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# Atomic Polarizabilities

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**Abstract.** The atomic dipole polarizability governs the first-order response of an atom to an applied electric field. Atomic polarization phenomena impinge upon a number of areas and processes in physics and have been the subject of considerable interest and heightened importance in recent years. In this paper, we will summarize some of the recent applications of atomic polarizability studies. A summary of results for polarizabilities of noble gases, monovalent, and divalent atoms is given. The development of the CI+all-order method that combines configuration interaction and linearized coupled-cluster approaches is discussed.

**Keywords:** Polarizabilities, coupled-cluster method, quantum information, atomic clocks, magic wavelengths, blackbody radiation shifts

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## INTRODUCTION

Many topics in the area of field-atom interactions have recently been the subject of much interest owing to the developments in cold-atom physics including Bose-Einstein condensation, development of optical frequency standards, preparation and manipulation of single quantum systems, studies of atoms in optical lattices, quantum information, and many other topics. Atomic polarization phenomena impinge upon a number of areas and processes in physics and have been the subject of considerable interest and heightened importance in recent years. For example, an imperfect knowledge of atomic polarizabilities presents a problem in accurate determination of the blackbody radiation shifts which are the largest source of uncertainty in the new generation of optical frequency standards. More precise atomic clocks will lead to more sensitive quantum-based standards for many applications such as searches for variation of the fundamental constants, testing of physics postulates, gravity gradiometry, inertial navigation, and tracking of deep-space probes.

There have been a number of reviews and tabulations of atomic and ionic polarizabilities [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. Some of these reviews, e.g. [3, 4, 10, 11] have largely focussed upon experimental developments while others [6, 8, 9, 13] have given theory more attention.

Accurate polarizabilities for the group I and II atoms and ions of the periodic table have recently become available by a variety of techniques [9]. These include refined many-body perturbation theory and coupled-cluster calculations sometimes combined with precise experimental data for selected transitions, *ab initio* calculations of atomic properties using explicitly correlated wave functions, microwave spectroscopy of Rydberg atoms and ions, interferometry with atom beams, refractive index measurements in microwave cavities, and velocity changes of laser cooled atoms induced by an electric field. In this paper, we review the present status of our knowledge of ground-state atomic polarizabilities for various types of systems.

The development of a novel theoretical method to accurately treat correlation corrections in atoms with a few valence electrons and its further extensions are discussed in detail. This method combines the linearized coupled-cluster method 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 Ra [14].

## APPLICATIONS OF ATOMIC POLARIZABILITIES

Accurate knowledge of atomic polarizabilities is important for variety of applications [9]: development of the next-generation atomic time and frequency standards, optical cooling and trapping schemes, quantum information with

neutral atoms, study of fundamental symmetries, thermometry and other macroscopic standards, study of cold degenerate gases, study of long-range interactions, atomic transition rate determinations, and benchmark comparisons of theory and experiment.

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  $^{133}\text{Cs}$  [15]. 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.

There are two main interconnecting areas of the theoretic atomic clock research: prediction of atomic properties required for new clock proposals and determination of the quantities contributing to the uncertainty budget of the existing schemes. New clock proposals require both estimation of the atomic properties for details of the proposals (magic wavelength, scattering rates, transition rates, lifetimes, branching ratios, etc.) and evaluation of the systematic shifts (blackbody radiation shift, ac Stark shifts due to various lasers fields, Zeeman shift, electric quadruple shift, etc.). While many of these quantities may be eventually measured, lack of knowledge of some of these properties may delay experimental realization of the new proposals by years. In the case of the well-developed proposals, one of the main uncertainty issues is the blackbody radiation (BBR) shift [16, 17, 18], i.e. the displacement of atomic energy levels due to universal ambient thermal fluctuations of the electromagnetic field. 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. Experimental measurements of the BBR shifts are difficult and high-precision theoretical calculations are presently needed.

The average electric field radiated by a blackbody at temperature  $T$  is [17]

$$\langle E^2 \rangle = (831.9 \text{ V/m})^2 \left( \frac{T(K)}{300} \right)^4. \quad (1)$$

Assuming that the system evolves adiabatically, the frequency shift of an atomic state due to such an electrical field can be related to the static electric-dipole polarizability  $\alpha_0$  by (see Ref. [18])

$$\delta\nu = -\frac{1}{2}(831.9 \text{ V/m})^2 \left( \frac{T(K)}{300} \right)^4 \alpha_0(1 + \eta), \quad (2)$$

where  $\eta$  is a small dynamic correction due to the frequency distribution and only the electric-dipole transition part of the contribution is considered. Therefore, the calculation of BBR shifts is reduced to the evaluation of the static polarizabilities of the two clock states and evaluation of the small dynamic correction. We refer the reader to the review [19] for a discussion of the current status of the BBR shift calculations.

The laser fields used to trap neutral atoms for the implementation of the optical frequency standards generally shift the energy levels of the lower and upper states by different amounts. This results in a wavelength (and intensity) dependent shift of the clock transition unless the laser is tuned to a magic wavelength  $\lambda_{\text{magic}}$ , where lattice potentials of equal depth are produced for the two electronic states of the clock transition. *Ab initio* calculations of the dynamic polarizability are needed to make an initial estimate of the magic wavelength. Such calculations involve the determination of the crossing points of the lower and upper state dynamic polarizability curves [20, 21, 22].

Development of more precise atomic clocks is also important for laboratory searches for variation of the fundamental constants, such as fine-structure constant  $\alpha$ . The astrophysical approach to such studies (involving study of absorption lines in the spectra of distant quasars) is complicated by the possible changes in isotopic abundances with time that may mimic the variance in the value of the fine-structure constant [23]. The laboratory searches for the variation of the fundamental constants are based on comparing the frequencies of two ultra-precise atomic clocks over time [24].

The precise calculation of atomic polarizabilities also has implications for quantum information processing and optical cooling and trapping schemes. One requirement for the experimental realization of the scalable quantum computer is the design of a quantum gate with low error rate which will allow for error correction. Therefore, it is important to study the various decoherence mechanisms and to search for ways to optimize gate performance. The issue of the mismatch of the polarizabilities of the ground and excited states has arisen in schemes to perform quantum logical operations where it is a source of decoherence [25].

Many other applications of the polarizability calculations are discussed in detail in the recent review [9].

**TABLE 1.** Ground state polarizabilities  $\alpha_0$  (in atomic units) of noble gases, monovalent, and divalent atoms. Uncertainties in the last digits are given in parentheses. References are given in square brackets. Method abbreviations: DC - dielectric constant, RI - refractive index, EH -  $E$ - $H$  balance or beam-deflection, sum-rule - hybrid  $f$ -sum rules with experimental data for primary contribution, RRPA - relativistic random-phase approximation, (R)(L)CCSDT - (relativistic) (linearized) coupled-cluster calculations. <sup>a</sup>Non-relativistic Hylleraas calculation for  $^{\infty}\text{Li}$ , <sup>b</sup>Hylleraas calculations for  $^7\text{Li}$  that includes estimate of relativistic effects, <sup>c</sup>CI, <sup>d</sup>Hybrid-RLCCSD data for the alkali ground states from [51] are listed as recommended “sum-rule” data, <sup>e</sup>interferometry, <sup>f</sup>interferometry ratio, <sup>g</sup>cold atom velocity change experiments, <sup>h</sup>RCCSDT, <sup>i</sup>MBPT, <sup>j</sup>Hybrid-RCI+MBPT data for the alkaline-earth ground states from [70] are listed as recommended “sum-rule” data

He	Ne	Ar	Kr	Xe	Method [Ref.]
1.322	2.38	10.77	16.47	26.97	Th. RRPA [26]
1.383763	2.6648	11.084			Th. CCSDT [27]
	2.697	11.22	16.80	27.06	Th. RCCSDT [28]
	2.665 [29]	11.085	Th. MBPT [30]		
	2.668(6) [31]				Th. RCCR12
1.38376079(23)[32]					Th.
1.383223(67) [33, 34]	2.670(3) [35]	11.081(5) [35]	16.766(8) [35]		Expt. DC
	2.66110(3)[36]				Expt. DC
1.3838	2.6680	11.091	16.740	27.340	Expt. RI [37]
1.384	2.663	11.080	16.734	27.292	Expt. RI [38]
1.383759(13) [39]		11.083(2) [40]			Expt. RI
Li	Na	K	Rb	Cs	Method
164.112(1) <sup>a</sup> [41]	164.50 <sup>c</sup> [42]			398.2(9) [43]	Th.
164.11(3) <sup>b</sup> [44]					Th. Hyl.
164.21 [45]	162.8 [46]	290.0 [46]	315.7 [46]		Th. CICP
	165.50 [47]	301.28 [48]			Th. CCSD
163.74 [48]	162.9(6) [49]	291.12 [50]	316.17 [50]	396.02 [50]	Th. RCCSDT
	163.0	289.1	316.4	401.5	Th. RLCCSD [51]
164.08 [52]		289.3 [53]		398.4(7) [54]	Th. RLCCSDT
164(3)	159(3)	293(6)	319(6)	402(8)	Expt. EH [55]
164.2(1.1) <sup>e</sup> [56]	162.7(8) <sup>e</sup> [57]	290.8(1.4) <sup>f</sup> [58]	318.8(1.4) <sup>f</sup> [58]	401.0(6) <sup>g</sup> [59]	Expt.
	162.6(3)	290.2(8)	318.6(6)	399.9(1.9)	Sum-rule <sup>d</sup> [51]
Be	Mg	Ca	Sr	Ba	Method
2s <sup>2</sup>	3s <sup>2</sup>	4s <sup>2</sup>	5s <sup>2</sup>	6s <sup>2</sup>	
37.755 [60]					Th. ECG
37.73(5) <sup>h</sup> [61]	71.7 <sup>i</sup> [62]	157 <sup>i</sup> [62]			Th.
37.807 [63]	70.90 [64]	171.7 [65]			Th. CI
37.29 [66]	70.74 [66]	156.0 [66]			Th. CICP
37.69 [46]	71.35 [46]	159.4 [46]	201.2 [46]		Th. CICP
		158.00 [67]	198.85 [67]	273.9 [67]	Th. RCCSDT
		152 [68]	190 [68]	275.5 [69]	Th. RCCSDT
37.76 [70]	71.33 [70]	159.0 [70]	202.0 [70]	272.1 [70]	Th. RCI+MBPT
		169(17) [71]	186(15) [72]	268(22) [72]	Expt. EH
	74.9(2.7) [73]	157.1(1.3) [70]	197.2(2) [70]	273.5(2.0) [70]	Sum-rule <sup>j</sup>

## THEORETICAL METHODS AND RESULTS

Most methods used to determine atomic wave functions and energy levels can be adapted to generate polarizabilities. A brief description of the applications of the following methods to the polarizability calculations has been given in the review [9]: configuration interaction (CI), CI calculations with a semi-empirical core potential (CICP), density functional theory, correlated basis functions, many-body perturbation theory (MBPT), coupled-cluster methods, combined CI+MBPT, and combined CI+coupled-cluster approaches. This list is not exhaustive, and includes those methods that have achieved the highest accuracy or those methods that have been applied to a number of different atoms and ions.

The results for the ground state polarizabilities  $\alpha_0$  (in atomic units) of He, Ne, Ar, Kr, Xe, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, and Ba are listed in Table 1. Uncertainties in the last digits are given in parentheses. References are given in square brackets. Method abbreviations: DC - dielectric constant, RI - refractive index, RRPA - relativistic

random-phase approximation, (R)CCSDT - (relativistic) coupled-cluster calculations, EH -  $E-H$  balance or beam-deflection, sum-rule - hybrid  $f$ -sum rules with experimental data for primary contribution, RLCCSDT - linearized CCSD method with partial triple contributions included. The RCCR12 calculation is a CCSDT calculation which allows for explicitly correlated electron pairs. Hybrid-RCI+MBPT data for the alkaline-earth ground states from [70] are listed as recommended “sum-rule” data. All coupled-cluster calculations that include some triple excitations are listed as (RL)CCSDT.

The most precise calculations of the noble gas polarizabilities (apart from helium) have mostly been obtained with coupled-cluster type calculations. Particular care has to be taken to ensure that the basis set used in coupled-cluster calculations is of sufficiently high quality to obtain accurate values. Random-phase approximation (RPPA) values for polarizabilities of noble gases [26] appear to be in remarkably good agreement with the much more elaborate coupled-cluster and Hylleraas basis function calculations as well as with experimental data. Core polarizabilities are included into many calculations of the polarizabilities of alkali and alkaline-earth ions (see, for example, Refs. [51, 70, 18]). They are also important for the construction of CICIP type models of these atoms. RPPA data are used in many of these cases.

The sum-rule polarizabilities for the alkali-metal atoms [51] come from a hybrid calculation that use the RLCCSD calculation as a template with the matrix element for the resonance transition has been replaced by high accuracy experimental matrix elements compiled in [74]. The *ab initio* RLCCSD values are in excellent agreement (better than 1%) with these hybrid recommended values. The CI calculations with a semi-empirical core potential (CICIP) are in excellent agreement with RLCCSDT calculations and experiment for lighter systems.

The perturbative methods do not work well for strong valence-valence correlations, and the sub-1% agreement between the highest quality theory and experiment that occurred for the alkali atoms is not observed for the alkaline-earth atoms owing to their more complicated atomic structure and resulting mixing of configurations. The hybrid values for Ca and Sr based on the RCI+MBPT calculations with the matrix elements for the resonance transitions replaced by values derived from experiments are respectively 1.1% and 2.5% smaller than the *ab initio* RCI+MBPT estimates [70]. Therefore, the accurate determination of the possibilities for divalent and more complicated systems requires development of the novel approaches. A promising method [14] combining CI and linearized coupled-cluster approaches is described in the next section.

## DEVELOPMENT OF THE CI+ALL-ORDER METHOD

A combination of the configuration-interaction (CI) method and perturbation theory was developed in Ref. [75]. This approach has been later applied to the calculation of atomic properties of various systems in a number of works (see [9] for references). 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 [76]:

$$\Psi_J = \sum_i c_i \Phi_i.$$

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

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

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  $v_{ijkl}$ ). The precision of the CI method is drastically limited for large systems by the number of the configurations that can be included. The CI + MBPT approach allows one to incorporate core excitations in the CI method by including second-order (and some higher-order) terms in an effective Hamiltonian. The one-body part  $H_1$  is modified to include the correlation potential  $\Sigma_1$  that accounts for part of the core-valence correlations,

$$H_1 \rightarrow H_1 + \Sigma_1.$$

Either the second-order expression,  $\Sigma_1^{(2)}$ , or all-order chains of such terms can be used (see, for example, Ref. [75]). 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  $g_{ijkl}$  Coulomb interaction by valence electrons;

$$H_2 \rightarrow H_2 + \Sigma_2,$$

where  $\Sigma_2$  is calculated in second-order MBPT in CI+MBPT approach. The CI method is then applied as usual with the modified  $H^{\text{eff}}$  to obtain improved energies and wave functions.

The second-order matrix elements  $(\Sigma_1^{(2)})_{yx}$  are given by [14]

$$\left(\Sigma_1^{(2)}\right)_{yx} = \sum_{mab} \frac{g_{myab} \tilde{g}_{mxab}}{\varepsilon_{ab} - \varepsilon_{xm} + \tilde{\varepsilon}_y - \varepsilon_y} + \sum_{mna} \frac{g_{mna} \tilde{g}_{mna}}{\tilde{\varepsilon}_y + \varepsilon_a - \varepsilon_{mn}}. \quad (3)$$

In the equation above, 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  $\varepsilon_i$  are written together as  $\varepsilon_{ij} = \varepsilon_i + \varepsilon_j$  for brevity. The summation over index  $i$  implies the sum over the quantum numbers  $n_i \kappa_i m_i$ . Ideally, the energy  $\tilde{\varepsilon}_y$  should be calculated from the particular eigenvalue of the effective Hamiltonian. In practice, we set the energy  $\tilde{\varepsilon}_y$  to the Dirac-Fock energy of the lowest orbital for the particular partial wave. For example, we use  $\tilde{\varepsilon}_{ns} = \varepsilon_{4s}$  for all  $ns$  orbitals of Ca system.

The second-order matrix elements  $(\Sigma_2^{(2)})_{mvmw}$  are given by [14]

$$\left(\Sigma_2^{(2)}\right)_{mvmw} = \sum_{cd} \frac{g_{vwcd} g_{mncd}}{\varepsilon_{cd} - \varepsilon_{mn} + \tilde{\varepsilon}_v - \varepsilon_v + \tilde{\varepsilon}_w - \varepsilon_w} + \left[ \sum_{rc} \frac{\tilde{g}_{wrnc} \tilde{g}_{mrvc}}{\tilde{\varepsilon}_v + \varepsilon_c - \varepsilon_{mr} + \tilde{\varepsilon}_w - \varepsilon_w} + \left( \begin{array}{c} m \leftrightarrow n \\ v \leftrightarrow w \end{array} \right) \right]. \quad (4)$$

In the CI+MBPT approach, MBPT corrections associated with terms  $\Sigma_1$  and  $\Sigma_2$  typically grow with nuclear charge  $Z$  leading to a deterioration of the accuracy of the results for heavier, more complicated systems requiring introduction of the intrinsically all-order treatment of the effective Hamiltonian.

In the CI + all-order approach [14] most important corrections to the effective Hamiltonian are calculated using the (linearized single-double coupled cluster) all-order method.

In the linearized single-double (SD) coupled-cluster method, the many-body wave function of a monovalent atom in a state  $v$  is represented by

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

where the indices  $m$  and  $n$  range over all possible virtual states while indices  $a$  and  $b$  range over all occupied core states. The lowest-order wave function is  $|\Psi_v^{(0)}\rangle = a_v^\dagger |\Psi_C\rangle$ , where  $|\Psi_C\rangle$  is the lowest-order frozen-core wave function. The quantities  $\rho_{ma}$ ,  $\rho_{mv}$  are single-excitation coefficients for core and valence electrons;  $\rho_{mnab}$  and  $\rho_{mna}$  are core and valence double-excitation coefficients, respectively. To derive equations for the excitation coefficients, the state vector  $|\Psi_v\rangle$  is substituted into the many-body Schrödinger equation  $H|\Psi_v\rangle = E|\Psi_v\rangle$ . The 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 [77]. First, the resulting system for the core excitations  $\rho_{ma}$  and  $\rho_{mnab}$  is solved iteratively until the core correlation energy converges. Next, the system of equations for the valence excitation coefficients  $\rho_{mv}$  and  $\rho_{mna}$  is solved iteratively with the used of the stored core coefficients. The iteration procedure continues until the valence energy converges. The single valence coefficients  $\rho_{mv}$  are directly used in the CI+all-order method, so we list the corresponding equation below:

$$(\varepsilon_v - \varepsilon_m + \delta E_v) \rho_{mv} = \sum_{bn} \tilde{g}_{mbvn} \rho_{nb} + \sum_{bnr} g_{mbnr} \tilde{\rho}_{nrvb} - \sum_{bcn} g_{bcvn} \tilde{\rho}_{mncb}, \quad (6)$$

where  $\tilde{\rho}_{nrvb} = \rho_{nrvb} - \rho_{mvb}$  and  $\delta E_v$  is the valence correlation energy.

The effective Hamiltonian in the CI+all-order method contains dominant core and core-valence correlation corrections to all orders. 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. Therefore, the resulting CI+all-order wave function contains all-order correlation corrections from all interaction sectors. In actual implementation, we first modify the effective Hamiltonian in second order using our version of the very fast MBPT code. The second-order modifications are done for nearly complete CI space. Then, a subset of effective Hamiltonian matrix is modified using

the all-order method. We have carried out extensive tests to verify that modifying larger subset of Hamiltonian via the all-order approach does not change results within the expected accuracy of the method.

To implement CI+all-order method, the all-order equations are re-written in terms of the quantities  $\Sigma$  instead of the excitation coefficients  $\rho$  as follows:

$$\begin{aligned}\Sigma_{ma} &= \rho_{ma}(\epsilon_a - \epsilon_m), \\ \Sigma_{mnab} &= \rho_{mnab}(\epsilon_{ab} - \epsilon_{mn}), \\ \Sigma_{mnva} &= \rho_{mnva}(\tilde{\epsilon}_v + \epsilon_a - \epsilon_{mn}).\end{aligned}\quad (7)$$

The quantities  $\Sigma_{ma}$ ,  $\Sigma_{mnab}$ , and  $\Sigma_{mnva}$  are used in the all-order iteration procedure but do not explicitly appear in the effective Hamiltonian. The one-body correction to the effective Hamiltonian  $\Sigma_1$  is given by

$$(\Sigma_1)_{mv} = \rho_{mv}(\tilde{\epsilon}_v - \epsilon_m), \quad (8)$$

where  $\rho_{mv}$  are valence excitation coefficients given by Eq. (6).

The two-body correction to the effective Hamiltonian  $\Sigma_2$  is given by [14]

$$\begin{aligned}(\Sigma_2)_{mrvw} &= \sum_{cd} \frac{g_{cdvw} \Sigma_{mncd}}{\epsilon_{cd} - \epsilon_{mn} + \tilde{\epsilon}_v - \epsilon_v + \tilde{\epsilon}_w - \epsilon_w} - \sum_c \frac{g_{cnvw} \Sigma_{mc}}{\epsilon_c - \epsilon_m + \tilde{\epsilon}_v - \epsilon_v + \tilde{\epsilon}_w - \epsilon_w} \\ &- \sum_c \frac{g_{mrvw} \Sigma_{nc}}{\epsilon_c - \epsilon_n + \tilde{\epsilon}_v - \epsilon_v + \tilde{\epsilon}_w - \epsilon_w} + \sum_{cr} \frac{\tilde{g}_{cnrw} \Sigma_{mrvc}}{\tilde{\epsilon}_v + \epsilon_c - \epsilon_{mr} + \tilde{\epsilon}_w - \epsilon_w} \\ &- \sum_{cr} \frac{g_{cnrw} \Sigma_{rmvc}}{\tilde{\epsilon}_v + \epsilon_c - \epsilon_{mr} + \tilde{\epsilon}_w - \epsilon_w} - \sum_{cr} \frac{g_{mcrw} \Sigma_{rmvc}}{\tilde{\epsilon}_v + \epsilon_c - \epsilon_{nr} + \tilde{\epsilon}_w - \epsilon_w} \\ &+ \sum_{cr} \frac{\tilde{g}_{mrvr} \Sigma_{rncw}}{\epsilon_c + \tilde{\epsilon}_w - \epsilon_{nr} + \tilde{\epsilon}_v - \epsilon_v} - \sum_{cr} \frac{g_{mrvr} \Sigma_{rncw}}{\epsilon_c + \tilde{\epsilon}_w - \epsilon_{nr} + \tilde{\epsilon}_v - \epsilon_v} \\ &- \sum_{cr} \frac{g_{cnvr} \Sigma_{rmvc}}{\epsilon_c + \tilde{\epsilon}_w - \epsilon_{mr} + \tilde{\epsilon}_v - \epsilon_v}.\end{aligned}\quad (9)$$

where all of the quantities  $\Sigma$  are given by Eq. (7) and are obtained as the result of the SD all-order iteration procedure. The Eq. (9) does not appear in the monovalent all-order method. This equation is not iterative, unlike the equation for  $\Sigma_1$  given by (8).

We note that rather large basis sets and CI space have to be used to achieve sufficient numerical accuracy. The MBPT correction to the effective Hamiltonian has to be done for nearly entire CI space.

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, In<sup>+</sup>, Ba, Hg, and Ra with experiment in Table 2. Some of these values were published in Ref. [14]. The energy values are given in cm<sup>-1</sup>. Relative differences of all results with experiment are given in the last three columns of Table 1 to illustrate the accuracy of each approach. We find that the all-order results are in significantly better agreement with experiment in comparison with the CI+MBPT values. We also find almost no deterioration in the accuracy of the two-electron binding energies from Ca to Ra; 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 as illustrated in Ref. [14].

While we have demonstrated a success of the CI + all-order method for divalent systems and obtained significant improvement of accuracy with comparison to the best know approaches for a number of properties, we found that a number of the additional all-order corrections have to be added to achieve the precision needed for accurate calculations of polarizabilities in heavy systems with a few valence electrons. Further proposed extensions of the present CI+all-order method are outlined below.

## Inclusion of the Valence Triple Excitations

The next version of the CI+all-order method will be based on the SDpT all-order version rather than the SD version of the all-order code (which is used at the present time). In the SDpT method [74], the triple valence term is added to the SD wave function:

$$|\Psi_v\rangle = |\Psi_v^{\text{SD}}\rangle + \frac{1}{6} \sum_{mnrab} \rho_{mnrab} a_m^\dagger a_n^\dagger a_r^\dagger a_b a_a a_v |\Psi_v^{(0)}\rangle,$$

**TABLE 2.** 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, In<sup>+</sup>, Ba, Hg, and Ra with experiment. CI+all-order results are listed in column labeled “CI+all”. The energies are given in cm<sup>-1</sup>. The relative difference with experimental values is given in the last three columns in %.

Atom	State	Energies				Differences with experiment (%)		
		Expt.	CI	CI+MBPT	CI+all	CI	CI+MBPT	CI+all
Mg	3s <sup>2</sup>	182939	179537	182717	182877	1.86	0.12	0.03
Ca	4s <sup>2</sup>	145058	139068	145985	145517	4.13	-0.64	-0.32
Zn	4s <sup>2</sup>	220662	204083	218521	219442	7.51	0.97	0.55
Sr	5s <sup>2</sup>	134896	127858	136082	135322	5.22	-0.88	-0.32
Cd	5s <sup>2</sup>	208915	188884	210716	208620	9.59	-0.86	0.14
In <sup>+</sup>	5s <sup>2</sup>	378299	356232	382436	379259	5.83	-1.09	-0.25
Ba	6s <sup>2</sup>	122721	114898	124956	123363	6.37	-1.82	-0.52
Hg	6s <sup>2</sup>	235469	207652	241152	236626	11.81	-2.41	-0.49
Ra	7s <sup>2</sup>	124416	115334	127302	125227	7.3	-2.23	-0.65

to the SD wave function  $|\Psi_v^{SD}\rangle$ . 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  $\rho_{mnrva}$  are the triples valence excitation coefficients. The SDpT extension will directly modify  $\Sigma_1$  corrections to the effective Hamiltonian and will produce significantly improved energies. While the SD approximation includes important high-order corrections, it omits certain third-order energy terms. The addition of the triple excitations will automatically add these contributions as well as other important higher-order corrections. The additions of the triple excitations should also significantly improve properties of levels that include  $d$  orbitals, based on our knowledge of the SDpT results for monovalent systems.

### All-order Corrections to the Matrix Elements

In the current CI + all-order approach, matrix elements of the one-body operators  $Z$ , such as electric-dipole or parity-nonconservation operators are calculated by replacing “bare” matrix elements by the “dressed” matrix elements using the random-phase approximations (RPA). The all-order corrections are included to the effective Hamiltonian, and consequently to the wave functions, but not to the effective  $Z$  operators. Such treatment omits all structure radiation, normalization, and other all-order corrections to the matrix elements (see Ref. [78] for definitions of these terms). We propose to remedy this problem by performing complete SD all-order “dressing” of all one-body matrix elements. The “bare” one-body matrix elements  $z_{vw}$  have to be modified as follows:

$$\begin{aligned}
Z_{vw}^{\text{eff}} &= z_{vw} + \sum_{ma} z_{am} \tilde{\rho}_{wmva} + \sum_{ab} z_{ab} \rho_{vb}^* \rho_{wa} + \sum_{mna} z_{mn} \rho_{ma}^* \tilde{\rho}_{wnva} \\
&- \sum_{mab} z_{ab} \rho_{mb}^* \tilde{\rho}_{wmva} + \sum_{mab} z_{am} \rho_{vb}^* \tilde{\rho}_{wmab} - \sum_{mab} z_{av} \rho_{mb}^* \tilde{\rho}_{wmab} \\
&+ \sum_{mnab} z_{ab} \rho_{mnwb}^* \tilde{\rho}_{nmva} + \sum_{mabc} z_{ab} \tilde{\rho}_{vmcb}^* \tilde{\rho}_{wmac} + \sum_{mnra} z_{mn} \tilde{\rho}_{rmwa}^* \tilde{\rho}_{rnva} \\
&+ \sum_{mnab} z_{mn} \rho_{vmab}^* \tilde{\rho}_{wnba} - \sum_{mnab} z_{am} \tilde{\rho}_{vmvb}^* \tilde{\rho}_{nmab} + \sum_{mnab} z_{av} \rho_{mnwb}^* \tilde{\rho}_{nmab} + (c.c.), \tag{10}
\end{aligned}$$

where (c.c.) stands for a complex conjugate part of certain terms (generally, these terms are the same with  $v \leftrightarrow w$ ).

Using “dressed” SD all-order one-body matrix elements given by Eq. (10) will make these quantities complete at the SD all-order level. Such treatment produced extremely accurate matrix elements for the monovalent systems [77]. It has never been implemented for more complicated systems. The excitation coefficients  $\rho$  in Eq. (10) are the same  $\rho$  used in the  $\Sigma_1$  and  $\Sigma_2$  correction of the effective Hamiltonian given by the Eqs. (8, 9).

The one-body part of the Breit interaction can be included on the same footing as the Coulomb potential via the modification of the B-spline basis set orbitals. The effect of the two-body part of Breit interaction on the matrix elements is generally small and can be included perturbatively.



## CONCLUSION

Further progress in experimental precision will require to make more detailed corrections of the effects of electromagnetic fields that are used for manipulation and investigation of atoms. Accurate determination of polarizabilities will become increasingly important in the future. New all-order approaches need to be developed to significantly improve precision of the polarizability calculations for systems with a few valence electrons.

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