Relativistic Equation of Motion Coupled-Cluster Method: Application to the closed-shell atomic systems

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We report our successful implementation of the full fledged relativistic equation of motion coupled cluster (EOMCC) method. This method is employed to compute the principal ionization potentials (IPs) of closed-shell rare gas atoms, He-like ions, Be-like ions along with Na+, Al+, K+, Be, and Mg. Four component Dirac spinors are used in the calculations and the one and two electron integrals are evaluated using the Dirac Coulomb Hamiltonian. Our results are in excellent agreement with those available measurements, which are taken from the National Institute of Science and Technology database (NIST). We also present results using the second order many-body perturbation theory (MBPT(2)) and random phase approximation (RPA) in the EOMCC framework. These results are compared with those of EOMCC at the level of single and double excitations in order to assess the role of the electron correlation effects in the intermediate schemes considered in our calculations.

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I. INTRODUCTION

High precision calculations of the spectroscopic properties of heavy atomic and molecular systems are challenging due to the complex interplay between relativistic and correlation effects. However, with the extension of several well established non relativistic many-body methods to the relativistic regime and the recent advances in high performance computing techniques, such calculations are no longer insurmountable. Studies of atomic parity non-conservation (PNC) and permanent electric dipole moments (EDMs) due to the violation of parity and time reversal symmetries, requirement of very accurate atomic properties for the precise estimate of systematic effects in the atomic clock experiments, determination of nuclear moments, calculations of sensitive coefficients to probe the variation of the fine structure constant etc. require the development of powerful relativistic many-body methods. The spectra of multi-charge ions are of immense interest in many areas of physics; particularly in x-ray space astronomy, plasma physics and laser physics. Accurate values of ionization potentials (IPs), double ionization potentials (DIPs), and excitation energies (EEs), especially from the deep core orbitals, are required for setting up the probe and its tunability of the ionizing beam in experiments like e-2e, e-3e, γ-2e, double Auger decay etc.

Among the various wave function based methods, the coupled-cluster (CC) theory within the singles and doubles (CCSD) approximation is the most elegant way of calculating energy or energy differences of atoms and molecules in the ground state as well as in the excited states. Green’s function and propagator techniques are the two traditional approaches to calculate direct energy differences. In the propagator approaches, the ground and excited states are treated simultaneously and due to the cancellation of common correlation effects, these approaches provide satisfactory results of these energy differences in a direct manner. In the CC domain, the Fock space multi-reference CC (FSMRCC) and the EOMCC method are the two most familiar variants for the calculation of direct energy differences. Many non-relativistic calculations of IPs, and EEs both in the FSMRCC and EOMCC frameworks are available, but their relativistic counterparts are far fewer for the former case and none for the latter.

Relativistic calculations are necessary for the spectral properties of heavy atoms and molecules as well as for highly stripped heavy ions. It is therefore desirable in such cases to have a theory which can simultaneously treat the electron correlation and the effects of relativity on the same footing as they are non-additive in nature. Kaldor and coworkers were the first to develop a relativistic coupled-cluster theory for this purpose. They applied the relativistic FSMRCC method to atoms as well as molecules. The effective Hamiltonian formalism of the FSMRCC theory, based on the Bloch equation, acts within a model space. It uses a common vacuum with respect to which holes and particles are defined. The holes and particles are further classified into active and inactive depending on the requirements of the problem. While an increase in the size of the model space can target more states, it can lead to convergence problems, which is well known in the literature as the intruder state problem. The EOMCC method is basically single reference in nature and is closely related to the CC linear response theory (CCLRT). Chaudhuri et al. had applied the relativistic CCLRT to the ionization...
Making our concluding remarks in Sec V. Unless stated otherwise we have used atomic units (a.u.) through out the paper.

II. GENERATION OF RELATIVISTIC ORBITALS

The four component DC Hamiltonian used to evaluate the atomic integrals is given by

\[ H = \sum_i \left[ c \alpha_i \cdot p_i + (\beta_i - 1)c^2 + V_{\text{nuc}}(r_i) + \sum_{j>i} \frac{1}{r_{ij}} \right] \] (1)

where \( \alpha_i \) and \( \beta_i \) are the usual Dirac matrices, \( V_{\text{nuc}}(r_i) \) is the nuclear potential and \( \frac{1}{r_{ij}} \) is the electron-electron repulsion potential. Subtraction of the identity operator from \( \beta \) means that the energies are scaled with reference to the rest mass energy of the electron. The nuclear potential is evaluated considering the Fermi-charge distribution of the nuclear density as given by

\[ \rho_{\text{nuc}}(r) = \frac{\rho_0}{1 + e^{(r-c)/a}} \] (2)

where the parameter 'c' is the half-charge radius as \( \rho_{\text{nuc}}(r) = \rho_0/2 \) for \( r = c \) and 'a' is related to the skin thickness which are evaluated by

\[ a = 2.3/4(n3) \] (3)

and \( c = \sqrt{5/3 \overline{r_{\text{rms}}} - 7/3 a^2 \pi^2} \) (4)

with \( r_{\text{rms}} \) is the root mean square radius of the nucleus.

In relativistic quantum mechanics, the four component single particle electron orbital is given by

\[ |\phi(r)\rangle = \frac{1}{r} \left( \begin{pmatrix} P(r) \\ iQ(r) \end{pmatrix} \chi_{n,m}(\theta, \phi) \right) \] (5)

where \( P(r) \) and \( Q(r) \) are the large and small components of the wave function and the angular functions are given.
The Pauli two-component spinors $\kappa_\sigma$, $\sigma$, are given by

$$\begin{align*}
\kappa & = \sum_{\sigma = \pm \frac{1}{2}} C(\sigma j; m - \sigma, \sigma) Y^{m-\sigma}_l(\theta, \phi) \phi_\sigma
\end{align*}$$

(6)

for the Clebsch-Gordan (Racah) coefficient $C(\sigma j; m - \sigma, \sigma)$, the normalized spherical harmonics $Y^{m-\sigma}_l(\theta, \phi)$, the Pauli two-component spinors $\phi_\sigma$, and the relativistic quantum number $\kappa = -(j + \frac{1}{2})\alpha$ satisfying the condition for the orbital angular momentum $l = j - \frac{1}{2}$ with the total angular momentum $j$.

To generate the single particle orbitals, we use the relativistic Hartree-Fock (Dirac-Fock (DF)) Hamiltonian given by

$$\begin{align*}
H_{DF} & = \sum_j [c \, \vec{\alpha} \cdot \vec{p}_j + (\beta - 1) c^2 + V_{nuc}(r_j) + U(r_j)] \\
& = \sum_j h_0(r_j)
\end{align*}$$

(7)

where $h_0$ is the single particle Fock operator with the DF potential

$$U(\phi_j) = \sum_{a=1}^{occ} \langle \phi_a | \frac{1}{r_{ja}} | \phi_a \rangle \phi_j - \langle \phi_a | \frac{1}{r_{ja}} | \phi_j \rangle \phi_a$$

(8)

for all the occupied orbitals $occ$ that leaves out contributions from the residual interaction $V_{rs} = \sum_{j', \sigma} \langle j', \sigma | \vec{p} \cdot \vec{a} | j, \sigma \rangle$ which is incorporated through the EOMCC method.

To retain the atomic spherical symmetry property in our calculations, the matrix form of the Coulomb interaction operator using the above single particle wave functions are expressed as

$$\langle \phi_a \phi_b | \frac{1}{r_{12}} | \phi_c \phi_d \rangle = \int dr_1 \{P_a(r_1)P_c(r_1) + Q_a(r_1)Q_c(r_1)\} \times \int dr_2 \{P_b(r_2)P_d(r_2) + Q_b(r_2)Q_d(r_2)\} \times \frac{r_k}{r_{12}^{k+1}} \times Ang,$$

(9)

with the multipole $k$ determined by $|j_a - j_c| \leq k \leq j_a + j_c$ and $|j_b - j_d| \leq k \leq j_b + j_d$. The angular momentum factor of the above expression is given by

$$Ang = \delta(m_a - m_c, m_d - m_b) \sum_k \Pi^\nu(k_a, k_c, k) \times \Pi^\nu(k_b, k_d, k) d^k(j_a, j_c, j_d, m_a) d^k(j_b, j_d, m_b)$$

(10)

where the coefficient $d^k(jm, jm')$ is defined as

$$d^k(jm, jm') = (-1)^{m+k} \frac{[(2j+1)(2j'+1)]^k}{(2k+1)!} C(jk'; \frac{1}{2}, -\frac{1}{2})$$

(11)

with $\Pi^\nu(k', k, k') = \frac{1}{2} \Gamma(1 - aa'(-1)^{j+j'-k})$ for $l + l' + k = even$.

The DF single particle orbitals, $|\phi_{n,\kappa}(r)\rangle$s, with principal quantum number $n$ and angular quantum number $\kappa$ are initially constructed as linear combinations of Gaussian type orbitals (GTOs) by writing

$$|\phi_{n,\kappa}(r)\rangle = \frac{1}{\sqrt{\pi}} \sum_{\nu} C_{\kappa,n}^{\nu} N_{\nu} f_{\nu}(r) \chi_{\kappa,m},$$

(12)
where $C_{n,s}$ are the expansion coefficients, $N_{L(S)}$ is the normalization constant for the large (small) component of the wave function and $\alpha_{\nu}$ is a suitably chosen parameter for orbitals of different angular momentum symmetries and $f_{\nu}(r) = r^\nu e^{-\alpha_{\nu} r^2}$ is a GTO. For the exponents, we use the even tempering condition $\alpha_{\nu} = a_0 \beta^{-\nu-1}$ with two parameters $a_0$ and $\beta$. It can be noticed in the above expression that the large and small components of the wave function satisfy the kinetic balance condition. The orbitals are finally obtained after solving the matrix eigenvalue form of the DF equation by a self-consistent procedure.

III. METHOD OF CALCULATIONS: EOM-CCSD

In the CC method, the ground state wave function of a closed-shell atomic system is defined as

$$|\Psi_0\rangle = e^T |\Phi_0\rangle,$$

where $|\Phi_0\rangle$ is the DF wave function. The excited states is defined as

$$H |\Psi_\mu\rangle = E_\mu |\Psi_\mu\rangle = E_\mu R_\mu |\Psi_0\rangle,$$

for a linear CI like excitation operator $R_\mu$.

The operators $R_\mu$ commute with $T$ as they are strings of quasi-particle creation operators (but not necessarily particle conserving). Pre-multiplying the above equation with the non-singular operator $e^{-T}$ leads to

$$[\mathcal{H}, R_\mu] |\Psi_0\rangle = \Delta E_\mu R_\mu |\Psi_0\rangle,$$

where $\Delta E_\mu$ is the energy change associated with the ionization process. and $\mathcal{H} = e^{-T} H e^T - \langle \phi_0 | e^{-T} H e^T | \phi_0 \rangle$ is a non-Hermitian operator. This approach is usually known as EOM method for the excitation operators in analogy to the Heisenberg’s equation of motion. In the EOM-MBPT(2) and EOM-RPA methods, the matrix elements of the effective Hamiltonian $\mathcal{H}$ are replaced accordingly in the above equation.

In the EOM-CCSD method, the cluster operators are defined as

$$T = T_1 + T_2 = \sum_{i,a} t_{i,a} a^+_i a_i + \sum_{a<b<j} t_{a,b} a^+_a a^+_b a_i a_j$$

and

$$R_\mu = R_{1\mu} + R_{2\mu} = \sum_i r_i a_i + \sum_{i<j} \sum_a r_{ij} a^+_a a_i a_j,$$

where $i, j$ indices are used for the occupied and $a, b$ are used for the virtual orbitals.

The matrix elements of the effective Hamiltonian for the present ionization problem are constructed in the (1h-0p) and (2h-1p) space and diagonalized to get the desired roots. The Davidson algorithm has been implemented for the diagonalizing $\mathcal{H}$. This is an iterative diagonalization scheme through which eigenvalues and eigenvectors are obtained. It avoids computation, storage and diagonalization of the full matrix. The considered EOM-CC methods can be regarded as the diagonalization of the coupled cluster similarity transformed Hamiltonian in the CI configuration space.

IV. RESULTS AND DISCUSSION

To test the performance of our newly implemented four component relativistic EOM-CCSD method, we present numerical results of principal ionization potentials. The calculations are performed for the closed-shell rare gas atoms (He through Rn), beryllium like ions (B through Ar and Kr), helium like ions (Li, Ne, Na, Ar, Kr) along with Na+, Al+, K+, Be and Mg. These calculations are compared with the results obtained using the EOM-MBPT(2) and EOM-RPA methods to assess the role of electron correlation. All these results are compared with those of the measurements, which are taken from the National Institute of Science and Technology (NIST) database. For the construction of the single particle orbitals, we have used both even tempered (ET) and universal basis (UB) functions depending on the convergence of the results. For Be-like systems, we use UB basis with $a_0 = 0.004$ and $\beta = 2.23$. We have used ET basis for other atomic systems. The corresponding $a_0$ and $\beta$ parameters for ET basis for different atoms are given in Table I. The use of total number of orbitals generated at the SCF level is impractical in the CC calculations as the contributions from the high lying orbitals are very small in the present calculations owing to their large energy values, we consider only the orbitals that are significant of the calculations and they are termed as the active orbitals. In Table II, we present (SCF) energy which is our zeroth energy (E_{corr}) and the correlation energies from the MBPT(2) (E_{corr}^{MBPT}) and CCSD (E_{corr}^{CCSD}) methods along with the number of active orbitals of different symmetries used in the calculations.

All the Gaussian type of functions generated at the SCF level are not important for the ionization potential calculations. To investigate this, we have studied the
ing that the calculated EOM-CCSD IP results are larger
calculations of the excited states. It is worth mention-
tion that the EOM-RPA method. This suggests that
MBPT(2) method seems to be a more valid approxima-
tion of the dynamical correlations for which the EOM-
function at the CCSD level is responsible for the major
into account in this approach. The ground state wave
major source of non-dynamical correlations, is not taken
be over estimating is that the 2h-1p block, which is the
CCSD. The reason why the EOM-RPA calculations may
EOM-MBPT(2) results are always less than the EOM-
32+
least accurate is 0.15% for Kr
which is also in the accuracy limit of 0
and the result for Li
Table IV. All the results are sub-one percent accurate
Table III.

We present the IP values of the helium like ions in
Table V. All the results are sub-one percent accurate
for the 1s orbital and it is found to be 1.76 × 10−2, which is also in the accuracy limit of 0.1%. As we are more interested in the valence ionization potential in the present work, an active space of similar basis set is suf-
cient to construct the orthogonal space for the inclusion
of the correlation effects for all the systems without com-
promising the desired accuracy. The results are given in
Table III.

We present the IP values of the helium like ions in
Table IV. All the results are sub-one percent accurate
and the result for Li+ is the most accurate and the
least accurate is 0.15% for Kr32+. This table shows that
EOM-MBPT(2) results are always less than the EOM-
CCSD whereas the EOM-RPA method over estimates
them compared to the NIST values. Also, the differ-
cences in the results between the EOM-MBPT(2) and
EOM-CCSD are less than those of EOM-RPA and EOM-
CCSD. The reason why the EOM-RPA calculations may
be over estimating is that the 2h-1p block, which is the
major source of non-dynamical correlations, is not taken
into account in this approach. The ground state wave
function at the CCSD level is responsible for the major
part of the dynamical correlations for which the EOM-
MBPT(2) method seems to be a more valid approxima-
tion than the EOM-RPA method. This suggests that
the non-dynamical correlations are also important for
the calculations of the excited states. It is worth mention-
ing that the calculated EOM-CCSD IP results are larger
than the NIST values for Ne8+ onwards and the deviation
gets larger as the nuclear charge increases.

In Table V, we give the IP results for the beryllium
like systems. The 2s valence IPs of these systems are in
excellent agreement with the NIST values. Our results
for the 1s orbital match reasonably well with the NIST
data. We find that the relative average deviation of the
IP values of beryllium like systems (∼ 0.03%) are less
than helium like (0.05%) systems with reference to the
the NIST data.

The results for the rare gas atoms are given in Table
VI. For the Kr, Xe, and Rn atoms, we have calculated

TABLE V: Ionization potentials (IPs) of beryllium (Be) like systems in eV using MBPT(2), RPA and CCSD methods in the
EOM procedure.

| Ion   | MBPT(2)  | RPA   | CCSD  | NIST [51] |
|-------|----------|-------|-------|-----------|
|       | 1s       | 2s    | 1s    | 2s        | 1s     | 2s     | 1s    | 2s     |
| B+    | 218.7753 | 24.6024 | 223.7170 | 25.4600 | 218.6932 | 25.1510 | 217.8827 | 25.1548 |
| C2+   | 340.5912 | 47.1763 | 345.3340 | 48.1961 | 340.5074 | 47.8838 | 47.8877  |
| N3+   | 489.5193 | 76.6082 | 494.3701 | 77.7833 | 489.3987 | 77.4732 | 77.4735  |
| O4+   | 665.8043 | 112.8779 | 670.6873 | 114.2098 | 665.6751 | 113.9003 | 113.8900 |
| P5+   | 869.6607 | 155.9937 | 874.4161 | 157.4809 | 869.5295 | 157.1714 | 157.1631 |
| Ne6+  | 1100.7242 | 205.9558 | 1105.5077 | 207.5972 | 1100.5835 | 207.2874 | 1098.7791 | 207.2710 |
| Na7+  | 1359.1193 | 262.7653 | 1363.9246 | 264.5086 | 1358.9780 | 264.2504 | 1357.1716 | 264.1920 |
| Mg8+  | 1644.9936 | 326.4618 | 1649.9248 | 328.4010 | 1644.8387 | 328.0902 | 327.9000  |
| Al9+  | 1958.6549 | 397.0176 | 1963.5520 | 399.1102 | 1958.5119 | 398.7986 | 398.7986  |
| Si10+ | 2299.5858 | 474.4895 | 2304.3242 | 476.7141 | 2299.4367 | 476.4017 | 476.4017  |
| P11+  | 2668.1363 | 558.8627 | 2672.8963 | 561.2228 | 2667.9846 | 560.9095 | 561.2228  |
| S12+  | 3064.3424 | 650.1586 | 3069.1229 | 652.6532 | 3064.1883 | 652.3391 | 652.3391  |
| Cl13+ | 3488.2444 | 748.3994 | 3493.0728 | 751.0246 | 3488.0867 | 750.7090 | 751.0246  |
| Ar14+ | 3941.3783 | 856.3104 | 3944.8161 | 856.5389 | 3941.4781 | 856.0432 | 856.0432  |
| Kr32+ | 16934.9486 | 3972.1671 | 16939.9718 | 3975.7297 | 16934.8134 | 3975.7297 | 3971.0000 |

TABLE VI: Ionization potentials (IPs) of noble gas atoms in eV using MBPT(2), RPA and CCSD methods in the EOM
procedure.

| Atom | Orbital | MBPT(2)  | RPA   | CCSD  | NIST [51] |
|------|---------|----------|-------|-------|-----------|
| He   | 1s1/2   | 24.5450  | 26.1086 | 24.5802 | 24.5870   |
| Ne   | 2p1/2   | 21.4439  | 25.5832 | 21.4503 | 21.5642   |
|      | 2p1/2   | 21.5499  | 25.7096 | 21.5560 | 21.6613   |
|      | 2s1/2   | 48.5478  | 54.3474 | 48.6207 | 48.4746   |
|      | 1s1/2   | 872.6377 | 894.5355 | 872.3581 |
| Ar   | 3p1/2   | 15.8278  | 18.0023 | 15.7951 | 15.7594   |
|      | 3p1/2   | 16.0152  | 18.2136 | 15.9817 | 15.9369   |
|      | 3s1/2   | 30.0706  | 36.3317 | 30.0656 | 29.2390   |
|      | 2p1/2   | 250.1420 | 261.8999 | 249.7786 |
|      | 2p1/2   | 252.3757 | 264.2143 | 252.0114 |
| Kr   | 4p1/2   | 14.1339  | 15.8840 | 13.9963 | 13.9996   |
| Xe   | 5p1/2   | 12.3916  | 13.7572 | 12.1294 | 12.1298   |
| Rn   | 6p1/2   | 10.8604  | 11.9900 | 10.5847 | 10.7485   |
only the outer valence IPs. The most accurate EOM-CCSD result we obtain among them is for Xe atom. The 2p_{3/2} valence ionization energy for the Ne atom differs from the experimental result by 0.1139 eV. The differences are 0.0357 eV, 0.0033 eV and 0.0004 eV for the Ar, Kr and Xe atoms respectively for their valence orbitals. The reason for these differences could be due to the possible double excitation character of the \( p \) orbitals and it decreases along the group. The IPs of the EOM-CCSD method predominantly account for contributions from the single excitations and to some extent from the double excitations. The discrepancies could be mitigated on inclusion of the triple excitations in the ground as well as in the EOM part which is computationally very expensive for the relativistic calculations and are not incorporated in the present implementation. The deviation is 1.54\% for Rn atom, which is expected as higher order relativistic effects are non negligible for heavy elements and also due to the finite size of the basis sets.

In Table VII we present the results for Na\(^+\), Al\(^+\), K\(^+\), Be and Mg. The largest deviation is found in the 2p_{3/2} state of Na\(^+\) which is about to be 0.33\%. This could be due to the possible dominance of the double excitations. In the case of K\(^+\) it is reduces to 0.05\% and for Mg it is 0.06\%.

V. CONCLUSION

The present work describes the four component relativistic implementation of the equation of motion coupled-cluster method at the level of single and double excitations for the ionization problem in closed-shell atomic systems. To test the reliability of this method, we have computed the ionization potentials of atomic systems from different groups in the periodic table. The calculations are performed using EOM-MBPT(2) and EOM-RPA besides EOM-CCSD to understand the role of electron correlation at all the three levels of approximation. The second order many-body perturbation method is found to under estimate the results, whereas the random phase approximation over estimates them. The EOM-CCSD results are in excellent agreement with the NIST data wherever available.

**Table VII:** Ionization potentials (IPs) of Na\(^+\), Al\(^+\), K\(^+\), Be and Mg in eV using MBPT(2), RPA and CCSD methods in the EOM procedure.

| Atom | Orbital | MBPT(2) | RPA | CCSD | NIST [51] |
|------|---------|---------|-----|------|-----------|
| Na\(^+\) | 2p_{3/2} | 47.1177 | 51.2511 | 47.1286 | 47.2863 |
|       | 2p_{1/2} | 47.3000 | 51.4556 | 47.3105 | 47.4557 |
|       | 2s_{1/2} | 79.9745 | 85.4228 | 80.0303 | 80.0741 |
|       | 1s_{1/2} | 1090.5239 | 1112.3845 | 1090.3169 | |
| Al\(^+\) | 3s_{1/2} | 18.6480 | 19.1227 | 18.8248 | 18.8285 |
|       | 2p_{3/2} | 92.0692 | 97.8533 | 91.9647 | 91.7116 |
|       | 2p_{1/2} | 92.5141 | 98.3291 | 92.4092 | 92.1604 |
|       | 2s_{1/2} | 137.4759 | 143.6488 | 137.4202 | |
|       | 1s_{1/2} | 1582.3139 | 1605.2003 | 1582.0885 | |
| K\(^+\) | 3p_{3/2} | 31.6687 | 33.9023 | 31.6434 | 31.6249 |
|       | 3p_{1/2} | 31.9497 | 34.2071 | 31.9232 | 31.8934 |
|       | 3s_{1/2} | 48.4814 | 55.1066 | 48.4795 | 47.8182 |
|       | 2p_{3/2} | 309.0471 | 320.6904 | 308.7081 | |
|       | 2p_{1/2} | 311.9336 | 323.6488 | 311.5935 | |
| Be | 2s_{1/2} | 8.9442 | 9.6603 | 9.3247 | 9.3226 |
| Mg | 3p_{3/2} | 124.7175 | 129.7139 | 124.6463 | 123.6344 |
|       | 2p_{3/2} | 58.3976 | 64.1697 | 58.2235 | 57.5603 |
|       | 2p_{1/2} | 58.6898 | 64.4875 | 58.5154 | 57.7983 |
|       | 2s_{1/2} | 98.3383 | 104.1001 | 98.2824 | |

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