

# An *ab initio* relativistic coupled-cluster theory of dipole and quadrupole polarizabilities: Applications to a few alkali atoms and alkaline earth ions

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We present an approach within the relativistic coupled-cluster theory framework to calculate the first order wave functions due to a general perturbative operator. Using the proposed method, we calculate the static dipole and quadrupole polarizabilities in some alkali atoms and alkaline earth-metal ions. This is a good test of the given theory for both parities and two different rank interaction operators. The present theory has a wide range of applications including the high precision calculations of very tiny but finite parity non-conserving and CP violating amplitudes those are useful to probe new physics beyond the standard model of the particle physics. Details of theoretical approach have been discussed and the role of correlation effects in the calculations of above properties of the ground states in the considered systems are given explicitly in terms of RCC operators. We have also compared these results with other calculations and available experimental results.

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Since years, studies of dipole and quadrupole polarizabilities have been highly interesting in many important aspects for both neutral atoms and ions [1–6]. These quantities are used in the case of ions to remove the quadratic Stark shifts in the recent proposed optical frequency standards, but experimentally it is very difficult to measure them precisely [7]. In some cases, relativistic effects are also investigated for these properties [8, 9]. Often theoretical calculations of these quantities are limited by many approximations restricting to the accuracy of the results. Moreover, it does not describe exactly the role of correlation effects which can only be understood using an *ab initio* method that is capable of considering correlation effects due to two-body interactions to all orders and contributions from all the allowed electronic configurations. In many theoretical studies, semiempirical methods combining the calculated E1 and E2 matrix elements of important states with their experimental excitation energies are used to determine these quantities [11, 12]. As a result, core electron correlations are usually estimated approximately in such approaches [11]. Therefore, an *ab initio* method is necessary to be able to, in principle, explain the importance of the electron correlation effects in the determination of above properties and also test the many-body theories employed. These results are largely used to determine the van der Waals coefficients, also known as dispersion factors [12–14]. The Dirac-Fock (DF) method and relativistic random-phase approximations (RPA) for the Dalgarno-Lewis [13–15] or scalar relativistic Douglas-Kroll [9, 16] effective Hamiltonians are sometime used to determine these quantities. A number of calculations on these quantities using molecular codes and pseudo-potentials have also been reported [5, 9, 10, 16]. A complete theory with fully atomic symmetry properties is, henceforth, required at this stage to determine the polarizabilities.

We propose here a novel approach using the four component relativistic coupled-cluster (RCC) theory, to calculate wave functions up to all orders in the residual Coulomb interaction and first order due to a perturbed operator in an equal footing making a common ansatz in the expression of wave function. This takes care of the sum-over-states approach of the many-body perturbation theory (MBPT) as an exact solution. Indeed, this method can be applied to calculate the first order wave function due to dipole and quadrupole transition operators. Hence, polarizabilities can be obtained by calculating the expectation values with respect to the total wave functions of the corresponding operators as given below. In fact, the same procedure can be easily extended to calculate polarizabilities in alkali clusters [17]. As an *ab initio* test of the theory, it is also possible to calculate the light shift ratio using the present method in ions and match with their measured values as called for Ba<sup>+</sup> [18]. Additionally, parity non-conserving (PNC) and CP violating amplitudes can also be determined very precisely using the same method due to rank zero or rank one weakly interacting Hamiltonians, which are the most challenging problems during the last three decades [19, 20]. Again, polarizabilities of negative ions like Ba<sup>-</sup>, Mg<sup>-</sup>, Ca<sup>-</sup> and Sr<sup>-</sup> can also be determined using the same procedure.

To demonstrate the application of the method, we consider three different sizes of systems each from neutral alkali atoms (Li, Na and K) and alkaline earth ions (Be<sup>+</sup>, Mg<sup>+</sup> and Ca<sup>+</sup>) to calculate their dipole and quadrupole

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polarizabilities which, in fact, inherently posses different types of angular momentum selection rules.

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  $\vec{\mathbf{E}} = \mathcal{E}\hat{\mathbf{z}}$  can be expressed as

$$\Delta E(J_n, M_n) = -\frac{1}{2}\alpha^1(J_n, M_n)\mathcal{E}^2, \quad (0.1)$$

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

$$\alpha^1(J_n, M_n) = \alpha_0^1(J_n) + \frac{3M_n^2 - J_n(J_n + 1)}{J_n(2J_n - 1)}\alpha_2^1(J_n), \quad (0.2)$$

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

$$\alpha_i^1(J_n) = -2 \sum_{k \neq n} C_i^1 \frac{|\langle J_n J_n | z | J_k J_k \rangle|^2}{E_n - E_k}, \quad (0.3)$$

where  $i$  represents either 0 or 2,  $C_i^1$  are the appropriate angular coefficients,  $z$  is the  $\hat{\mathbf{z}}$  component of the position vector  $\vec{\mathbf{r}}$  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  $\alpha_i$ 's can be expressed in terms of the reduced matrix elements of the E1 operator ( $D = e\vec{\mathbf{r}}$ ) as follows

$$\alpha_0^1(J_n) = \frac{-2}{3(2J_n + 1)} \sum_{k \neq n} \frac{|\langle J_n || D || J_k \rangle|^2}{E_n - E_k} \quad (0.4)$$

and

$$\alpha_2^1(J_n) = \left( \frac{40J_n(2J_n - 1)}{3(2J_n + 3)(2J_n + 1)(J_n + 1)} \right)^{1/2} \sum_{k \neq n} (-1)^{J_n + J_k + 1} \left\{ \begin{matrix} J_n & 1 & J_k \\ 1 & J_n & 2 \end{matrix} \right\} \frac{|\langle J_n || D || J_k \rangle|^2}{E_n - E_k}. \quad (0.5)$$

Similarly, the static quadrupole polarizability can be expressed as

$$\begin{aligned} \alpha_0^2(J_n) &= -2 \sum_{k \neq n} C_0^2 \frac{|\langle J_n J_n | Q | J_k J_k \rangle|^2}{E_n - E_k} \\ &= \frac{-2}{5(2J_n + 1)} \sum_{k \neq n} \frac{|\langle J_n || Q || J_k \rangle|^2}{E_n - E_k}, \end{aligned} \quad (0.6)$$

where  $C_0^2$  is the corresponding angular factor and  $Q = -\frac{e}{2}(3z^2 - r^2)$  is the E2 operator which has different selection rules than the E1 operator.

In a general form, the above expressions for the polarizabilities can be expressed as

$$\begin{aligned} \alpha(J_n M_n) &= \langle \Psi_n | O | \Psi_n \rangle \\ &= \langle \Psi_n^{(0)} | O | \Psi_n^{(1)} \rangle + \langle \Psi_n^{(1)} | O | \Psi_n^{(0)} \rangle \\ &= 2\langle \Psi_n^{(1)} | O | \Psi_n^{(0)} \rangle, \end{aligned} \quad (0.7)$$

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

$$|\Psi_n \rangle = |\Psi_n^{(0)} \rangle + |\Psi_n^{(1)} \rangle. \quad (0.8)$$

It has to be noticed that the  $C$  angular factors from the  $\alpha$ 's are absorbed in the first order wave functions.

Now, we proceed to demonstrate how it is possible to calculate  $\alpha(J_n M_n)$ 's exactly by calculating both the  $|\Psi_n^{(0)} \rangle$  and  $|\Psi_n^{(1)} \rangle$  using a single many-body approach that can evaluate the unperturbed wave function exactly and determines the first order wave function accurately avoiding the sum-over-states approach that overcomes the limitations in the

calculations as discussed earlier. In the proposed method, we would like to obtain the first order perturbed wave function as a solution to the following equation

$$(\mathbf{H}_0^{(\text{DC})} - E_n^{(0)})|\Psi_n^{(1)}\rangle = (E_n^{(1)} - \mathbf{H}_{\text{int}})|\Psi_n^{(0)}\rangle, \quad (0.9)$$

where  $\mathbf{H}_0^{(\text{DC})}$  and  $\mathbf{H}_{\text{int}}$  are the Dirac-Coulomb (DC) and perturbed interaction Hamiltonians due to 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. The unperturbed wave functions and energies are obtained using the RCC method that is known as an order perturbative theory with size consistent and extensivity behavior.

The starting point of our development is the relativistic generalization of the valence universal coupled-cluster (CC) theory introduced by Mukherjee et al [21] which was put later in a more compact form by Lindgren [22]. In the relativistic analogous of CC theory, called as RCC theory in this paper, the atomic wave function  $|\Psi_n^{(0)}\rangle$  for a single valence ( $n$ ) open-shell system is expressed as

$$|\Psi_n\rangle = e^T \{1 + S_n\} |\Phi_n\rangle, \quad (0.10)$$

where  $|\Phi_n\rangle$  is the open-shell reference state constructed by appending the valence electron ( $n$ ) orbital to the closed-shell Dirac-Hartree-Fock (DF) wave function ( $|\Phi_0\rangle$ ; i.e.  $|\Phi_n\rangle = a_n^\dagger |\Phi_0\rangle$ ). In the above expression, the CC excitation operators,  $T$  excites only the core electrons and  $S_n$  excites either only the valence electron ' $n$ ' or along with the necessary core electrons.

To get both the unperturbed and perturbed wave functions of Eq. (0.8), we make an ansatz by expressing the  $T$  and  $S_n$  operators as

$$T = T^{(0)} + T^{(1)} \quad (0.11)$$

$$S_n = S_n^{(0)} + S_n^{(1)}, \quad (0.12)$$

where  $T^{(0)}$  and  $S_n^{(0)}$  are the CC operators for the DC Hamiltonian and  $T^{(1)}$  and  $S_n^{(1)}$  are the corresponding first order excitation operators due to the interaction Hamiltonian. To calculate  $\alpha_i(J_n M_n)$ , only linear terms involving  $T^{(1)}$  or  $S_n^{(1)}$  operators are kept from the exponential function of Eq. (0.10)

$$|\Psi_n\rangle = e^{T^{(0)}} \{1 + S_n^{(0)} + (1 + S_n^{(0)})T^{(1)} + S_n^{(1)}\} |\Phi_n\rangle. \quad (0.13)$$

Hence, the unperturbed and perturbed wave functions can be separated as

$$|\Psi_n^{(0)}\rangle = e^{T^{(0)}} \{1 + S_n^{(0)}\} |\Phi_n\rangle, \quad (0.14)$$

$$|\Psi_n^{(1)}\rangle = e^{T^{(0)}} \{(1 + S_n^{(0)})T^{(1)} + S_n^{(1)}\} |\Phi_n\rangle. \quad (0.15)$$

We consider only the single and double excitations from the RCC method (CCSD method) in our calculations, which is proved successful to cope with the electron correlation effects in most one valence systems; i.e.

$$T = T_1 + T_2 \quad (0.16)$$

$$S_n = S_{1n} + S_{2n}. \quad (0.17)$$

First we solve the unperturbed  $T^{(0)}$  and  $S_v^{(0)}$  amplitudes by solving usual CC equations, then these amplitudes are used to determine the  $T^{(1)}$  and  $S_v^{(1)}$  amplitudes in the following equations

$$\langle \Phi_0^* | \overline{\mathbf{H}_N^{(\text{DC})}} T^{(1)} | \Phi_0 \rangle = -\langle \Phi_0^* | \overline{\mathbf{H}_{\text{int}}} | \Phi_0 \rangle \quad (0.18)$$

$$\langle \Phi_n^* | (\overline{\mathbf{H}_N^{(\text{DC})}} + \Delta E_n) S_n^{(1)} | \Phi_n \rangle = -\langle \Phi_n^* | \left[ \overline{\mathbf{H}_{\text{int}}} \{1 + S_n^{(0)}\} + \overline{\mathbf{H}_N^{(\text{DC})}} T^{(1)} \right] | \Phi_n \rangle, \quad (0.19)$$

where the subscript  $N$  represents normal order form of the operators,  $\Delta E_n$  is the  $n$  valence electron affinity energy to the closed-shell core and the symbol \* represents excited states with respect to the corresponding reference states. In the above equations, we define  $\overline{\mathbf{H}} = e^{-T^{(0)}} \mathbf{H} e^{T^{(0)}} = ((\mathbf{H} e^{T^{(0)}})_c)$ , with the subscript 'c' representing connected terms.

After getting both the unperturbed and perturbed amplitudes, we evaluate the polarizabilities using the following expression

$$\begin{aligned} \alpha_i(J_n) &= \frac{\langle \Phi_n | \{1 + S_n^\dagger\} e^{T^\dagger} O e^T \{1 + S_n\} | \Phi_n \rangle}{\langle \Phi_n | \{1 + S_n^\dagger\} e^{T^\dagger} e^T \{1 + S_n\} | \Phi_n \rangle} \\ &= \frac{\langle \Phi_n | S_n^{(1)\dagger} \overline{\mathbf{O}^{(0)}} \{1 + S_n^{(0)}\} + \{1 + S_n^{(0)\dagger}\} \overline{\mathbf{O}^{(0)}} S_n^{(1)} + \{1 + S_n^{(0)\dagger}\} (T^{(1)\dagger} \overline{\mathbf{O}^{(0)}} + \overline{\mathbf{O}^{(0)}} T^{(1)}) \{1 + S_n^{(0)}\} | \Phi_n \rangle}{N_n^{(0)}} \end{aligned} \quad (0.20)$$

TABLE I: Static dipole and quadrupole polarizabilities in alkali atoms: Li, Na and K.

Atoms	Expts	Others	This work
<u>Dipole polarizabilities</u>			
Li	164(3.4) [24] 164.2(1.1) [25]	163.73 [9], 164.6 [5] 165.01 [10], 164.111 [4]	162.48
Na	159.2(3.4) [24] 164.6(11.5) [26]	163.07 [11], 164.89 [9] 160.7 [5], 165.88 [10]	163.78
K	292.8(6.1) [24] 305(21.6) [26]	290.1 [11], 289.5 [5] 301.28 [9], 285.23 [10]	290.42
<u>Quadrupole polarizabilities</u>			
Li		1424(4) [13], 1393 [5] 1423.266(5) [4], 1424 [27] 1423 [28]	1421.37
Na		1885(26) [13], 1796 [5] 1878 [27], 1879 [28]	1901.51
K		5000(45) [13], 4703 [5] 5000 [27], 5001 [28]	4933.19

where for computational simplicity we define  $\overline{O^{(0)}} = e^{T^{(0)\dagger}} O e^{T^{(0)}}$  and  $N_n^{(0)} = e^{T^{(0)\dagger}} e^{T^{(0)}} + S_n^{(0)\dagger} e^{T^{(0)\dagger}} e^{T^{(0)}} S_n^{(0)}$ . The fully contracted term of  $\overline{O}_c = e^{T^\dagger} O e^T$  represents the contributions from the pure core orbitals and calculated separately. We compute then the  $\overline{O}^{(0)}$  in two steps as effective one-body and two-body terms and substitute in the above equation. We account for contributions from the normalization (Norm) factor expressed as

$$\text{Norm} = \langle \Psi_n | O | \Psi_n \rangle \left\{ \frac{1}{N_n} - 1 \right\}. \quad (0.21)$$

The above approach is an exact theory to evaluate the polarizabilities, but it can easily be extended to calculate the first order wave functions due to nuclear spin independent (NSI) and nuclear spin dependent (NSD) weakly interaction Hamiltonians for the determination of PNC amplitudes [19] and CP violating electric dipole moments (EDMs) [20] precisely in atoms those are crucial in other contexts. It was not our aim to discuss these properties here, but we mentioned them in order to highlight the broader applications of the proposed theory.

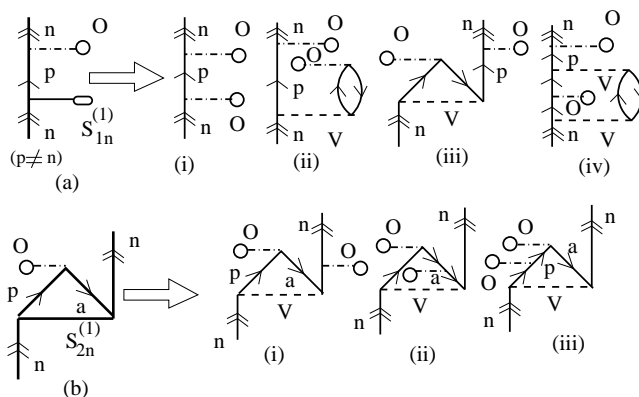


FIG. 1: Break down of important perturbed CC diagrams into some of the important lowest order MBPT diagrams. The V represents Coulomb operator and a and p represent, occupied and unoccupied orbitals, respectively.

We construct the relativistic single particle orbitals using the Gaussian type orbitals (GTOs) and we consider the finite size of the nucleus assuming a Fermi charge distribution as discussed in [23]. One can calculate E1 and E2

TABLE II: Static dipole and quadrupole polarizabilities in alkaline earth-metal ions: Be<sup>+</sup>, Mg<sup>+</sup> and Ca<sup>+</sup>.

Atoms	Expts	Others	This work
		<u>Dipole polarizabilities</u>	
Be <sup>+</sup>		24.93 [5], 24.63 [29] 25.04 [30], 16.74 [31]	24.16
Mg <sup>+</sup>	34.62(26) [3] 33.0(5) [32] 33.8(8) [33]	34.144 [3], 38.7 [34] 33.68 [5], 37.2 [31] 34.0 [35], 38.9 [36]	35.04
Ca <sup>+</sup>	70.89(15) [3] 75.3(4) [32] 72.5(19) [32]	70.872 [3], 112.4 [34] 71.01 [5], 87(2) [2] 76.9 [35], 96.2 [31]	76.68
		<u>Quadrupole polarizabilities</u>	
Be <sup>+</sup>		52.93 [5], 55.42 [30] 55.71 [31], 52.4 [1]	53.81
Mg <sup>+</sup>		150.2 [5], 187.66 [31] 150.15 [35]	156.02
Ca <sup>+</sup>		1171 [5], 727.55 [31] 1303.51 [35]	712.91

TABLE III: Contributions from DF and important perturbed CC terms for the dipole and quadrupole polarizabilities.

Atoms	DF	$\bar{O}_c$	$\bar{O}_{S_{1n}^{(1)}} + cc$	$\bar{O}_{S_{2n}^{(1)}} + cc$	Norm	Others
		<u>Dipole polarizabilities</u>				
Li	168.95	0.19	164.21	-0.40	-0.08	-1.44
Na	188.17	0.89	169.09	-1.26	-0.29	-4.65
K	398.15	4.41	313.32	-6.93	-2.11	-18.28
Be <sup>+</sup>	24.81	0.05	24.33	-0.08	-0.01	-0.13
Mg <sup>+</sup>	38.39	0.45	35.57	-0.43	-0.04	-0.51
Ca <sup>+</sup>	94.62	2.82	79.84	-1.48	-0.32	-4.18
		<u>Quadrupole polarizabilities</u>				
Li	1484.98	0.09	1444.87	0.00	-0.72	-22.87
Na	2230.62	1.84	2012.95	0.00	-3.34	-109.94
K	7099.70	13.48	5562.48	0.00	-36.38	-606.39
Be <sup>+</sup>	54.97	0.01	54.23	0.00	-0.02	-0.41
Mg <sup>+</sup>	171.34	-0.15	161.09	0.00	-0.18	-4.74
Ca <sup>+</sup>	952.65	6.32	750.39	0.00	-3.07	-40.73

amplitudes using both length and velocity gauge expressions in order to justify the accuracy of the polarizabilities, but we have taken only the length gauge expression which converges faster with the basis functions. Again, we have calculated only the ground state polarizabilities in the considered systems, although the presented approach is also valid for the excited states having one valence electron configurations. In these ground states, tensor polarizabilities are zero due to the forbidden rules in the angular momentum coefficients. It may also worthwhile to mention here that polarizabilities of the closed-shell systems can be evaluated using this approach by just considering the  $T-$  operators in Eq. (0.10). We present our results in Tables I and II, and compare these results with the available experimental and other calculated values. Many calculations are available for the dipole polarizabilities in the neutral systems, however we present only a few recent calculations in these tables. To our knowledge, there are only a few experimental results

available for the dipole polarizabilities whereas no results are found for the quadrupole polarizabilities, though there exist a couple of calculations.

We present the DF results and contributions from individual RCC terms in Table III to investigate the role of electron correlation effects. The contributions given by  $\overline{O}_c$  are nothing but the pure core orbital correlations which are generally determined approximately in the sum-over-states approach. As seen from this table,  $OS_{1n}^{(1)}$  and its complex conjugate (*cc*) terms contribute predominantly. To interpret these contributions, we break down this RCC term into some of the leading order MBPT diagrams as shown in the Fig. (1(a)). It is obvious from this relationship that the above term consists of dominant DF (Fig.1(ai)), core-polarization (Fig.1(aii) and 1(aiii)) and pair-correlation (Fig.1(aiv)) effects, therefore it contributes larger than other terms in all systems. Again, we also show another important RCC term diagrammatically ( $OS_{2n}^{(1)}$ ) in Fig. (1(b)) as the sum of different types of core-polarization effects. From Table III, we find that contributions from other higher order terms are non-negligible especially in the large systems. We also find from this table that the amount of correlation effects in neutral and ionic systems with the same electronic configurations are different.

Conclusively, We have developed a new approach to calculate the first order wave functions exactly due to a general rank operator with any parity function for the first time in the atomic theory using the relativistic coupled-cluster theory that can be employed in diverse areas of physics ranging from polarizabilities to probe physics beyond the standard model of particle physics. We have demonstrated the method by calculating the dipole and quadrupole polarizabilities in six different systems and investigated role of electron correlation effects in these properties. In these studies, we observed that higher order correlation effects will be crucial in large systems to determine these quantities precisely. This suggests that the method will serve as an *ab initio* test of the many-body theory in the similar studies. Indeed, this approach can also be extended to determine frequency dependent (dynamic) polarizabilities which we defer to our next studies. The many-body aspects presented here would certainly be of interesting for both physicists and quantum chemists.

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