A relativistic equation-of-motion coupled-cluster investigation of the trends of single and double ionization potentials in the He and Be isoelectronic systems

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Abstract
We employ a four-component spinor relativistic equation-of-motion coupled-cluster (EOMCC) method within the single- and double-excitation approximation to calculate the single ionization potentials (IPs) and double ionization potentials (DIPs) of the He and Be isoelectronic sequences up to Ne. The obtained results are compared with the available results from the National Institute of Standards and Technology (NIST) database to test the performance of the EOMCC method. We also present intermediate results at different levels of approximations in the EOMCC framework to gain insight of the effect of electron correlation. Furthermore, we investigate the dependence of the IPs and DIPs of these ions on the ionic charge and observe that these follow parabolic trends. Similarities between the trends of IPs and DIPs in both the classes of considered systems are categorically demonstrated.

Keywords: double ionization potentials, equation-of-motion theory, coupled-cluster method

1. Introduction
In recent years, there have been significant advances in the experimental techniques such as time-of-flight photoelectron-photoelectron coincidence (TOF-PEPECO) spectroscopy [1, 2] which allows high precision measurements of multi-ionization processes stimulated by single photons from synchrotron sources. Sources like the x-ray free electron laser of the linac coherent light sources of SLAC [3, 4] are capable of producing sequential and direct multiphoton-multielectron interactions. A single photon having sufficient energy may eject two electrons to the continuum orbitals which can be treated as a topological three-body quantal problem. The mutual interaction between the electrons (electron correlation) play a major role in these processes.

The highly charged ions are of significant interest in diverse areas of physics, starting from x-ray space astronomy, plasma physics to laser physics [5, 6]. In a recent work [7], it has been demonstrated that the highly charged ions of C, N, O and Ne are the constituents of warm-hot intergalactic medium and are distributed mainly between their He and H like species. These highly charged ions be significant in determining the mass of missing baryons [8, 9].

The wave function constructed using a non-relativistic theory is not adequate for the accurate description of the energy spectrum of highly charged ions, and a relativistic description is imperative in this case [10]. On the other hand, accurate description of the relaxation effects along with the electron correlation effects are essential for explaining multiple ionization processes precisely. Therefore, calculations
based on the lower order many-body theories are not reliable enough and may not be able to complement to describe the quality of results that are anticipated from the on-going sophisticated experiments [11]. Kaldor and coworkers have made significant contributions in addressing the simultaneous treatment of relativistic and electron correlation effects using coupled-cluster (CC) methods. They extended the effective Hamiltonian variant of the Fock-space multi-reference theory to the relativistic domain and applied to both atomic and molecular systems [12–17]. A brief overview of the effective Hamiltonian variant of the Fock-space multi-reference coupled-cluster (FSMRCC) method is given in [18]. A detailed description of the effective Hamiltonian variant of the FSMRCC can be found in [19–26]. The challenging problem associated with the effective Hamiltonian theory is the problem of intruder states which arises due to the presence of quasi-degeneracy in the eigenstates leading to the failure in convergence [27–31]. The intermediate Hamiltonian variant of the FSMRCC (IHFSMRCC) theory is a solution to address the problem of intruder states [32–39]. The eigenvalue independent partitioning technique (EIP) of Mukherjee in the multi-reference coupled-cluster (EIP-MRCC) approach is also a specific variant of IHFSMRCC to take care of the intruder state problem [40, 41]. It converts the non-linear FSMRCC equations for a given model space into a set of linear CI-like non hermitian eigenvalue equations. The solution can be reached by solving one root at a time preserving the norm of the corresponding eigenvector. This makes EIP-MRCC free from the problem of intruder and achieving faster convergence as compared to the effective Hamiltonian based FSMRCC.

On the other hand, a fully four-component relativistic method in the equation-of-motion coupled-cluster (EOMCC) framework [18, 42–44] is an alternative potential choice to treat different many-body effects in a balanced manner. It describes the complex multi-configurational wave function within a single reference description. The key feature of the EOMCC method is that its reference wave function is obtained using the CC method, which takes care of the dynamical parts of the electron correlations while the non-dynamic counterparts are incorporated through the diagonalization of matrix elements of an effective Hamiltonian in the configuration space [45–52]. Furthermore, the EOMCC method is free from the intruder state problem due to its CI-like structure. This method scales properly at the non-interacting limit and does not satisfy the requirement of linkedness rigorously ensuring the size extensivity [53, 54]. It is worth mentioning that EOMCC method is equivalent to an effective Hamiltonian variant of the FSMRCC method for the single ionization or attachment problem [55], whereas it is not so in the case of double ionization or attachment (DI/DE-EOMCC) [56–58]. The reason behind is that the FSMRCC theory requires the amplitude equations of all the lower sectors along with the amplitudes of the sector of interest, whereas EOMCC requires only the amplitudes of the (0,0) sector and that of the considered sector.

Another important aspect of EOMCC is it directly gives the eigenstates in contrast to the propagator based approaches [59, 60] although these also have equation-of-motion (EOM) structure. Coupled cluster linear response theory (CCLRT) [61–65] is closely related to EOMCC in nature and produces identical results for the energy differences. A comparative discussion on EOMCC and CCLRT can be found in [66–68]. Choudhury et al applied the relativistic CCLRT to calculate ionization potentials and related phenomena [69–74]. Symmetry adapted cluster expansion configuration interaction (SAC-CI) [75–77] is also very similar to EOMCC. These two methods differ in the description of the ground state wave-function.

In this work, we employ our recently developed fully four-component relativistic EOMCC method to calculate core as well as valence ionization potentials (IPs) and double ionization potentials (DIPs) of He-like and Be-like atomic systems with atomic number $Z \leq 10$. The results of our calculations are compared with the available results from the National Institute of Standards and Technology (NIST) database [78]. To understand the role of electron correlations, we followed different approximate schemes in the EOMCC framework. We call these as MBPT2-RPA, MBPT2-EOMCC and CCSD-RPA. In the MBPT2-RPA scheme the ground state wave-function is constructed at the first order perturbation theory level and the EOM matrix is constructed in the one-hole (1 h) or two-hole (2 h) space for the ionization and double ionization potential respectively. MBPT2-EOMCC uses first order perturbation wave function and the EOM matrix is constructed in 1 h and two-hole and one-particle (2 h-1p) space for the ionization problem, whereas it is 2 h and 3 h-1p space for the double ionization problem. The CCSD-RPA scheme uses the ground state wave-function in the coupled-cluster singles and doubles level and EOM matrix is constructed in the 1 h and 2 h space for single ionization and double ionization respectively. All these results are compared with the results calculated using CCSD-EOMCC method to understand passage of the electron correlation effects at various levels of approximation.

The paper is organized as follows: a brief discussion on the relativistic method to generate atomic single particle orbital is presented in section 2. This is followed by a description of the EOMCC theory in the context of evaluation of IPs and DIPs in section 3. We present the results and discuss about their trends in section 4 before making our final remarks in section 5. Atomic units (a.u.) are used consistently unless stated otherwise.

2. Generation of basis and nuclear potential

We use the Dirac–Coulomb (DC) Hamiltonian in our calculations which, after scaling with the rest mass energy of the
electrons ($c^2$), is given by

$$H = \sum_i \left[ \mathbf{a}_i \cdot \mathbf{p}_i + (\beta_i - 1)c^2 \right] + V_{\text{muc}}(r_i) + \sum_{j \neq i} \left\{ \frac{1}{r_{ij}} \right\} \tag{1}$$

where $\mathbf{a}_i$ and $\beta_i$ are the Dirac matrices, $V_{\text{muc}}(r_i)$ is the nuclear potential and $\frac{1}{r_{ij}}$ is the electron-electron repulsion potential.

Obviously, the above Hamiltonian takes into account the spin-orbit interaction through the Dirac Hamiltonian of the electron [79, 80] and the dominant Coulomb interaction. The spin-orbit interaction through the Dirac Hamiltonian of the electron [82]. This interaction may not directly influence the calculations of IPs and DIPs in the He- and Be-like systems, however they still contribute in these systems via the correlation effects of the electrons from different virtual orbitals.

The four-component Dirac wave function for an electron is given by

$$\psi(r) = \frac{1}{r} \begin{pmatrix} P(r) X_{n,m} (\theta, \phi) \\ iQ(r) Z_{-n,-m} (\theta, \phi) \end{pmatrix} \tag{2}$$

with $P(r)$ and $Q(r)$ are the large and small components of the wave function and $X_{n,m}$ and $Z_{-n,-m}$ are the angular functions of the relativistic quantum number $k = -(j + \frac{1}{2})\alpha$ satisfying the condition for the orbital angular momentum $l = j - \frac{1}{2}$ and total angular momentum $\ell$. A linear combination of Gaussian type orbitals (GTOs) is used to obtain the DF single particle orbitals $|\phi_{n,k}(r)\rangle$ as

$$|\phi_{n,k}(r)\rangle = \sum_{x} \left\{ C_{n,k} F_{n,k} (r) X_{n,m} \right\} \tag{3}$$

where $n$ is the principal quantum number of the orbital, $C_{n,k}$ is the expansion coefficients, $N_{n,k}$ is the normalization constant for the large (small) component of the wave function and $\alpha$ is a suitably chosen parameter for orbitals of different angular momentum symmetries and $F_{n,k} (r) = r^l e^{-\alpha r^2}$ is a GTO. The even tempering parameter $\alpha = \alpha_0 \beta^{n-1}$ with two parameters $\alpha_0$ and $\beta$ used for the exponents. The small component and large component of the wave function are related through the kinetic balance condition. The two parameter Fermi-charge distribution

$$\rho_{\text{muc}} (r) = \frac{\rho_0}{1 + e^{r - b/a}} \tag{4}$$

with the normalization factor $\rho_0$, the half-charge radius $b$ and $a = 2.34/(\ln 3)$ is related to the skin thickness of the atomic nucleus, is considered for the evaluation of the nuclear potential.

After obtaining the single particle orbitals, we calculate the matrix element of the Coulomb interaction operator using the expression

$$\langle \phi_{\alpha} | \phi_{\beta} \left\{ \frac{1}{r_{\ell_2}} \right\} | \phi_{\gamma} \rangle = \delta (m_{\alpha} - m_{\gamma}, m_{\beta} - m_{\gamma}) \times \sum_{k=0}^{\infty} (-1)^{m_{\alpha}+m_{\beta}} \times \int d\mathbf{r} [P_{\alpha}(r)P_{\beta}(r) + Q_{\alpha}(r)Q_{\beta}(r)] \times \int d\mathbf{r} [P_{\gamma}(r)P_{\gamma}(r) + Q_{\gamma}(r)Q_{\gamma}(r)] \times \frac{r_k}{r_{\ell_1} + 1} \times X_k \Pi (k, k, l, k) \Pi (k, k, l, k) \tag{5}$$

with the multipole $k$ determined by the triangular conditions $|j_a - j_b| \leq k \leq j_a + j_b$ and $|j_a - j_b| \leq k \leq j_b + j_b$ satisfying the condition for the function $\Pi (k, k', l) = \frac{1}{2} [1 - \alpha'(-1)^{l+k+1}]$ for $l + l' + k = \text{even}$. The angular momentum factor $X_k$ is given by

$$X_k = (-1)^{l+1} \sqrt{(2j_a + 1)(2j_b + 1)(2j_a + 1)} \begin{pmatrix} j_a \quad j_b \quad j_d \quad j_c \\ m_a \quad m_b \quad -m_d \quad m_c \end{pmatrix} \begin{pmatrix} 1/2 \quad 0 \quad -1/2 \quad 1/2 \quad 0 \quad -1/2 \quad 1/2 \quad 0 \quad -1/2 \end{pmatrix} \tag{6}$$

3. Brief description of the EOMCC theory

In the EOMCC approach, the wave function for the $k^{th}$ target state is created by the action of a linear operator ($\Omega_k$) on the single reference CC wave function $|\Psi_0\rangle = \exp(\hat{T})|\Phi_0\rangle$, i.e.

$$|\Psi_k\rangle = \Omega_k |\Psi_0\rangle = \Omega_k \exp(\hat{T})|\Phi_0\rangle \tag{7}$$

where $|\Phi_0\rangle$ is a reference determinant which is taken as the Dirac–Fock (DF) wave function in the present case and the CC operator $\hat{T}$ accounts for the hole (h) to particle (p) excitations. The $T$ operators are given as

$$\hat{T} = \sum_{i < j} \sum_i \sum_{\ell} a^i b^j c^i \delta^{\ell} \cdots \tag{8}$$

in terms of strings of creation and annihilation operators for the holes (denoted by indices $i, j, \cdots$) and particles (denoted by indices $(a, b, \cdots)$ for total $N$ number of electrons of a system. We start with the energy eigenvalue equation

$$\hat{H} \Omega_k \exp(\hat{T}) |\Phi_0\rangle = E_k \Omega_k \exp(\hat{T}) |\Phi_0\rangle \tag{9}$$
By operating on both the sides of the equations with \( \exp(-\hat{T}) \) from the left-hand side and considering \( \Omega_k \) and \( \hat{T} \) commute each other owing to the fact that they are made up of strings of same quasi-particle creation and annihilation operators, we get

\[
\hat{H}\Omega_k \ket{\Phi_0} = E_k \Omega_k \ket{\Phi_0},
\]

for \( \hat{H} \equiv \exp(-\hat{T})\hat{H}\exp(\hat{T}) \). The above equation is projected onto the basis of excited determinants those are accessible by the action of \( \Omega_k \) on \( \ket{\Phi_0} \). To simplify the notations, we denote the IP evaluating EOMCC operators as

\[
\Omega_k^{IP} \equiv R_1 + R_2 + \ldots = \sum_i r_i + \sum_{i<j} r_{ij} a^* a_{ji} + \ldots,
\]

whereas for DIP evaluation, we define

\[
\Omega_k^{DIP} \equiv S_2 + S_3 + \ldots = \sum_{i<j} s_{ij} a^* a_{ji} a^* a_{kj} + \ldots.
\]

We project on to the set of excited determinants \( \{\Phi_i\} \) and \( \{\Phi_{ij}^a\} \) representing the 1 h and 2 h-1p determinants, respectively, for the evaluation of the \( R_1 \) and \( R_2 \) amplitudes as

\[
\bra{\Phi_i} \hat{H} R_1 \ket{\Phi_0} = E_i \bra{\Phi_i} R_1 \ket{\Phi_0}
\]

and

\[
\bra{\Phi_{ij}^a} \hat{H} R_2 \ket{\Phi_0} = E_1 \bra{\Phi_{ij}^a} R_2 \ket{\Phi_0}.
\]

Similarly, we project \( \ket{\Phi_0} \) and \( \ket{\Phi_{ij}^a} \) representing 2 h and 3 h-1p determinants, respectively, to determine the \( S_1 \) and \( S_2 \) amplitudes as

\[
\bra{\Phi_0} \hat{H} S_1 \ket{\Phi_0} = E_1 \bra{\Phi_0} S_1 \ket{\Phi_0},
\]

and

\[
\bra{\Phi_{ij}^a} \hat{H} S_2 \ket{\Phi_0} = E_1 \bra{\Phi_{ij}^a} S_2 \ket{\Phi_0}.
\]

It has to be noted that the 3 h-1p excitations for the He-like systems are absent, hence only the 2 h projections are made in this case after performing the CC calculations. All these equations are expressed in the matrix form as

\[
\hat{H}_N \Omega_k = \Omega_k \Delta E_k \Omega_k
\]

to solve for the eigenvalues \( \Delta E_k = E_k - E_0 \), the energy difference between the \( \ket{\Omega_k} \) state \( E_0 \) and the ionized \( \ket{\Omega_k} \) state \( E_k \), and their corresponding eigenvectors by using the normal order Hamiltonian \( \hat{H}_N \). The Davidson algorithm [83], which is an iterative diagonalization scheme, is implemented to diagonalize the non-hermitian matrix elements of the effective Hamiltonian \( \hat{H}_N \). We have constructed the EOMCC matrix in the opted space but solve only for the principal peaks.

### 4. Results and discussions

Here, we present and discuss about the numerical results of the calculated IPs and DIPs of the He-like and Be-like systems considering atoms up to Ne using the relativistic EOMCC methods at different levels of approximations. To carry out these calculations, we construct the single particle orbitals in the universal basis (UB) method using GTOs with \( \alpha_0 = 0.004 \) and \( \beta = 2.23 \) for all the considered systems. For each of the atomic systems, we use 40, 39, 38, 37 and 36 number of GTOs for the s, p, d, f and g symmetry waves in the DF method to obtain the self-consistent field (SCF) solutions for the orbitals. For the EOMCC calculations, we only correlate electrons belonging to the low-lying orbitals up to 16s, 14p, 13d, 11f and 10g as high-lying orbitals contribute less in the calculations of IPs and DIPs owing to their high energy values. In table 1, we present the SCF \( (E_{DF}) \) and correlation energies calculated at the the second order perturbation theory approximation \( (E_{corr}) \) and from the CC method considering only the singles and doubles excitations, which is referred to as the CCSD method in the literature, \( (E_{corr}^{CCSD}) \).

In table 2, we present IPs of the He-like systems starting from He to Ne. In the same table, we also compare our results with the values listed in the NIST database [78] and the deviations of our results from the NIST values are given in percentages as \( \delta \). Three intermediate calculations are also done for the Be like ions. In MBPT2-RPA scheme both dynamic and non-dynamic parts of the correlations are missing in comparison to the CCSD-EOMCC method. It is observed that the MBPT2-RPA values are overestimated than CCSD-EOMCC. It is also true for the scheme CCSD-RPA. Missing non-dynamic correlations leads to these over-estimations. The MBPT2-EOMCC scheme underestimates the results but these values are in better agreement than the other two schemes in comparison to the experimental values from NIST. It is observed from this table that with the increase in the atomic charge the deviation increases, except for He for which it comparatively shows large discrepancy. We attribute the reason for this to the same as orbitals of the

### Table 1. SCF energy \( (E_{DF}) \), correlation energies from the MBPT(2) \( (E_{corr}^{(2)})) \) and CCSD \( (E_{corr}^{CCSD}) \) methods for different systems obtained using our calculations.

| System   | \( E_{DF} \) | \( E_{corr}^{(2)} \) | \( E_{corr}^{CCSD} \) |
|----------|-------------|-----------------|-----------------|
| He       | -2.8618     | -0.0368         | -0.0417         |
| Li\textsuperscript{+} | -7.2372    | -0.0394         | -0.0429         |
| Be\textsuperscript{2+} | -13.6139   | -0.0406         | -0.0434         |
| B\textsuperscript{3+} | -21.9931   | -0.0412         | -0.0435         |
| C\textsuperscript{4+} | -32.3759   | -0.0415         | -0.0435         |
| N\textsuperscript{5+} | -44.7641   | -0.0416         | -0.0434         |
| O\textsuperscript{6+} | -59.1597   | -0.0416         | -0.0432         |
| F\textsuperscript{7+} | -75.5650   | -0.0415         | -0.0429         |
| Ne\textsuperscript{8+} | -93.9827   | -0.0412         | -0.0426         |
| Be       | -14.5758   | -0.0745         | -0.0927         |
| B\textsuperscript{+}  | -24.2451   | -0.0856         | -0.1091         |
| C\textsuperscript{2+} | -36.4251   | -0.0948         | -0.1236         |
| N\textsuperscript{3+} | -51.1114   | -0.1029         | -0.1371         |
| O\textsuperscript{4+} | -68.3143   | -0.1104         | -0.1500         |
| F\textsuperscript{5+} | -88.0271   | -0.1173         | -0.1623         |
| Ne\textsuperscript{6+} | -110.2559  | -0.1238         | -0.1742         |
ions are more contracted towards the nucleus than He. Again, increase in discrepancies in ions with higher Z values indicates that contributions from the neglected Breit interaction and quantum electrodynamic (QED) corrections are important to be considered to improve accuracies in these results. Similarly, we present DIPs of the He-like ions in Table 3 and compare them with the data available in the NIST database. Also, results from our calculations using MBPT2-DIP scheme are presented where the ground state wave function is the first order perturb wave function. In DIP calculations of He like systems the 3h-1p block does not contribute naturally. Deviations of our DIP results from the NIST values, are given as δ in percentage in the same table. This comparison between the MBPT2-DIP and CCSD-DIP results shows that MBPT2-DIP values are underestimated than the CCSD-DIP values. This study demonstrates that though MBPT2-DIP method constructs the ground state wave function at the first order perturbation level but it gives reasonably accurate results by saving enormous computational time.

In order to assess the trends followed by the calculated results using different employed methods with the ionic charge (q) of the considered atomic systems, we plot the calculated IPs and DIPs of the He-like systems as a function of q as shown in Figure 1. We found that both the IPs and DIPs follow the standard quadratic equations \( aq^2 + bq + c \) with arbitrary parameters \( a, b \) and \( c \). It is found that DIPs of He-like ions satisfy the relationship \( 27q^2 + 92q + 79 \) while for the IPs obey \( 14q^2 + 37q + 25 \) trend. The reason for a large \( a \) coefficient for DIPs may be because of the large kinetic energies of the electrons in the doubly ionized systems rather than the singly ionized systems. The presence of linear terms in \( q \) with different magnitudes of \( b \) coefficient for IPs and DIPs correspond to the role of the Coulomb interactions. The larger ratios of \( b/a \) and \( c/b \) in DIPs imply dominant role by the kinetic energies than the Coulomb interactions in the evaluation of DIPs in the heavier ions.

In table 4, we tabulate the IP values for both the \( 1s \) and \( 2s \) orbitals of the considered Be-like ions. The results of the \( 2s \) orbitals are compared with the NIST values and the deviations, given in percentage as \( \delta \) from the NIST values, are found to be very small. The DIP values are given in Table 5 and are compared with the NIST data. As can be seen, we have achieved accuracies of less than \( \sim 0.01\% \) for all the Be-like systems. For Ne\(^{6+}\), the absolute value differs by 0.04 eV and for the rest it is only about 0.01 eV. For Be like systems we also present intermediate results using MBPT2-RPA, MBPT2-EOMCC and CCSD-RPA schemes. It has been observed that the RPA values are overestimated than the CCSD-EOMCC results. On the other hand MBPT2-EOMCC results. On the other hand MBPT2-EOMCC and CCSD-RPA schemes. It has been observed that the RPA values are overestimated than the CCSD-EOMCC results. On the other hand MBPT2-EOMCC values are lower than the CCSD-RPA values. The differences between the results from these two schemes are more observed that the RPA values are overestimated than the CCSD-EOMCC results.

Figure 1. Trends of IPs and DIPs in the He-like systems as a function of their ionic charge (q).

### Table 2. Comparison of our calculated IPs of He-like ions (in eV) with the NIST database. Differences are given as \( \delta \) in %.

| System  | MBPT2-RPA  | MBPT2-EOMCC | CCSD-RPA  | CCSD-EOMCC | NIST [78] | \( \delta \) |
|---------|------------|-------------|-----------|------------|-----------|---------|
| He      | 78.8769    | 79.0141     | 79.0051   | 0.011      |
| Li\(^+\) | 198.0081   | 198.1053    | 198.0935  | 0.005      |
| Be\(^{2+}\) | 371.5618  | 371.6384    | 371.6152  | 0.006      |
| B\(^{3+}\) | 599.5864  | 599.6502    | 599.5977  | 0.008      |
| C\(^{4+}\) | 882.1263  | 882.1813    | 882.0847  | 0.010      |
| N\(^{5+}\) | 1219.2303 | 1219.2788   | 1219.1142 | 0.013      |
| O\(^{6+}\) | 1610.9541 | 1610.9977   | 1610.7380 | 0.016      |
| F\(^{7+}\) | 2057.3616 | 2057.4013   | 2057.0158 | 0.018      |
| Ne\(^{8+}\) | 2558.5256 | 2558.5621   | 2558.0076 | 0.021      |

### Table 3. Comparison of DIPs of He-like ions (in eV) from our calculations and IERM method with NIST database. Differences between our values with NIST data are given as \( \delta \) in %.

| System  | MBPT2-DIP  | CCSD-DIP  | NIST [78] | \( \delta \) |
|---------|------------|-----------|-----------|---------|
| He      | 78.8769    | 79.0141   | 79.0051   | 0.011   |
| Li\(^+\) | 198.0081   | 198.1053  | 198.0935  | 0.005   |
| Be\(^{2+}\) | 371.5618  | 371.6384  | 371.6152  | 0.006   |
| B\(^{3+}\) | 599.5864  | 599.6502  | 599.5977  | 0.008   |
| C\(^{4+}\) | 882.1263  | 882.1813  | 882.0847  | 0.010   |
| N\(^{5+}\) | 1219.2303 | 1219.2788 | 1219.1142 | 0.013   |
| O\(^{6+}\) | 1610.9541 | 1610.9977 | 1610.7380 | 0.016   |
| F\(^{7+}\) | 2057.3616 | 2057.4013 | 2057.0158 | 0.018   |
| Ne\(^{8+}\) | 2558.5256 | 2558.5621 | 2558.0076 | 0.021   |
| System | MBPT2-RPA 1s | MBPT2-RPA 2s | MBPT2-EOMCC 1s | MBPT2-EOMCC 2s | CCSD-RPA 1s | CCSD-RPA 2s | CCSD-EOMCC 1s | CCSD-EOMCC 2s | NIST [78] 1s | NIST [78] 2s | NIST [78] 2s | δ       |
|--------|-------------|-------------|----------------|---------------|-------------|-------------|-------------|---------------|--------------|--------------|--------------|---------|
| Be     | 129.9469    | 9.3047      | 124.7181       | 8.9465        | 129.7176    | 9.3252      | 124.6451    | 9.3226        | 9.3226       | 0.028        |           |         |
| B⁺     | 223.9840    | 24.9441     | 218.8594       | 24.6074       | 223.7854    | 25.4713     | 218.7644    | 25.1534       | 25.1548       | 0.005        |           |         |
| C²⁺    | 345.5711    | 47.5097     | 340.6506       | 47.1797       | 345.3836    | 48.1981     | 340.5585    | 47.8859       | 47.8877       | 0.003        |           |         |
| C³⁺    | 494.5523    | 76.9378     | 489.5203       | 76.6103       | 494.3698    | 77.7834     | 489.3986    | 77.4733       | 77.4735       | ~0.000       |           |         |
| N³⁺    | 670.8905    | 113.2110    | 665.8323       | 112.8843      | 670.7105    | 114.2119    | 665.6995    | 113.9024      | 113.8989      | 0.003        |           |         |
| O⁴⁺    | 874.5887    | 156.3277    | 869.6562       | 156.0011      | 874.4103    | 157.4820    | 869.5240    | 157.1727      | 157.1631      | 0.006        |           |         |
| Ne⁶⁺   | 1105.6664   | 206.2915    | 1100.7049      | 205.9644      | 1105.4891   | 207.5978    | 1100.5646   | 207.2880      | 207.2710      | 0.008        |           |         |
Table 5. Comparison of our calculated DIPs of Be-like ions (in eV) with the NIST database. Differences are given as $\delta$ in %.

| System | MBPT2-RPA 1s | MBPT2-EOMCC 1s | CCSD-RPA 1s | CCSD-EOMCC 1s | NIST [78] 1s | $\delta$ |
|--------|--------------|----------------|-------------|---------------|----------------|------|
| Be     | 321.0077     | 27.1344        | 308.5294    | 27.0969       | 320.4761       | 27.5600 | 308.3921 | 27.5427 | 27.5338 | 0.032 |
| B$^+$  | 526.2121     | 62.5409        | 513.4659    | 62.4882       | 525.7490       | 63.1252 | 513.2750 | 63.0833 | 63.0869 | 0.005 |
| C$^{2+}$ | 786.4974    | 111.6955       | 773.6588    | 111.6329      | 786.0613       | 112.4343 | 773.4375 | 112.3789 | 112.3803 | 0.001 |
| N$^{3+}$ | 1101.5640   | 174.5374       | 1088.4372   | 174.4678      | 1101.1411      | 175.4290 | 1088.1864 | 175.3649 | 175.3638 | ~0.000 |
| O$^{4+}$ | 1471.3467   | 251.0545       | 1458.4205   | 250.9797      | 1470.9312      | 252.0981 | 1458.2743 | 252.0278 | 252.0183 | 0.003 |
| F$^{5+}$ | 1895.8582   | 341.2520       | 1882.5409   | 341.1733      | 1895.4476      | 342.4468 | 1882.2607 | 342.3718 | 342.3493 | 0.006 |
| Ne$^{6+}$ | 2375.1422   | 445.1430       | 2361.6537   | 445.0611      | 2374.7351      | 446.4879 | 2361.3575 | 446.4093 | 446.3676 | 0.009 |
as of the plot for the IPs of the Be-like ions. However, since the Coulomb potentials are larger in the Be-like systems for which its \( b \) coefficient is found to be larger. In the same figure, we also give the plot for IPs of the outer 2s electrons from the respective Be-like systems and find again a parabolic trend but with much smaller \( a \), \( b \) and \( c \) coefficients. This may be due to the the fact that the outer 2s electrons are loosely bound with their nucleus. Similarly, we plot the DIPs of Be-like systems for both the 1s and 2s orbital electrons in figure 3. We see like-wise plots with figure 2 and find for the 1s orbital electrons it follows the relationship 27q^2 + 180q + 310 while for the 2s orbital electrons it obeys 6.8q^2 + 29q + 28 relation with their ionic charges. These coefficients are almost twice than that of their corresponding IPs. Again, when we compare trends of DIPs of the 1s orbital electrons of Be-like ions with the He-like ions, we find the corresponding \( a \) coefficient is same but the \( b \) coefficient value is large.

5. Conclusion

We have developed and applied four-component EOM methods at different levels of approximations to evaluate IPs and DIPs of the He-like and Be-like isoelectronic sequences up to Ne. Comparison between our results with the NIST database shows that EOMCC results are in very good agreement with the values tabulated in NIST database. It has been demonstrated that both IPs and DIPs of He-like and Be-like isoelectronic sequences follow parabolic trends and the magnitudes of the coefficients of the parabolas are attributed to the role of the kinetic energies and Coulomb interactions of the systems. These coefficients for the 1s orbital electrons are almost twice than those of the 2s orbital electrons in the Be-like systems. Excellent agreement of our calculated results with the NIST values implies that our EOMCC method is capable of accounting for both the relativistic and electron correlation effects accurately. Observation of slight deviations in the values for heavier ions imply that inclusion of higher order relativistic corrections may be required to improve accuracies of those results.

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References

[1] Eland J H D, Vieuxmaire O, Kinugawa T, Lablanquie P, Hall R I and Penent F 2003 Phys. Rev. Lett. 90 053003
[2] Eland J H D, Ho S S W and Worthington H L 2003 Chem. Phys. 290 27
[3] Ackermann W et al 2007 Nat. Photonics. 1 336
[4] Rohringer N et al 2012 Nature 481 488
[5] Gillaspy J D 2001 J. Phys. B 34 R93
[6] Chutjian A 2003 The Physics of Multiply and Highly Charged Ions ed F J Currell (London: Kluwer)
[7] McLaughlin B M 2013 J. Phys. B 46 075204
[8] Nicastro F, Smita M, Elvis M, Drake J, Taotao F, Antonella F, Yair K, Hermann M, Rik W and Andreas Z 2005 Nature 433 495
[9] Zappacosta L, Nicastro F, Kronggold Y and Maiolino R 2012 Astrophys. J. 753 137
[10] Grant I P 2010 Relativistic Quantum Theory of Atoms and Molecules: Theory and Computation (New York: Springer)
[11] Seakins M, Griffiths W J, Harris F M, Andrews S R and Parry D E 1993 Org. Mass. Spectr. 28 1144
[12] Eliav E, Kaldor U and Ishikawa Y 1994 Phys. Rev. A 49 1724
[13] Eliav E, Kaldor U and Ishikawa Y 1994 Phys. Rev. A 50 1121
[14] Visscher L, Eliav E and Kaldor U 2001 J. Chem. Phys. 115 9720
[15] Ilyabaev E and Kaldor U 1992 Chem. Phys. Letters. 194 95
[16] Ilyabae E and Kaldor U 1992 J. Chem. Phys. 97 8455
[17] Ilyabae E and Kaldor U 1993 Phys. Rev. A 47 137
[18] Pathak H, Sasmal S, Nayak M K, Vaval N and Pal S 2014 Phys. Rev. A 90 062501
[19] Lindgren I 1978 J. Int. Quantum Chem 14 33
[20] Haque M and Mukherjee D 1984 J. Chem. Phys. 80 5058
[21] Stolarczyk L Z and Monkhorst H J 1985 Phys. Rev. A 32 725
[22] Pal S, Rittby M, Bartlett R J, Sinha D and Mukherjee D 1987 Chem. Phys. Lett. 137 273
[23] Mukherjee D and Lindgren I 1987 Phys Rep 151 93
[24] Pal S, Rittby M, Bartlett R J, Sinha D and Mukherjee D 1988 J. Chem. Phys. 88 4357
[25] Jeziorski B and Paldus J 1989 J. Chem. Phys. 90 2714
[26] Mukherjee D and Pal S 1989 Adv. Quantum. Chem. 20 291
[27] Schucan T H and Weidemann H A 1972 Ann. Phys. 73 108
[28] Schucan T H and Weidemann H A 1973 Ann. Phys. 76 483
[29] Baker H, Robb M A and Slattery Z 1981 Mol. Phys. 44 1035
[30] Salomonsen S, Lindgren I and Martensson A M 1980 Phys. Scr 21 351
[31] Kaldor U 1988 Phys. Rev. A 38 6013
[32] Malrieu J P, Durand P H and Daudey J P 1985 J. Phys. A 18 S09
[33] Meissner L 1998 J. Chem. Phys. 108 9227
[34] Musial M, Meissner L, Kucharski S A and Bartlett R J 2005 J. Chem. Phys. 122 224110
[35] Meissner L and Nooijen M 1995 J. Chem. Phys. 102 9604
[36] Meissner L and Malinowski P 2000 Phys. Rev. A 61 062510
[37] Musial M and Bartlett R J 2008 Chem. Phys. Lett. 457 267
[38] Landau A, Eliav E and Kaldor U 1999 Chem. Phys. Lett. 313 399
[39] Landau A, Eliav E and Kaldor U 2001 Adv. Quantum. Chem. 39 171
[40] Sinha D, Mukhopadhyay S, Chaudhuri R and Mukherjee D 1989 Chem. Phys. Lett. 154 544
[41] Chattopadhyay S, Mitra A and Sinha D 2006 J. Chem. Phys. 125 244111
[42] Pathak H, Sahoo B K, Das B P, Vaval N and Pal S 2014 Phys. Rev. A 89 042510
[43] Nandy D K, Singh Y and Sahoo B K 2014 Phys. Rev. A 89 062509
[44] Pathak H, Ghosh A, Sahoo B K, Das B P, Vaval N and Pal S 2014 Phys. Rev. A 90 010501
[45] Sekino H and Bartlett R J 1984 Int. J. Quantum. Chem. 26 255
[46] Bartlett R J and Stanton J F 1994 Reviews in Computational Chemistry ed K B Lipkowitz and D B Boyd vol 5 (New York: VCH) pp 65
[47] Stanton J F and Bartlett R J 1993 J. Chem. Phys. 98 7029
[48] Bartlett R J 2012 Comput. Mol. Sci. 2 126
[49] Musial M, Kucharski S A and Bartlett R J 2003 J. Chem. Phys. 118 1128
[50] Musial M and Bartlett R J 2003 J. Chem. Phys. 119 1901
[51] Musial M, Perera A and Bartlett R J 2011 J. Chem. Phys. 134 114108
[52] Meissner L and Bartlett R J 1995 J. Chem. Phys. 102 7490
[53] Nooijen M and Bartlett R J 1995 J. Chem. Phys. 102 3629
[54] Kr Mukhopadhyay, Choudhuri R, Mukhopadhyay D Jr and Mukherjee D 1990 Chem. Phys. Lett. 173 181
[55] Mukhopadhyay D, Mukhopadhyay S K, Choudhuri R and Mukherjee D 1991 Theor. Chim. Acta. 80 441
[56] Tomasz Kus and Krylov Anna I 2011 J. Chem. Phys. 135 084109
[57] Jun Shen Piotr Piecuch 2013 J. Chem. Phys. 138 194102
[58] Mustia M, Perera A and Bartlett R J 2011 J. Chem. Phys. 134 114108
[59] Lindenberg J and Ohn Y 1973 Propagators in Quantum Chemistry (New York: Academic)
[60] Cederbaum L S and Domcke W 1977 Adv. Chem. Phys. 35 108
[61] Koch H, Jensen H A, Jorgensen P and Helgaker 1993 J. Chem. Phys. 93 3335
[62] Koch H, Jensen H A, Jorgensen P and Helgaker 1993 J. Chem. Phys. 93 3345
[63] Mukherjee D and Mukherjee P K 1979 Chem. Phys. 39 325
[64] Koch H, Kobayashi R, deMers A S and Jorgensen P 1994 J. Chem. Phys. 100 4393
[65] Kobayashi R, Koch H and Jorgensen P 1994 Chem. Phys. Lett. 219 30
[66] Sekino H and Bartlett R J 1994 Chem. Phys. Lett. 225 486
[67] Chaudhuri R K, Panda P K, Das B P, Mahapatra U S and Mukherjee D 1999 Phys. Rev. A 60 246
[68] Chaudhuri R K, Panda P K, Merlitz H, Das B P, Mahapatra U S and Mukherjee D 3200 33 5129
[69] Das M, Chaudhuri R K, Chattopadhyay S, Mahapatra U S and Mukherjee D 2011 J. Phys. B 44 165701
[70] Chaudhuri R, Datta B, Das K and Mukherjee D 1996 Int. J. Quantum. Chem. 60 347
[71] Chaudhuri R, Chattopadhyay S and Mahapatra U S 2013 J. Phys. Chem. A 117 12616
[72] Chaudhuri R K, Chattopadhyay S and Mahapatra U S 2012 Phys. Plasmas 19 082701
[73] Nakatsuji H 1978 Chem. Phys. Lett. 59 362
[74] Nakatsuji H and Hirao K 1978 J. Chem. Phys. 68 2053
[75] Nakatsuji H 1979 Chem. Phys. Lett. 74 329
[76] http://physics.nist.gov/PhysRefData/ASD/ionEnergy.html
[77] Sakurai J J 1967 Advanced Quantum Mechanics 1st edition (Addison Wesley)
[78] Grant I P 2007 Relativistic Quantum Theory of Atoms and Molecules, Springer series on Atomic Optical and Plasma Physics 40 173
[79] Das B P, Hata J and Grant I P 1984 J. Phys. B 17 L1
[80] Bernath P F 2005 Spectra of Atoms and Molecules (Oxford University Press) 137
[81] Davidson E R 1975 J. Comput. Phys. 17 87