Atomic Calculations for Future Technology and Study of Fundamental Problems

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Abstract. Selected modern applications of the atomic calculations ranging from the study of fundamental interactions to applications of atomic physics to future technological developments are reviewed. The coupled-cluster approach to high-precision calculation of various atomic properties of monovalent systems is discussed. The computational challenges in the implementation of the all-order approaches including the development of the computer programs capable of performing complicated symbolic calculations, automatic generation of the computer codes are discussed. Novel approach to calculation of the atomic properties of more complicated systems that combines configuration interaction and all-order methods is discussed and preliminary results are presented.

INTRODUCTION

One of the unique attractions of atomic physics is the possibility of the extremely accurate theoretical predictions and stingiest experimental tests of those predictions. There are numerous observable quantities which can be accurately calculated and measured. The advancements in the experimental technologies and further development of the high-precision atomic theory methodologies lead not only to our better understanding of atomic properties but also to remarkable opportunities for applications in many areas. In this talk, I report on various modern applications of the atomic calculations ranging from the study of fundamental interactions to applications of atomic physics to future technological developments, such as quantum computing and optical atomic clocks.

One of such applications is the study of fundamental symmetries with atomic systems. For example, the study of parity nonconservation (PNC) in cesium provided an atomic-physics test of the standard model of the electroweak interactions and tested our understanding of weak hadronic interactions. Another test of fundamental science where atomic physics calculations are important is the search for the variation of the fundamental constants, such as fine-structure constant.

In this talk, I also review applications of the atomic calculations to the fields of quantum information and atomic clocks. Quantum computation is a new field of research that is aimed at using quantum nature of matter to produce fundamentally new methods of computation and simulation of physical systems. New generation of atomic clocks, based on optical rather than microwave frequency standards will allow to increase the accuracy and stability of the atomic clocks by orders of magnitude and will lead to new technological and scientific developments such as tracking of deep-space probes, searches for gravitational waves and nonlinearity of the quantum mechanics, as well as other applications.

The applications mentioned above require precise calculations of atomic properties and evaluation of the accuracy of the results. I describe the computational challenges in the implementation of the computational methods used by our group including the development of the computer programs capable of performing complicated symbolic calculations and automatic generation of the computer codes.

SELECTED APPLICATIONS OF THE ATOMIC CALCULATIONS

Study of fundamental symmetries with heavy atoms

There are two separate reasons for PNC studies in an atom: to search for new physics beyond the standard model of the electroweak interaction by precise evaluation of the weak charge Q_w, and to probe parity violation in the nucleus

by evaluating the nuclear anapole moment. The study of PNC in cesium involving both high-precision measurement [1] and several high-precision calculations provided an atomic-physics test of the standard model of the electroweak interactions [2]. To conduct such a test, both high-precision theory and experiment were required.

The precise measurement of PNC amplitudes in Cs [1] also led to an experimental value of the small contribution from the nuclear-spin dependent PNC accurate to 14%. The constraints on weak nucleon-nucleon coupling constants derived from this experiment and calculations in Cs were found to be inconsistent with constraints from deep inelastic scattering and other nuclear experiments [3, 4]. This analysis was based on the calculations of the spin-depended PNC amplitude from [5, 6].

The spin-dependent contribution to the PNC amplitude has three distinct sources: the nuclear anapole moment, the Z exchange interaction from nucleon axial-vector currents ($A_n V_e$), and the combined action of the hyperfine interaction and spin-independent Z exchange from nucleon vector ($V_n A_e$) currents. The anapole moment contribution strongly dominates. The first two of the above-mentioned interactions can be represented by the same Hamiltonian

$$H^{(i)} = \frac{G}{\sqrt{2}} \kappa_i \boldsymbol{\alpha} \cdot \boldsymbol{I} \rho(r),$$

(1)

where the subscript $i = a, 2$ refers to the anapole moment and the axial-vector contributions, respectively. In the equation above, G is the universal weak coupling constant, $\boldsymbol{I}$ is the nuclear spin, and $\rho(r)$ is a normalized density function. The dimensionless constant κ_a is used to characterize anapole moment [4].

We have carried out preliminary all-order calculation of the spin-dependent PNC amplitude in Cs in an attempt to understand discrepancies in weak nucleon-nucleon coupling constants derived from atomic and nuclear experiments. We find that individual PNC matrix elements significantly change with more complete inclusion of the correlation corrections, whereas changes in the total spin-dependent PNC amplitude are relatively small. Our preliminary value of the anapole coupling constant $\kappa_a = 0.88(12)$ Ref. [7] is only 5% lower than the value used by Haxton and Wieman [3].

More PNC experiments in other atomic systems, such as Ba^+, Yb, Fr are currently in progress. The experiments in Pb, Bi, and Tl have been conducted but no theoretical calculations of comparable accuracy exist to allow to fully analyze those experiments to test the standard model.

Another test of the fundamental physics where the atomic physics calculations are important is the search for the variation of the fundamental constants, such as fine-structure constant [8]. The astrophysical approach to such test (involving looking at the spectra of distant objects) requires the calculation of the isotope shifts in many systems since the possible changes in isotopic abundances with time may mimic the variance in the value of the fine-structure constant. The calculations of the isotope shifts also can be used to infer the difference in the values of the charge radii between different isotopes which both provides importance information for the nuclear physics and for the PNC experiments with chains of isotopes.

Quantum Information

Quantum computation is a field of research which is aimed at using quantum nature of matter to produce fundamentally new methods of computation. The quantum computer is a device which manipulates quantum states in order to solve a computational problem. Quantum computers may be used to solve various problems, ranging from simulating quantum systems to breaking widely used RSA encryption, currently intractable on the best classical computers.

There are various approaches to the experimental realization of the quantum computation. In the quantum computation scheme with neutral atoms the qubits are realized as internal states of neutral atoms trapped in optical lattices or microtraps. This approach to quantum computation has many advantages, such as scalability, possible massive parallelism, long decoherence times of the internal states of the atoms, flexibility in controlling atomic interactions, and well-developed experimental techniques.

One of the possible quantum logic gates to be considered is a Rydberg gate [9], realized by excitations to Rydberg states. The choice of this particular scheme results from its potential for fast (sub-microsecond) gate operations. In the Rydberg gate scheme, the basic qubit is based on two ground hyperfine states of neutral atoms confined in an optical lattice. A two-qubit phase gate may be realized by conditionally exciting two atoms to relatively low-lying Rydberg states.

One of the requirements for the experimental realization of the scalable quantum computer is the design of quantum gate with low error rate which will allow for error correction. Therefore, it is important to study various decoherence

mechanisms and search for ways to optimize gate performance. The atomic calculations are needed for understanding of various decoherence mechanisms and realizing schemes for optimization of gate operations.

There are different proposals for specific realization of Rydberg gate citeRgate. In those schemes, either one or both atoms may occupy the Rydberg state for much of the duration of the gate operation. However, an atom in a Rydberg state will, in general, move in different optical lattice potential than that experienced by the ground state. Therefore, the vibrational state of the atom in the lattice may change after the gate operation is completed, leading to decoherence due to motional heating. The optical potential for a given state depends on its ac polarizability, so we can seek to minimize this motional heating effect by the choice of a particular Rydberg state or of the lattice photon frequency ω. We described a method for accomplishing this by matching the frequency-dependent polarizabilities $\alpha(\omega)$ of the atomic ground state and Rydberg state [10].

One of the current goals of the quantum information projects is to design an apparatus capable of interconnecting "flying" and "stationary" qubits. The ability to trap neutral atoms inside high-Q cavities in the strong coupling regime is of particular importance for such schemes. In a far-detuned optical dipole trap, the potential experienced by an atom can be either attractive or repulsive depending on the sign of the ac Stark shift due to the trap light. The excited states may experience an ac Stark shift with an opposite sign of the ground state Stark shift affecting the fidelity of the experiments.

We evaluated the magic wavelengths in Na, K, Rb, and Cs atoms for which the ns ground state and either of the first two np_j excited states experience the same optical potential for state-insensitive cooling and trapping [11]. We accomplished this by matching the ac polarizabilities of the atomic ns and np_j states. We conducted extensive calculations of the relevant electric-dipole matrix elements using the relativistic all-order method and evaluated the uncertainties of the resulting ac polarizabilities.

We also proposed to design schemes to minimize decoherence by using two-color light for state-insensitive trapping at convenient wavelengths. In such scheme, a combination of trapping and control lasers will allow to minimize the variance of the potential experienced by the atom in ground and excited states leading to minimizing the resulting decoherence [12].

Atomic clocks

The current definition of a second in the International System of Units (SI) is based on the microwave transition between the two hyperfine levels of the ground state of ^{133}Cs [13]. The present relative standard uncertainty of Cs microwave frequency standard is around 5×10^{-16}. More precise frequency standards will open ways to improve global positioning systems and tracking of deep-space probes, and perform more accurate measurements of the fundamental constants and postulates of physics. The frequencies of feasible optical clock transitions are five orders of magnitude greater than the standard microwave transitions. Therefore, optical frequency standards may achieve even smaller relative uncertainties. Significant recent progress in optical spectroscopy and measurement techniques has led to the achievement of relative standard uncertainties in optical frequency standards that are comparable to the Cs microwave benchmark. With extremely low systematic perturbations and better stability and accuracy, such optical frequency standards can reach a systematic fractional uncertainty of the order of 10^{-18} [14, 15]. Currently, the ultranarrow electric-dipole forbidden transitions in single trapped ^{199}Hg$^+$ [14, 16], ^{88}Sr$^+$ [17, 18], ^{171}Yb$^+$ ions, and ^{87}Sr [19, 20] atoms have been recommended for secondary realizations of the SI second by a Joint Working Group of the Consultative Committees for Length (CCL) and Time and Frequency (CCTF).

The operation of atomic clocks is generally carried out at room temperature, whereas the definition of the second refers to the clock transition in an atom at absolute zero. This implies that the clock transition frequency should be corrected for effects of finite temperature, of which the leading contributor is the blackbody radiation (BBR) shift. The BBR shift at room temperature effecting the Cs microwave frequency standard has been calculated to high accuracy (0.35% and 1%) in Refs. [21, 22], respectively, implying a 6×10^{-17} fractional uncertainty. These calculations are in agreement with a 0.2% measurement [23]. The BBR shift is a major component in the uncertainty budget of the optical frequency standard based on these trapped ions. Experimental measurements of the BBR shifts are difficult.

We calculated the BBR shifts for optical frequency standards based on the $4s - 3d_{5/2}$ transition in Ca$^+$ [24] and the $5s - 4d_{5/2}$ transition in Sr$^+$ [25]. We note that while the calculations were conducted for ^{43}Ca$^+$ and ^{88}Sr$^+$, we have verified that the final results do not depend on the particular isotope. The calculation of the BBR shift for these transitions requires the calculation of the lowest-order atomic polarizability (unlike the cases of the hyperfine transitions, it does not cancel out for optical frequency standards) and the evaluation of the very small dynamic

correction η. Therefore, the evaluation of the BBR shift requires an accurate calculation of static scalar polarizabilities of the $ns_{1/2}$ ground and $(n-1)d_{5/2}$ excited states. The effect of the tensor part of the $(n-1)d_{5/2}$ polarizability averages out due to the isotropic nature of the electric field radiated by the blackbody.

The blackbody radiation (BBR) shift of the $5s - 4d_{5/2}$ clock transition in $^{88}Sr^+$ was calculated to be 0.250(9) Hz at room temperature, $T = 300$ K, using the relativistic all-order method where all single and double excitations of the Dirac-Fock wave function are included to all orders of perturbation theory [25]. The BBR shift for the $4s - 3d_{5/2}$ transition in Ca^+ [24] was calculated to be 0.38(1) Hz.

We have significantly improved the accuracy of the BBR shifts in these systems in comparison to previous estimates. We have increased the accuracy of the polarizability values as compared to any other previous calculation by using more accurate dipole-matrix element values calculated using relativistic all-order single-double method. Our results are accurate enough for the present level of projected performance of Ca^+ and Sr^+ single-ion frequency standards at room temperature.

ALL-ORDER METHOD

Brief overview

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

$$|\Psi\rangle = \exp(S)|\Psi^{(0)}\rangle, \tag{2}$$

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, $\cdots$, N-electron excitations of the lowest-order state vector $|\Psi^{(0)}\rangle$: $S = S_1 + S_2 + \cdots + S_N$. The exponential in Eq. (2), when expanded in terms of the n-body excitations S_n, becomes

$$|\Psi\rangle = \left\{ 1 + S_1 + S_2 + S_3 + \frac{1}{2}S_1^2 + S_1 S_2 + \frac{1}{2}S_2^2 + \cdots \right\} |\Psi^{(0)}\rangle. \tag{3}$$

In the linearized coupled-cluster method described in detail in Refs. [27, 28], all non-linear terms are omitted and the wave function takes the form

$$|\Psi\rangle = \{ 1 + S_1 + S_2 + S_3 + \cdots + S_N \} |\Psi^{(0)}\rangle. \tag{4}$$

Restricting the sum in Eq. (4) to single, double, and valence triple excitations yields the following expansion for the state vector of a monovalent atom in state v:

$$|\Psi_v\rangle = \left[1 + \sum_{ma} \rho_{ma} a_m^\dagger a_a + \frac{1}{2} \sum_{mnab} \rho_{mnab} a_m^\dagger a_n^\dagger a_b a_a + \right. \tag{5}$$
$$\left. + \sum_{m \neq v} \rho_{mv} a_m^\dagger a_v + \sum_{mna} \rho_{mnva} a_m^\dagger a_n^\dagger a_a a_v + \frac{1}{6} \sum_{mnrab} \rho_{mnrvab} a_m^\dagger a_n^\dagger a_r^\dagger a_b a_a a_v \right] |\Psi_v^{(0)}\rangle,$$

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 quantities ρ_{ma}, ρ_{mv} are single-excitation coefficients for core and valence electrons and ρ_{mnab} and ρ_{mnva} are double-excitation coefficients for core and valence electrons, respectively, and ρ_{mnrvab} are the triples valence excitation coefficients.

We use the relativistic no-pair Hamiltonian $H = H_0 + V_I$ obtained from QED by Brown and Ravenhall [29]:

$$H_0 = \sum_i \varepsilon_i : a_i^\dagger a_i :, \tag{6}$$

$$V_I = \frac{1}{2} \sum_{ijkl} v_{ijkl} : a_i^\dagger a_j^\dagger a_l a_k : + \sum_{ij} (V_{HF} - U)_{ij} : a_i^\dagger a_j :, \tag{7}$$

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

TABLE 1. Comparison of the excited state theoretical scalar α_0 and tensor α_2 polarizabilities in alkali-metal atoms with experiment. The experimental values are from compilation of Ref. [33]. Theoretical all-order values have been previously published in Ref. [11].

Atom	Polarizability	Theory	Experiment
Na	$\alpha_0(3p_{1/2})$	359.9(4)	359.2(6)
	$\alpha_0(3p_{3/2})$	361.6(4)	360.4(7)
	$\alpha_2(3p_{3/2})$	-88.4(10)	-88.3(4)
K	$\alpha_0(4p_{1/2})$	606(6)	606.7(6)
	$\alpha_0(4p_{3/2})$	616(6)	614(10)
	$\alpha_2(4p_{3/2})$	-109(2)	-107(2)
Rb	$\alpha_0(4p_{1/2})$	606(6)	606.7(6)
	$\alpha_0(4p_{3/2})$	616(6)	614(10)
	$\alpha_2(4p_{3/2})$	-109(2)	-107(2)

over states in the closed core. The quantity ε_i in Eq. (6) is the eigenvalue of the Dirac equation. We take U to be *frozen-core* V^{N-1} potential, $U = V_{HF}$. Such choice of the potential greatly simplifies the calculations as the second term in Eq. (7) vanishes in this case.

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 Ref. [28].

We have completed the addition of all non-linear single-double (SD) terms into the all-order method [30]. It was shown in Refs. [31] that both non-linear terms and triple excitations have to be added to improve accuracy of the linearized coupled-cluster SD method. The details of the all-order method and its applications are discussed in our review Safronova and Johnson [32] and references therein.

The matrix elements for any one-body operator $Z = \sum_{ij} z_{ij} a_i^\dagger a_j$ are obtained within the framework of the linearized coupled-cluster method as

$$Z_{wv} = \frac{\langle \Psi_w | Z | \Psi_v \rangle}{\sqrt{\langle \Psi_v | \Psi_v \rangle \langle \Psi_w | \Psi_w \rangle}}, \tag{8}$$

where $|\Psi_v\rangle$ and $|\Psi_w\rangle$ are given by the expansion (5). In the SD approximation, the resulting expression for the numerator of Eq. (8) consists of the sum of the DF matrix element z_{wv} and 20 other terms that are linear or quadratic functions of the excitation coefficients. The all-order method yielded results for the properties of alkali-metal atoms ([28]) in excellent agreement with experiment. The expression in Eq. (8) does not depend on the nature of the operator Z, only on its rank and parity. Therefore, electric and magnetic multipole transition matrix elements, magnetic-dipole, electric-quadrupole, and magnetic-octupole hyperfine matrix elements, and nuclear spin-dependent and spin-independent PNC matrix elements, are all calculated using the same general code.

Table 1 gives comparison of the excited state scalar α_0 and tensor α_2 polarizabilities in alkali-metal atoms with experimental values compiled in [33]. The polarizabilities are computed using sum-over-states approach with all-order values of the matrix elements and experimental energies.

Computational challenges

The derivation of the formulas for the addition of the triple excitations and non-linear terms into the formulation of the all-order method requires extremely lengthy analytical calculations that involve thousands of terms. Therefore, we have developed a symbolic computer package that carries out required analytical calculations. The code implements Wick's theorem and performs all required simplifications of the resulting expressions. For example, the program will evaluate the term

$$g_{ijkl}\rho_{mnwa} : a_i^\dagger a_j^\dagger a_l a_k : : a_m^\dagger a_n^\dagger a_a a_w : |0\rangle, \tag{9}$$

TABLE 2. Uncertainty estimate of the dominant contribution to the atomic quadrupole moment of the $3d_{5/2}$ state in Ca^+.

Approximation	*ab initio*	Scaled
Lowest-order	2.451	
Third-order	1.610	
LCCSD	1.785	1.849
LCCSDpT	1.837	1.836
CCSD	1.822	1.851
Final		1.849(13)

where $|0\rangle$ is the lowest-order core wave function, and produce the following output (LaTex formatted):

$$g_{ijkl}\rho_{mnwa} : a_i^\dagger a_j^\dagger a_l a_k : : a_m^\dagger a_n^\dagger a_a a_w : |0\rangle$$

$$= g_{mnba}\rho_{rswc} a_m^\dagger a_n^\dagger a_r^\dagger a_s^\dagger a_a a_b a_c a_w |0\rangle - \tilde{g}_{cmba}\rho_{nrwc} a_m^\dagger a_n^\dagger a_r^\dagger a_a a_b a_w |0\rangle$$

$$+ \tilde{g}_{mnas}\tilde{\rho}_{srwb} a_m^\dagger a_n^\dagger a_r^\dagger a_a a_b a_w |0\rangle + \tilde{g}_{wmba}\rho_{nrwc} a_m^\dagger a_n^\dagger a_r^\dagger a_a a_b a_c |0\rangle$$

$$- \tilde{g}_{cwba}\rho_{mnwc} a_m^\dagger a_n^\dagger a_a a_b |0\rangle + 2\tilde{g}_{wmar}\tilde{\rho}_{rnwb} a_m^\dagger a_n^\dagger a_a a_b |0\rangle - 2\tilde{g}_{bmar}\tilde{\rho}_{rnwb} a_m^\dagger a_n^\dagger a_a a_w |0\rangle$$

$$- g_{mnrs}\tilde{\rho}_{srwa} a_m^\dagger a_n^\dagger a_a a_w |0\rangle - 2\tilde{g}_{bwan}\tilde{\rho}_{nmwb} a_m^\dagger a_a |0\rangle - \tilde{g}_{wmnr}\tilde{\rho}_{rnwa} a_m^\dagger a_a |0\rangle$$

$$+ \tilde{g}_{amnr}\tilde{\rho}_{rnwa} a_m^\dagger a_w |0\rangle + \tilde{g}_{awmn}\tilde{\rho}_{nmwa} |0\rangle \tag{10}$$

The quantity $\tilde{g}$ is given by $\tilde{g}_{mnab} = g_{mnab} - g_{mnba}$.

Even when all possible simplifications are carried out, the number of the terms for the numerical evaluation remains very large representing a daunting task. Therefore, we have developed a computer code that is capable of generating most of the needed FORTRAN subroutines for subsequent numerical evaluation.

EVALUATION OF THE THEORETICAL UNCERTAINTY

The applications listed above also require evaluation of the uncertainties of the theoretical results. Firstly, the evaluation of the theoretical uncertainty is necessary for the analysis of the PNC experiments. Secondly, recommended values that are produced with the all-order method have more value when they contain uncertainty estimates. Uncertainty bounds of recommended values are important for use by both experimentalists and other theorists in their research and for making benchmark comparisons. Accuracy estimates of theoretical data are particularly important when significant discrepancies exist between results from different experiments.

Evaluation of theoretical uncertainties is a very difficult problem since it essentially involves evaluation of the quantity that is not known beforehand. Several strategies can be used in evaluating the uncertainties of the all-order results:

- approximate evaluation of the size of the correlation correction;
- evaluation of the size of the higher-order corrections;
- study of the order-by-order convergence of perturbation theory;
- study of the breakdown of the various all-order contributions and identification of the most important terms;
- semi-empirical determination of important missing contributions.

We illustrate the evaluation of the uncertainty in the theoretical values on the example of the atomic quadrupole moment of the $3d_{5/2}$ state in Ca^+ [34]. Summary of the uncertainty estimate of the dominant contribution to this quantity is given in Table 2in atomic units. The quadrupole moment is defined as as

$$\Theta(\gamma J) = \frac{(2J)!}{\sqrt{(2J-2)!(2J+3)!}} \langle \Psi(\gamma J) \| Q \| \Psi(\gamma J) \rangle. \tag{11}$$

The following values are listed: lowest-order Dirac-Hartree-Fock, third-order relativistic many-body perturbation theory (RMBPT), linearized coupled-cluster with single-double excitations (LCCSD), linearized coupled-cluster with

TABLE 3. 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 experimental energies are given in cm^{-1}. The relative differences of the CI, CI+MBPT, CI + all-order values [44] with experimental data are given in the last three columns in %.

Element	State	Experiment	Differences with experiment (%)		
			CI	CI + MBPT	CI + all-order
Mg	$3s^2\,^1S_0$	182939	1.86	0.12	0.03
Ca	$4s^2\,^1S_0$	145058	4.13	-0.64	-0.32
Zn	$4s^2\,^1S_0$	220662	7.51	0.97	0.55
Sr	$5s^2\,^1S_0$	134896	5.22	-0.88	-0.32
Cd	$5s^2\,^1S_0$	208915	9.59	-0.86	0.14
Ba	$6s^2\,^1S_0$	122721	6.37	-1.82	-0.52
Hg	$6s^2\,^1S_0$	235469	11.81	-2.41	-0.49

single-double and partial triple excitations (LCCSDp), full coupled-cluster with single-double excitations (CCSD), and the corresponding scaled all-order values. The final error of the dominant correlation correction is obtained as the maximum difference of the final (LCCSD scaled) value and LCCSDpT, LCCSDpT scaled, and CCSD scaled results. A detailed knowledge of the more important correlation corrections is crucial in developing procedures for estimating uncertainties in theoretical data, especially in cases where one wishes to provide recommended values.

DEVELOPMENT OF CI + ALL-ORDER METHOD

The all-order method described above is designed to treat core-core and core-valence correlations with high accuracy. 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 making it impractical to attempt direct extensions of the all-order approach to more complicated systems. For example, the expression for all-order matrix elements in divalent systems contains several hundred terms instead of the twenty terms in the corresponding monovalent expression. Moreover, use of the Rayleigh-Schrödinger RMBPT for heavy systems with more than one valence electron leads to a non-symmetric effective Hamiltonian and to the problem of "intruder states".

A combination of the configuration-interaction method and perturbation theory was developed in Ref. [35] and later applied to the calculation of atomic properties of various systems in a number of works (see [36, 37, 38, 39, 40, 41, 42, 43] and references therein).

In the configuration-interaction (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 [41]

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

i.e. a linear combination of Slater determinants from a model subspace [35]. Energies and wave functions of low-lying states are determined by diagonalizing the effective Hamiltonian. Then, the resulting wave functions are used to calculate matrix elements. The precision of the CI method is 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 are 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 constructing an effective Hamiltonian that incorporates certain perturbation theory terms. The CI method is then applied to the modified H^{eff} to obtain improved energies and wave functions.

The Hamiltonian given by the Eqs. (6, 7) separates into a sum of the one-body and two-body interactions,

$$H = H_1 + H_2.$$

In the above equation, H_2 contains the Coulomb (or Coulomb + Breit) matrix elements v_{ijkl}. 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, $H_1 \to H_1 + \Sigma_1$. Either the second-order expression for $\Sigma_1^{(2)}$ or all-order chains of such terms can

TABLE 4. Comparison of the CI, CI+MBPT and CI+all-order *ab initio* results for the energy levels of Mg, Ca, and Cd [44] with experiment. The experimental values are given in cm^{-1}. The energies are counted from the ground state. The relative difference with experimental values is given in the last three columns in %.

Element	State	Experiment	Differences with experiment (%)		
			CI	CI+MBPT	CI+all-order
Mg	$3s4s\,^3S_1$	41197	1.91	0.16	0.05
	$3s4s\,^1S_0$	43503	1.87	0.10	0.00
	$3s3d\,^1D_2$	46403	2.77	0.18	0.04
	$3s3d\,^3D_1$	47957	2.05	0.14	0.04
	$3s3d\,^3D_2$	47957	2.05	0.14	0.04
	$3s3d\,^3D_3$	47957	2.05	0.14	0.04
	$3s3p\,^3P_0$	21850	4.32	0.32	0.08
	$3s3p\,^3P_1$	21870	4.32	0.32	0.08
	$3s3p\,^3P_2$	21911	4.31	0.30	0.07
	$3s3p\,^1P_1$	35051	1.61	0.00	-0.04
Ca	$3d4s\,^3D_1$	20335	-19.00	2.01	0.00
	$3d4s\,^3D_2$	20349	-18.93	1.97	-0.03
	$3d4s\,^3D_3$	20371	-18.81	1.91	-0.07
	$3d4s\,^1D_2$	21850	-9.17	1.05	-0.53
	$4s5s\,^3S_1$	31539	4.42	-0.72	-0.49
	$4s5s\,^1S_0$	33317	4.27	-0.70	-0.45
	$4s4p\,^3P_0$	15158	10.88	-2.08	-1.19
	$4s4p\,^3P_1$	15210	10.87	-2.09	-1.15
	$4s4p\,^3P_2$	15316	10.85	-2.10	-1.19
	$4s4p\,^1P_1$	23652	2.54	-0.50	-0.32
Cd	$5s6s\,^3S_1$	51484	14.48	-0.84	0.17
	$5s6s\,^1S_0$	53310	13.43	-0.90	0.07
	$5s5d\,^1D_2$	59220	14.50	-0.81	0.35
	$5s5d\,^3D_1$	59486	13.77	-0.66	0.38
	$5s5d\,^3D_2$	59498	13.77	-0.66	0.38
	$5s5d\,^3D_3$	59516	13.77	-0.66	0.38
	$5s5p\,^3P_0$	30114	18.92	-2.62	-0.09
	$5s5p\,^3P_1$	30656	18.86	-2.59	0.03
	$5s5p\,^3P_2$	31827	18.83	-2.60	-0.03
	$5s5p\,^1P_1$	43692	10.96	-0.64	0.20

be used (see, for example, Ref. [45]). The two-body Coulomb interaction term in H_2 is modified by including the two-body part of core-valence interaction that represents screening of the Coulomb interaction by valence electrons; $H_2 \rightarrow H_2 + \Sigma_2$. The quantity Σ_2 is calculated in second-order MBPT. The CI+MBPT approach is based on the Brilloiun-Wigner variant of the MBPT, rather than the Rayleigh-Schrödinger variant. In the Brilloiun-Wigner variant of MBPT, the effective Hamiltonian is symmetric and accidentally small denominators do not arise; however, Σ_1 and Σ_2 became energy dependent.

The CI+MBPT approach includes only a limited number of the core-valence excitation terms (mostly in second order) and deteriorates in accuracy for heavier, more complicated systems.

In the CI+all-order approach, the effective Hamiltonian is constructed using fully converged all-order excitations coefficients ρ_{ma}, ρ_{mnab}, ρ_{mv}, and ρ_{mnva}. 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 the monovalent systems. The CI method will then be used to treat valence-valence correlations. This method will yield accurate wave functions for subsequent calculations of matrix elements (PNC, transition E1, E2, M1, hyperfine, $\cdots$).

The comparison of the CI, CI+MBPT and CI+all-order *ab initio* results [44] for the two-electron binding energies of Mg, Ca, Zn, Sr, Cd, Ba, and Hg with experiment [46] is given in Table 3. The experimental energies are given in cm^{-1}. The relative differences of the CI, CI+MBPT, CI + all-order values [44] with experimental data is given in the last

three columns in %. Comparison of the CI, CI+MBPT and CI+all-order *ab initio* results for the energy levels of Mg, Ca, and Cd [44] with experiment [46] is given in Table 4. The energies are counted from the ground state. The relative difference with experimental values is given in the last three columns in %. We find that the all-order two-electron binding energy 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 factor of three in comparison with the second-order data. Similar improvements are observed for most of the excited states listed in Table 4. We refer the reader to Ref. [44] for a detailed discussion of the CI+all-order approach.

CONCLUSION

We reviewed selected modern applications of the atomic calculations ranging from the study of fundamental interactions to applications of atomic physics to future technological developments. The coupled-cluster approach to high-precision calculation of various atomic properties of monovalent systems is discussed. The computational challenges in the implementation of the all-order approach including the development of the computer programs capable of performing complicated symbolic calculations and automatic generation of the computer codes were discussed. New high-precision method combining the all-order approach currently used in precision calculations of properties of monovalent atoms with the configuration-interaction method is presented. This method 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 three in agreement with experimental values for the two-electron binding energies and most excited state energies in comparison with the CI + MBPT method.

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REFERENCES

1. C. S. Wood, S. C. Bennett, D. Cho, B. P. Masterson, J. L. Roberts, C. E. Tanner, and C. E. Wieman, *Science* **275**, 1759 (1997).
2. S. G. Porsev, K. Beloy, and A. Derevianko, *Phys. Rev. Lett.* **102**, 181601 (2009).
3. W. C. Haxton, and C. E. Wieman, *Ann. Rev. Nucl. Part. Sci.* **51**, 261 (2001).
4. W. C. Haxton, C.-P. Liu, and M. J. Ramsey-Musolf, *Phys. Rev. Lett.* **86**, 5247 (2001).
5. P. A. Frantsuzov, and I. B. Khriplovich, *Z. Phys. D* **7**, 297 (1998).
6. A. Y. Kraftmaker, *Phys. Rev. Lett.* **132**, 167 (1988).
7. M. Safronova, R. Pal, D. Jiang, M. Kozlov, W. Johnson, and U. Safronova, *Nucl. Phys. A* **827**, 411c (2009).
8. J. K. Webb, M. T. Murphy, V. V. Flambaum, V. A. Dzuba, J. D. Barrow, C. W. Churchill, J. X. Prochaska, and A. M. Wolfe, *Phys. Rev. Lett.* **87**, 091301 (2001).
9. D. Jaksch, H.-J. Briegel, J. I. Cirac, C. W. Gardiner, and P. Zoller, *Phys. Rev. Lett.* **82**, 1975 (1999).
10. M. Safronova, C. J. Williams, and C. W. Clark, *Phys. Rev. A* **67**, 040303 (2003).
11. B. Arora, M. S. Safronova, and C. W. Clark, *Phys. Rev. A* **76**, 052509 (2007).
12. B. Arora, M. S. Safronova, and C. W. Clark (2009), to be submitted to Phys. Rev. A.
13. M. Lombardi, T. Heavner, and S. Jefferts, *Measure: J. Meas. Sci.* **2**, 74 (2007).
14. S. A. Diddams, T. Udem, J. C. Bergquist, E. A. Curtis, R. E. Drullinger, L. Hollberg, W. M. Itano, W. D. Lee, C. W. Oates, K. R. Vogel, and D. J. Wineland, *Science* **293**, 825 (2001).
15. H. S. Margolis, G. Barwood, G. Huang, H. A. Klein, S. N. Lea, K. Szymaniec, and P. Gill, *Science* **306**, 19 (2004).
16. M. Petersen, R. Chicireanu, S. T. Dawkins, D. V. Magalhães, C. Mandache, Y. L. Coq, A. Clairon, and S. Bize, *Phys. Rev. Lett.* **101**, 183004 (2008).
17. A. A. Madej, J. E. Bernard, P. Dube, and L. Marmet, *Phys. Rev. A* **70**, 012507 (2004).
18. H. S. Margolis, G. Huang, G. barwood, S. N. Lea, H. A. Klein, W. R. C. Rowley, and P. Gill, *Phys. Rev. A* **67**, 032501 (2003).
19. M. M. Boyd, A. D. Ludlow, S. Blatt, S. M. Foreman, T. Ido, T. Zelevinsky, and J. Ye, *Phys. Rev. Lett.* **98**, 083002 (2007).

20. R. L. Targat, X. Baillard, M. Fouché, A. Brusch, O. Tcherbakoff, G. D. Rovera, and P. Lemonde, *Phys. Rev. Lett.* **97**, 130801 (2006).
21. K. Beloy, U. I. Safronova, and A. Derevianko, *Phys. Rev. Lett.* **97**, 040801 (2006).
22. E. J. Angstmann, V. A. Dzuba, and V. Flambaum, *Phys. Rev. Lett.* **97**, 040802 (2006).
23. E. Simon, P. Laurent, and A. Clairon, *Phys. Rev. A* **57**, 426 (1998).
24. B. Arora, M. Safronova, and C. W. Clark, *Phys. Rev. A* **76**, 064501 (2007).
25. D. Jiang, B. Arora, M. Safronova, and C. W. Clark, *J. Phys. B* **42**, 154020 (2009).
26. F. Coester, and H. Kümmel, *Nucl. Phys.* **17**, 477 (1960).
27. S. A. Blundell, W. R. Johnson, and J. Sapirstein, *Phys. Rev. A* **43**, 3407 (1991).
28. M. S. Safronova, W. R. Johnson, and A. Derevianko, *Phys. Rev. A* **60**, 4476 (1999).
29. G. E. Brown, and D. G. Ravenhall, *Proc. Roy. Soc. A* **208**, 552 (1951).
30. R. Pal, M. S. Safronova, W. R. Johnson, A. Derevianko, and S. G. Porsev, *Phys. Rev. A* **75**, 042515 (2007).
31. S. G. Porsev, and A. Derevianko, *Phys. Rev. A* **73**, 012501 (2006).
32. M. S. Safronova, and W. R. Johnson, *Adv. At. Mol., OPt. Phys.* **55**, 191 (2007).
33. C. Zhu, A. Dalgarno, S. G. Porsev, and A. Derevianko, *Phys. Rev. A* **70**, 032722 (2004).
34. D. Jiang, B. Arora, and M. S. Safronova, *Phys. Rev. A* **78**, 022514 (2008).
35. V. A. Dzuba, V. V. Flambaum, and M. G. Kozlov, *Phys. Rev. A* **54**, 3948 (1996).
36. S. G. Porsev, M. G. Kozlov, Y. G. Rakhlina, and A. Derevianko, *Phys. Rev. A* **64**, 012508 (2001).
37. M. G. Kozlov, and S. G. Porsev, *Eur. Phys. J. D* **5**, 59 (1999).
38. M. G. Kozlov, and S. G. Porsev, *J. Expt. Theor. Phys.* **84**, 461 (1997).
39. V. A. Dzuba, and V. V. Flambaum, *Phys. Rev. A* **75**, 052504 (2007).
40. V. A. Dzuba, and V. V. Flambaum, *J. Phys. B* **40**, 227 (2007).
41. I. M. Savukov, and W. R. Johnson, *Phys. Rev. A* **65**, 042503 (2002).
42. I. M. Savukov, W. R. Johnson, and H. G. Berry, *Phys. Rev. A* **66**, 052501 (2002).
43. I. M. Savukov, *J. Phys. B* **36**, 4789 (2003).
44. M. Safronova, M. G. Kozlov, W. Johnson, and D. Jiang, *Phys. Rev. A* **80**, 012516 (2009).
45. V. A. Dzuba, and J. S. M. Ginges, *Phys. Rev. A* **73**, 032503 (2006).
46. C. E. Moore, *Atomic Energy Levels*, vol. 35 of *Natl. Bur. Stand. Ref. Data Ser.*, U.S. Govt. Print. Off., 1971.