

INVITED PAPER
A coupled-cluster approach to polarizabilities:
Computational aspects

B. K. Sahoo¹

Max-Planck Institute for the Physics of Complex Systems, Nöthnitzer Straße 38, D-01187
Dresden, Germany

B. P. Das²

Non-Accelerator Particle Physics Group, Indian Institute of Astrophysics, Bangalore-34, India

R. K. Chaudhuri³

Non-Accelerator Particle Physics Group, Indian Institute of Astrophysics, Bangalore-34, India

D. Mukherjee⁴

Department of Physical Chemistry, Indian Association for Cultivation of Science, Kolkata - 700
032, India

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Abstract: We present *ab initio* calculations of both the dipole and quadrupole polarizabilities within the framework of the relativistic coupled-cluster theory. We directly solve the first order perturbed equation arising from a general one-electron perturbation, thereby avoiding an explicit summation over intermediate states. This method can be applied to a wide range of problems including the high precision calculations of very small but finite parity non-conserving and CP violating amplitudes. We discuss in detail the computational methods used in the calculations and investigate the trends of electron correlation effects for the dipole and quadrupole polarizabilities.

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1 Introduction

There have been continuous attempts to improve the calculations of polarizabilities in atoms [1]-[8]. Due to their wide range of applications, both atomic physicists and quantum chemists have applied

¹Corresponding author: E-mail - bijaya@mpipks-dresden.mpg.de

²E-mail - das@iiap.res.in

³E-mail - rkchaudh@iiap.res.in

⁴E-mail - pcdm@mahendra.iacs.res.in

various types of theories to determine them accurately [7]-[12]. A knowledge of these quantities is useful in optical frequency standards [13, 14], parity non-conservation [2, 15], and in testing the accuracy of the lifetimes of the excited atomic states [4, 7] etc. A fairly common approach that is used in the calculation of polarizabilities is the sum-over-states approach, where one needs to calculate the intermediate states that make significant contributions and also the excitation energies [7, 8]. A possible advantage of this approach is that in certain cases one can use the experimental energies to obtain accurate values of the polarizabilities [7]. On the other hand, it has two major drawbacks: First, this is not an *ab initio* method and second it is not possible to include contributions from all the intermediate states, but rather a selective number of states for practical reasons. In some cases, non-relativistic theories have been employed to calculate polarizabilities and the relativistic corrections are considered in an approximate manner [16, 17]. These quantities have been calculated using the scalar relativistic Douglas-Kroll [17, 18, 19] and the Dalgarno-Lewis [5, 10, 20] approaches [11, 12, 17]. Sometimes molecular codes with pseudopotentials [18, 21] and finite field coupled-cluster (CC) method [22] have been used.

Relativistic coupled-cluster (RCC) theory has been employed recently to calculate a variety of atomic properties [23, 24]. This method is capable of treating electron correlation rigorously as it is equivalent to all order many-body perturbation theory [25, 26]. We generate our wave functions for the calculations in the present work using this method. To calculate both dipole and quadrupole polarizabilities, we present a new approach based on the RCC theory. The key aspect of this approach is that it implicitly includes all intermediate states in the first order perturbed wave functions. By calculating these wave functions with dipole or quadrupole operators as perturbations and evaluating the expectation values of the corresponding operators, it is possible to determine the dipole and quadrupole polarizabilities, respectively. In this approach, one does not have to consider the core-orbital contributions separately. It clearly has the potential to yield accurate *ab initio* results. This method can be extended to evaluate dynamic polarizabilities and hence to determine the van der Waal's co-efficients for like atom alkali-metal pairs [5, 8, 20, 27] and hetero-nuclear alkali-metal interactions [12]. A similar approach can also be applied to calculate polarizabilities in alkali clusters [28]. In addition, this method can be used to calculate the first order perturbed wave functions due to parity non-conserving (PNC) and CP violating amplitudes. Interestingly, polarizabilities of negative ions like Be^- , Mg^- , Ca^- and Sr^- can also be determined in this approach.

We have applied our method to three alkali atoms (Li, Na and K) and alkaline earth ions (Be^+ , Mg^+ and Ca^+) to calculate their dipole and quadrupole polarizabilities for ground and excited states. We consider dipole polarizabilities for the ground states and two excited states. Quadrupole polarizabilities are calculated only for the ground states in these systems.

First, we discuss the theory underlying atomic polarizabilities. In sec. 3, we give the details of our computational procedure for determining the unperturbed and first order perturbed wave functions. We then proceed to present our results in the next section and that is followed by some concluding remarks.

2 Theory

The energy shift, $\Delta E(J_n, M_n)$ of any state $|J_n M_n\rangle$, with principal quantum number n , in a direct current (dc) electric field $\vec{\mathcal{E}} = \mathcal{E}\hat{z}$ can be expressed as

$$\Delta E(J_n, M_n) = -\frac{1}{2}\alpha^1(J_n, M_n)\mathcal{E}^2, \quad (1)$$

where $\alpha^1(J_n, M_n)$ is defined as the static polarizability of state $|J_n M_n\rangle$. Further, $\alpha^1(J_n, M_n)$ can be divided as

$$\alpha^1(J_n, M_n) = \alpha_0^1(J_n) + \frac{3M_n^2 - J_n(J_n + 1)}{J_n(2J_n - 1)}\alpha_2^1(J_n), \quad (2)$$

Here $\alpha_0^1(J_n)$ and $\alpha_2^1(J_n)$ are known as the scalar and tensor polarizabilities, respectively. From the first order perturbation equations, these parameters can be expressed as the sum over intermediate states

$$\alpha_i^1(J_n) = -2 \sum_{k \neq n} \frac{|\langle J_n J_n | z | J_k J_k \rangle|^2}{E_n - E_k}, \quad (3)$$

where i represents either 0 or 2, z is the \hat{z} component of the position vector \vec{r} and E 's are the unperturbed energy levels. Since z can be expressed in terms of the spherical harmonics of rank one ($Y_{10}(\theta, \phi)$), the above matrix elements will be non-zero between opposite parity states satisfying the E1 transition selection rules. The α_i 's can be expressed in terms of the reduced matrix elements of the E1 operator ($D = e\vec{r}$) as follows

$$\alpha_0^1(J_n) = \frac{-2}{3(2J_n + 1)} \sum_{k \neq n} \frac{|\langle J_n || D || J_k \rangle|^2}{E_n - E_k} \quad (4)$$

and

$$\alpha_2^1(J_n) = \left(\frac{40J_n(2J_n - 1)}{3(2J_n + 3)(2J_n + 1)(J_n + 1)} \right)^{1/2} \sum_{k \neq n} (-1)^{J_n + J_k + 1} \begin{Bmatrix} J_n & 1 & J_k \\ 1 & J_n & 2 \end{Bmatrix} \frac{|\langle J_n || D || J_k \rangle|^2}{E_n - E_k}. \quad (5)$$

Similarly, the static quadrupole polarizability can be expressed as

$$\begin{aligned} \alpha_0^2(J_n) &= -2 \sum_{k \neq n} \frac{|\langle J_n J_n | Q | J_k J_k \rangle|^2}{E_n - E_k} \\ &= \frac{-2}{5(2J_n + 1)} \sum_{k \neq n} \frac{|\langle J_n || Q || J_k \rangle|^2}{E_n - E_k}, \end{aligned} \quad (6)$$

where $Q = -\frac{e}{2}(3z^2 - r^2)$ is the E2 operator which has different selection rules than the E1 operator.

3 Computational method

The above expressions for both the polarizabilities can be expressed in a general form as

$$\begin{aligned} \alpha(J_n M_n) &= \langle \Psi_n | O | \Psi_n \rangle \\ &= \langle \Psi_n^{(0)} | O | \Psi_n^{(1)} \rangle + \langle \Psi_n^{(1)} | O | \Psi_n^{(0)} \rangle \\ &= 2\langle \Psi_n^{(1)} | O | \Psi_n^{(0)} \rangle, \end{aligned} \quad (7)$$

where the wave function of the n th state can be written in terms of the original atomic wave function and the first order correction due to the corresponding dipole or quadrupole operators $O(= D \text{ or } Q)$; i.e.

$$|\Psi_n\rangle = |\Psi_n^{(0)}\rangle + |\Psi_n^{(1)}\rangle. \quad (8)$$

We show that it is possible to calculate $\alpha(J_n M_n)$'s by calculating both the $|\Psi_n^{(0)}\rangle$ and $|\Psi_n^{(1)}\rangle$ using a coupled-cluster method which circumvents the sum-over-states approach mentioned above. In our approach, we obtain the first order perturbed wave function as a solution to the following equation

$$(H_0^{(DC)} - E_n^{(0)})|\Psi_n^{(1)}\rangle = (E_n^{(1)} - H_{int})|\Psi_n^{(0)}\rangle, \quad (9)$$

where $H_0^{(DC)}$ and H_{int} are the Dirac-Coulomb (DC) and the E1 or E2 operators, respectively. The $E_n^{(0)}$ and $E_n^{(1)}$ are the zeroth and first order energies of the n th state, respectively.

3.1 Calculations of unperturbed wave functions

The starting point of our development is the relativistic generalization of the valence universal coupled-cluster theory introduced by Mukherjee et al [29, 30] which was put later in a more compact form by Lindgren [25, 31]. In the relativistic analogous of CC theory, to be hereafter called as the RCC theory, the atomic wave function $|\Psi_v^{(0)}\rangle$ for a single valence (v) open-shell system is expressed as

$$|\Psi_v^{(0)}\rangle = e^{T^{(0)}}\{1 + S_v^{(0)}\}|\Phi_v\rangle, \quad (10)$$

where we define $|\Phi_v\rangle = a_v^\dagger|\Phi_0\rangle$, with $|\Phi_0\rangle$ as the Dirac-Fock (DF) state for the closed-shell system, which is taken as the vacuum with respect to the DF vacuum. The curly bracket in the above expression represents normal ordered form.

In the single and double excitations approximation coupled-cluster (CCSD) method, we have

$$\begin{aligned} T^{(0)} &= T_1^{(0)} + T_2^{(0)}, \\ S_v^{(0)} &= S_{1v}^{(0)} + S_{2v}^{(0)}, \end{aligned} \quad (11)$$

where $T_1^{(0)}$ and $T_2^{(0)}$ are the single and double hole-particle excitation operators for the core electrons and $S_{1v}^{(0)}$ and $S_{2v}^{(0)}$ are the single and double excitation operators for the valence electron along with necessary core electrons, respectively. The energies and RCC operator amplitudes can be determined by solving the coupled-cluster singles and doubles equations as given below:

$$\langle\Phi_0^L|H^{(0)}\widehat{e^{T^{(0)}}}|\Phi_0\rangle = \delta_{L,0} E_0^{(0)} \quad (12)$$

$$\begin{aligned} \langle\Phi_v^K|H^{(0)}\widehat{e^{T^{(0)}}}S_v^{(0)}|\Phi_v\rangle &= -\langle\Phi_v^K|H^{(0)}\widehat{e^{T^{(0)}}}|\Phi_v\rangle + \langle\Phi_v^K|\{1 + S_v^{(0)}\}|\Phi_v\rangle E_v^{(0)} \\ &= -\langle\Phi_v^K|H^{(0)}\widehat{e^{T^{(0)}}}|\Phi_v\rangle + E_v^{(0)} + \langle\Phi_v^K|S_v^{(0)}|\Phi_v\rangle\langle\Phi_v|(H^{(0)}\widehat{e^{T^{(0)}}})\{1 + S_v^{(0)}\}|\Phi_v\rangle, \end{aligned} \quad (13)$$

where $L = 1, 2$ represents single and double excitations from the closed-shell state and $K = 1, 2$ represents single and double excitations from a single valence state. For $L = 0$, we get the closed-shell energy $E_0^{(0)}$ and for $K = 0$, we get the energy $E_v^{(0)}$ with the valency electron ' v '. The difference between these two energies give the ionization potential (IP) energy of the corresponding valence electron. In the above equation, the wide-hat notation represents contraction and we have used the relation: $(e^{-T^{(0)}}H^{(0)}e^{T^{(0)}})_c = H^{(0)}\widehat{e^{T^{(0)}}}$, where the subscript ' c ' represents only the connected terms for the expression of the left hand side.

We consider the Dirac-Coulomb (DC) Hamiltonian for the calculation of unperturbed wave-functions given by

$$\begin{aligned} H^{(0)} &= [H_0^{(0)}] + [V_{es}^{(0)}] \\ &= \sum_i^N [c\alpha \cdot p_i + (\beta - 1)c^2 + V_n(r_i) + U(r_i)] + \left[\sum_{i>j}^N \frac{1}{r_{ij}} - \sum_i^N U(r_i)\right], \end{aligned} \quad (14)$$

where $H_0^{(0)}$ is the DF Hamiltonian and $V_{es}^{(0)}$ is the Coulomb residual term in atomic unit (au) obtained using the mean field potential $U(r_i)$ that is included perturbatively to all orders in the RCC method. Here α and β are the universal Dirac matrices.

To solve the amplitude equation given by Eq. (12), we formulate the following matrix equation

$$\begin{pmatrix} \langle \Phi_a^p | \overbrace{H_N(e^{T^{(0)}} - 1)} | \Phi_a^p \rangle & \langle \Phi_a^p | \overbrace{H_N(e^{T^{(0)}} - 1)} | \Phi_{ab}^{pq} \rangle \\ \langle \Phi_a^p | \overbrace{H_N(e^{T^{(0)}} - 1)} | \Phi_{ab}^{pq} \rangle & \langle \Phi_{ab}^{pq} | \overbrace{H_N(e^{T^{(0)}} - 1)} | \Phi_{ab}^{pq} \rangle \end{pmatrix} \begin{pmatrix} t_a^{p(0)} \\ t_{ab}^{pq(0)} \end{pmatrix} = - \begin{pmatrix} \langle \Phi_a^p | H_N | \Phi_0 \rangle \\ \langle \Phi_{ab}^{pq} | H_N | \Phi_0 \rangle \end{pmatrix}, \quad (15)$$

where we have used $a, b, c \dots$ and $p, q, r \dots$ indices for occupied and unoccupied orbitals, respectively. $|\Phi_a^p\rangle$ and $|\Phi_{ab}^{pq}\rangle$ are the single and double excitation wave functions, respectively, with respect to $|\Phi_0\rangle$. The above equation in vector form can be expressed as

$$\mathbf{A}(\mathbf{X}) \cdot \mathbf{X} = -\mathbf{B}. \quad (16)$$

The matrix \mathbf{A} itself depends explicitly on the $T^{(0)}$ operator amplitudes. The non-linear terms present in \mathbf{A} can be split up as effective one-body terms and two-body terms. First these effective one-body and two-body terms can be calculated and stored in RAM on the computer. These intermediate parts can be contracted further with respective $T^{(0)}$ operators of the \mathbf{X} vector. The solution of the above matrix equation can be expressed as

$$X_j(i) = \frac{-B_j - \sum_{l \neq j} A_{jl}(X) X_l(i-1)}{A_{jj}}, \quad (17)$$

where A_{jj} and A_{jl} are the diagonal and off-diagonal element of the matrix \mathbf{A} , respectively. The diagonal elements are determined from the effective one-body terms and off-diagonal elements are determined from effective one-body and two-body terms. The off-diagonal contributions are shown diagrammatically in Fig. 1. The above equation is solved self-consistently using Jacobi iterative method with i representing iteration number for the j th element. Initial guesses for the first iteration are given by

$$\begin{aligned} (t_a^p)^{(0)}(1) &= 0 \\ (t_{ab}^{pq})^{(0)}(1) &= \frac{\langle pq | \frac{1}{r_{12}} | ab \rangle}{\epsilon_a + \epsilon_b - \epsilon_p - \epsilon_q}, \end{aligned} \quad (18)$$

respectively. The initial value for the $(t_a^p)^{(0)}(1)$ is zero which follows from the *Brillouin's condition* [25, 26] and ϵ 's are the DF single particle orbital energies. Zero in the superscript represents for the unperturbed states.

The open-shell CC amplitudes determining Eq. (13) can be expressed in a similar approach as

$$\begin{pmatrix} \langle \Phi_v^p | \overbrace{H_N e^{T^{(0)}} - \Delta E_v} | \Phi_a^p \rangle & \langle \Phi_v^p | \overbrace{H_N e^{T^{(0)}}} | \Phi_{vb}^{pq} \rangle \\ \langle \Phi_{vb}^{pq} | \overbrace{H_N e^{T^{(0)}}} | \Phi_v^p \rangle & \langle \Phi_{vb}^{pq} | \overbrace{H_N e^{T^{(0)}} - \Delta E_v} | \Phi_{vb}^{pq} \rangle \end{pmatrix} \begin{pmatrix} s_v^{p(0)} \\ s_{vb}^{pq(0)} \end{pmatrix} = - \begin{pmatrix} \langle \Phi_v^p | \overbrace{H_N e^{T^{(0)}}} | \Phi_v \rangle \\ \langle \Phi_{vb}^{pq} | \overbrace{H_N e^{T^{(0)}}} | \Phi_v \rangle \end{pmatrix}. \quad (19)$$

Or, in vector form

$$(\mathbf{A} - \Delta E_v \mathbf{I}) \cdot \mathbf{X} = -\mathbf{B}, \quad (20)$$

where \mathbf{I} is the identity operator. In fact, in this equation \mathbf{A} and \mathbf{B} are known quantities as $T^{(0)}$ -amplitudes are already evaluated. The above equation is non-linear because of the fact that the

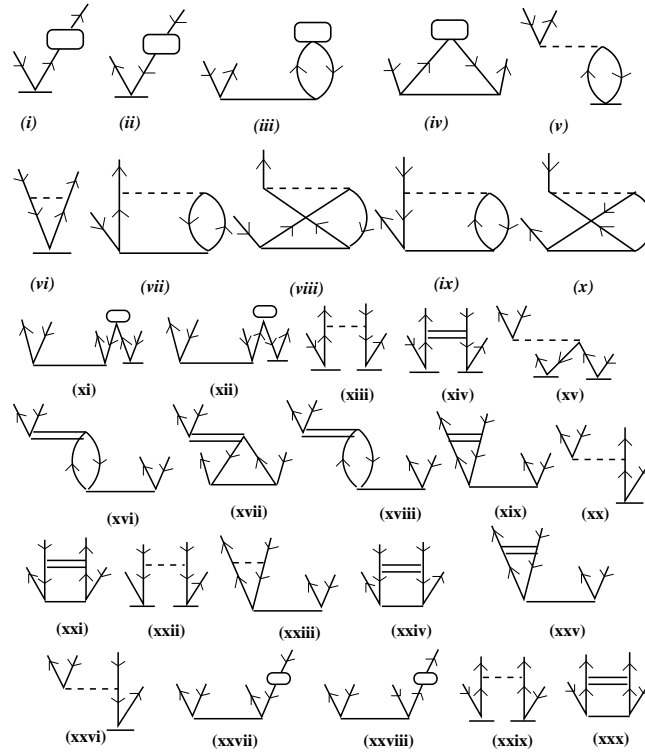


Figure 1: Goldstone diagrammatic representation of off-diagonal elements for singles (a) and doubles (b) unperturbed $T^{(0)}$ - operators. Boxes and double lines are the necessary effective one-body and two-body terms, respectively. Dotted line represents bare two-body term (V_{es} and solid line represents $T^{(0)}$ - operators.

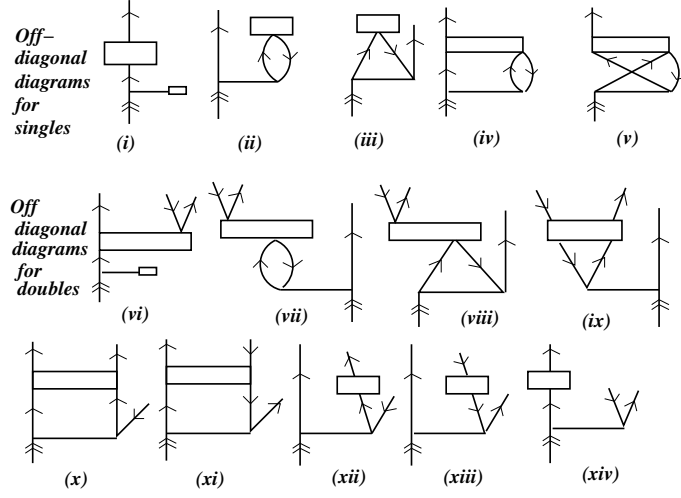


Figure 2: Goldstone diagrams for off-diagonal elements $S_v^{(0)}$ determining equations. Boxes with two open-lines and four open-lines represent effective one-body and two-body terms with $T^{(0)}$ -operators which are known for the open-shell RCC equations. Operator diagram with double arrow represents $S_v^{(0)}$ - operators and lines with double arrow represent valence orbital.

electron affinity energy (ΔE_v) itself depends on $S_v^{(0)}$ operator amplitudes. For the Jacobi iterative method, the above equation can be solved by expressing

$$X_j(i) = \frac{-B_j + (\Delta E_v - \epsilon_v)X_j(i-1) - \sum_{l \neq j} A_{jl}X_l(i-1)}{A_{jj}}. \quad (21)$$

The initial values of the above equation are taken as

$$\begin{aligned} s_v^{p(0)}(1) &= \frac{f(p, v)}{f(v, v) - f(p, p)} \\ s_{vb}^{pq(0)}(1) &= \frac{\langle pq|V(pq, vb)|vb\rangle}{f(v, v) + f(b, b) - f(p, p) - f(q, q)}, \end{aligned} \quad (22)$$

where $f(i, j)$ and $V(pq, vb)$ are elements of effective one-body and two-body terms of \mathbf{A} . The off-diagonal elements are shown diagrammatically in Fig. 2.

To illustrate the fact that the RCC method is an all order perturbative method, we decompose our RCC operators in terms of many-body perturbation theory (MBPT) and show diagrammatically in Fig. 3. It implies that our $S_{1v}^{(0)}$ operator (Fig. 3(a)) contains leading order pair-correlation effects and $S_{1v}^{(0)}$ operator (Fig. 3(b)) contains leading order core-polarization effects of the MBPT method, respectively.

The most important triple excitations have been considered by constructing the excitation operators from V_{es} , $T_2^{(0)}$ and $S_{v2}^{(0)}$ [32] as

$$S_{vbc}^{pqr(0)} = \frac{\{\widehat{V_{es}T_2^{(0)}}\}_{3body} + \{\widehat{V_{es}S_{v2}^{(0)}}\}_{3body}}{\epsilon_v + \epsilon_b + \epsilon_c - \epsilon_p - \epsilon_q - \epsilon_r}, \quad (23)$$

where $\{\dots\}_{3body}$ are the appropriate three-body excitation operators from $vbr \rightarrow pqr$.

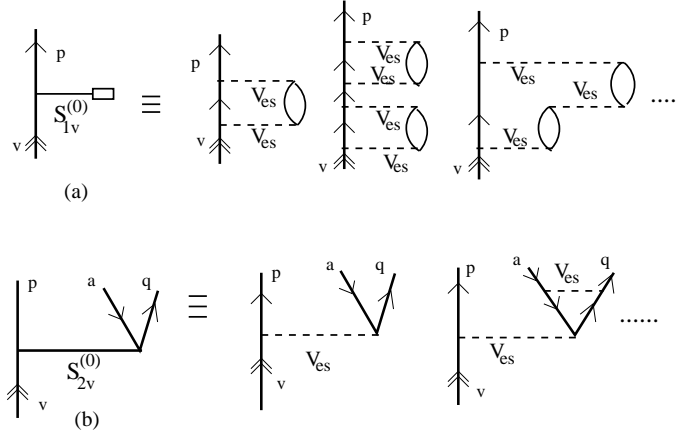


Figure 3: A schematic diagrammatic representation of RCC diagrams for $S_{1v}^{(0)}$ and $S_{2v}^{(0)}$ in terms of lower order MBPT diagrams. Here we have used 'a' represents occupied (core) orbital, 'p' and 'q' represent unoccupied (particle) orbitals and 'v' represents valence orbital. For $S_{1v}^{(0)}$, we have the restriction $p \neq v$.

The above operators are used to construct the single and double open-shell cluster amplitudes by connecting further with the CCSD operators and they are solved self-consistently. For the element X_j at i th iteration, we have

$$X_j(i) = \frac{-B_j + (S_{vbc}^{pqr})_j^{(i-1)} X_j(i-1) + (\Delta E_v - \epsilon_v) X_j(i-1) - \sum_{l \neq j} A_{jl} X_l(i-1)}{A_{jj}}, \quad (24)$$

and the approach is known as CCSD(T) method. Typical excitation operators those are considered in these calculations are shown diagrammatically in Fig. 4.

3.2 Calculations of perturbed wave functions

In the presence of an external perturbation, it is possible to express the exact wave function of the system in the presence of weak perturbed source as

$$|\Psi_v\rangle = e^T \{1 + S_v\} |\Phi_v\rangle, \quad (25)$$

where the cluster amplitudes are given by

$$\begin{aligned} T &= T^{(0)} + \lambda T^{(1)}, \\ S_v &= S_v^{(0)} + \lambda S_v^{(1)}. \end{aligned} \quad (26)$$

Here λV_{ext} is taken as external perturbation. The $T^{(1)}$ and $S_v^{(1)}$ operators are the corrections to the cluster operators $T^{(0)}$ and $S_v^{(0)}$, respectively. If λ is very small, of the order of electron charge, one can consider only the first order terms in Eq. (26). Therefore, Eq. (25) can be written as

$$|\Psi_v\rangle = [e^{T^{(0)}} T^{(1)} \{1 + S_v^{(0)}\} + e^{T^{(0)}} \{S_v^{(1)}\}] |\Phi_v\rangle, \quad (27)$$

which can be explicitly separated as given in Eq. (8).

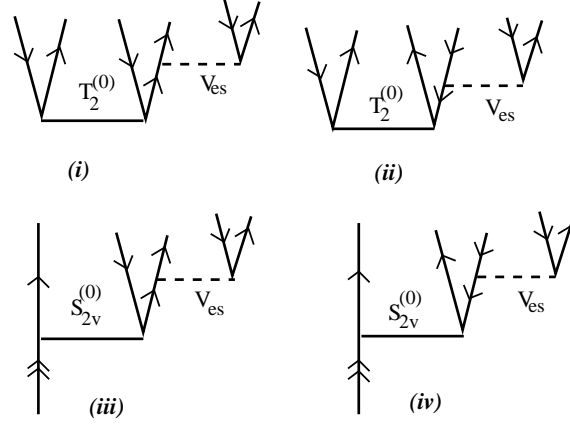


Figure 4: Typical Goldstone diagrams representing leading order triple excitations over the CCSD method. Double arrow in the diagrams represents valence electron v and V_{es} is the residual interaction.

The perturbed amplitudes for $T^{(1)}$ and $S_v^{(1)}$ operators are solved using the following equations

$$\langle \Phi_0^L | \widehat{H^{(0)}} T^{(1)} + \widehat{H_{int}} | \Phi_0 \rangle = 0, \quad (28)$$

$$\langle \Phi_v^K | (\widehat{H^{(0)}} - \widehat{E_v^{(0)}}) S_v^{(1)} + \widehat{H^{(0)}} T^{(1)} + \widehat{H^{(0)}} T^{(1)} S_v^{(0)} + \widehat{H_{int}} + \widehat{H_{int}} S_v^{(0)} | \Phi_v \rangle = 0, \quad (29)$$

where $L, K = 1, 2$ and the effective Hamiltonian operators with overline defined as $\widehat{H^{(0)}} = (e^{-T^{(0)}} H^{(0)} e^{T^{(0)}})_c$. These are computed after determining $T^{(0)}$ amplitudes. The wide-hat symbol as usual represents the connected terms. Here H_{int} is the interaction Hamiltonian for the external potential λV_{ext} .

In the matrix representation, with the CCSD approximation, one can express Eq. (28) as

$$\begin{pmatrix} \langle \Phi_a^p | \widehat{H_N^{(0)}} | \Phi_a^p \rangle & \langle \Phi_a^p | \widehat{H_N^{(0)}} | \Phi_{ab}^{pq} \rangle \\ \langle \Phi_{ab}^{pq} | \widehat{H_N^{(0)}} | \Phi_a^p \rangle & \langle \Phi_{ab}^{pq} | \widehat{H_N^{(0)}} | \Phi_{ab}^{pq} \rangle \end{pmatrix} \begin{pmatrix} t_a^{p(1)} \\ t_{ab}^{pq(1)} \end{pmatrix} = - \begin{pmatrix} \langle \Phi_a^p | \widehat{H_{int}} | \Phi_0 \rangle \\ \langle \Phi_{ab}^{pq} | \widehat{H_{int}} | \Phi_0 \rangle \end{pmatrix}, \quad (30)$$

where $t_a^{p(1)}$ and $t_{ab}^{pq(1)}$ are the perturbed single and double excitation amplitudes, respectively. Or, in vector form one writes

$$\mathbf{A} \cdot \mathbf{X} = -\mathbf{B}. \quad (31)$$

The j^{th} element of the vector \mathbf{X} , which represents $T^{(1)}$ operator, can be solved using the Jacobi iterative method by expressing

$$X_j(i) = \frac{-B_j - \sum_{l \neq j} A_{jl} X_l(i-1)}{A_{jj}}, \quad (32)$$

where i represents iteration number and j the element number. A_{jl} and A_{jj} are the off-diagonal and diagonal elements of the matrix \mathbf{A} . B_j is the j^{th} element of the matrix \mathbf{B} .

The initial values for these elements are considered as,

$$\begin{aligned} t_a^{p(1)}(1) &= \frac{\langle \Phi_a^p | \widehat{H_{int}} | \Phi_0 \rangle}{f(a, a) - f(p, p)} \\ t_{ab}^{pq(1)}(1) &= \frac{\langle \Phi_{ab}^{pq} | \widehat{H_{int}} | \Phi_0 \rangle}{f(a, a) + f(b, b) - f(p, p) - f(q, q)}. \end{aligned} \quad (33)$$

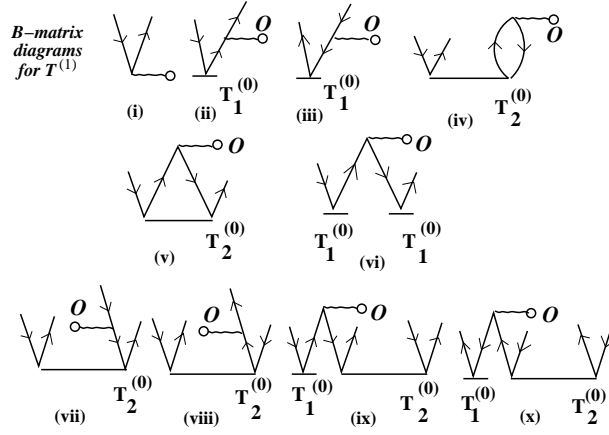


Figure 5: B- matrix diagrams for $T^{(1)}$ - determining equation. O represents the perturbed interaction operator D or Q .

Here superscript (1) represents the perturbed operator and ordinary (1) in the parenthesis stands for the first iteration. Similarly for the open-shell Eq. (29), we can have

$$\begin{pmatrix} \langle \Phi_v^p | \overline{H_N^{(0)}} - \Delta E_v | \Phi_v^p \rangle & \langle \Phi_v^p | \overline{H_N^{(0)}} | \Phi_{vb}^{pq} \rangle \\ \langle \Phi_{vb}^{pq} | \overline{H_N^{(0)}} | \Phi_v^p \rangle & \langle \Phi_{vb}^{pq} | \overline{H_N^{(0)}} - \Delta E_v | \Phi_{vb}^{pq} \rangle \end{pmatrix} \begin{pmatrix} s_v^{p(1)} \\ s_{vb}^{pq(1)} \end{pmatrix} = - \begin{pmatrix} \langle \Phi_v^p | \overline{H_N^{(0)}} T^{(1)} + \overline{H_{int}} | \Phi_v \rangle \\ \langle \Phi_{vb}^{pq} | \overline{H_N^{(0)}} T^{(1)} + \overline{H_{int}} | \Phi_v \rangle \end{pmatrix}, \quad (34)$$

where $s_v^{p(1)}$ and $s_{vb}^{pq(1)}$ are the perturbed single and double excitation amplitudes, respectively, with the valence electron 'v'.

In vector notation, the above matrix can be expressed as

$$\mathbf{A} \cdot \mathbf{X} = -\mathbf{B}. \quad (35)$$

The j^{th} element of the vector \mathbf{X} , which represents $S_v^{(1)}$ operator, can be solved using the Jacobi iterative method by expressing

$$X_j(i) = \frac{-B_j - \sum_{l \neq j} A_{jl} X_l(i-1)}{A_{jj}}. \quad (36)$$

The initial values for these elements are considered as

$$\begin{aligned} s_v^{p(1)}(1) &= \frac{\langle \Phi_v^p | \overline{H_N^{(0)}} T^{(1)} + \overline{H^{(1)}} | \Phi_0 \rangle}{\Delta E_v - f(p, p)}, \\ s_{vb}^{pq(1)}(1) &= \frac{\langle \Phi_{vb}^{pq} | \overline{H_N^{(0)}} T^{(1)} + \overline{H^{(1)}} | \Phi_0 \rangle}{\Delta E_v + f(b, b) - f(p, p) - f(q, q)}. \end{aligned} \quad (37)$$

To calculate the polarizabilities, one now takes H_{int} as dipole (D) or quadrupole (Q) operators. For atomic PNC or CP violating studies the corresponding weak interaction Hamiltonian has to be considered. Now, considering the interaction Hamiltonian H_{int} due to dipole or quadrupole operators, it is possible to express the polarizabilities as given in Eq. (7). i.e.

$$\alpha_i(J_v M_v) = \frac{\langle \Phi_v | \{1 + S_v^\dagger\} e^{T^\dagger} O e^T \{1 + S_v\} | \Phi_v \rangle}{\langle \Phi_v | \{1 + S_v^\dagger\} e^{T^\dagger} e^T \{1 + S_v\} | \Phi_v \rangle}$$

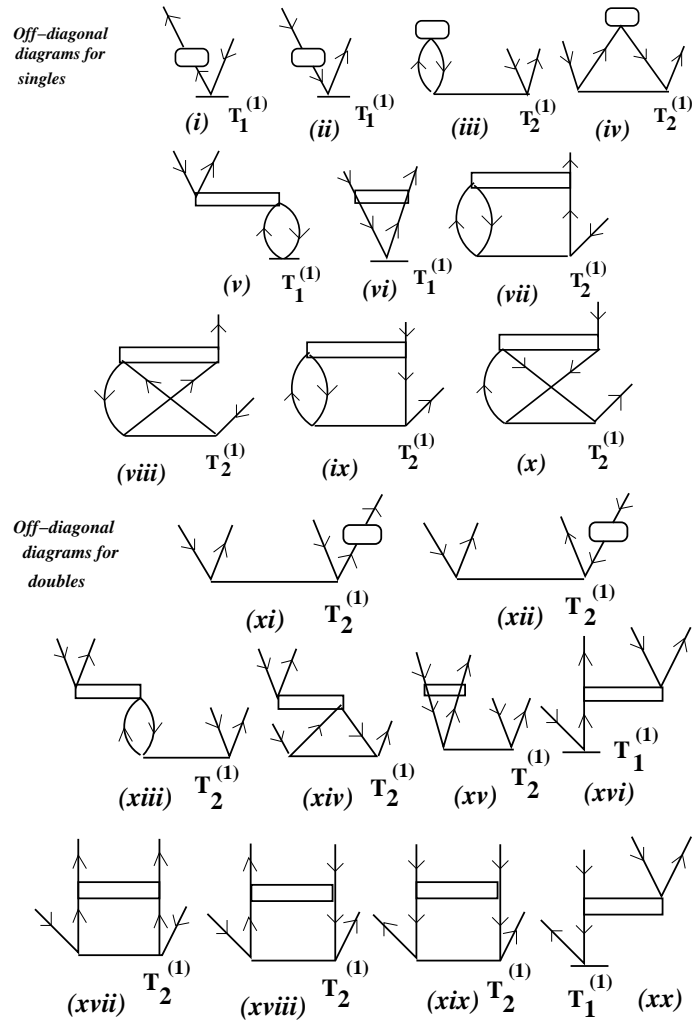


Figure 6: The off-diagonal elements for $T^{(1)}$ - determining equations.

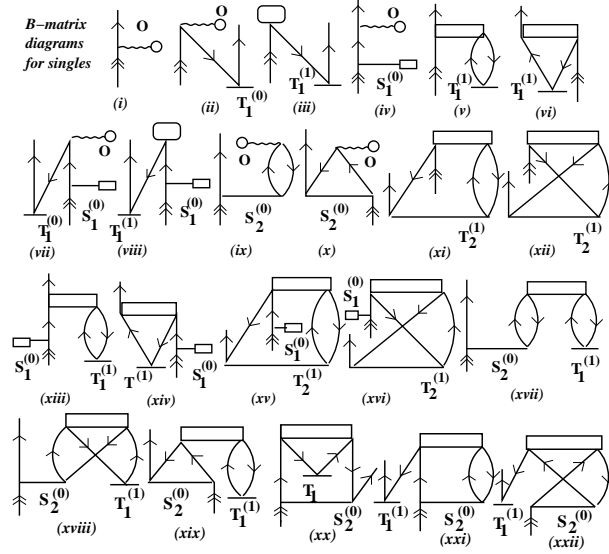


Figure 7: The B- matrix diagrams for singles equation. These are the most dominant contributing terms than the doubles diagrams.

$$\begin{aligned}
&= \frac{\langle \Phi_v | \{1 + S_v^{(1)\dagger} + T^{(1)\dagger} S_v^{(0)\dagger} + T^{(1)\dagger}\} e^{T^{(0)\dagger}} O e^{T^{(0)}} \{1 + T^{(1)} + T^{(1)} S_v^{(0)} + S_v^{(1)}\} | \Phi_v \rangle}{\langle \Phi_v | \{1 + S_v^{(0)\dagger}\} e^{T^{(0)\dagger}} e^{T^{(0)}} \{1 + S_v^{(0)}\}} \\
&= \frac{\langle \Phi_v | S_v^{(1)\dagger} \overline{O^{(0)}} \{1 + S_v^{(0)}\} + \{1 + S_v^{(0)\dagger}\} \overline{O^{(0)}} S_v^{(1)} + \{1 + S_v^{(0)\dagger}\} (T^{(1)\dagger} \overline{O^{(0)}} + \overline{O^{(0)}} T^{(1)}) \{1 + S_v^{(0)}\} | \Phi_v \rangle}{1 + N_v^{(0)}}.
\end{aligned} \tag{38}$$

where we have defined $\overline{O^{(0)}} = e^{T^{(0)\dagger}} O e^{T^{(0)}}$.

For computational simplicity, we compute the above expression in stepwise. We define $\overline{O} (= e^{T^{(0)\dagger}} O e^{T^{(0)}})$, which can be expanded using the Wick's general theorem [25] as

$$\overline{O} = \overline{O}_{f.c.} + \overline{O}_{o.b.} + \overline{O}_{t.b.} + \dots, \tag{39}$$

where we have used the abbreviations *f.c.*, *o.b.* and *t.b.* for fully contracted, effective one-body and effective two-body terms, respectively. In this expansion of \overline{O} , the effective one-body terms are computed first keeping terms up to

$$\overline{O}_{o.b.} = O + T^{(0)\dagger} O + O T^{(0)} + T^{(0)\dagger} O T^{(0)}. \tag{40}$$

Obviously, the fully contracted (*f.c.*) terms will not contribute in the calculation based on the linked-diagram theorem [25]. These terms are finally contracted with the $S_v^{(1)}$ and $S_v^{(1)\dagger}$ operators in the final calculation. Contributions from the effective two-body terms of \overline{O} are computed directly. The following types of RCC terms are considered for the construction of effective two-body terms

$$\overline{O}_{t.b.} = O T_1^{(0)} + T_1^{(0)\dagger} O + O T_2^{(0)} + T_2^{(0)\dagger} O. \tag{41}$$

Similarly, we also construct effective one-body and two-body terms combining O and $T^{(1)}$ operators. These operators again contracted with the $S_v^{(0)}$ and $S_v^{(0)\dagger}$ operators. Other neglected

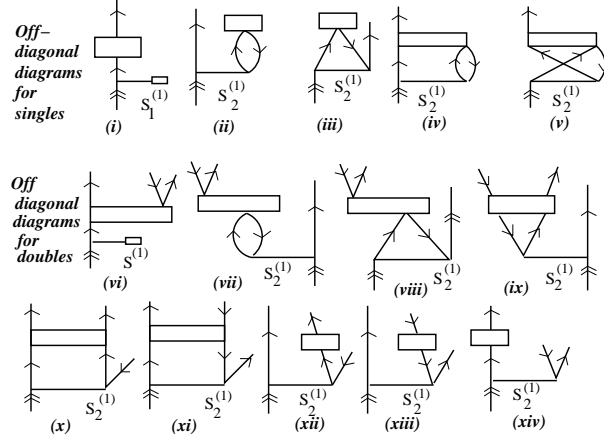


Figure 8: Off-diagonal elements for the $S_v^{(1)}$ determining equations.

terms correspond to higher order in residual Coulomb interaction and are neglected in the present calculation.

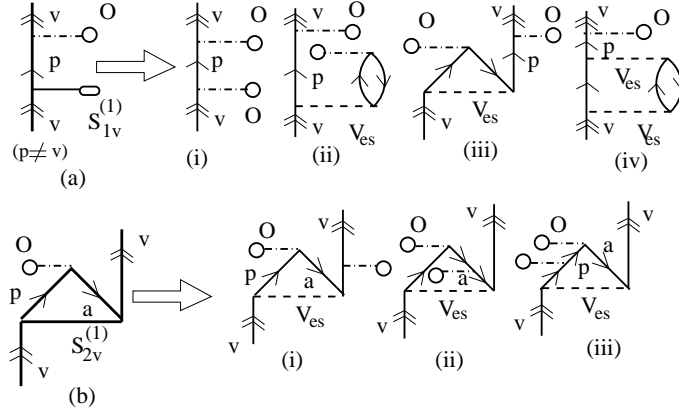


Figure 9: Break down of important perturbed RCC diagrams into some of the important lowest order MBPT diagrams. The V_{es} represents residual Coulomb operator and a and p represent, occupied and unoccupied orbitals, respectively.

Contributions from normalization factors ($Norm$) are obtained using the following relation

$$Norm = \langle \Psi_f | O | \Psi_i \rangle \left\{ \frac{1}{\sqrt{(1 + N_f^{(0)})(1 + N_i^{(0)})}} - 1 \right\}, \quad (42)$$

with $N_v^{(0)} = \{ S_v^{(0)\dagger} e^{T^{(0)\dagger}} e^{T^{(0)}} S_v^{(0)} \}$ for the valence electron v .

In Fig. 8, we have contracted pair-correlation and core-polarization as diagrams as has been shown by Fig. 3 with the dipole/quadrupole operators and have demonstrated how these effects to all orders in the final calculations ensuring inclusion of large physical effects.

4 Basis functions

The DF single particle orbital $|\phi_i\rangle$ is constructed as linear combinations of Gaussian type orbitals (GTOs) as [33, 34]

$$|\phi_i(r)\rangle = \sum_{\nu} c_{i\nu} |f_{i,\nu}(r)\rangle \quad (43)$$

where the GTOs are given by

$$f_{i,k}(r) = r^k e^{-\alpha_i r^2}, \quad (44)$$

where $k = 0, 1, \dots$ for s, p, \dots type orbital symmetries, respectively. For the exponents, we have used [33, 34]

$$\alpha_i = \alpha_0 \beta^{i-1}. \quad (45)$$

In the present calculations, we have considered $\alpha_0 = 0.00525$ and $\beta = 2.73$ for all the systems.

Therefore, we can express the DF orbitals as

$$\begin{aligned} |\phi_i(r)\rangle &= \sum_{\nu} c_{i\nu} |f_{i,\nu}(r)\rangle \\ \Rightarrow \frac{1}{r} \begin{pmatrix} P_i(r) & \chi_{\kappa,m} \\ iQ_i(r) & \chi_{-\kappa,m} \end{pmatrix} &= \frac{1}{r} \begin{pmatrix} \sum_{\nu} c_{i\nu}^L f_{i,\nu}(r) & \chi_{\kappa,m} \\ i \sum_{\nu} c_{i\nu}^S f_{i,\nu}(r) & \chi_{-\kappa,m} \end{pmatrix}, \end{aligned} \quad (46)$$

where $c_{i\nu}^L$ and $c_{i\nu}^S$ are the coefficients for the large (L) and small (S) components of the DF orbitals. These coefficients are determined by diagonalizing the DF equation.

The kinetic balance condition [35, 36] has been imposed between the large and small components of the GTOs in order to avoid divergence of the self-consistent solution of the above DF equation. For a finite nucleus all orbitals are generated on a grid using a two-parameter Fermi nuclear distribution approximation given by

$$\rho = \frac{\rho_0}{1 + e^{(r-c)/a}}, \quad (47)$$

where the parameter 'c' is the *half-charge radius*, and 'a' is related to the *skin thickness* which is defined as the interval of the nuclear thickness over which the nuclear charge density falls from near one to near zero. These values are tabulated by Vries *et al.* [37] for many atomic systems. We determine 'c' and 'a' for various atomic systems as given by Mohanty and Parpia [38]. The equations determining these parameters are

$$\begin{aligned} a &= 2.3/4(\ln 3) \\ c &= \sqrt{\frac{5}{3} r_{rms}^2 - \frac{7}{3} a^2 \pi^2} \end{aligned} \quad (48)$$

where r_{rms} is the root mean square radius of the nucleus.

5 Results and Discussions

In table 1, we present the results of our dipole polarizability calculations for the ground states and two excited states of the systems we have considered. These results are compared with experimental data. We have also presented results of selected calculations which were obtained by a variety of non-relativistic and relativistic many-body methods. Hartree-Fock results for many of the systems can be found in [71] and some theoretical results using different perturbation theories

Table 1: Dipole polarizabilities in alkali atoms and alkaline-earth-metal ions in a_0^3 .

Transitions	Expts	Others	This work
Li			
$2s \ ^2S_{1/2}$	164(3.4) [39], 148(13) [40] 164.2(1.1) [41]	164.111 [1], 165.01 [11], 164.6 [12] 163.73 [17], 165.2 [42], 164.5 [43] 170.43 [44], 169.55 [45], 165.8 [46] 164.1 [47], 163.91 [48], 164.08 [49] 164.8 [50], 164.21 [51], 164.0 [52]	162.29
$3s \ ^2S_{1/2}$		4136 [53], 4135 [54], 4121 [55] 4088, 3770 [56], 3832 [57]	4121.80
$4s \ ^2S_{1/2}$			12270.58
Na			
$3s \ ^2S_{1/2}$	159.2(3.4) [39], 164.6(11.5) [40]	163.07 [7], 165.88 [11], 160.7 [12] 164.89 [17], 168.41 [44], 162.8 [51] 159.2 [52]	162.89
$4s \ ^2S_{1/2}$		3100.66 [7], 3389.0 [53]	3099.37
$5s \ ^2S_{1/2}$			1290.31
K			
$4s \ ^2S_{1/2}$	292.8(6.1) [39], 305(21.6) [40] 292.9(59) [58]	290.1 [7], 285.23 [11], 289.5 [12] 301.28 [17]	286.01
$5s \ ^2S_{1/2}$		4958.40 [7]	4837.18
$6s \ ^2S_{1/2}$			826.44
Be ⁺			
$2s \ ^2S_{1/2}$		24.93 [12], 25.04 [44], 24.63 [45] 16.74 [59]	24.11
$3s \ ^2S_{1/2}$		635 [57]	575.70
$4s \ ^2S_{1/2}$			4935.78
Mg ⁺			
$3s \ ^2S_{1/2}$	34.62(26) [60], 33.0(5) [61] 33.8(8) [62]	33.68 [12], 37.2 [59], 34.144 [60] 34.0 [66], 38.7 [63], 38.9 [64]	34.59
$4s \ ^2S_{1/2}$			538.17
$5s \ ^2S_{1/2}$			4024.27
Ca ⁺			
$4s \ ^2S_{1/2}$	70.89(15) [60], 75.3(4) [61] 72.5(19) [61]	71.01 [12], 96.2 [59], 70.872 [60] 76.9 [66], 112.4 [63], 75.88 [65] 87(2) [67], 75.71 [68]	73.86
$5s \ ^2S_{1/2}$			951.97
$6s \ ^2S_{1/2}$			7597.05

Table 2: Quadrupole polarizabilities in alkali atoms and alkaline-earth-metal ions in a_0^5 .

Atoms	Others	This work
Li	1423.266(5) [1], 1424(4) [5], 1448.11 [9], 1393 [12] 1383 [21], 1428 [43], 1519.80 [44], 1486 [46] 1423 [47], 1430 [50], 1424 [52], 1423 [69]	1421.28
Na	1885(26) [5], 1383 [9], 1796 [12], 1806.57 [21] 2194.73 [44], 1878 [52], 1879 [69]	1899.67
K	5000(45) [5], 5105.43 [9], 4703 [12], 4597 [21] 5000 [52], 5001 [69]	4919.71
Be ⁺	52.93 [12], 55.52 [44] 55.71 [59], 52.4 [70]	53.80
Mg ⁺	150.2 [12], 187.66 [59], 150.15 [66], 137.0 [70]	156.17
Ca ⁺	1171 [12], 727.55 [59], 1303.51 [66]	706.59

are discussed by Schwerdtfeger [72]. Only a few experimental results are available for the excited states.

We have also presented quadrupole polarizabilities in table 2. To our knowledge, no experimental results are available for these quantities. These quantities are useful for determining van der Waal's coefficients. We have compared our results with those of other calculations. They are in reasonable agreement with our calculations.

6 Conclusion

We have developed for the first time a general method in the framework of relativistic coupled-cluster theory to obtain the first order wave functions due to any one electron perturbation. This approach can be applied to diverse problems in physics ranging from polarizabilities to probes of physics beyond the Standard Model of particle physics. We have also investigated electron correlation effects from the dipole and quadrupole polarizabilities calculations in six different systems and highlighted their behavior. We have observed that higher order correlation effects for polarizabilities are important for the relatively larger systems we have considered, thereby suggesting the suitability of our relativistic coupled-cluster method for the present studies. Indeed, this approach can also be extended to determine frequency dependent (dynamic) polarizabilities which we defer to our future studies. The computational aspects of our work presented in this paper would certainly be of interest to theoretical atomic physicists and quantum chemists.

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