.04
	$3s3d\ ^3D_2$	47957	46972	47892	47936	2.05	0.14	0.04
	$3s3d\ ^3D_3$	47957	46972	47892	47936	2.05	0.14	0.04
	$3s3p\ ^3P_0$	21850	20906	21780	21833	4.32	0.32	0.08
	$3s3p\ ^3P_1$	21870	20926	21801	21852	4.32	0.32	0.08
	$3s3p\ ^3P_2$	21911	20967	21844	21897	4.31	0.30	0.07
	$3s3p\ ^1P_1$	35051	34488	35053	35065	1.61	0.00	−0.04
Ca	$4s^2\ ^1S_0$	145058	139068	145985	145517	4.13	−0.64	−0.32
	$3d4s\ ^3D_1$	20335	24200	19927	20335	−19.00	2.01	0.00
	$3d4s\ ^3D_2$	20349	24201	19949	20355	−18.93	1.97	−0.03
	$3d4s\ ^3D_3$	20371	24203	19982	20386	−18.81	1.91	−0.07
	$3d4s\ ^1D_2$	21850	23853	21620	21965	−9.17	1.05	−0.53
	$4s5s\ ^3S_1$	31539	30147	31765	31694	4.42	−0.72	−0.49
	$4s5s\ ^1S_0$	33317	31893	33552	33466	4.27	−0.70	−0.45
	$4s4p\ ^3P_0$	15158	13509	15474	15338	10.88	−2.08	−1.19
	$4s4p\ ^3P_1$	15210	13557	15528	15385	10.87	−2.09	−1.15
	$4s4p\ ^3P_2$	15316	13655	15638	15498	10.85	−2.10	−1.19
	$4s4p\ ^1P_1$	23652	23052	23771	23729	2.54	−0.50	−0.32
Cd	$5s^2\ ^1S_0$	208915	188884	210716	208620	9.59	−0.86	0.14
	$5s6s\ ^3S_1$	51484	44027	51916	51395	14.48	−0.84	0.17
	$5s6s\ ^1S_0$	53310	46153	53788	53272	13.43	−0.90	0.07
	$5s5d\ ^1D_2$	59220	50634	59697	59015	14.50	−0.81	0.35
	$5s5d\ ^3D_1$	59486	51292	59881	59259	13.77	−0.66	0.38
	$5s5d\ ^3D_2$	59498	51303	59893	59271	13.77	−0.66	0.38
	$5s5d\ ^3D_3$	59516	51320	59911	59291	13.77	−0.66	0.38
	$5s5p\ ^3P_0$	30114	24417	30903	30141	18.92	−2.62	−0.09
	$5s5p\ ^3P_1$	30656	24875	31451	30646	18.86	−2.59	0.03
	$5s5p\ ^3P_2$	31827	25833	32656	31838	18.83	−2.60	−0.03
	$5s5p\ ^1P_1$	43692	38902	43970	43607	10.96	−0.64	0.20
Ba	$6s^2\ ^1S_0$	122721	114898	124956	123363	6.37	−1.82	−0.52
	$6s5d\ ^3D_1$	9034	11524	9276	9249	−27.57	−2.67	−2.38
	$6s5d\ ^3D_2$	9216	11603	9489	9441	−25.91	−2.97	−2.45
	$6s5d\ ^3D_3$	9597	11780	9941	9840	−22.75	−3.59	−2.54
	$6s5d\ ^1D_2$	11395	12753	11878	11727	−11.92	−4.24	−2.91
	$6s6p\ ^3P_0$	12266	9938	13112	12556	18.98	−6.90	−2.36
	$6s6p\ ^3P_1$	12637	10269	13484	12919	18.73	−6.70	−2.23
	$6s6p\ ^3P_2$	13515	11010	14391	13819	18.53	−6.48	−2.25
	$6s6p\ ^1P_1$	18060	16908	18621	18292	6.38	−3.11	−1.28

TABLE III. Comparison of the CI + all-order results for the energy levels of Ba with experiment. Two-electron binding energies are given in the first row; the other values are counted from the ground state. The one-particle $\tilde{\epsilon}$ energies for ns and np orbitals are set to $\tilde{\epsilon}_{ns}=-0.48$ a.u. and $\tilde{\epsilon}_{np_{1/2,3/2}}=-0.40$ a.u.; the energies for the other partial waves are set to the Dirac-Fock values for the lowest orbital. The energies are given in cm^{-1}. The relative difference with experimental values is given in the last column in %.

State	Expt.	CI + all-order	Δ (%)
$6s^2\ ^1S_0$	122721	122757	−0.03
$6s5d\ ^3D_1$	9034	9012	0.25
$6s5d\ ^3D_2$	9216	9202	0.14
$6s5d\ ^3D_3$	9597	9603	−0.07
$6s5d\ ^1D_2$	11395	11407	−0.11
$6s6p\ ^3P_0$	12266	12235	0.26
$6s6p\ ^3P_1$	12637	12602	0.27
$6s6p\ ^3P_2$	13515	13491	0.18
$6s6p\ ^1P_1$	18060	18120	−0.33
$5d6p\ ^3F_2$	22065	22201	−0.62
$5d6p\ ^3F_3$	22947	23174	−0.99
$5d6p\ ^3F_4$	23757	24005	−1.04
$\Delta(^3D_1-^3P_0)$	3232	3223	0.28

tion of black-body radiation shifts and the study of fundamental symmetries.

VI. CONCLUSION

We have developed a theoretical method combining the all-order approach currently used in precision calculations of properties of monovalent atoms with the configuration-interaction approach that is applicable for many-electron systems. This approach has been tested on the calculation of energy levels of divalent systems from Mg to Hg. We have demonstrated an improvement of at least a factor of 3 in agreement with experimental values for the two-electron binding energies and most excited-state energies in comparison with the CI+MBPT method. Further work on this method will include an addition of the all-order terms beyond the RPA in the treatment of the transition amplitudes and other matrix elements for the precision calculation of atomic properties of systems with few valence electrons.

ACKNOWLEDGMENTS

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