Relativistic coupled-cluster studies of dipole polarizabilities in closed-shell atoms

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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 metals, helium, and ytterbium 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 approximations. The perturbed wave functions 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

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 preeminent role of polarizabilities in the determination of interatomic interactions has assumed special significance in the context of research on ultracold atoms [2].

Calculations of atomic polarizabilities have come along 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 [5–7]. 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 nonlinearized [9] relativistic coupled-cluster (RCC) theory. These are based on approaches that sum over a set of intermediate states. Liu and Kelly used a coupled-cluster linear-response-based approach to calculate the static and dynamic polarizabilities of He [10]. In contrast, we have obtained the first-order perturbed wave function by solving the first-order perturbed CC equation and used it to obtain the dipole polarizabilities of the closed-shell alkaline earth metals, helium (He), and ytterbium (Yb). Information on these quantities is useful for frequency standards experiments that have been proposed for Mg [11], Ca [12], Sr [13], and Yb [11,14] as well as the search for the electric-dipole moment [15] and parity non-conservation experiments [16–18] in Yb.

There has been considerable interest in accurate calculations of the dipole polarizabilities of alkaline earth metals, He, and Yb. The dipole polarizability of He is available to high precision both experimentally [19] and theoretically [20]. Sadlej et al. have calculated these quantities for Ca, Sr, and Ba using a quasirelativistic approach, but their treatment of correlation is rigorous [21]. Their calculations have been carried out at the finite-order many-body perturbation theory and CC levels. Porsev and Derevianko have performed calculations of the dipole polarizabilities of Mg, Ca, Sr, and Yb using a hybrid approach involving many-body perturbation theory and the configuration-interaction method [11]. A calculation of the dipole polarizability of Yb based on the time-dependent density functional theory (TDDFT) has been reported recently [22].

II. THEORY AND METHOD OF CALCULATIONS

In a uniform dc electric field \( \mathbf{E} = \epsilon \mathbf{z} \), the energy shift \( \Delta E \) of the ground state \( |\Psi_0^{(0)}(\pi, J_0, M_0)\rangle \) with the parity eigenvalue \( \pi \) and angular momentum \( J_0 = 0 \) and its azimuthal value \( M_0 = 0 \) is given by

\[
\Delta E = - \frac{1}{2} \alpha \epsilon^2 ,
\]

(2.1)

where \( \alpha \) is the static polarizability and can be expressed as

\[
\alpha = - 2 \sum_I \left| \langle \Psi_0^{(0)}(\pi, J_0, M_0) | D_I | \Psi_0^{(0)}(\pi', J_I, M_I) \rangle \right|^2 E_0 - E_I ,
\]

(2.2)

where the subscripts 0 and I represent ground and excited states of the Dirac-Coulomb (DC) Hamiltonian \( H_0^{(DC)} \), respectively, the superscript \( (0) \) represents unperturbed wave functions, \( D_I \) is the \( I \) th component of the electric-dipole operator, \( J_0 \) and \( M_0 \) are the angular momentum quantum numbers of the intermediate states, \( \pi \) and \( \pi' \) are the parity quantum numbers for states of opposite parity, and \( E_0 \) and \( E_I \) are the energies of the ground and intermediate states, respectively.

In a more explicit form, the above expression can be written as

\[ \alpha = - 2 \sum_I \left| \langle \Psi_0^{(0)}(\pi, J_0, M_0) | D_I | \Psi_0^{(0)}(\pi', J_I, M_I) \rangle \right|^2 \]
\[ \alpha = -2 \sum_i \frac{(\Psi_0^{(0)}(\pi, J_0, M_0)D_i \Psi_0^{(0)}(\pi', J_1, M_1))(\Psi_0^{(0)}(\pi', J_1, M_1)D_i \Psi_0^{(0)}(\pi, J_0, M_0))}{E_0 - E_i} \]

\[ = - \sum_i \frac{(\Psi_0^{(0)}(\pi, J_0, M_0)D_i \Psi_0^{(0)}(\pi', J_1, M_1))(\Psi_0^{(0)}(\pi', J_1, M_1)D_i \Psi_0^{(0)}(\pi, J_0, M_0))}{E_0 - E_i} \]

\[ = \langle \Psi_0^{(0)}(\pi, J_0, M_0)|D_i \Psi_0^{(0)}(\pi', J_1, M_1)\rangle \langle \Psi_0^{(0)}(\pi', J_1, M_1)|D_i |\Psi_0^{(0)}(\pi, J_0, M_0)\rangle \]  

where we define

\[ |\Psi_0\rangle = |\Psi_0^{(0)}(\pi, J_0, M_0)\rangle + |\Psi_0^{(1)}(\pi', J', M')\rangle, \]

with \( |\Psi_0^{(1)}(\pi', J', M')\rangle \) as the first-order perturbation with the angular momentum \( J' = 1 \) and \( M' \) due to the operator \( D_i \) to the original unperturbed wave function, \( |\Psi_0^{(0)}(\pi, J_0, M_0)\rangle \), in the presence of an external dc electric field and given by

\[ |\Psi_0^{(1)}(\pi', J', M')\rangle = \sum_i |\Psi_0^{(0)}(\pi', J_1, M_1)\rangle i \frac{(\Psi_0^{(0)}(\pi', J_1, M_1)D_i |\Psi_0^{(0)}(\pi, J_0, M_0)\rangle)}{E_0 - E_i} \delta(J) \delta(M') \delta(M_0, M_1). \]

The first-order perturbed wave function \( |\Psi_0^{(1)}(\pi', J', M')\rangle \) can be obtained using an approach that avoids explicitly summing over intermediate states.

A. Unperturbed wave function

Using the CC ansatz, the all-order unperturbed wave function \( |\Psi_0^{(0)}(\pi, J_0, M_0)\rangle \) for closed-shell atoms can be expressed as [23]

\[ |\Psi_0^{(0)}(\pi, J_0, M_0)\rangle = e^{-i\theta_0} |\Phi_0(\pi, J_0, M_0)\rangle, \]

where \( |\Phi_0(\pi, J_0, M_0)\rangle \) are the Dirac-Fock (DF) wave functions determined using the mean-field approximation and \( T^{(0)} \) are the electron excitation operators due to Coulomb interaction from the corresponding DF states.

In the present work, we have considered all possible single and double excitations (CCSD approach) in the calculations. We obtain the \( T^{(0)} \) amplitudes by solving the following equations using the Jacobi iterative method:

\[ \langle \Phi_0^N | H_D^{(DC)} | \Phi_0 \rangle = 0, \]

where \( |\Phi_0^N\rangle \) represents the singly and doubly excited states with respect to \( |\Phi_0\rangle \), the subscript \( N \) represents the normal-order form of the operators, and we have defined \( \tilde{H} = e^{-i\theta_0}H e^{i\theta_0} = (H e^{i\theta_0})_{\text{cont}} \) with the subscript “cont” representing connected terms.

B. First-order perturbed wave function

To obtain the \( |\Psi_0^{(1)}(\pi', J', M')\rangle \), we proceed as follows. Let us operate \( (H^{(DC)}_0 - E_0) \) on both sides of Eq. (2.5); i.e.,

\[ (H^{(DC)}_0 - E_0)|\Psi_0^{(1)}(\pi', J_1, M_1)\rangle = \sum_i (H^{(DC)}_0 - E_0)|\Psi_0^{(0)}(\pi', J_1, M_1)\rangle \langle \Psi_0^{(0)}(\pi', J_1, M_1)|D_i |\Psi_0^{(0)}(\pi, J_0, M_0)\rangle \frac{(\Psi_0^{(0)}(\pi', J_1, M_1)|D_i |\Psi_0^{(0)}(\pi, J_0, M_0)\rangle)}{E_0 - E_i} \]

\[ = \sum_i (E_i - E_0)|\Psi_0^{(0)}(\pi', J_1, M_1)\rangle \langle \Psi_0^{(0)}(\pi', J_1, M_1)|D_i |\Psi_0^{(0)}(\pi, J_0, M_0)\rangle \frac{(\Psi_0^{(0)}(\pi', J_1, M_1)|D_i |\Psi_0^{(0)}(\pi, J_0, M_0)\rangle)}{E_0 - E_i} \]

\[ = - \sum_i |\Psi_0^{(0)}(\pi', J_1, M_1)\rangle \langle \Psi_0^{(0)}(\pi', J_1, M_1)|D_i |\Psi_0^{(0)}(\pi, J_0, M_0)\rangle \frac{(\Psi_0^{(0)}(\pi', J_1, M_1)|D_i |\Psi_0^{(0)}(\pi, J_0, M_0)\rangle)}{E_0 - E_i} \frac{(\Psi_0^{(0)}(\pi', J_1, M_1)|D_i |\Psi_0^{(0)}(\pi, J_0, M_0)\rangle)}{E_0 - E_i} \]

Using the completeness principle of the atomic states of the DC Hamiltonian, \( \sum_a |\Psi_a^{(0)}\rangle \langle \Psi_a^{(0)}| = 1 \), we get

\[ \sum_i |\Psi_0^{(0)}(\pi', J_1, M_1)\rangle \langle \Psi_0^{(0)}(\pi', J_1, M_1)| = 1 - \sum_{K \neq i} |\Psi_K^{(0)}(\pi, J_K, M_K)\rangle \langle \Psi_K^{(0)}(\pi, J_K, M_K)|. \]

Substituting Eq. (2.9) into Eq. (2.8), we get
\[
(H_0^{\text{DC}} - E_0)|\Psi_0^{(1)}(\pi', J', M')\rangle = -D_z|\Psi_0^{(0)}(\pi, J_0, M_0)\rangle + \sum_K |\Psi_K^{(0)}(\pi, J_K, M_K)\rangle \langle \Psi_K^{(0)}(\pi, J_K, M_K)|D_z|\Psi_0^{(0)}(\pi, J_0, M_0)\rangle
\]
\[
 = -D_z|\Psi_0^{(0)}(\pi, J_0, M_0)\rangle,
\]  

(2.10)

where the second term does not contribute since \(|\Psi_K^{(0)}(\pi, J_K, M_K)\rangle\) and \(|\Psi_0^{(0)}(\pi, J_0, M_0)\rangle\) have the same parity.

The above equation represents a first-order perturbed equation with \(D_z\) as the perturbation and the first-order energy equal to zero. The unperturbed wave function is represented by \(|\Psi_0^{(0)}(\pi, J_0, M_0)\rangle\), and \(|\Psi_0^{(1)}(\pi', J', M')\rangle\) is its first-order correction. In order to solve for \(|\Psi_0^{(1)}(\pi', J', M')\rangle\), we solve Eq. (2.10) using the following (RCC) approach.

Using the above CC ansatz for closed-shell atoms, we can express the total wave function \(|\Psi_0\rangle\), which is of mixed parity and angular momentum, by

\[
|\Psi_0\rangle = e^{\hat{T}}|\Phi_0(\pi, J_0, M_0)\rangle,
\]

(2.11)

where we define

\[
\hat{T} = T^{(0)} + T^{(1)},
\]

(2.12)

with \(T^{(1)}\) representing the excitation operators containing all orders in the Coulomb interaction and one order in \(D_z\). Substituting Eq. (2.12) into Eq. (2.11), we get

\[
|\Psi_0\rangle = e^{\hat{T}^{(0)} + \hat{T}^{(1)}}|\Phi_0(\pi, J_0, M_0)\rangle = e^{\hat{T}^{(0)}}(1 + \hat{T}^{(1)})|\Phi_0(\pi, J_0, M_0)\rangle,
\]

(2.13)

where only terms up to linear in \(\hat{T}^{(1)}\)—i.e., those terms up to one order in \(D_z\)—are retained.

It is clear from Eq. (2.13) that the first-order perturbed wave function can now be written as

\[
|\Psi_0^{(1)}(\pi', J', M')\rangle = e^{\hat{T}^{(0)}}\langle \hat{T}^{(1)}|\Phi_0(\pi, J_0, M_0)\rangle.
\]

(2.14)

The \(T^{(1)}\) amplitudes are determined using the equations

\[
\langle \Phi_0|H_0^{\text{DC}}T^{(1)}|\Phi_0\rangle = -\langle \Phi_0|\hat{D}_z|\Phi_0\rangle,
\]

(2.15)

where we have used the relation \(\hat{O}=e^{\hat{T}^{(0)}}\hat{O}e^{\hat{T}^{(0)}}=(\hat{O}e^{\hat{T}^{(0)}})_{\text{con}}.\) A detailed description for evaluating these amplitudes and the corresponding Goldstone diagrams in the closed-shell and one valence systems are given elsewhere [24,25].

C. (R)CC expression for \(\alpha\)

Using Eqs. (2.6) and (2.14), the expression for the polarizabilities using the (R)CC operators can be expressed as

\[
\alpha = \frac{\langle \Phi_0|e^{\hat{T}}\hat{D}_ze^{\hat{T}}|\Phi_0\rangle}{\langle \Phi_0|e^{\hat{T}}e^{\hat{T}}|\Phi_0\rangle} = \frac{\langle \Phi_0|(T^{(1)}D_z^{(0)} + D_z^{(0)}T^{(1)})|\Phi_0\rangle}{N_0},
\]

(2.16)

where for computational simplicity we define \(D_z^{(0)}=e^{T^{(0)}}\hat{D}_ze^{T^{(0)}}\) and \(N_0=\langle \Phi_0|e^{T^{(0)}}e^{T^{(0)}}|\Phi_0\rangle.\) We compute these terms by expressing them as effective one-body and two-body terms using the generalized Wick’s theorem [26].

III. RESULTS AND DISCUSSIONS

In Table I, we present our results of electric-dipole polarizabilities and compare them with those available in the literature. The error bars in the experimental results are large for all the systems except in He, and our results lie within them. The results of the calculations that are given in Table I are obtained using a variety of many-body theories. Our results are in reasonable agreement with most of them. We have also estimated the contributions from the important triple excitations in addition to the CCSD contributions and taken them as the upper limits of the errors associated in our calculations. They are mentioned in the parentheses next to our results presented in Table I.

There are several calculations of the ground-state He polarizability available using different methods, and some of them have also included certain QED contributions [20]. Similarly, a number of precise measurements are listed in [20] among which the latest result is reported in [19]. It is therefore desirable to calculate He polarizability using our method. A linear response approach derived from time-dependent CC theory was also earlier used by Liu and Kelly.

<table>
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<th>Atoms</th>
<th>Expt.</th>
<th>Others</th>
<th>This work</th>
</tr>
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<tbody>
<tr>
<td>He</td>
<td>1.383746(7)(^a)</td>
<td>1.383193,(^b) 1.389(^c)</td>
<td>1.382(1)</td>
</tr>
<tr>
<td>Be</td>
<td>37.755,(^d) 37.69,(^e) 37.9(^f)</td>
<td>37.80(47)</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>71.5(3.1)(^g)</td>
<td>71.35,(^h) 72.0,(^i) 71.3(0)(^j)</td>
<td>73.41(2.32)</td>
</tr>
<tr>
<td>Ca</td>
<td>169(17)(^k)</td>
<td>159.4,(^l) 152.7,(^m) 157.1(1.3),(^n)</td>
<td>154.58(5.42)</td>
</tr>
<tr>
<td>Sr</td>
<td>186(15)(^o)</td>
<td>201.2,(^p) 193.2,(^q) 197.2(2),(^r)</td>
<td>199.71(7.28)</td>
</tr>
<tr>
<td>Ba</td>
<td>268(22)(^s)</td>
<td>264,(^t) 273,(^u) 273.9(^v)</td>
<td>268.19(8.74)</td>
</tr>
<tr>
<td>Yb</td>
<td>142(36)(^w)</td>
<td>111.3(5),(^x) 141.7,(^y) 157.3(0)(^z)</td>
<td>144.59(5.64)</td>
</tr>
</tbody>
</table>

\(^a\)Reference [19]. \(^b\)Reference [34]. \(^c\)Reference [36]. \(^d\)Reference [20]. \(^e\)Reference [35]. \(^f\)Reference [29].
\(^g\)Reference [10]. \(^h\)Reference [11]. \(^i\)Reference [37]. \(^j\)Reference [33]. \(^k\)Reference [21]. \(^l\)Reference [31].
\(^m\)Reference [27]. \(^n\)Reference [30]. \(^o\)Reference [22].
We have carried out calculations of electric-dipole polarizabilities for many alkaline earth metals, helium, and ytterbium using the RCC method and highlighted the importance of the correlation effects. These calculations avoid the sum-over-states approach in determining polarizabilities and implicitly consider all the intermediate states by solving the perturbed RCC wave function to first order in the dipole and all orders in the residual Coulomb interaction. 

*Note added.* We recently became aware of a recent calculation of the polarizability of the ground state of Yb [38]. It was performed using full and approximate relativistic *ab initio* methods, and the result is in good agreement with ours.

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