Electric dipole polarizability from perturbed Relativistic Coupled-Cluster Theory: application to Neon

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We develop a method based on the relativistic coupled-cluster theory to incorporate a perturbative interaction to the no-pair Dirac-Coulomb atomic Hamiltonian. The method is general and suitable to incorporate any perturbation Hamiltonian in a many electron atom or ion. Using this perturbed relativistic coupled-cluster (PRCC) theory we calculate the electric dipole polarizability, \( \alpha \), of Neon. The linearized PRCC results are in very good agreement with the experimental value. However, the results of the nonlinear PRCC shows larger uncertainty but it is consistent with the observations from earlier works.

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I. INTRODUCTION

The electric dipole polarizability, \( \alpha \), of an atom or molecule is an important property as it describes the interaction with an external electric field. Knowing accurate value of atomic \( \alpha \) is imperative in different areas of research. To mention a few, the parity nonconservation experiment which involves the atom interacting with an external electric field. Knowing accurate value of atomic \( \alpha \) is essential in any experiment which involves the atom interacting with an external electric field. Theoretically, \( \alpha \) is calculated using the first order time-independent perturbation theory. A recent review gives a detailed account of the current status of the theoretical results of atomic and ionic polarizabilities. An excellent source of information related to atomic polarizability is ref. [6].

In the present work we extend the standard relativistic coupled-cluster (RCC) theory to include an additional perturbation Hamiltonian. Here, it must emphasized that the coupled-cluster (CC) theory is one of the most reliable quantum many body theory. We refer to the CC theory with the additional perturbation as PRCC method. The theory is flexible and formulated to incorporate multiple perturbations which may have different tensor structures in the electronic sector. The perturbation could be internal, like hyperfine interaction or external like the static electric field. For the present work, as \( \alpha \) is the quantity of interest, we take an external electric field as the perturbation. The coupled-cluster theory has been widely used for atomic [9, 10], molecular [11], nuclear [12], condensed matter physics [13] calculations. The previous approaches of CC theory for atomic calculations are conceptually different from the PRCC method in one aspect. In PRCC, the CC single and double (CCSD) excitation operators within the electron sector could be tensor operators of higher ranks. In which case the associated angular factors are complicated and are evaluated using diagrammatic method [14]. The PRCC equations are, at first glance, complicated in appearance as it involves two sets of cluster operators. However, the equations are linear and not nonlinear as in the full RCC theory. For calculations, we used the equivalent of standard CC single and double but the theory can be extended to higher orders.

The paper is organized as follows. In the Section. II we provide a brief description of the PRCC method and examine the structure of the cluster equations. This is followed with a short presentation of the details of the numerical aspects and actual models used in Section. III. The Section. IV discusses the results and we end with the conclusions.

II. THEORETICAL METHODS

The Dirac-Coulomb Hamiltonian \( H^{DC} \), consisting of relativistic one-electron terms and electrostatic electron-electron interaction, is the starting point of our calculation. For an \( N \)-electron atom

\[
H^{DC} = \sum_{i=1}^{N} [c\alpha_i \cdot p_i + (\beta_i - 1)c^2 - V_N(r_i)] + \sum_{i<j} \frac{1}{r_{ij}},
\]

where, \( \alpha_i \)'s and the \( \beta_i \) are the Dirac matrices, \( V_N(r_i) \) is the nuclear potential and the last term represents the electron-electron Coulomb interactions. For a closed-shell atom the eigen-value equation is

\[
H^{DC}|\Psi_i\rangle = E_i|\Psi_i\rangle.
\]

In the RCC theory the ground state wave-function of an atom is written as

\[
|\Psi_o\rangle = e^{T(0)}|\Phi_o\rangle,
\]

here \( |\Phi_o\rangle \) is the ground state reference state. In the CCSD approximation the cluster operator \( T(0) = T_1^{(0)} + T_2^{(0)} \). The advantage of CC theory is, it is an all order non-perturbative theory and ensures that electron-electron correlation diagrams is accounted fully. For future reference \( T(0) \) are referred to as the unperturbed
cluster operator. In the CCSD approximation the amplitude equations are written as
\[
\langle \Phi^p_0 | \tilde{H}_N | \Phi_0 \rangle = 0, \quad (4)
\]
\[
\langle \Phi^p_0 | \tilde{H}_N | \Phi_0 \rangle = 0. \quad (5)
\]
Here \( \tilde{H}_N = e^{-\lambda H_0} H_N e^{\lambda H_0} \) is the similarity transformed Hamiltonian and \( H_N = H_{DC} - \langle \Phi_0 | H_{DC} | \Phi_0 \rangle \) is the normal ordered Hamiltonian [15].

In the presence of an additional interaction, which could be an internal or external perturbation Hamiltonian \( \lambda H' \), \( | \Psi_0 \rangle \) is modified. Examples of internal perturbations are hyper-fine interaction, Breit interaction, etc. And examples of external perturbations are Stark effect, Zeeman effect, etc. The perturbation Hamiltonian, in the electron sector, can be a tensor operator of rank one or higher. The effect of these perturbations, although important, are less in magnitude than the residual Coulomb interaction and a first order treatment is sufficient. To incorporate \( H' \), we have developed a perturbed RCC (PRCC) theory.

For the present work we take an external electric field as the perturbation in an \( N \)-electron atom. The atomic Hamiltonian is then modified to
\[
H = H_{DC} + \lambda H_{int}, \quad (6)
\]
where \( H_{int} = \sum_{i=1}^{N} r_i E \), with \( E \) as the external electric field and \( \lambda \) is the perturbation parameter. Eigenvalue equation with the modified Hamiltonian is \( H | \tilde{\Psi}_0 \rangle = E_0 | \tilde{\Psi}_0 \rangle \). In the PRCC theory the new ground state wavefunction is
\[
| \tilde{\Psi}_0 \rangle = e^{-\lambda T(0)} | \Phi_0 \rangle. \quad (7)
\]
Here we have introduced the PRCC operator \( T(1) \), which incorporates the many-body effects of \( H_{int} \). It operates on the electronic sector and is a rank one operator as the electronic part of \( H_{int} \) is a tensor operator of rank one.

To first order in \( \lambda \) we have \( | \tilde{\Psi}_0 \rangle = e^{-\lambda T(0)} \langle 1 + \lambda T(1) | \Phi_0 \rangle \) and in the CCSD approximation \( T(1) = T_1(1) + T_2(1) \). More detailed description on the structures of \( T_1(1) \) and \( T_2(1) \) operators are given our previous publication [10].

The PRCC amplitude are solutions of the equations
\[
\langle \Phi^p_0 | \tilde{H}_N T(1) + H_N T(0) \rangle | \Phi_0 \rangle = -\langle \Phi^p_0 | \tilde{H}_N T(0) \rangle | \Phi_0 \rangle, \quad (8)
\]
\[
\langle \Phi^p_{ab} | \tilde{H}_N T(1) + H_N T(0) \rangle | \Phi_0 \rangle = -\langle \Phi^p_{ab} | \tilde{H}_N T(0) \rangle | \Phi_0 \rangle, \quad (9)
\]
where, \( \tilde{AB} \) represents all possible contractions between the two operators \( A \) and \( B \). These are non-linear coupled equations. However, \( T(0) \) are solutions of the unperturbed RCC equations [12] which are solved separately. With this consideration, the \( T(1) \) equations are reduce to a set of linear algebraic equations. The terms on the left hand side of Eq. (8) and (9) can be simplified to
\[
\{ \tilde{H}_N T(1) \} = \{ H_N T_1(1) \} + \{ H_N T_2(1) \},
\]
\[
\{ H_N T(0) \} = \{ H_N T_1(0) \} + \{ H_N T_2(0) \},
\]
\[
\{ H_N T(0) \} = \{ H_N T_1(0) \} + \{ H_N T_2(0) \} + \{ H_N T_2(1) \}.
\]

For further evaluation we use diagrammatic techniques to calculate the contributions from these terms. In total there are 42 single diagrams and 102 doubles diagrams.

From the time independent perturbation theory the dipole polarizability of an atom is
\[
\alpha = -2 \sum_i \langle \Psi_i | D | \Psi \rangle \langle \Psi | D | \Psi \rangle / E_0 - E_i, \quad (10)
\]
where, \( | \Psi_i \rangle \) are the intermediate atomic states. In the PRCC theory the sum over states is implicit and \( \alpha \) is the expectation value of the operator \( e^{-\lambda T(1)} \langle D e^{-\lambda T(0)} + e^{-\lambda T(0)} D e^{-\lambda T(1)} \rangle \). After expansion, collecting terms up to second order in cluster operators
\[
\alpha = \frac{1}{N} \langle \Phi_0 | \{ T_1(1) | D \} + \{ D T_1(1) \} + \{ T_1(1) D T_1(1) \} + \{ T_2(0) T_1(1) \} + \{ T_1(0) T_2(1) \} + \{ T_2(0) T_2(1) \} | \Phi_0 \rangle, \quad (11)
\]
where \( N = \langle \Phi_0 | \{ T_1(0) | T_1(0) \} + \{ T_2(0) T_2(0) \} | \Phi_0 \rangle \) is the normalization constant. The unperturbed wave-function is normalized, but we have to normalize the perturbed wave-function.

### III. CALCULATIONAL DETAILS

Using PRCC we have done a systematic study of dipole polarizability of Neon. For precision atomic theory calculation the orbital basis set is an important factor. In
our calculations we use even tempered Gaussian type orbitals (GTOs) \cite{18}. The radial part of the Dirac bi-spinor is expressed in terms of the linear combination of GTOs. The GTOs

\[ g_{\alpha p}^L(r) = C_{\alpha L}^r \rho_n e^{-\alpha_p r^2}. \]  

(12)

The index \( p \) is the number of basis functions. The exponent \( \alpha_p \) depends on two parameters \( \alpha_0 \) and \( \beta \) and are related as \( \alpha_p = \alpha_0 \beta^{p-1} \), where \( p = 0, 1 \ldots m \) and \( m \) is the number of \( g_{\alpha_p}^L(r) \) considered. For present calculations we use even tempered basis, where \( \alpha_0 \) and \( \beta \) are unique for each of the symmetries. The symmetry wise values of the parameters are listed in Table. I. Although, in principle, a complete set of orbitals are needed, it is near impossible to go beyond a few hundred. Even at a few hundred the computational requirements is very high. Another practical consideration, with further increase the gain in accuracy is marginal or non-existent once the basis set converges. The basis parameters are optimized such that the core orbital energies are in good agreement with the GRASP92 \cite{19} results. For information, the orbital energies are listed in Table. II.

| Table I. The GTO even tempered basis parameters used in the present calculations. |
| Symmetry | \( s_{1/2} \) | \( p_{1/2} \) | \( p_{3/2} \) | \( d_{3/2} \) | \( d_{5/2} \) | \( f_{7/2} \) |
|---|---|---|---|---|---|---|
| \( \alpha_0 \) | 0.0925 | 0.1951 | 0.1917 | 0.0070 | 0.0070 | 0.0069 |
| \( \beta \) | 1.45 | 2.71 | 2.71 | 2.70 | 2.70 | 2.69 |

| Table II. Orbital energies of obtained from GRASP92 and GTO in atomic units. |
| Orbital | \( 1s_{1/2} \) | \( 2s_{1/2} \) | \( 2p_{1/2} \) | \( 2p_{3/2} \) |
|---|---|---|---|
| GTO | -32.8177 | -1.9357 | -0.8526 | -0.8480 |
| GRASP92 | -32.8145 | -1.9387 | -0.8528 | -0.8482 |

To test and check the theory, we consider the linearized PRCC theory. There are then 10 singles and 10 doubles diagrams each. However, only 6 of the singles diagram but all the doubles diagrams contribute when DHF orbitals are used. Detailed descriptions of the diagrammatic calculations are given in ref. \cite{19}. The result, along with previous and experimental values, are given in Table. III. It shows that our results agree very well with the experimental data and indicates that the PRCC theory, even at the linear level, gives accurate results for a single reference system like Ne. To analyze the impact of basis set truncation, we examine the convergence of \( \alpha \) with the size of basis set. For this we start with a basis set of 50 GTOs and do a series of calculations by increasing the basis size in steps. The value of \( \alpha \) converges to 2.6695 when the basis set size is 124. However, for confirmation we increase the basis set size upto 171 and results are listed in Table. IV. In this calculation we have considered finite size Fermi density distribution for the nucleus.

\[ \rho_{nuc}(r) = \frac{\rho_0}{1 + e^{r-r_0/a}}. \]  

(13)

Here, \( a = t 4 \ln(3) \). The parameter \( c \) is the half charge radius so that \( \rho_{nuc}(c) = \rho_0/2 \) and \( t \) is the skin thickness. The PRCC equations are solved iteratively using Jacobi method, we have chosen this method as it is parallelizable. The method, however, is slow to converge. So, we use direct inversion in the iterated subspace (DIIS) \cite{24} to accelerate the convergence.

| Table IV. Convergence pattern of \( \alpha \) of Ne as a function of the Basis set size. |
| No. of orbitals | Basis size | Polarizability |
|---|---|---|
| 50 | (10s, 6p, 6d, 4f, 4g) | 2.7279 |
| 60 | (12s, 7p, 7d, 5f, 5g) | 2.7087 |
| 75 | (13s, 9p, 9d, 7f, 6g) | 2.6849 |
| 91 | (15s, 11p, 11d, 8f, 8g) | 2.6712 |
| 108 | (20s, 13p, 11d, 11f, 9g) | 2.6696 |
| 124 | (22s, 14p, 14d, 13f, 10g) | 2.6695 |
| 145 | (27s, 17p, 16d, 14f, 12g) | 2.6695 |
| 163 | (29s, 21p, 17d, 16f, 13g) | 2.6695 |
| 171 | (31s, 23p, 18d, 16f, 13g) | 2.6695 |

IV. RESULTS AND DISCUSSIONS

In the properties calculations the CC expression of the polarizability operator, \( e^{T(1)^{+}D}e^{T(0)} + e^{T(0)^{+}D}e^{T(1)} \), is a nonterminating series. However, as described earlier, in the present calculations we consider up to second order in \( T \). The contributions from the higher order terms, based on previous studies with an iterative all order method \cite{25}, is negligible. The contributions from different terms in Eq. (11) are listed in Table. V. As evident from the table, the dominant contribution arises from \( T_{1}^{(1)}D \) and its hermitian conjugate. This is not surprising as these terms subsume the DF contribution and core-polarization effects. The general trend is, for closed-shell atoms, the DF and core-polarization effects are the leading order and next to leading order, respectively. Coming to the pair correlation effects, the leading contribution arise from \( T_{2}^{(0)}D \) and its hermitian conjugate. This is along the expected lines as the \( T_{2}^{(0)} \) amplitude is larger, compared to \( T_{1}^{(0)} \), on account of pair-correlations. The contributions from the remaining terms
are small and cancellations reduce the combined contribution even further.

The next level of calculation is to consider all the terms in the Eq. (5) and (9), which we refer to as the non-linear PRCC. The term wise contributions are listed in Table V.

TABLE V. Contribution to $\alpha$ of Ne from different terms of the dressed dipole operator in the linearized PRCC theory.

| Contributions from $T$ | $\alpha$ |
|------------------------|----------|
| $\{T_1^{(1)} D\} + h.c.$ | 2.6610 |
| $\{T_1^{(1)} D T_2^{(0)}\} + h.c.$ | -0.0478 |
| $\{T_1^{(1)} D T_1^{(0)}\} + h.c.$ | 0.0644 |
| $\{T_2^{(1)} D T_1^{(0)}\} + h.c.$ | -0.0062 |
| $\{T_2^{(1)} D T_2^{(0)}\} + h.c.$ | 0.0961 |
| Normalization | 1.0367 |
| Total | 2.6695 |

TABLE VI. Contribution from all the terms in the nonlinear PRCC theory.

| CC terms | $\alpha$ |
|----------|----------|
| $\{T_1^{(1)} D\} + h.c.$ | 2.7344 |
| $\{T_1^{(1)} D T_2^{(0)}\} + h.c.$ | -0.0492 |
| $\{T_1^{(1)} D T_1^{(0)}\} + h.c.$ | 0.0670 |
| $\{T_2^{(1)} D T_1^{(0)}\} + h.c.$ | -0.0058 |
| $\{T_2^{(1)} D T_2^{(0)}\} + h.c.$ | 0.0924 |
| Normalization | 1.0367 |
| Total | 2.7383 |

VI and the net result of 2.7383 is 2.6% larger than the linearized PRCC result. As evident from the table, most of the change is attributed to $\{T_1^{(1)} D\}$ and hermitian conjugate. Contribution from this term is 2.7% larger in the nonlinear PRCC, which is comparable to the change in the value of $\alpha$. This is one of the case where higher order calculations does not translate into improved accuracy. A similar situation, but in a different context, was observed in a detailed analysis of contributions from nonlinear terms in the CCSD and dressing to calculate the magnetic dipole hyperfine constant of Li $^{26}$. Like in the work referred, the contributions from higher order cluster operators, triple and quadruple excitations, could be of different phase and bring $\alpha$ closer to experimental data. However, to examine or confirm this requires more detailed analysis and is beyond the scope of the present work.

Through a series of rigorous calculations, we examine the changes in $\alpha$, and associate it with a nonlinear term in Eq. (5) and (9). At the second order, there is an anomalously large contribution from $\{H N T_2^{(0)} T_1^{(1)}\}$, it induces a changes of 0.0808 a.u. to the net result of $\alpha$. This term accounts for the large change of $\alpha$ in the nonlinear PRCC calculations. Compared to this term, the contribution from other terms at this order are marginal. The next largest contribution arises from $\{H N T_1^{(0)} T_1^{(1)}\}$, it contributes 0.0086 a.u. The other contributions are 0.0004 and 0.0034 a.u. from $\{H N T_1^{(0)} T_1^{(1)}\}$ and $\{H N T_2^{(0)} T_1^{(1)}\}$, respectively.

At the third order $\{H N T_1^{(0)} T_1^{(1)} T_1^{(1)}\}$ and $\{H N T_2^{(0)} T_2^{(0)} T_1^{(1)}\}$ contribute equally, 0.0077 a.u. each. The contribution from the last term at this order, $\{H N T_1^{(0)} T_2^{(0)} T_1^{(1)}\}$, is -0.0018 a.u. To illustrate the relative changes arising from the third order terms, we list the contributions from the leading order terms in the second order and third order in Table VII. It is evident from the table that the difference between the second and third order contributions arises from the $\{T_1^{(1)} D\}$ and its hermitian conjugate.

At the fourth order there is only one term $\{H N T_1^{(0)} T_1^{(1)} T_1^{(1)} T_1^{(1)}\}$ and contributes 0.0077 a.u. This detailed study implies that the higher order terms in the PRCC equations, third and fourth order, have negligible effect on the electric dipole polarizability. Since the effect of the higher terms are tightly coupled to the electron correlation effects, a similar trend may occur in other properties as well.

To estimate the uncertainty in our calculations, we have identified two sources in the calculations using PRCC with CCSD approximation. First type of error is associated with the orbital basis set truncation and the termination of iteration while solving the cluster amplitudes. Based on the basis set convergence, as described earlier, the uncertainty from the basis set truncation is negligible. Similarly, the uncertainty from the termination of cluster amplitude calculation is negligible as we set $10^{-6}$ as the convergence criterion. The second type of error arises from the truncation of the CC theory at double excitations and the truncation of $e^{T^{(1)}} D e^{T^{(0)}} + e^{T^{(0)^\dagger}} D e^{T^{(1)}}$. Based on other detailed studies on the contributions from the triples and quadruple excitations could be in the range of $\approx 2.6\%$. So that
TABLE VIII. The contribution to $\alpha$ from the fourth order term in nonlinear PRCC theory.

| Contributions From | \( \{H_N T_1^{(0)} T_1^{(0)} T_1^{(0)} T_1^{(1)} \} \) |
|-------------------|--------------------------------------------------|
| \( T_1^{(1)} D \) + h.c. | 2.6688 |
| \( T_1^{(1)} D T_1^{(0)} \) + h.c. | -0.0478 |
| \( T_1^{(1)} D T_1^{(0)} \) + h.c. | 0.0645 |
| \( T_1^{(1)} D T_1^{(0)} \) + h.c. | -0.0062 |
| \( T_1^{(1)} D T_1^{(0)} \) + h.c. | 0.0962 |
| Normalization | 1.0367 |
| Total | 2.6772 |

it balances the larger error arising from the inclusion of the nonlinear terms in the PRCC theory. Again, based on other studies with iterative method [22] to incorporate higher order terms in the properties calculations with CC theory, the contributions from the third or higher order in \( e T_1^{(1)} D T_1^{(0)} + e T_1^{(1)} D T_1^{(0)} \) is negligibly small. The contribution from Breit and QED corrections could be another source of error. However, as \( Z \alpha \ll 1 \), where \( \alpha \) is the fine structure constant for Ne the uncertainty from excluding Breit and QED correction could easily be sub 0.01%. This is consistent with the estimates of the contribution from the Breit interaction to correlation energy [27]. Combining all the sources of error, the uncertainty for the calculations with nonlinear PRCC is \( \approx 2.6\% \). But due to possible fortuitous cancellations, the uncertainty with linearized PRCC calculations is sub 0.1%.

V. CONCLUSION

The PRCC theory provides a consistent approach within CC theory to calculate atomic properties. Although, in this paper we have demonstrated the use of PRCC to calculate \( \alpha \) of Ne. The method is applicable to any atomic property. In PRCC theory, the number of cluster amplitudes is larger than the RCC theory but the PRCC equations are linear. The main feature of the method is accounting of all possible intermediate states within the basis set chosen for the calculations. With converged basis sets, the intermediate states incorporated in the properties calculations is practically complete.

From the detailed calculations presented in this work, it can be concluded that inclusion of the nonlinear terms does not improve the accuracy of the properties calculated with PRCC theory. However, The linearized PRCC provides results which are in excellent agreement with the experimental data. The lower accuracy with the nonlinear PRCC may be attributed to large cancellations between contributions from different nonlinear terms. As to be expected, the leading order term is \( \{T_1^{(1)} D\} \). It accounts for, in the linearized PRCC calculations, 96% of the total value.

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