PHYSICAL REVIEW A **89**, 042510 (2014)

Relativistic equation-of-motion coupled-cluster method: Application to closed-shell atomic systems

Himadri Pathak,[1,*] B. K. Sahoo,[2] B. P. Das,[3] Nayana Vaval,[1] and Sourav Pal[1,†]

[1]*Electronic Structure Theory Group, Physical Chemistry Division, CSIR-National Chemical Laboratory, Pune, 411008, India*

[2]*Theoretical Physics Division, Physical Research Laboratory, Ahmedabad, 380009, India*

[3]*Theoretical Physics and Astrophysics Group, Indian Institute of Astrophysics, Bangalore, 560034, India*

(Received 6 January 2014; published 22 April 2014)

We report our successful implementation of the 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 available measurements, which are taken from the National Institute of Science and Technology database. The accuracies of the calculations are estimated to be within one half of a percent for He-like and Be-like ions and 1% for the heavier systems. We also present results using the second-order many-body perturbation theory and random-phase approximation 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.

DOI: 10.1103/PhysRevA.89.042510 PACS number(s): 31.10.+z

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 [1]. However, with the extension of several well-established nonrelativistic 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 nonconservation (PNC) and permanent electric dipole moments (EDMs) due to the violation of parity and time-reversal symmetries [2,3], the requirement of very accurate atomic properties for a precise estimate of systematic effects in atomic clock experiments [4–6], the determination of nuclear moments [7], calculations of coefficients that are sensitive to relativistic effects to probe the variation of the fine-structure constant [8–10], etc., require the development of powerful relativistic many-body methods. The spectra of multicharged ions are of immense interest in many areas of physics, particularly x-ray space astronomy, plasma physics, and laser physics [11,12]. 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 such as *e*-2*e*, *e*-3*e*, γ-2*e*, double Auger decay, etc. [13,14].

Among the various wave-function-based methods, the coupled-cluster (CC) theory within the single- and double-excitation (CCSD) approximation is the most elegant way of calculating the energy or energy differences of atoms and molecules in the ground state as well as in the excited states [15]. Green's function and propagator techniques [16,17] 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 multireference CC (FSMRCC) [18–24] and the equation-of-motion coupled-cluster (EOMCC) method [25–27] are the two most familiar variants for the calculation of direct energy differences. Many nonrelativistic calculations of IPs and EEs in both the FSMRCC [28] and EOMCC [29,30] frameworks are available, but full-fledged relativistic counterparts are far fewer for the former method, and there are 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 nonadditive 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 [31–34]. The effective Hamiltonian formalism of the FSMRCC theory, based on the Bloch equation, acts within a model space [35,36]. It uses a common vacuum with respect to which holes and particles are defined. The holes and particles are further classified as 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 [37,38]. The EOMCC method is basically single reference in nature and is closely related to the CC linear response theory (CCLRT) [39–41]. Chaudhuri *et al.* applied the relativistic CCLRT to the ionization problem [42]. Hirata *et al.* [43] employed the relativistic EOMCC method using two-component valence spinors along with a relativistic effective core potential (RECP) which was supplemented by the spin-orbit interaction [44]. The approach of Hirata *et al.* is clearly not a rigorous description of the relativistic effects, which can be taken into account by using four-component orbitals and the Dirac-Coulomb Hamiltonian. An approach called the configuration interaction (CI) plus the all-order method has been used to perform several relativistic atomic

---

[*] h.pathak@ncl.res.in

[†] s.pal@ncl.res.in

structure calculations [45]. It appears operationally similar to the EOMCC method, but the treatment of correlation effects in the two approaches is different. The CI plus all-order method divides the system into core and valence sectors and then proceeds in two steps: (i) solution of the linear CCSD (LCCSD) equations for the closed-shell core and (ii) construction and diagonalization of an effective Hamiltonian which has the frozen-core Hamiltonian containing core-valence excitations and another part that includes the valence-valence interactions screened by the core electrons. The wave function in the CI plus all-order method contains the core-valence correlation at the LCCSD level, while in the EOMCC method, it is computed using the full CCSD approach. The former is a Hilbert space approach as calculations based on it are carried out in a space comprising N electrons. At the CI level, this method suffers from the redundancy problem, which stems from the same excited determinant arising from two different reference determinants. As the EOMCC method treats two Hilbert spaces in a particular problem (N and $N-1$ electron spaces), it is a Fock-space approach. It also accounts for the relaxation effects, which is more important for the core spectrum, and it is free from the redundancy problem. It is well established that a Fock-space approach performs better than its Hilbert-space counterpart for the calculations of energy differences [46]. This method becomes less reliable when the number of valence electrons is more than 3 or 4 [47]. The lower part of the valence spectrum can be calculated accurately, but for energies above the excitation energies of the core, the results may not be very reliable [48]. EOMCC, on the other hand, performs well for the whole spectrum and is applicable for any number of valence electrons.

In the present work, we consider the EOMCC method in the four-component relativistic framework within the single- and double-excitation approximation (EOM-CCSD method) to calculate IPs by removing one electron from a closed-shell atomic system. This EOMCC method for the ionization problem is size consistent and is equivalent to the (0,1) sector of the FSMRCC theory [49,50]. It is capable of providing the principal as well as shake-up IP values. The (0,1) sector FSMRCC theory does not address the shake-up states. Although the EOM-CCSD method is a size-extensive method for the principal valence sector [51,52], it is not so for the shake-up states. The error due to the size extensivity is reduced due to the presence of the two-hole–one-particle (2h-1p) block. Being an eigenvalue problem, it is not affected by numerical instabilities due to the intruder states, which are very common in the FSMRCC method. Two intermediate calculations are employed to assess the effects of electron correlation. We refer to these as the EOM-MBPT(2) and EOM-RPA methods, which are the second-order many-body perturbation theory [MBPT(2)] and random phase approximation (RPA) in the EOMCC framework. The former uses a first-order perturbed ground-state wave function which corresponds to the MBPT(2) energy as the ground-state energy, and in the latter, the EOM matrix elements are constructed in the one-hole (1h-0p) space.

This paper is organized as follows. A brief discussion of the relativistic method used to obtain the single-particle orbitals is presented in Sec. II. This is followed by a description of the EOMCC theory of the ionization problem, and the computational details are presented in Sec. III. In Sec. IV, we give our results and discuss them before making our concluding remarks in Sec V. Unless stated otherwise, we have used atomic units throughout the paper.

II. GENERATION OF RELATIVISTIC ORBITALS

The Dirac-Coulomb (DC) Hamiltonian is given by

$$H = \sum_i \left[c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + (\beta_i - 1)c^2 + V_{\text{nuc}}(r_i) + \sum_{j>i} \frac{1}{r_{ij}} \right], \quad (1)$$

where $\boldsymbol{\alpha}_i$ and β_i are the usual Dirac matrices, $V_{\text{nuc}}(r_i)$ is the nuclear potential, and $\frac{1}{r_{ij}} = \frac{1}{\vec{r}_i - \vec{r}_j}$ is the electron-electron repulsion potential. Subtraction of the identity operator from β means that the energies are scaled with reference to the rest mass energy of the electron. The nuclear potential is evaluated using the Fermi-charge distribution of the nuclear density, which is given by

$$\rho_{\text{nuc}}(r) = \frac{\rho_0}{1 + e^{(r-b)/a}}, \quad (2)$$

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

$$a = 2.3/4(\ln 3), \quad (3)$$

$$b = \sqrt{\tfrac{5}{3} r_{\text{rms}}^2 - \tfrac{7}{3} a^2 \pi^2}, \quad (4)$$

with r_{rms} being the root-mean-square radius of the nucleus.

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

$$|\phi(r)\rangle = \frac{1}{r} \begin{pmatrix} P(r) & \chi_{\kappa,m}(\theta,\phi) \\ i\,Q(r) & \chi_{-\kappa,m}(\theta,\phi) \end{pmatrix}, \quad (5)$$

where $P(r)$ and $Q(r)$ are the large and small components of the wave function and the angular functions are given by

$$\chi_{\kappa,m}(\theta,\phi) = \sum_{\sigma=\pm\frac{1}{2}} C(l\sigma j; m-\sigma,\sigma) Y_l^{m-\sigma}(\theta,\phi)\phi_\sigma \quad (6)$$

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

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

$$\begin{aligned} H_{\text{DF}} &= \sum_j [c\,\vec{\alpha} \cdot \vec{p}_j + (\beta - 1)c^2 + V_{\text{nuc}}(r_j) + U(r_j)] \\ &= \sum_j h_0(r_j) \end{aligned} \quad (7)$$

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

$$U|\phi_j\rangle = \sum_{a=1}^{occ} \langle\phi_a|\frac{1}{r_{ja}}|\phi_a\rangle|\phi_j\rangle - \langle\phi_a|\frac{1}{r_{aj}}|\phi_j\rangle|\phi_a\rangle \quad (8)$$

for all the occupied orbitals *occ* and the residual interaction $V_{es} = \sum_{j<l} \frac{1}{r_{jl}} - \sum_j U(r_j)$, 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 is expressed as

$$\begin{aligned}\langle \phi_a \phi_b | \frac{1}{r_{12}} | \phi_c \phi_d \rangle = & \int dr_1 [P_a(r_1) P_c(r_1) + Q_a(r_1) Q_c(r_1)] \\ & \times \int dr_2 [P_b(r_2) P_d(r_2) + Q_b(r_2) Q_d(r_2)] \\ & \times \frac{r_<^k}{r_>^{k+1}} \times \text{Ang},\end{aligned} \tag{9}$$

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

$$\begin{aligned}\text{Ang} = & \, \delta(m_a - m_c, m_d - m_b) \sum_k \Pi^e(\kappa_a, \kappa_c, k) \\ & \times \Pi^e(\kappa_b, \kappa_d, k) d^k(j_c m_c, j_a m_a) d^k(j_b m_b, j_d m_d),\end{aligned} \tag{10}$$

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

$$\begin{aligned}d^k(jm, j'm') = & (-1)^{m+\frac{1}{2}} \frac{[(2j+1)(2j'+1)]^{\frac{1}{2}}}{(2k+1)} \\ & \times C\left(jkj'; \frac{1}{2}, -\frac{1}{2}\right) C(jkj'; -m, m'),\end{aligned} \tag{11}$$

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

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

$$|\phi_{n,\kappa}(r)\rangle = \frac{1}{r} \sum_\nu \begin{pmatrix} C^L_{n,\kappa} N_L f_\nu(r) & \chi_{\kappa,m} \\ i C^S_{n,-\kappa} N_S \left(\frac{1}{dr} + \frac{\kappa}{r}\right) f_\nu(r) & \chi_{-\kappa,m} \end{pmatrix}, \tag{12}$$

where $C_{n,\kappa}$ are the expansion coefficients, $N_{L(S)}$ is the normalization constant for the large (small) component of the wave function, α_ν is a suitably chosen parameter for orbitals of different angular momentum symmetries, and $f_\nu(r) = r^l e^{-\alpha_\nu r^2}$ is a GTO. For the exponents, we use the even-tempering condition $\alpha_\nu = \alpha_0 \beta^{\nu-1}$ with two parameters, α_0 and β. 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 CALCULATION: EOM-CCSD

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

$$|\Psi_0\rangle = e^T |\Phi_0\rangle, \tag{13}$$

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

$$H|\Psi_\mu\rangle = E_\mu |\Psi_\mu\rangle = E_\mu R_\mu |\Psi_0\rangle \tag{14}$$

for a linear excitation operator R_μ.

The operators R_μ commute with T as they are strings of quasiparticle creation operators (but not necessarily particle conserving). Premultiplying the above equation with the nonsingular operator e^{-T} leads to

$$[\overline{H}, R_\mu]|\Phi_0\rangle = \Delta E_\mu R_\mu |\Phi_0\rangle, \tag{15}$$

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

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

$$T = T_1 + T_2 = \sum_{i,a} t_i^a a_a^+ a_i + \sum_{a<b} \sum_{i<j} t_{ij}^{ab} a_a^+ a_b^+ a_i a_j, \tag{16}$$

$$R_\mu = R_{1\mu} + R_{2\mu} = \sum_i r_i a_i + \sum_{i<j} \sum_a r_{ij}^a a_a^+ a_i a_j, \tag{17}$$

TABLE I. The α_0 and β parameters of the even-tempered basis used in calculations.

	s		*p*		*d*		*f*		*g*	
Atom	α_0	β	α_0	β	α_0	β	α_0	β	α_0	β
He	0.00075	2.075	0.00155	2.080	0.00258	2.180	0.00560	2.300	0.00765	2.450
Li	0.00750	2.075	0.00755	2.070	0.00758	2.580	0.00760	2.600	0.00765	2.650
Be	0.00500	2.500	0.00615	2.650	0.00505	2.550	0.00500	2.530	0.00480	2.500
Ne	0.00753	2.075	0.00755	2.070	0.00758	2.580	0.00800	2.720	0.00800	2.720
Na	0.00250	2.210	0.00955	2.215	0.00700	2.750	0.00710	2.760	0.00715	2.765
Mg	0.02950	1.630	0.09750	1.815	0.00750	2.710	0.00780	2.730	0.00800	2.750
Ar	0.09850	1.890	0.00720	2.965	0.00700	2.700	0.00700	2.690	0.00700	2.696
K	0.00550	2.250	0.00995	2.155	0.00690	2.550	0.00700	2.600	0.00700	2.600
Kr	0.00020	2.022	0.00720	2.365	0.00700	2.550	0.00700	2.695	0.00700	2.695
Xe	0.00010	2.022	0.00720	2.365	0.00700	2.550	0.00700	2.695	0.00700	2.695
Rn	0.00010	2.280	0.00671	2.980	0.00715	2.720	0.00720	2.710	0.00720	2.695

where indices i,j are used for the occupied orbitals 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 are diagonalized to get the desired roots. The Davidson algorithm [53] has been implemented for the diagonalization of $\overline{H}$. This is an iterative diagonalization scheme through which eigenvalues and eigenvectors are obtained. It avoids computation, storage, and diagonalization of the full matrix. The EOM-CC method can be regarded as the diagonalization of the coupled-cluster similarity-transformed Hamiltonian in 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), and heliumlike 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 approaches 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 [54], where many are measured values and a few are the results of calculations based on different theoretical approaches.

TABLE II. SCF energy E^0_{DF} and correlation energies from the MBPT(2) ($E^{(2)}_{\mathrm{corr}}$) and CCSD ($E^{(\mathrm{ccsd})}_{\mathrm{corr}}$) methods, along with the numbers of active orbitals from various symmetries taken in the calculations for different atoms.

	Number of active orbitals							
Atom	s	p	d	f	g	E^0_{DF}	$E^{(2)}_{\mathrm{corr}}$	$E^{(\mathrm{ccsd})}_{\mathrm{corr}}$
He	16	14	12	9	7	−2.8618	−0.0365	−0.0415
Li^+	15	14	10	9	8	−7.2372	−0.0395	−0.0430
Ne^{8+}	16	15	11	9	8	−93.9827	−0.0421	−0.0434
Na^{9+}	16	15	13	10	9	−114.4158	−0.0414	−0.0426
Ar^{16+}	14	11	11	10	8	−314.1995	−0.0409	−0.0417
Kr^{34+}	22	13	11	10	9	−1296.1641	−0.0237	−0.0240
Be	13	11	11	9	8	−14.5758	−0.0742	−0.0924
B^+	15	14	10	9	8	−24.2451	−0.0824	−0.1062
C^{2+}	15	13	11	10	9	−36.4251	−0.0924	−0.1215
N^{3+}	15	14	13	10	9	−51.1144	−0.1026	−0.1369
O^{4+}	15	14	12	10	9	−68.3143	−0.1089	−0.1487
F^{5+}	15	14	13	10	9	−88.0271	−0.1168	−0.1621
Ne^{6+}	16	15	13	10	9	−110.2559	−0.1237	−0.1744
Na^{7+}	15	14	11	10	9	−135.0042	−0.1266	−0.1829
Mg^{8+}	15	14	13	11	9	−162.2763	−0.1352	−0.1966
Al^{9+}	15	14	13	10	9	−192.0767	−0.1404	−0.2072
Si^{10+}	15	14	13	11	9	−224.4105	−0.1461	−0.2177
P^{11+}	15	14	13	11	10	−259.2833	−0.1513	−0.2278
S^{12+}	15	14	13	11	10	−296.7011	−0.1561	−0.2374
Cl^{13+}	15	14	13	11	9	−336.6703	−0.1606	−0.2466
Ar^{14+}	15	14	13	11	10	−379.1979	−0.1650	−0.2554
Kr^{32+}	16	15	14	11	10	−1593.0492	−0.2316	−0.3630
Ne	17	17	13	11	10	−128.6919	−0.3736	−0.3732
Na^+	17	15	11	10	9	−161.8958	−0.3691	−0.3715
Mg	20	14	11	10	8	−199.9350	−0.4074	−0.4174
Al^+	15	14	13	10	9	−242.1290	−0.3951	−0.4065
Ar	14	11	11	10	8	−528.6657	−0.6513	−0.6640
K^+	15	14	12	10	8	−601.3780	−0.6664	−0.6799
Kr	22	13	11	9	8	−2788.8492	−1.5247	−1.4622
Xe	23	13	12	9	7	−7446.8108	−2.1180	−2.0009
Rn	21	13	12	10	9	−23595.8070	−3.7880	−3.4583

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 with $\alpha_0 = 0.004$ and $\beta = 2.23$. We have used the ET basis for other atomic systems. The corresponding α_0 and β parameters for the 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 to the calculations, and they are called the active orbitals. In Table II, we present (SCF) energy which is our zeroth energy (E^0_{DF}) and the correlation energies from the MBPT(2) (E^2_{corr}) and CCSD ($E^{\mathrm{CCSD}}_{\mathrm{corr}}$) methods along with the number of active orbitals of different symmetries used in the calculations.

All the Gaussian-type of orbitals generated at the SCF level are not important for the ionization potential calculations. To investigate this, we have studied the convergence pattern of ionization potentials as a function of basis set through a series of calculations. The Be atom is chosen for the convergence study. We started our calculations with 91 GTOs and gradually increased them to 145 GTOs. It is found that the IP value of the $2s$ orbital changes by 8×10^{-4} when the number of basis functions increases from 91 to 145. The change is more for the $1s$ orbital, and it is found to be 1.89×10^{-2}, which is also in the accuracy range of 0.01%. We have also investigated our results by increasing the number of diffuse s and p

TABLE III. Convergence pattern of ionization potentials of the Be atom (in eV) as a function of the active orbitals using the EOM-CCSD method.

	IP values	
Number of active orbitals	$1s$	$2s$
91 $(13s,11p,11d,9f,8g)$	124.6463	9.3247
100 $(14s,12p,12d,10f,9g)$	124.6565	9.3248
109 $(15s,13p,13d,11f,10g)$	124.6620	9.3249
116 $(16s,14p,13d,12f,11g)$	124.6639	9.3249
118 $(16s,14p,14d,12f,11g)$	124.6639	9.3248
125 $(17s,15p,15d,12f,12g)$	124.6630	9.3249
132[a] $(20s,17p,15d,12f,12g)$	124.6991	9.3249
135[b] $(21s,18p,15d,12f,12g)$	124.6992	9.3250
141 $(17s,15p,15d,12f,12g,8h)$	124.6632	9.3255
145 $(17s,15p,15d,12f,12g,10h)$	124.6652	9.3255
145[b] $(23s,20p,16d,13f,12g)$	124.6992	9.3250

[a] The α_0 for the s and p orbitals are taken as 0.000 50 and 0.000 615, respectively.

[b] The α_0 for the s and p orbitals are taken as 0.000 20 and 0.000 415, respectively.

TABLE IV. Ionization potentials (IPs) of He-like systems (in eV) using the MBPT(2), RPA, and CCSD methods in the EOM procedure.

Atom	MBPT(2)	RPA	CCSD	NIST [54]
Li^{+}	75.5517	77.1594	75.6399	75.6400
Ne^{8+}	1196.1770	1197.7308	1196.2113	1195.8078
Na^{9+}	1465.6073	1467.1611	1465.6401	1465.1344
Ar^{16+}	4123.5442	4125.1003	4123.5661	4120.6654
Kr^{34+}	17323.3995	17324.9869	17323.4104	17296.4200

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

Atom	Orbital	MBPT(2)	RPA	CCSD	NIST [54]
He	$1s_{1/2}$	24.4560	26.1086	24.5802	24.5870
Ne	$2p_{3/2}$	21.4439	25.5832	21.4503	21.5642
	$2p_{1/2}$	21.5499	25.7096	21.5560	21.6613
	$2s_{1/2}$	48.5478	54.3474	48.6207	48.4746
	$1s_{1/2}$	872.6377	894.5355	872.3581	
Ar	$3p_{3/2}$	15.8278	18.0023	15.7951	15.7594
	$3p_{1/2}$	16.0152	18.2136	15.9817	15.9369
	$3s_{1/2}$	30.0706	36.3317	30.0656	29.2390
	$2p_{3/2}$	250.1420	261.8999	249.7786	
	$2p_{1/2}$	252.3757	264.2143	252.0114	
Kr	$4p_{3/2}$	14.1339	15.8840	13.9963	13.9996
Xe	$5p_{3/2}$	12.3916	13.7572	12.1294	12.1298
Rn	$6p_{3/2}$	10.8604	11.9900	10.5847	10.7485

functions by decreasing the exponent α_0. It is observed that the 2s ionization-potential value remains almost unchanged with more diffuse s and p functions, whereas the maximum change for the 1s orbital is found to be 0.0529 eV. The deviation from the NIST value increases when more diffuse s and p functions are included. The inclusion of higher-order relativistic effects becomes relevant for inner-core orbitals. As we are more interested in the valence ionization potential in the present work, an active space of a similar basis set is sufficient to construct the orthogonal space for the inclusion of the correlation effects for all the systems without compromising the desired accuracy. The results are given in Table III.

We present the IP values of the heliumlike ions in Table IV. All the results are sub-1% accurate; the result for Li^{+} is the most accurate, and the least accurate is 0.15% for Kr^{34+}. Table IV shows that EOM-MBPT(2) results are always less than those of EOM-CCSD, whereas the EOM-RPA method overestimates them. Also, the differences in the results between 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 overestimating the results is that the 2h-1p block, which is the major source of nondynamical correlations, is not taken into account in this approach. The ground-state wave function at the CCSD level is responsible for the major source of the dynamical correlations for which the EOM-MBPT(2) method seems to be a more valid approximation than the EOM-RPA method. This suggests that the nondynamical correlations are also important for the calculations of the excited states. It is worth mentioning that the calculated EOM-CCSD IP results are larger than the NIST values for Ne^{8+} onwards and the deviations are larger in the heavier systems.

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%) is less than that of heliumlike (0.05%) systems with reference to the NIST data. A relatively larger deviation is found for the highly charged ions, which also increases with an increase in the ionic charge of the atom. The QED effects are non-negligible for the highly charged ions, where the effects of relativity are greater and increase with an increase in the ionic charge.

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

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

	MBPT(2)		RPA		CCSD		NIST [54]	
Ion	1s	2s	1s	2s	1s	2s	1s	2s
B^{+}	218.7753	24.6024	223.7170	25.4690	218.6932	25.1510	217.8827	25.1548
C^{2+}	340.5912	47.1763	345.3340	48.1961	340.5074	47.8838		47.8877
N^{3+}	489.5193	76.6082	494.3701	77.7833	489.3987	77.4732		77.4735
O^{4+}	665.8043	112.8779	670.6873	114.2098	665.6751	113.9003		113.8990
F^{5+}	869.6607	155.9937	874.4161	157.4809	869.5295	157.1714		157.1631
Ne^{6+}	1100.7242	205.9558	1105.5077	207.5972	1100.5835	207.2874	1098.7791	207.2710
Na^{7+}	1359.1193	262.7653	1363.9246	264.5608	1358.9780	264.2504	1357.1716	264.1920
Mg^{8+}	1644.9936	326.4618	1649.9248	328.4010	1644.8387	328.0902		327.9900
Al^{9+}	1958.6549	397.0176	1963.3552	399.1102	1958.5119	398.7986	1955.7950	398.6500
Si^{10+}	2299.5858	474.4895	2304.3242	476.7141	2299.4367	476.4017	2296.5894	476.1800
P^{11+}	2668.1363	558.8627	2672.8963	561.2228	2667.9846	560.9095	2664.7632	560.6200
S^{12+}	3064.3424	650.1586	3069.1229	652.6532	3064.1883	652.3391	3059.9469	651.9600
Cl^{13+}	3488.2444	748.3994	3493.0728	751.0246	3488.0867	750.7090		750.2300
Ar^{14+}	3941.3783	853.6104	3944.8161	856.3589	3941.4781	856.0432	3934.7226	855.4700
Kr^{32+}	16934.9486	3972.1671	16939.9718	3976.0698	16934.8134	3975.7297	16902.8643	3971.0000

TABLE VII. IPs of Na^+, Al^+, K^+, Be, and Mg (in eV) using the MBPT(2), RPA, and CCSD methods in the EOM procedure.

Atom	Orbital	MBPT(2)	RPA	CCSD	NIST [54]
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	323.6745	311.5935	
Be	$2s_{1/2}$	8.9442	9.6603	9.3247	9.3226
	$1s_{1/2}$	124.7175	129.7139	124.6463	123.6344
Mg	$3s_{1/2}$	7.5057	7.9519	7.6508	7.6462
	$2p_{3/2}$	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	

outer-valence IPs. The most accurate EOM-CCSD result we obtain among them is for the 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, 0.0033, 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 the difference 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 by the inclusion of the triple excitations in the ground and excited states, which is computationally very expensive for relativistic calculations, so they are not incorporated in the present implementation. The deviation is 1.54% for the Rn atom, which is expected as higher-order relativistic effects are non-negligible for heavy elements and also because of 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^+ and is about 0.33%. This could be due to the possible dominance of the double excitations. In the case of K^+ it is reduced to 0.05%, and for Mg it is 0.06%.

In order to quantify the errors in our calculations, we take into account the close agreement of our EOM-MBPT(2) and EOM-CCSD results, the convergence obtained using the basis sets in our calculations, and the omitted higher-order relativistic and correlation effects. We estimate the uncertainties in the results of the He-like ions reported in Table IV to be below one half of a percent based on the above-mentioned factors. It has been found recently that the dominant contributions to the IPs of the Be-like ions given in Table V come from electron correlation effects at the DC level, which have been taken into account in this work to all orders via the EOM-CCSD method, and contributions from the QED effects are reported to be below one half of a percent [55]. We therefore assign a conservative uncertainty estimate of 0.5% to the IPs of the He-like systems that we have calculated. Unlike in the highly charged ions, correlation effects play a dominant role in the evaluations of the atomic properties of the neutral and singly charged atomic systems. Our EOM-CCSD method is capable of accounting for the correlation effects very accurately for light and medium-size atoms and ions, but triple and other higher higher-order excitations could become non-negligible as the system gets heavier. It would therefore be reasonable to estimate the errors in these calculations for such systems to be within 1%.

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 in addition to EOM-CCSD to understand the role of electron correlation at all three levels of approximation. The second-order many-body perturbation method is found to underestimate the results, while the random-phase approximation overestimates them. The EOM-CCSD results are in excellent agreement with the NIST data wherever available, and we estimate the errors to be within one half of a percent and 1% for the light and heavy systems, respectively.

ACKNOWLEDGMENTS

H.P., N.V., and S.P. acknowledge a grant from the CSIR XIIth five year plan project on Multi-scale Simulations of Material (MSM) and the use of the facilities of the Center of Excellence in Scientific Computing at CSIR-NCL. H.P. acknowledges the Council of Scientific and Industrial Research (CSIR) for his fellowship. S.P. acknowledges a grant from DST and a J. C. Bose fellowship project towards completion of the work. Part of the computations were carried out using the 3T-Flop HPC cluster at Physical Research Laboratory.

---

[1] I. P. Grant, *Relativistic Quantum Theory of Atoms and Molecules: Theory and Computation* (Springer, New York, 2010).

[2] J. Engel, M. J. Ramsey-Musolf, and U. van Kolck, Prog. Part. Nucl. Phys. **71**, 21 (2013).

[3] J. S. M. Ginges and V. V. Flambaum, Phys. Rep. **397**, 63 (2004).

[4] M. Kallay, H. S. Nataraj, B. K. Sahoo, B. P. Das, and L. Visscher, Phys. Rev. A **83**, 030503 (2011).

[5] B. K. Sahoo, R. G. E. Timmermans, B. P. Das, and D. Mukherjee, Phys. Rev. A **80**, 062506 (2009).

[6] B. K. Sahoo, B. P. Das, R. K. Chaudhuri, D. Mukherjee, R. G. E. Timmermans, and K. Jungmann, Phys. Rev. A **76**, 040504(R) (2007).

[7] C. S. Wood, S. C. Bennett, D. Cho, B. P. Masterson, J. L. Roberts, C. E. Tanner, and C. E. Wieman, Science **275**, 1759 (1997).

[8] J. P. Uzan, Rev. Mod. Phys. **75**, 403 (2003).

[9] D. K. Nandy and B. K. Sahoo, Phys. Rev. A **88**, 052512 (2013).

[10] H. Chand, R. Srianand, P. Petitjean, and B. Aracil, in *Proceedings of the ESO/Lisbon/Aveiro Conference, Aveiro, Portugal, 2006*, edited by B. Leibundgut (Springer, Berlin, Germany, 2008), p. 101.

[11] J. D. Gillaspy, J. Phys. B **34**, R93 (2001).

[12] A. Chutjian, in *The Physics of Multiply and Highly Charged Ions*, edited by F. J. Currell (Kluwer, London, 2003), p. 79.

[13] J. H. D. Eland, M. Tashiro, P. Linusson, M. Ehara, K. Ueda, and R. Feifel, Phys. Rev. Lett. **105**, 213005 (2010).

[14] J. P. Cryan *et al.*, Phys. Rev. Lett. **105**, 083004 (2010).

[15] R. J. Bartlett and M. Musiał, Rev. Mod. Phys. **79**, 291 (2007).

[16] J. Lindenberg and Y. Öhrn, *Propagators in Quantum Chemistry* (Academic, New York, 1973).

[17] L. S. Cederbaum and W. Domcke, Adv. Chem. Phys. **36**, 205 (1977).

[18] I. Lindgren, Int. J. Quantum Chem. **14**, 33 (1978).

[19] M. Haque and D. Mukherjee, J. Chem. Phys. **80**, 5058 (1984).

[20] L. Z. Stolarczyk and H. J. Monkhorst, Phys. Rev. A **32**, 725 (1985).

[21] D. Mukherjee and I. Lindgren, Phys. Rep. **151**, 93 (1987).

[22] S. Pal, M. Rittby, R. J. Bartlett, D. Sinha, and D. Mukherjee, Chem. Phys. Lett. **137**, 273 (1987).

[23] S. Pal, M. Rittby, R. J. Bartlett, D. Sinha, and D. Mukherjee, J. Chem. Phys. **88**, 4357 (1988).

[24] B. Jeziorski and J. Paldus, J. Chem. Phys. **90**, 2714 (1989).

[25] H. Sekino and R. J. Bartlett, Int. J. Quantum Chem. **26**, 255 (1984).

[26] R. J. Bartlett and J. F. Stanton, Rev. Comp. Chem. **5**, 65 (1994).

[27] J. F. Stanton and R. J. Bartlett, J. Chem. Phys. **98**, 7029 (1993).

[28] D. I. Lyakh, M. Musiał, V. F. Lotrich, and R. J. Bartlett, Chem. Rev. **112**, 182 (2012).

[29] R. J. Bartlett, Comput. Mol. Sci. **2**, 126 (2012).

[30] M. Musiał, S. A. Kucharski, and R. J. Bartlett, J. Chem. Phys. **118**, 1128 (2003).

[31] E. Ilyabaev and U. Kaldor, Chem. Phys. Lett. **194**, 95 (1992).

[32] E. Ilyabaev and U. Kaldor, J. Chem. Phys. **97**, 8455 (1992).

[33] E. Ilyabaev and U. Kaldor, Phys. Rev. A **47**, 137 (1993).

[34] L. Visscher, E. Eliav, and U. Kaldor, J. Chem. Phys. **115**, 9720 (2001).

[35] P. Durand and J.-P. Malrieu, in *Advances in Chemical Physics: Ab Initio Methods in Quantum Chemistry Part I*, edited by K. P. Lawley, Vol. 67 (John Wiley & Sons, Inc., Hoboken, NJ, 2007), p. 321.

[36] V. Hurtubise and K. F. Freed, in *Advances in Chemical Physics*, edited by I. Prigogine and S. A. Rice, Vol. 83 (John Wiley & Sons, Inc., Hoboken, NJ, 2007), p. 465.

[37] T. H. Schucan and H. A. Weidenmuller, Ann. Phys. (NY) **73**, 108 (1972).

[38] U. Kaldor, Phys. Rev. A **38**, 6013 (1988).

[39] H. J. Monkhorst, Int. J. Quantum Chem. **12**, 421 (1977).

[40] E. Dalgaard and H. J. Monkhorst, Phys. Rev. A **28**, 1217 (1983).

[41] D. Mukherjee and P. K. Mukherjee, Chem. Phys. **39**, 325 (1979).

[42] R. K. Chaudhuri, P. K. Panda, B. P. Das, U. S. Mahapatra, and D. Mukherjee, Phys. Rev. A **60**, 246 (1999).

[43] S. Hirata, T. Yanai, R. J. Harrison, M. Kamiya, and Peng-Dong Fan, J. Chem. Phys. **126**, 024104 (2007).

[44] P. A. Christiansen and K. S. Pitzer, J. Chem. Phys. **73**, 5160 (1980).

[45] M. S. Safronova, M. G. Kozlov, W. R. Johnson, and D. Jiang, Phys. Rev. A **80**, 012516 (2009).

[46] M. Musiał, A. Perera, and R. J. Bartlett, J. Chem. Phys. **134**, 114108 (2011).

[47] M. G. Kozlov, Int. J. Quantum Chem. **100**, 336 (2004).

[48] S. G. Porsev, Y. G. Rakhlina, and M. G. Kozlov, J. Phys. B **32**, 1113 (1999).

[49] D. Sinha, S. K. Mukhopadhyay, R. Chaudhuri, and D. Mukherjee, Chem. Phys. Lett. **154**, 544 (1989).

[50] D. Mukhopadhyay, S. K. Mukhopadhyay, R. Chaudhuri, and D. Mukherjee, Theor. Chim. Acta **80**, 441 (1991).

[51] S. Kr. Mukhopadhyay, R. Chaudhuri, D. Mukhopadhyay, Jr., and D. Mukherjee, Chem. Phys. Lett. **173**, 181 (1990).

[52] D. Mukherjee and S. Pal, Adv. Quantum Chem. **20**, 291 (1989).

[53] E. R. Davidson, J. Comput. Phys. **17**, 87 (1975).

[54] http://physics.nist.gov/PhysRefData/ASD/ionEnergy.html.

[55] J. Sapirstein and K. T. Cheng, Phys. Rev. A **83**, 012504 (2011).