Electric dipole polarizabilities of doubly ionized alkaline Earth metal ions from perturbed relativistic coupled-cluster theory

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Using perturbed relativistic coupled-cluster (PRCC) theory we compute the ground state electric dipole polarizability, \( \alpha \), of doubly ionized alkaline earth metal ions \( \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+} \) and \( \text{Ra}^{2+} \). In the present work we use the Dirac-Coulomb-Breit atomic Hamiltonian and we also include the Uehling potential, which is the leading order term in the vacuum polarization corrections. We examine the correction to the orbital energies arising from the Uehling potential in the self-consistent field calculations as well as perturbatively. Our results of \( \alpha \) are in very good agreement with the experimental data, and we observe a change in the nature of the orbital energy corrections arising from the vacuum polarization as we go from \( \text{Mg}^{2+} \) to \( \text{Ra}^{2+} \).

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I. INTRODUCTION

The static electric dipole polarizability, \( \alpha \), of an atom or ion is a measure of the first order response to an external electric field. It is an essential parameter to determine any property associated with atom-field or ion-field interactions as well as atom-atom and atom-ion interactions. The properties include the refractive indexes, dielectric constants, ion mobility in gases, and van der Waal’s constants. \( \alpha \) has been measured using a wide variety of experimental techniques. For closed-shell ions, like the doubly ionized alkaline-Earth-metal ions, \( \alpha \) is a good representative of the core-polarization effects.

Theoretically, \( \alpha \) of the many electron atoms and ions has been calculated using different many body methods. A recent review on atomic and ionic polarizabilities provide a description of the theoretical methods used in the calculation of \( \alpha \). However, among the various theoretical methods the ones based on coupled-cluster theory (CCT) are ideal for atoms and ions which are closed-shell or with few valence electrons. The CCT is, among the many body theories, one of the most reliable and powerful theory. It takes into account the electron correlation to all order. A detailed discussion on the CCT and different variants are given in a recent review, and very good descriptions of the application of non-relativistic CCT to atomic and molecular systems are given in ref. The CCT has been used with great success in atomic, molecular, nuclear and condensed matter physics calculations. For the theoretical calculations of \( \alpha \), the CCT based methods which have given very precise results are the finite field \( 10 \), sum over states \( 17 \) and perturbed relativistic coupled-cluster (PRCC) theory \( 19 \) \( 20 \). In a previous work, the CCT based finite field method with the Douglas-Kroll Hamiltonian was used to compute the \( \alpha \) of the alkaline-Earth metal ions. In this work we compute the \( \alpha \) of doubly ionized alkaline ions using the PRCC theory. The method was used in our previous works to calculate the \( \alpha \) of noble gas atoms \( 19 \) \( 20 \) and alkaline-Earth metal ions \( 21 \). The theory is the conventional relativistic coupled-cluster (RCC) theory with an additional perturbation. To account for the additional perturbation, we introduce a new set of cluster operators and accordingly, define a second set of cluster equations. The equations, however, are linear in the cluster operators and the new operators obey the same selection rules as the perturbation Hamiltonian. In the calculation of \( \alpha \) the perturbation is the external electric field \( E \). In the present work we use the Dirac-Coulomb-Breit atomic Hamiltonian along with the vacuum polarization (VP) potential. The VP potential is treated self consistently as well as perturbatively.

The paper is organised as follows. In Sec. II we give a brief discussion on RCC and PRCC theory along with the VP correction. The theoretical formulation of \( \alpha \) in the framework of PRCC theory is discussed in Sec. III. In Sec. IV we give the details of our calculational methodology. Next we discuss about the VP correction to the orbital energies of doubly ionized alkaline earth metal ions. In the subsequent sections we give the results of static polarizability and discuss it in great detail. Then we end with the conclusion. All the results presented in this work and related calculations are in atomic units \( ( \hbar = m_e = e = 4 \pi \epsilon_0 = 1 ) \). In this system of units the velocity of light is \( c \), the inverse of fine structure constant. For which we use the value of \( c = 137.035999974 \).

II. THEORETICAL METHODS

A detailed description of the RCC theory for closed-shell atoms is given in ref. and similarly, a detailed account of PRCC theory is given in our previous works \( 19 \) \( 21 \). However, for completeness and easy reference we provide a brief overview in this section.
A. RCC and PRCC theory

In the present work we use the Dirac-Coulomb-Breit no-virtual-pair Hamiltonian, \( H^\text{DCB} \), to incorporate the relativistic effects and avoid the difficulties associated with the negative continuum states \[25\]. For a doubly ionized atom with \( N \) electrons \[26\], it accounts for the electron correlations by adding a set of cluster operators introduced in our recent work \[20\]. The former is equivalent to the unperturbed and perturbed coupled-cluster operators, respectively. The latter is an elegant alternative to the projection operators, and better suited for numerical computations, is to use the kinetically balanced finite basis sets \[27\]. This is the method adopted in the present work to generate the orbital basis sets. Returning to \( H^\text{DCB} \), the last two terms, \( 1/r_{ij} \) and \( g^B(r_{ij}) \), are the Coulomb and Breit interactions, respectively. The latter, Breit interaction, represents the transverse photon interaction and is given by

\[
g^B(r_{12}) = -\frac{1}{2r_{12}} \left[ \alpha_1 \cdot \alpha_2 + \frac{(\alpha_1 \cdot r_{12})(\alpha_2 \cdot r_{12})}{r_{12}^2} \right].
\]

The general trends in the observables arising from the inclusion of Breit interaction in RCC and PRCC are discussed in our previous work on noble gas atoms \[20\]. For a closed-shell ion, the ground state eigen-value equation is

\[
H^\text{DCB}|\Psi_0\rangle = E_0|\Psi_0\rangle,
\]

where, \( |\Psi_0\rangle \) is the ground state of the ion. In the presence of a perturbation Hamiltonian, \( H_{\text{int}} \), the eigenvalue equation is modified to

\[
(H^\text{DCB} + \lambda H_{\text{int}})|\tilde{\Psi}_0\rangle = \tilde{E}_0|\tilde{\Psi}_0\rangle,
\]

where \( \lambda \) is the perturbation parameter, \( |\tilde{\Psi}_0\rangle \) is the perturbed ground state and \( \tilde{E}_0 \) is the corresponding eigen energy. The origin of \( H_{\text{int}} \) could be internal to the ion, like the hyperfine interaction or external, like the interaction with an external electromagnetic field \( \mathbf{E} \).

In the RCC and PRCC theories, we define two sets of coupled-cluster operators \( T^{(0)} \) and \( T^{(1)} \), which we refer to as the unperturbed and perturbed coupled-cluster operators, respectively. The former is equivalent to the conventional cluster operators, and the latter is an additional set of cluster operators introduced in our recent works \[19,21\]. It accounts for the electron correlations effects arising from \( H_{\text{int}} \) and follows the same selection rules as \( H_{\text{int}} \). To calculate \( \alpha \), consider the interaction of the ion with an electrostatic electric field \( \mathbf{E} \). The interaction Hamiltonian is then

\[
H_{\text{int}} = -\sum_i r_i \cdot \mathbf{E} = \mathbf{D} \cdot \mathbf{E},
\]

where \( \mathbf{D} \) is the many electron electric dipole operator. The cluster operators \( T^{(1)} \) are then rank one tensor operators in the electronic space and follow the same parity selection rule as \( H_{\text{int}} \). Consequently, as \( H_{\text{int}} \) is parity odd there is no first order perturbative correction to the energy, so to first order in \( \lambda \) we get \( \tilde{E}_0 = E_0 \). Using the cluster operators \( T^{(0)} \) and \( T^{(1)} \), the atomic states of unperturbed and perturbed atomic Hamiltonians are

\[
\begin{align*}
|\Psi_0\rangle &= e^{T^{(0)}}|\Phi_0\rangle, \\
|\tilde{\Psi}_0\rangle &= e^{[T^{(0)} + \lambda T^{(1)} \mathbf{E}]}|\Phi_0\rangle,
\end{align*}
\]

where \( |\Phi_0\rangle \) is the reference state wave-function. The cluster operators involve all possible excitations, however, a simplified but accurate representation is the coupled-cluster single and double (CCSD) excitation approximation. With this approximation

\[
\begin{align*}
T^{(0)} &= T_1^{(0)} + T_2^{(0)}, \\
T^{(1)} &= T_1^{(1)} + T_2^{(1)},
\end{align*}
\]

where, the subscripts represent the level of excitation. In the second quantized notations

\[
\begin{align*}
T_1^{(0)} &= \sum_{a,p} t_{a,p}^e \hat{a}_a^\dagger \hat{a}_p, \\
T_2^{(0)} &= \frac{1}{2} \sum_{a,b,p,q} t_{a,b,p,q}^{ep} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_p \hat{a}_q,
\end{align*}
\]

where \( t_{\cdots} \) are cluster amplitudes, \( \hat{a}_i^\dagger \) (\( a_i \)) are single particle creation (annihilation) operators and \( abc \ldots \) (\( pq \ldots \)) represent core (virtual) states. Similarly, the perturbed cluster operators are represented as

\[
\begin{align*}
T_1^{(1)} &= \sum_{a,p} t_{a,p}^e \mathbf{C}_1(\hat{r}) \hat{a}_p^\dagger \hat{a}_a, \\
T_2^{(1)} &= \sum_{a,b,p,q} \sum_{l,k} \tau_{ab}^{pq}(l,k) \{ \mathbf{C}_l(\hat{r}_1) \mathbf{C}_k(\hat{r}_2) \} \hat{a}_l^\dagger \hat{a}_b^\dagger \hat{a}_p \hat{a}_q.
\end{align*}
\]

Here, \( \mathbf{C}_l(\hat{r}) \), a C-tensor is used to represent the vector nature of \( T_1^{(1)} \). On the other hand, two C tensor operators of rank \( l \) and \( k \) are coupled together to form a rank one tensor operator, \( T_2^{(1)} \). For a more rigorous description of the tensor structure of the PRCC operators we refer to our previous work \[20\].

B. Vacuum Polarization

In the present work we incorporate the vacuum polarization (VP) corrections to the electron-nucleus interactions. It modifies the Coulomb potential between the
nucleus and electrons. For a point nucleus, to the order of \( Z \alpha \), it is given by the Uehling potential [31]

\[
V_{\text{Ue}}(r) = -\frac{2\alpha Z}{3r} \int_1^\infty dt \sqrt{t^2 - 1} \left( \frac{1}{t^2} + \frac{1}{2t^4} \right) \exp \left[ -\frac{2rt}{\alpha} \right],
\]

where \( Z \) is the nuclear charge and \( \alpha \), in this case, is the fine structure constant. The latter is not to be confused with the dipole polarizability. In heavy atoms a finite size Fermi charge distribution model of the nucleus is more appropriate and it is defined as

\[
\rho_{\text{nuc}}(r) = \frac{\rho_0}{1 + e^{(r-c)/a}},
\]

(9)

where \( a = t4 \ln(3) \). The parameter \( c \) is the half charge radius so that \( \rho_{\text{nuc}}(c) = \rho_0/2 \) and \( t \) is the skin thickness. For a consistent treatment of the nucleus-electron electrostatic interaction, \( V_{\text{Ue}}(r) \) must be modified to account for the finite nuclear size. This is done by folding \( V_{\text{Ue}}(r) \) with the \( \rho_{\text{nuc}}(r) \) [33]. The modified form of the Uehling potential is [34]

\[
V_{\text{Ue}}(r) = -\frac{2\alpha^2}{3} \int_0^\infty dx \rho(x) \int_1^\infty dt \sqrt{t^2 - 1} \left( \frac{1}{t^2} + \frac{1}{2t^4} \right) \left( e^{-2c\sqrt{(r-x)}} - e^{-2c\sqrt{(r+x)}} \right).
\]

We add this to the electron-nucleus Coulomb interaction potential in the self-consistent field computations to generate the single particle states. The Uehling potential is the leading order term in VP correction and it accounts for more than 90% of the VP correction in Hydrogen like ions. So we identify it as the VP correction in the subsequent sections.

C. Linearized PRCC Theory

In this section we describe in brief the linearized form of the PRCC (LPRCC) theory. It is much simpler than the complete PRCC but encompasses all the important many-body effects. To derive the LPRCC equations, as discussed earlier, consider \( E \) as the perturbation. The eigen-value equation is then

\[
(H_{\text{DCB}} + \lambda H_{\text{int}}) e^{T(0)} \left( 1 + \lambda T^{(1)} \cdot E \right) |\Phi_0\rangle = E_0 e^{T(0)} \left( 1 + \lambda T^{(1)} \cdot E \right) |\Phi_0\rangle,
\]

(10)

Using this expression, the PRCC eigen-value equation assumes the form

\[
\left( H_{\text{DCB}}^{\text{N}} + \lambda H_{\text{int}} \right) \Psi_0 = \Delta E_0 \Psi_0,
\]

(11)

where, \( \Delta E_0 = E_0 - \langle \Phi_0 | H_{\text{DCB}} | \Phi_0 \rangle \) is the ground state correlation energy of the many-electron ion. Using the PRCC wave-function in Eq. (13), we write the ground state as

\[
|\Psi_0\rangle \approx e^{T(0)} \left[ 1 + \lambda T^{(1)} \cdot E \right] |\Phi_0\rangle.
\]

(12)

Following the standard coupled-cluster ansatz, as the initial step to derive the cluster amplitude equations, we apply \( e^{-T(0)} \) from the left and get

\[
\left[ H_{\text{DCB}}^{\text{N}} + \lambda H_{\text{int}} \right] e^{\lambda T^{(1)} \cdot E} |\Phi_0\rangle = \Delta E_0 e^{\lambda T^{(1)} \cdot E} |\Phi_0\rangle,
\]

(14)

where \( H = e^{-T(0)} H e^{T(0)} \) is the similarity transformed Hamiltonian. After applying \( e^{-\lambda T^{(1)}} \) from the left and considering the terms linear in \( \lambda \), we obtain the PRCC equation

\[
\left( \left[ H_{\text{DCB}}^{\text{N}}, T^{(1)} \right] \cdot E + \tilde{H}_{\text{int}} \right) |\Phi_0\rangle = 0.
\]

(15)

The linearized PRCC is the approximation where we take \( \left[ H_{\text{DCB}}^{\text{N}}, T^{(1)} \right] \approx \left[ H_{\text{DCB}}^{\text{N}}, T^{(1)} \right] \) and \( \tilde{H}_{\text{int}} \approx D + [D, T^{(0)}] \). The eigenvalue equation is then reduced to

\[
\left[ H_{\text{DCB}}^{\text{N}}, T^{(1)} \right] |\Phi_0\rangle = \left( D + [D, T^{(0)}] \right) |\Phi_0\rangle.
\]

(16)

Where, for simplicity, we have dropped \( E \) from the equation. The equations of the cluster amplitudes \( T_1^{(1)} \) and \( T_2^{(1)} \) are obtained by projecting the above equation to single and double excited states \( |\Phi_a^{(1)}\rangle \) and \( |\Phi_b^{(1)}\rangle \), respectively. These states, however, must be opposite in parity to the reference state \( |\Phi_0\rangle \). The equations so obtained forms a set of linear algebraic equations and are solved using standard linear algebraic methods.

The other method of calculating \( \alpha \) which avoids summation over the intermediate states is the finite field method [16]. The method, however, requires evaluation of the energy for different values of \( E \) and this implies computing the cluster amplitudes multiple times. In the PRCC theory, however, the computations of the cluster amplitudes are limited to one time evaluation of \( T^{(0)} \) and \( T^{(1)} \). Although, the equations of \( T^{(1)} \) are linear, the tensor nature translates into angular factors consisting of a large numbers of \( 6j \)-symbols and \( 9j \)-symbols. So, for our present work we resort to a symmetry adapted storing of these angular factors.

III. DIPOLAR POLARIZABILITY

In the present calculation of \( \alpha \) we use the PRCC expression discussed and described in our previous works [19, 20]. Accordingly, the \( \alpha \) of the ground state of a doubly ionized alkaline atom is

\[
\alpha = -\frac{\langle \Phi_0 | T^{(1)} | D + \tilde{D} | T^{(1)} | \Phi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle},
\]

(17)
Here $\mathbf{D} = e^{r(0)} \mathbf{D} e^{r(0)}$ is a non-terminating series and we have considered only the leading order terms in this expression.

\[
\alpha = -\frac{1}{N} \langle \Phi_0 | T_1^{(1)} \mathbf{D} + DT_1^{(1)} + T_2^{(1)} DT_1^{(1)} + T_1^{(1)} DT_1^{(1)} + T_1^{(0)} DT_1^{(0)} + T_2^{(1)} DT_1^{(0)} + T_1^{(0)} DT_2^{(0)} + T_2^{(1)} DT_2^{(0)} + T_2^{(0)} DT_2^{(0)} | \Phi_0 \rangle,
\]

where $N = \langle \Phi_0 | \exp[T^{(0)}] \exp[T^{(0)}] | \Phi_0 \rangle$ is the normalization factor, which involves a non-terminating series of contractions between $T^{(0)}$ and $T^{(0)}$. However, in the present work we use $N \approx \langle \Phi_0 | 1 + T_1^{(0)} + T_1^{(1)} + T_1^{(2)} + T_1^{(3)} + \cdots | \Phi_0 \rangle$. In the PRCC expression of $\alpha$, the summation over intermediate states is subsumed within $T^{(1)}$ in a natural way and eliminates the need for a complete set of intermediate states. This is, however, with the condition of solving an additional set of cluster equations.

### IV. CALCULATIONAL DETAILS

#### A. Basis set

To get accurate results the first step is to generate an appropriate basis set of orbitals. Here we use the Gaussian type orbitals (GTO’s), in which the orbitals are expressed as a linear combination of Gaussian type functions of the form

\[
\Phi_i^\alpha(r) = C_{\alpha i} \exp(-\alpha_p r^2),
\]

where $p = 0, 1 \ldots m$ is the GTO index and $m$ is the number of Gaussian type functions. The exponent $\alpha_p = \alpha_0 \beta^{p-1}$, where $\alpha_0$ and $\beta$ are two independent parameters. The small component are constructed from the large component through the kinetic balance condition. The GTOs are calculated on a grid and we optimize the values of $\alpha_0$ and $\beta$ for individual atoms to reproduce the orbital energies of the core orbitals and self consistent field (SCF) energy from GRASP92 code. The comparison of the SCF energies for the doubly ionized alkaline atoms are given in Table. From the table it is evident that the results of the SCF energies from the GTOs are in agreement with the GRASP92 results to the accuracy of at least $10^{-3}$ Hartree. The symmetry wise values of the optimized $\alpha_0$ and $\beta$ are listed in Table.

#### TABLE I. Comparison between the ground state SCF energies obtained from the computations with GTO and GRASP92. The energies are in atomic units.

| Atom   | GTO   | GRASP92 |
|--------|-------|---------|
| Mg$^{2+}$ | $-199.1500$ | $-199.1501$ |
| Ca$^{2+}$ | $-679.1038$ | $-679.1038$ |
| Sr$^{2+}$ | $-3177.5218$ | $-3177.5218$ |
| Ba$^{2+}$ | $-8135.1421$ | $-8135.1421$ |
| Ra$^{2+}$ | $-26027.5632$ | $-26027.5634$ |

#### TABLE II. The $\alpha_0$ and $\beta$ parameters of the even tempered GTO basis for different ions used in the present calculations.

| Atom   | $\alpha_0$ | $\beta$ | $\alpha_0$ | $\beta$ | $\alpha_0$ | $\beta$ |
|--------|------------|--------|------------|--------|------------|--------|
| Mg$^{2+}$ | 0.00825 | 2.310 | 0.00715 | 2.365 | 0.00700 | 2.700 |
| Ca$^{2+}$ | 0.00895 | 2.110 | 0.00815 | 2.150 | 0.00750 | 2.500 |
| Sr$^{2+}$ | 0.00975 | 2.100 | 0.00915 | 2.010 | 0.00900 | 2.030 |
| Ba$^{2+}$ | 0.00985 | 2.150 | 0.00975 | 2.070 | 0.00995 | 2.010 |
| Ra$^{2+}$ | 0.00995 | 2.110 | 0.00925 | 2.090 | 0.00850 | 2.010 |

The number of Gaussian type functions with the optimized basis set parameters is large and not all the GTOs generated are important for the calculations. For the PRCC calculation we select the number of GTO’s for each symmetry such that the electron correlation is accounted accurately. In order to investigate this, we examine the convergence pattern of the $\alpha$ by varying the basis set size. Here we present the result for Sr$^{2+}$. We start with a basis set size of 95 GTOs and increase it in steps upto 155 GTO’s. For this the computations are done with the Dirac-Coulomb Hamiltonian and the results are listed in Table. Based on the table the optimal basis size to get converged result accurate upto $10^{-3}$ is 127.

#### TABLE III. Convergence pattern of $\alpha$ of Sr$^{2+}$ ion as a function of the basis set size. For this set of calculations we consider the Dirac-Coulomb Hamiltonian and result is in atomic units.

| No. of orbitals | Basis size | $\alpha$ |
|-----------------|------------|---------|
| 95              | (15s, 11p, 11d, 9f, 9g) | 5.762 |
| 113             | (17s, 13p, 13d, 11f, 11g) | 5.745 |
| 127             | (19s, 15p, 15d, 13f, 11g) | 5.743 |
| 137             | (21s, 17p, 17d, 13f, 11g) | 5.743 |
| 155             | (23s, 19p, 19d, 15f, 13g) | 5.743 |

To solve the PRCC equations for single and double excitations, we use Jacobi method. We chose this method as it can be parallelized without any difficulty. However, there is a major drawback of the method or performance penalty: slow convergence. To accelerate the convergence we use direct inversion of the iterated subspace (DIIS) and this improves the convergence significantly.

#### B. VP Corrections to the Orbital Energies

To study the VP corrections arising from $V_{\text{ee}}$, we compute the orbital energy corrections in the self consistent field (SCF) calculations. We also compute the first order correction using the many-body perturbative theory. In the former case, SCF calculations, the VP potential is considered along with the Dirac-Hartree-Fock (DHF)
potential, $U_{\text{DHF}}$. The orbital eigen-value equation is then
\[ [h_0 + V_{\text{Ue}}(r) + U_{\text{DHF}}(r)] |\psi_i\rangle = \epsilon_i |\psi_i\rangle, \]
where $h_0 = c \alpha \cdot \cdot + (\beta - 1)c^2 - V_{N-2}(r)$ is the single particle part of Dirac-Coulomb Hamiltonian, $U_{\text{DHF}}(r)$ is the Dirac-Hartree-Fock potential, $|\psi_i\rangle$ is a four component orbital and $\epsilon_i$ is the corresponding eigenvalue. Similarly, we use unprimed states, $|\psi'_i\rangle$, to represent orbitals which are eigenfunctions of the DHF Hamiltonian, that is
\[ [h_0 + U_{\text{DHF}}(r)] |\psi'_i\rangle = \epsilon'_i |\psi'_i\rangle, \]
where $\epsilon_i$ is the DHF energy of the orbital. To quantify the VP effect we define
\[ \Delta \epsilon_i = \epsilon'_i - \epsilon_i, \]
as the change in the orbital energy due to $V_{\text{Ue}}(r)$. Following the time-independent many-body perturbation theory, the first order energy correction associated with $V_{\text{Ue}}(r)$ is
\[ \langle V_{\text{Ue}} \rangle_i = \langle \psi | V_{\text{Ue}}(r) | \psi \rangle. \]
Since the VP potential is attractive and short range in nature, it has larger effect on the orbitals which have finite probability density within the nucleus. So, at the first order $\langle V_{\text{Ue}} \rangle_i$ is negative for orbitals, but only the $s_{1/2}$ orbitals have negative $\Delta \epsilon$ for all the ions. A similar pattern is reported in ref. [38] for the orbitals energies of Cs\(^{+}\). For the Ra\(^{2+}\) ion, in addition to $s_{1/2}$ the $p_{1/2}$ orbitals also have negative $\Delta \epsilon$. More details of the $\Delta \epsilon_i$ and $\langle V_{\text{Ue}} \rangle_i$ for the core orbitals of the Ca\(^{2+}\), Sr\(^{2+}\), Ba\(^{2+}\) and Ra\(^{2+}\), and are presented in the next section.

**TABLE IV.** Static dipole polarizability of doubly ionized alkaline-Earth metal ions and the values are in atomic units.

| Atom | This Work Method | Previous Works Method | Method |
|------|------------------|-----------------------|--------|
| Mg\(^{2+}\) | 0.489 (LPRCC) | 0.469\(^a\) | RRPA |
|      | 0.495 (PRCC) | 0.489(5)\(^b\) | Expt. |
| Ca\(^{2+}\) | 3.284 (LPRCC) | 3.262\(^c\) | RCCSDT |
|      | 3.387 (PRCC) | 3.254\(^d\) | RRPA |
|      | 3.26(3)\(^e\) | | Expt. |
| Sr\(^{2+}\) | 5.748 (LPRCC) | 5.792\(^c\) | RCCSDT |
|      | 5.913 (PRCC) | 5.813\(^e\) | RRPA |
| Ba\(^{2+}\) | 10.043 (LPRCC) | 10.491\(^c\) | RCCSDT |
|      | 10.426 (PRCC) | 10.61\(^d\) | RRPA |
| Ra\(^{2+}\) | 12.908 (LPRCC) | 13.361\(^c\) | RCCSDT |

\(^{a}\) Reference [40].
\(^{b}\) Reference [41].
\(^{c}\) Reference [23].

**V. RESULTS AND DISCUSSIONS**

As mentioned earlier, the expression of the $\alpha$ in PRCC theory is a non-terminating series of the cluster amplitudes. However, considering that the cluster operators $T_2^{(0)}$ and $T_1^{(1)}$ accounts for more than 95% of the many-body effects in RCC and PRCC, the terms considered in Eq. (15) give very accurate results. To verify, we have examined the leading terms which are third order in cluster amplitudes and find the contributions are $\sim 10^{-4}$. So, for the present work, as we consider $\alpha$ up to third decimal place, it is appropriate to neglect the contributions from terms which are third and higher order in cluster operators.

In table IV we list the $\alpha$ of alkaline-Earth metal ions Mg\(^{2+}\), Ca\(^{2+}\), Sr\(^{2+}\), Ba\(^{2+}\) and Ra\(^{2+}\) computed using Eq. (15). The results are based on two sets of calculations: one is based on the cluster amplitudes obtained from LPRCC and the other is based on PRCC. For a systematic comparison we also list the previous theoretical and experimental results. The results of $\alpha$ along with the orbital energy corrections arising from $V_{\text{Ue}}(r)$ for each of the ions are discussed in the subsequent sections.

**A. Mg\(^{2+}\)**

The $\alpha$ of Mg\(^{2+}\) computed with LPRCC is in excellent agreement with the experimental data. However, the PRCC result is 1.2% higher than the LPRCC result and experimental data. This may be due to a part of the additional many-body effects arising from the nonlinear terms in the cluster amplitude equations, but which may ultimately cancel with the contributions from the cluster amplitudes of higher excitations like $T_3^{(0)}$ and $T_3^{(1)}$. The RRPA result is 4.1% lower than the experimental data and it is also lower than both the LPRCC and PRCC results. It must be added that a similar trend is observed for the Na\(^{+}\) ion [21], which is isoelectronic with Mg\(^{2+}\), the RRPA result of $\alpha$ is lower than the experimental data [39]. This trend may be on account of the inherent strength and limitation of RRPA, the potential to incorporate core-polarization effects very accurately and weakness to account for pair correlation effects.

To estimate the contribution from the Breit interaction we consider the Dirac-Coulomb Hamiltonian with the VP potential. The contribution from the Breit interaction can be safely neglected for this ion as the contribution is less than 0.02%. Not surprisingly, the orbital energy corrections $\Delta \epsilon_i$ and $\langle V_{\text{Ue}} \rangle_i$ are very small and can be neglected. For this reason we have not listed the values of $\Delta \epsilon_i$ and $\langle V_{\text{Ue}} \rangle_i$ for Mg\(^{2+}\).
For Ca$^{2+}$, the LPRCC result of $\alpha$ is within the experimental uncertainty and it is in good agreement with the result from a previous work, which is based on the RCCSDT theory. The PRCC result is 3.1% larger than the LPRCC result and deviates from the experimental data by 3.7%. On the other hand, the result from the RRPA \[90\], like in Mg$^{2+}$, is lower than the experimental data.

Based on another set of calculations with the Dirac-Coulomb Hamiltonian, the contribution from the Breit interaction is estimated to be 0.004, which is a mere $\pm 0.1\%$ of the total value. Similarly, we can calculate the VP correction to the orbital energy with a series of SCF calculations and results are listed in Table. \[91\] As to be expected, the first order correction $\langle V_{ue} \rangle$ is negative for all the core orbitals. But the values of $\Delta \epsilon$ are negative only for the $s_{1/2}$ orbitals. Another important observation is, for $s_{1/2}$ orbitals $\langle V_{ue} \rangle_i$ and $\Delta \epsilon_i$ are similar in value. But for the other orbitals, besides the change in sign, the values of $\langle V_{ue} \rangle_i$ and $\Delta \epsilon_i$ are different by several orders of magnitude.

### C. Sr$^{2+}$

For Sr$^{2+}$ it is important to have accurate theoretical results as there are no experimental data of $\alpha$. From the

#### D. Ba$^{2+}$

Like in Sr$^{2+}$, there are no experimental data of $\alpha$ for Ba$^{2+}$. Hence, it is important to have accurate theoretical results and in this regard, it is pertinent to calculate $\alpha$.
with a reliable method like RCC. Here, computing with the relativistic version coupled-cluster is essential as the high Z implies that the relativistic corrections are important. From Table. [IV] it is evident that our LPRCC result of 10.043 is 4.3% lower than the RCCSDT result. However, our PRCC result is in very good agreement with the RCCSDT result, it is just 0.6% less. Examining the results discussed so far, there is a discernible trend when we compare the PRCC and RCCSDT results. The difference between the two results narrows with increasing Z. This may be due to the the basic property of the CCT, the inclusion of selected electron correlation effects to all order. So, with higher Z the importance of the correlation effects grows and the two coupled-cluster based methods incorporate the correlation effects to similar accuracy. The other theoretical result from the RRPA theory is larger than the other results.

Following the computations described earlier, we estimate the Breit contribution as 0.007, which is similar to the previous cases. Coming to the orbital energy corrections arising from the VP, we find an important change in the pattern of $\Delta \epsilon$. The $\Delta \epsilon$ of $p_{1/2}$ and $p_{3/2}$ continue to be positive, but $\Delta \epsilon_{n_{p_{1/2}}}$ is $\approx 72\%$ smaller than $\Delta \epsilon_{n_{p_{3/2}}}$. For the remaining $n_{p_{1/2}}$ and $n_{p_{3/2}}$, although the difference is not so dramatic, the differences are still large.

**TABLE VIII.** VP Corrections to the orbital energies of Ra$^{2+}$.

| Orbital  | $\Delta \epsilon$ | $(V_{\text{ho}})$ |
|---------|-------------------|------------------|
| $1s_{1/2}$ | -2.560 | -2.614 |
| $2s_{1/2}$ | -3.881[-1] | -3.999[-1] |
| $2p_{1/2}$ | -3.802[-2] | -5.753[-2] |
| $2p_{3/2}$ | 1.211[-2] | -2.707[-3] |
| $3s_{1/2}$ | -8.999[-2] | -9.315[-2] |
| $3p_{1/2}$ | -9.620[-3] | -1.504[-2] |
| $3p_{3/2}$ | 3.728[-3] | -7.545[-4] |
| $3d_{3/2}$ | 4.213[-3] | -1.330[-5] |
| $3d_{5/2}$ | 3.953[-3] | -2.385[-6] |
| $4s_{1/2}$ | -2.362[-2] | -2.451[-2] |
| $4p_{1/2}$ | -2.238[-3] | -3.938[-3] |
| $4p_{3/2}$ | 1.315[-3] | -1.999[-4] |
| $4d_{3/2}$ | 1.350[-3] | -3.943[-6] |
| $4d_{5/2}$ | 1.282[-3] | -7.062[-7] |
| $4f_{5/2}$ | 1.015[-3] | -1.647[-9] |
| $4f_{7/2}$ | 9.928[-4] | -4.229[-10] |
| $5s_{1/2}$ | -5.378[-3] | -5.633[-3] |
| $5p_{1/2}$ | -3.002[-4] | -8.438[-4] |
| $5p_{3/2}$ | 4.845[-4] | -4.200[-5] |
| $5d_{3/2}$ | 4.074[-4] | -6.735[-7] |
| $5d_{5/2}$ | 3.859[-4] | -1.187[-7] |
| $6s_{1/2}$ | -9.883[-4] | -9.951[-4] |
| $6p_{1/2}$ | -1.613[-5] | -1.290[-4] |
| $6p_{3/2}$ | 1.211[-4] | -5.949[-6] |

**E. Ra$^{2+}$**

Our PRCC result of $\alpha$ for Ra$^{2+}$ is $\approx 3.7\%$ larger than the LPRCC result. This trend is similar to the case of Ba$^{2+}$ and may be attributed to better accounting of correlation effects in PRCC. To be more precise, the importance of the correlation effects grows with increasing number of electrons, but, LPRCC theory is insufficient to incorporate the correlation effects as it considers only the linear terms. The PRCC theory, which includes the nonlinear terms, provides a better description of the electron correlations. This is borne by the fact that the PRCC results are in good agreement with the RCCSDT results, the difference between the two results is just $\approx 0.3\%$.

Like in the previous cases, the contribution from the Breit interaction is small and the value is 0.008. Coming to the orbital energy correction arising from VP, listed in Table. [VIII] there is a key difference from the other ions. The values of $\Delta \epsilon_{n_{p_{1/2}}}$ in addition to $\Delta \epsilon_{n_{p_{3/2}}}$ are negative.

**TABLE IX.** Contribution to $\alpha$ from different terms and their hermitian conjugates in the LPRCC and PRCC theory.

| Terms + h.c. | Mg$^{2+}$ | Ca$^{2+}$ | Sr$^{2+}$ | Ba$^{2+}$ | Ra$^{2+}$ |
|-------------|----------|----------|----------|----------|----------|
| $T_{1}^{(1)}D$ | 0.496 | 3.594 | 6.400 | 11.708 | 15.160 |
| $T_{1}^{(1)}D_{2}^{(0)}$ | -0.008 | -0.180 | -0.330 | -0.676 | -0.864 |
| $T_{2}^{(0)}D_{2}^{(0)}$ | 0.001 | -0.022 | -0.044 | -0.114 | -0.108 |
| $T_{2}^{(0)}D_{2}^{(0)}$ | -0.0001 | 0.004 | 0.008 | 0.020 | 0.018 |
| $T_{2}^{(1)}D_{2}^{(0)}$ | 0.008 | 0.098 | 0.174 | 0.370 | 0.470 |
| Normalization | 1.019 | 1.064 | 1.080 | 1.126 | 1.137 |
| Total | 0.489 | 3.284 | 5.748 | 10.043 | 12.908 |
| LPRCC results | | | | | |
| $T_{1}^{(1)}D$ | 0.502 | 3.718 | 6.606 | 12.214 | 15.820 |
| $T_{1}^{(1)}D_{2}^{(0)}$ | -0.008 | -0.188 | -0.344 | -0.710 | -0.908 |
| $T_{2}^{(0)}D_{2}^{(0)}$ | 0.002 | -0.022 | -0.046 | -0.120 | -0.114 |
| $T_{2}^{(0)}D_{2}^{(0)}$ | -0.0001 | -0.004 | 0.008 | 0.018 | 0.016 |
| $T_{2}^{(1)}D_{2}^{(0)}$ | 0.008 | 0.092 | 0.162 | 0.338 | 0.424 |
| Normalization | 1.019 | 1.064 | 1.080 | 1.126 | 1.137 |
| Total | 0.495 | 3.387 | 5.913 | 10.426 | 13.402 |

**F. Core-polarization and pair correlation effects**

In the previous sections we discussed the comparison between the results from different theories, general trends and orbital energy corrections from VP. To examine and investigate the contributions from various many-body effects, which are encapsulated in different terms of LPRCC and PRCC, we isolate the contributions from different terms through a series of computations. The results are listed in Table. [IX] From the table it is evident that the leading term in the LPRCC as well as PRCC
theory is \( \{ T^{(1)}_1 (D + h.c) \} \). This is not surprising as it is the term which subsumes the DF contribution and the RPA effects. Now to understand and quantify the RPA effects in these systems, we separate the core orbital contribution to \( \alpha \). The four dominant contributions from

|            | Mg\(^{2+}\) | Ca\(^{2+}\) | Sr\(^{2+}\) |
|------------|-------------|-------------|-------------|
|            |             |             |             |
|            | 0.312 (2p\(_3/2\)) | 2.376 (3p\(_3/2\)) | 4.344 (4p\(_3/2\)) |
|            | 0.154 (2p\(_1/2\)) | 1.148 (3p\(_1/2\)) | 1.940 (4p\(_1/2\)) |
|            | 0.028 (2s\(_1/2\)) | 0.056 (3s\(_1/2\)) | 0.048 (4s\(_1/2\)) |
|            | 0.002 (1s\(_1/2\)) | 0.006 (2p\(_3/2\)) | 0.034 (3d\(_5/2\)) |
| Ba\(^{2+}\) | 8.182 (6p\(_3/2\)) | 11.766 (6p\(_3/2\)) |             |
| Ra\(^{2+}\) | 3.188 (5p\(_1/2\)) | 2.822 (6p\(_1/2\)) |             |
|            | 0.162 (4d\(_5/2\)) | 0.338 (5d\(_5/2\)) |             |
|            | 0.102 (4d\(_3/2\)) | 0.192 (5d\(_3/2\)) |             |

TABLE X. Four leading contributions to \( \{ T^{(1)}_1 (D + h.c) \} \) to \( \alpha \) in terms of the core spin-orbitals.

To study the pair-correlation effects we examine the next to leading order term, \( T_1^{(1)} D T_2^{(0)} \) in more detail. In Table XI we list the four leading order core-orbital pairs which contribute to \( \alpha \). The \( (np_{3/2}, np_{3/2}) \) orbital pairing gives the most dominant contribution. The next leading order contribution arises from \( (np_{3/2}, np_{1/2}) \) orbital pairing. The same pattern is observed for all the doubly charged ions. For Ra\(^{2+}\) the fourth largest contribution arise from \( (6p_{3/2}, 5d_{5/2}) \) orbital pairing, but for other ions it is from \( (np_{1/2}, np_{1/2}) \) orbital pairing. This is because of the relativistic effects, which contracts the outer \( s_{1/2} \) orbital in Ra\(^{2+}\) more than the other ions. One important point to notice here is the higher order terms does not translate to higher accuracy as observed in the case of Mg\(^{2+}\) and Ca\(^{2+}\).

|            | Mg\(^{2+}\) | Ca\(^{2+}\) | Sr\(^{2+}\) |
|------------|-------------|-------------|-------------|
|            |             |             |             |
|            | -0.002 (2p\(_3/2\), 2p\(_3/2\)) | -0.038 (3p\(_3/2\), 3p\(_3/2\)) |             |
|            | -0.001 (2p\(_3/2\), 2p\(_1/2\)) | -0.022 (3p\(_3/2\), 3p\(_1/2\)) |             |
|            | -0.001 (2p\(_1/2\), 2p\(_3/2\)) | -0.022 (3p\(_1/2\), 3p\(_3/2\)) |             |
|            | -0.0004 (2p\(_1/2\), 2p\(_1/2\)) | -0.009 (3p\(_1/2\), 3p\(_1/2\)) |             |

TABLE XI. Core orbitals contribution from \( T_1^{(1)} D T_2^{(0)} \) to \( \alpha \) of Mg\(^{2+}\) and Ca\(^{2+}\).

G. Theoretical Uncertainty

We have isolated the following sources of uncertainty in the present calculations. The first is the truncation of the numerical basis set. We start our calculations with calculation with 9 symmetry and increase up to 13 symmetry. Along with this we also increase the number of orbitals per symmetry and we observe that our value of \( \alpha \) converges for all the doubly charged ions. So we can neglect this error safely. The second source of error is associated with the truncation of RCC theory at the single and doubles excitation in both the unperturbed and at the perturbed level. Based on a series of test calculations, we estimate the contribution from triple excited
cluster amplitudes to less than 0.2% of the total value. So, we can consider the upper bound on the uncertainty from the truncation of the RCC and PRCC theories as 0.4% for the heavier ions Sr$^{2+}$, Ba$^{2+}$ and Ra$^{2+}$. Examining the trend in the results of Mg$^{2+}$ and Ca$^{2+}$, the uncertainty is likely to be higher for the PRCC results of these ions. But, the LPRCC results could have an uncertainty less than ±0.4%. The third source of error is the truncation of the non-terminating series of $\alpha$. We terminate $e^{T(0)} e^{T(0)} e^{T(0)}$ at the second order in cluster operator. However, based on our earlier study [41], we reported an iterative technique to calculate properties to all order, the contribution from the third and higher order terms is negligible. So, the uncertainty arising from the truncation in the expression of $\alpha$ can be neglected. Quantum electrodynamic (QED) corrections is another source of uncertainty in the present calculation. We include the VP potential in the present work but the self-energy part of the radiative corrections is neglected. The self-energy correction is important for the heavy atoms [42]. We can, however, safely neglect it from the error estimates as the contribution is less than at the most 0.1% of the total value. So, considering all the sources, the upper bound on the uncertainty of the present calculations is ±0.4% for the LPRCC results of Mg$^{2+}$ and Ca$^{2+}$, and PRCC results of Sr$^{2+}$, Ba$^{2+}$ and Ra$^{2+}$ ions.

VI. CONCLUSION

The electric dipole polarizability of doubly ionized alkaline-Earth-metal ions calculated using the PRCC theory are in very good agreement with the previous theoretical results and experimental data. An important observation is, for the lighter ions Mg$^{2+}$ and Sr$^{2+}$ the inclusion of nonlinear terms in PRCC does not translate to better agreement with the experimental data. However, for the heavier ions, the nonlinear terms are essential to obtain results which are in agreement with the other results based on relativistic coupled-cluster theory. The correction from Breit interaction is shown marginal increase with atomic number and this may be due to the radial dependence of the $\alpha$.

The changes in orbital energies, SCF and first order correction, with the VP potential reflects the short range nature of this potential. Further more, there is an important change in the SCF energy correction $\Delta E$ with increasing $Z$. For lighter atoms only the $\Delta E$ of the core $ns_{1/2}$ are negative. But, for Ra$^{2+}$ in addition to the core $ns_{1/2}$, the core np$1/2$ orbitals also have negative $\Delta E$.

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