Electron correlation effects in the dipole polarizabilities of the ground states of Be, Mg, Ca, Sr, Ba and Yb

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We investigate the role of electron correlation effects in the electric dipole polarizabilities of the ground states of the alkaline earth and ytterbium atoms by employing the relativistic coupled-cluster (RCC) theory. These effects are incorporated via the residual Coulomb interaction to all orders in the RCC singles and doubles approximation. The perturbed wavefunctions used in the calculations of the polarizabilities are obtained by directly solving the first order perturbed RCC equations, thereby avoiding the sum-over-states approach. Our results are compared with other calculations and available experimental data.

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I. INTRODUCTION

A knowledge of electric dipole polarizabilities is necessary in many areas of physics and chemistry. In particular it is required in studies of collisions involving atoms and molecules [1]. In recent years, the pre-eminent role of polarizabilities in the determination of inter atomic interactions has assumed special significance in the context of research on ultra-cold atoms [2].

Calculations of atomic polarizabilities have come a long way since the classic work of Dalgarno and Lewis [3]. Following a series of calculations using the coupled Hartree-Fock method (see for example, [4]), a number of state-of-the art methods including the coupled-cluster (CC) theory have been used to calculate atomic and molecular polarizabilities [5, 6, 7]. A few calculations of the polarizabilities of heavy atomic systems have been performed in the past few years using the linearized [8] as well as the non-linearized [9] relativistic CC theory. These are based on approaches that sum over a set of intermediate states. In contrast, we have obtained the first order perturbed wavefunction by solving the first order perturbed CC equation and used it to obtain the dipole polarizabilities of the closed-shell alkaline earth atoms and ytterbium (Yb). Information on these quantities is useful for the frequency standards experiments that have been proposed for Mg [10], Ca [11], Sr [12] and Yb [13] as well as the search for the electric dipole moment in Yb [14].

There has been considerable interest in accurate calculations of the dipole polarizabilities of alkaline earth atoms and Yb. Sadlej et al have calculated these quantities for Ca, Sr and Ba using a quasi relativistic approach but their treatment of correlation is rigorous [15]. Their calculations have been carried out at the finite order many-body perturbation theory and CC levels. Por-
where we define $|\Psi(1)(\gamma', J_0, M_0)\rangle$ as the first order correction to the original unperturbed wavefunction $|\Psi(0)(\gamma, J_0, M_0)\rangle$ due to the operator $D_z$ and hence the total wavefunction in the presence of an external DC electric field is given by

$$\Psi(\gamma, J_0, M_0) = |\Psi(0)(\gamma, J_0, M_0)\rangle + |\Psi(1)(\gamma', J_0, M_0)\rangle. \quad (2.4)$$

Our aim in this work is to obtain the exact wavefunction $|\Psi(\gamma, J_0, M_0)\rangle$ by calculating both $|\Psi(0)(\gamma, J_0, M_0)\rangle$ and $|\Psi(1)(\gamma', J_0, M_0)\rangle$ wavefunctions using an approach which can rigorously incorporate the relativistic and correlation effects. In other words, we would like to obtain $|\Psi(1)(\gamma', J_0, M_0)\rangle$ for the Dirac-Coulomb (DC) wavefunction $|\Psi(0)(\gamma, J_0, M_0)\rangle$ as the solution of the following equation

$$\left(H_0^{(DC)} - E_n^{(0)}\right)|\Psi(1)(\gamma', J_0, M_0)\rangle = (E_0 - E_{\text{int}})|\Psi(0)(\gamma, J_0, M_0)\rangle, \quad (2.5)$$

where $H_0^{(DC)}$ and $E_{\text{int}}$ correspond to the DC Hamiltonian and interaction due to $D_z$, respectively.

Using the CC ansatz, we express wavefunctions $|\Psi(\gamma, J_0, M_0)\rangle$ by

$$|\Psi(\gamma, J_0, M_0)\rangle = e^T |\Phi_0(\gamma, J_0, M_0)\rangle, \quad (2.6)$$

where $|\Phi_0(\gamma, J_0, M_0)\rangle$ are the Dirac-Fock (DF) wavefunctions determined using the mean-field approximation and $T$ are the electron excitation operators from the corresponding DF states.

To obtain both the unperturbed and perturbed wavefunctions of Eq. (2.4) separately, we divide the excitation operators $T$ as

$$T = T^{(0)} + \lambda T^{(1)} \quad (2.7)$$

where $T^{(0)}$ and $T^{(1)}$ are the all order excitation operator of the relativistic coupled-cluster (RCC) method and its first order correction arising in the presence of $D_z$, respectively. $\lambda$ represents the perturbation parameter. More explicitly, we can write the unperturbed and perturbed wavefunctions in terms of the RCC excitation operators as

$$|\Psi(0)(\gamma, J_0, M_0)\rangle = e^{T^{(0)}} |\Phi_0(\gamma, J_0, M_0)\rangle, \quad (2.8)$$
$$|\Psi(1)(\gamma, J_0, M_0)\rangle = e^{T^{(0)}} T^{(1)} |\Phi_0(\gamma, J_0, M_0)\rangle, \quad (2.9)$$

where the exponential function of $T^{(1)}$ reduces to the linear term since we have considered only one order of $D_z$ operator in Eq. (2.5).

In the present work, we have considered all possible single and double excitations (CCSD approach) in the calculations. We obtain first the unperturbed $T^{(0)}$ amplitudes by solving the usual (R)CC equations, then these amplitudes are used to determine the $T^{(1)}$ amplitudes. The corresponding equations to solve these amplitudes are given by

$$\langle \Phi_0 | H_{N}^{(DC)}^{T^{(0)}} | \Phi_0 \rangle = 0 \quad (2.10)$$
$$\langle \Phi_0 | H_{N}^{(DC)} T^{(1)} | \Phi_0 \rangle = -\langle \Phi_0 | H_{\text{int}} | \Phi_0 \rangle \quad (2.11)$$
where the subscript $N$ represents normal order form of the operators and we have defined $\mathbb{P} = e^{-T^{(0)}} H e^{T^{(0)}} = (H e^{T^{(0)}})_{\text{con}}$, with the subscript 'con' representing connected terms.

The polarizabilities are determined by evaluating the following expression
\[
\alpha = \frac{\langle \Phi_0 | e^{T^{(1)}} D e^{T} | \Phi_0 \rangle}{\langle \Phi_0 | e^{T^{(0)}} e^{T} | \Phi_0 \rangle} = \frac{\langle \Phi_0 | (T^{(1)} D^{(0)} + \overline{D^{(0)}} T^{(1)}) | \Phi_0 \rangle}{\langle \Phi_0 | e^{T^{(0)}} e^{T} | \Phi_0 \rangle}, \tag{2.12}
\]
where for computational simplicity we define $\overline{D^{(0)}} = e^{T^{(0)}} D e^{T^{(0)}}$. We compute these terms after expressing them as effective one-body and two-body terms using the generalized Wick’s theorem [18].

### III. RESULTS AND DISCUSSIONS

In Table I, we present our results of electric dipole polarizabilities and compare with those available in the literature. The error bars in the experimental results are large for all the systems and our results lie within them. The results of the calculations that are given in the above table are obtained using a variety of many-body theories. Our results are in reasonable agreement with them except for a few cases where they differ by more than 5%.

Mitroy and Bromley [19] have used oscillator strengths from a semiempirical approach to obtain these quantities. Some results based on an \textit{ab initio} method that combines the configuration interaction (CI) method and many-body perturbation theory (MBPT) are available [10, 20, 21]. In these calculations, the valence electrons correlation effects are evaluated by the CI method whereas the core electrons correlation effects are calculated using the MBPT method. However, these calculations consider the core-polarization effects in the framework of finite order MBPT, while our CC method takes them into account to all orders. Lim and Schwerdtfeger had employed the scalar-relativistic Douglas-Kroll Hamiltonian to determine some of these quantities [22].

In these calculations, they had shown the importance of the relativistic effects. There are also a few calculations available for the Yb polarizabilities using the CC method [23, 24], where the atomic orbitals are evaluated using the molecular symmetries. Recently TDDFT was used for calculating the same quantities [10], but this method treats exchange and correlation effects via local potentials. The main difference between the methods on which all these calculations are based and ours is that we calculate both the unperturbed and the first order perturbed wavefunctions using a RCC approach that implicitly takes into consideration all the intermediate states.

To emphasize the importance of correlation effects in these calculations, we present the DF and the leading RCC contributions in Table III for the electric dipole polarizabilities. For all the cases that have been considered, the DF results are larger than the total results. From the individual RCC contributions, we find that only the terms arising from $\overline{D T^{(1)}}$ and its conjugate $(cc)$ are significant. Given that these terms include the DF, leading core-polarization and other important correlation effects to all orders, it is not surprising that they should collectively make up the largest contribution. In Fig IV we give the breakdown of $\overline{D T^{(1)}}$ in terms of the DF, random phase approximation (RPA) and other diagrams. All the above mentioned calculations where these terms contribute.

### Table I: Static dipole polarizabilities in divalent atoms: Be, Mg, Ca, Sr, Ba and Yb (in au).

| Atoms | Expts | Others | This work |
|-------|-------|--------|-----------|
| Be    | 37.755$^a$, 37.69$^b$, 37.9$^c$ | 37.80 |
| Mg    | 71.5(3.1)$^d$ | 73.41 |
| Ca    | 169(17)$^e$ | 154.58 |
| Sr    | 186(15)$^f$ | 199.71 |
| Ba    | 268(22)$^g$ | 268.19 |
| Yb    | 142(36)$^i$ | 144.59 |

$^a$Reference: [25], $^b$Reference: [26], $^c$Reference: [27], $^d$Reference: [28], $^e$Reference: [29], $^f$Reference: [30], $^g$Reference: [31], $^h$Reference: [32], $^i$Reference: [33]

### Table II: Contributions from DF and important perturbed CC terms (in au) for the dipole polarizabilities.

| Atoms | DF | $\overline{D T^{(1)}} + cc$−DF | $\overline{T^{(1)}} + cc$ | Norm |
|-------|----|---------------------------------|-----------------|------|
| Be    | 45.82 | −7.94 | −0.09 | 0.02 |
| Mg    | 82.44 | −8.77 | −0.21 | 0.03 |
| Ca    | 184.14 | −29.23 | −0.07 | −0.26 |
| Sr    | 234.41 | −34.46 | −0.17 | −0.08 |
| Ba    | 328.32 | −61.18 | 0.09 | 0.81 |
| Yb    | 183.32 | −39.86 | 0.032 | 1.10 |
TABLE III: Contributions from important \( nsmp \) \(^3\)P\(^0\) and \( n\bar{smp} \) \(^1\)P\(^1\) states in the form of single particle orbitals through the \((\overline{DT}_1^{(1)} + cc)\) CC terms to the dipole polarizabilities.

| Atoms | ns     | mp     | DF   | \( \overline{DT}_1^{(1)} + cc \) |
|-------|--------|--------|------|-----------------------------------|
| Be    | 2s1/2  | 2p1/2  | 1.154 | 0.893                             |
|       | 2s1/2  | 3p1/2  | 8.261 | 6.596                             |
|       | 2s1/2  | 4p1/2  | 5.529 | 4.583                             |
|       | 2s1/2  | 2p3/2  | 2.308 | 1.816                             |
|       | 2s1/2  | 3p3/2  | 16.521| 13.484                            |
|       | 2s1/2  | 4p3/2  | 11.059| 9.390                             |
| Mg    | 3s1/2  | 3p1/2  | 3.521 | 2.292                             |
|       | 3s1/2  | 4p1/2  | 15.701| 10.279                            |
|       | 3s1/2  | 5p1/2  | 7.780 | 5.254                             |
|       | 3s1/2  | 3p3/2  | 7.009 | 6.742                             |
|       | 3s1/2  | 4p3/2  | 31.351| 31.308                            |
|       | 3s1/2  | 5p3/2  | 15.605| 17.030                            |
| Ca    | 4s1/2  | 4p1/2  | 20.550| 17.790                            |
|       | 4s1/2  | 5p1/2  | 32.290| 29.712                            |
|       | 4s1/2  | 6p1/2  | 6.928 | 8.073                             |
|       | 4s1/2  | 4p3/2  | 40.358| 32.079                            |
|       | 4s1/2  | 5p3/2  | 64.805| 53.218                            |
|       | 4s1/2  | 6p3/2  | 14.097| 13.437                            |
| Sr    | 5s1/2  | 5p1/2  | 30.288| 25.795                            |
|       | 5s1/2  | 6p1/2  | 38.465| 35.555                            |
|       | 5s1/2  | 7p1/2  | 6.838 | 8.402                             |
|       | 5s1/2  | 5p3/2  | 56.608| 45.432                            |
|       | 5s1/2  | 6p3/2  | 78.344| 67.307                            |
|       | 5s1/2  | 7p3/2  | 14.665| 15.247                            |
| Ba    | 6s1/2  | 6p1/2  | 55.019| 47.128                            |
|       | 6s1/2  | 7p1/2  | 45.796| 45.569                            |
|       | 6s1/2  | 8p1/2  | 4.631 | 8.292                             |
|       | 6s1/2  | 6p3/2  | 95.404| 71.484                            |
|       | 6s1/2  | 7p3/2  | 98.613| 81.924                            |
|       | 6s1/2  | 8p3/2  | 11.420| 11.623                            |
| Yb    | 6s1/2  | 6p1/2  | 26.578| 19.824                            |
|       | 6s1/2  | 7p1/2  | 29.112| 24.629                            |
|       | 6s1/2  | 8p1/2  | 3.234 | 3.925                             |
|       | 6s1/2  | 6p3/2  | 43.498| 32.953                            |
|       | 6s1/2  | 7p3/2  | 61.077| 52.816                            |
|       | 6s1/2  | 8p3/2  | 5.548 | 9.522                             |

have been evaluated are based on finite order MBPT, but in our present method, we treat them to all orders in the residual Coulomb interaction. The \(^3\)P\(_1\) and \(^1\)P\(_1\) configurations are of crucial importance for the leading term of \(\overline{DT}_1^{(1)}\) and its conjugate. In Table III we present the contributions arising from different combinations of single particle orbitals.

\[ \text{(i)} + \text{(ii)} + \text{(iii)} + \text{(iv)} + \text{(v)} + \text{(vi)} + \text{(vii)} + \text{(viii)} + \text{(ix)} \]

FIG. 1: Breakdown of the \(\overline{DT}_1^{(1)}\) CC diagram in terms of lower order MBPT and RPA diagrams that contribute significantly to the polarizability calculations. Here, D and V\(_N\) represent the dipole and normal order Coulomb interaction operators which are shown as single dotted and dashed lines, respectively.

IV. CONCLUSION

We have carried out calculations of electric dipole polarizabilities for many alkaline earth atoms and ytterbium using the RCC method and highlighted the importance of the correlation effects. The novelty in these calculations is that it avoids the sum-over-states approach in determining polarizabilities and implicitly considers all the intermediate states by solving the perturbed RCC wavefunction to first order in the dipole and all orders in the residual Coulomb interaction.

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