Relativistic double-ionization equation-of-motion coupled-cluster method: Application to low-lying doubly ionized states

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The article deals with the extension of the relativistic double-ionization equation-of-motion coupled-cluster (DI-EOMCC) method [H. Pathak et al. Phys. Rev. A 90, 010501(R) (2014)] for the molecular systems. The Dirac-Coulomb (DC) Hamiltonian with four-component spinors is considered to take care of the relativistic effects. The implemented method is employed to compute a few low-lying doubly ionized states of noble gas atoms (Ar, Kr, Xe, and Rn) and Cl2, Br2, HBr, and HI. Additionally, we presented results with two intermediate schemes in the four-component relativistic DI-EOMCC framework to understand the role of electron correlation. The computed double ionization spectra for the atomic systems are compared with the values from the non-relativistic DI-EOMCC method with spin-orbit coupling (SOC) [Z. Wang et al. J. Chem. Phys. 142, 144109 (2015)] and the values from the National Institute of Science and Technology (NIST) database. Our atomic results are found to be in good agreement with the NIST values. Further, the obtained results for the molecular systems agree well with the available experimental values.

I. INTRODUCTION

There has been considerable progress in the last few decades in the experimental techniques for the study of di-cationic ions.1–6 The doubly charged ions are highly reactive, and they play an important role in ionized gases, excimer lasers, plasmas, and interstellar clouds, which attracted much attention from both experimentalists and theoreticians.7–10

The unambiguous theoretical prediction of the double-ionization spectra demands a reliable theory. The correctness and authenticity of the calculated values depend on the quality of the wavefunction in describing the quantum systems. Therefore, it is obligatory to have a highly correlated method that can provide a better description of the ionized states. Besides, electron correlation, relativistic effects has a significant contribution to describe the simultaneous removal of two electrons. Thus, concurrent treatment of both the effects of relativity and electron correlation is mandatory due to their intertwined nature.11,12

The self-consistent-field (SCF) solution considering Dirac-Coulomb Hamiltonian with four-component spinors provides the best possible single determinantal description of the effects of relativity in a quantum many-body calculations. On the other hand, coupled-cluster theory13–15 becomes the most acceded many-body method while dealing with the electron correlation. Therefore, the development of a relativistic coupled-cluster theory will be the means to engage with these problems.

Kaldor and coworkers extensively worked on the relativistic coupled-cluster theory.16–22 They extended the Fock-space multireference coupled-cluster theory (FSMRCC)23–30 to the relativistic framework to calculate transition energies.17,20–22 The effective Hamiltonian variant of the FSMRCC theory encounters convergence difficulty with an increase in the size of the model space. The intermediate Hamiltonian Fock-space multireference coupled-cluster (IHFSMRCC) theory31–33 and the MRCC theory based on eigenvalue independent partitioning (EIP-MRCC)34,35 are quite impressive in predicting spectroscopic properties in an intruder-free manner.

As an alternative, the equation-of-motion coupled-cluster (EOMCC) method42–60 becomes popular due to its simple CI-like eigenvalue structure, hassle-free convergence, and the possibility of obtaining shake-up states those are important in explaining photoionization spectra,61 and various radiation-less decay mechanism.62 Furthermore, the EOMCC method directly provides the eigenstates contrary to the propagator based approaches,63,64 even though these methods share similar EOM structure. We would like to emphasis that the EOMCC method works well at the noninteracting limit; however, it lacks the rigorous definition of

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| Atom/ Molecule | Basis | Virtual Cutoff (a.u.) | Spinor | Correlation Energy |
|---------------|-------|----------------------|--------|--------------------|
|               |       |                      | Occupied | Virtual | MBPT(2) | CCSD     |
| Ar            | dyall.cv3z36 | 500.0               | 18      | 146   | -0.59324132 | -0.60681938 |
| Kr            | dyall.acv3z37 | 500.0               | 36      | 230   | -1.46015195 | -1.39817620 |
| Xe            | dyall.acv3z37 | 500.0               | 54      | 242   | -1.62810633 | -1.53775344 |
| Rn            | dyall.acv4z37 | 200.0               | 86      | 364   | -2.38266005 | -2.16144919 |
| Cl₂           | dyall.av3z36 | 500.0               | 34      | 242   | -0.71772024 | -0.74479386 |
| Br₂           | dyall.cv3z37 | 500.0               | 70      | 402   | -2.88914902 | -2.75863049 |
| HBr           | H: aug-cc-pVTZ38, Br: dyall.av3z37 | 500.0 | 36  | 222   | -0.95277980 | -0.91704702 |
| HI            | H: aug-cc-pVTZ38, I: dyall.ae3z37 | 500.0 | 54  | 308   | -2.27780739 | -2.16475927 |

| TABLE II. Comparison of DIP values (in eV) of Kr with various schemes in the EOMCCSD approximation |
|-----------------------------------------------|
| Scheme                                      | States                      |
| basis: aug-cc-pVTZ30                       | $^3P_2$, $^3P_1$, $^3P_0$, $^1D_2$, $^1S_0$ |
| contracted basis, point nucleus, No of virtual spinor=82 | |
| ECPDS10MDFSF60 (spin free)                  | 38.067($^3P$)               | 39.514($^1D$) | 41.740($^1S$) |
| ECPDS10MDFS060 (spin orbit)                | 37.663                      | 38.389         | 38.460         | 39.631         | 41.993         |
| Dirac-Coulomb (1$s^22s^22p^53p^1/23p^1/2$ core frozen) | 38.203                      | 38.670         | 38.775         | 40.005         | 42.316         |
| Dirac-Coulomb                               | 38.202                      | 38.669         | 38.774         | 40.004         | 42.315         |
| basis: Dyall.av3z37                         |                            |                |                |                |
| finite nucleus, virtual cutoff =500 Hartree, No of virtual spinor=170 | |
| Dirac-Coulomb                               | 38.177                      | 38.754         | 38.853         | 40.057         | 42.388         |
| Dirac-Coulomb-Gaunt                         | 38.165                      | 38.730         | 38.831         | 40.035         | 42.362         |
| basis: Dyall.acv3z37                        |                            |                |                |                |
| finite nucleus, virtual cutoff =500 Hartree, No of virtual spinor=230 | |
| Dirac-Coulomb                               | 38.341                      | 38.930         | 39.028         | 40.218         | 42.566         |
| Dirac-Coulomb-Gaunt                         | 38.329                      | 38.906         | 39.005         | 40.196         | 42.539         |
| basis: Dyall.ae3z37                         |                            |                |                |                |
| finite nucleus, virtual cutoff =500 Hartree, No of virtual spinor=244 | |
| Dirac-Coulomb                               | 38.342                      | 38.931         | 39.028         | 40.219         | 42.567         |
| Dirac-Coulomb-Gaunt                         | 38.330                      | 38.907         | 39.006         | 40.196         | 42.540         |
| no virtual cutoff, No of virtual spinor=326 | |
| Dirac-Coulomb                               | 38.344                      | 38.933         | 39.031         | 40.224         | 42.569         |
| Dirac-Coulomb-Gaunt                         | 38.332                      | 38.909         | 39.008         | 40.199         | 42.542         |
| NIST41                                      | 38.359                      | 38.923         | 39.018         | 40.175         | 42.461         |

the size-extensivity. The values computed by the FSM-RCC theory and the EOMCC method cease to agree with each other beyond the principal peaks of the one-valence sector. Coupled-cluster linear response theory (CCLRT)65–68 and symmetry adapted cluster configuration interaction (SAC-CI) method69–71 are the alterna-
It is desirable to introduce the effects of relativity in the electronic structure calculations by choosing an appropriate relativistic Hamiltonian. The use of relativistic effective-core-potential (RECP) with spin-orbit coupling (SOC) is the most common in molecular relativistic calculations. A wide range of RECPs are available, depending on how the RECPs are optimized. It helps to exclude a large number of chemically inert electrons from the SCF calculations to reduce the computational costs for the correlation calculation as compared to the fully relativistic counterparts. The effects of SOC has been introduced in different variants of the EOMCC method. However, the inclusion of the SOC with RECP does not address the intricate coupling between the relativistic and correlation effects. Therefore, it is essential to have a more robust theory considering relativistic Hamiltonian with four-component wavefunction and a highly correlated method for the treatment of the electron correlation. Further, we would like to categorically point out that the SOC effect is naturally taken care of by the Dirac-Hamiltonian. The use of Dirac-Coulomb Hamiltonian is most common in relativistic electronic structure calculation where the two-body Coulomb operator is added with the one-body Dirac-Hamiltonian. The mathematical form of the Coulomb operator is the same as in the non-relativistic theory; however, the physical meaning is different as it takes care of the spin-same orbit interaction. The relativistic Hamiltonian containing up to Coulomb term is sufficient for almost all chemical purposes. However, if unprecedented accurate results are sought especially for the fine-structure splitting from the deep core orbitals, in such a case consideration of the spin-other-orbit interaction and spin-spin interaction become relevant which require full inclusion of the Breit part of the two-body interaction.

The four-component relativistic EOMCC method has been implemented for the computation of ionization potential, electron affinity, and excitation energies of closed-shell heavy atomic systems, as well as for highly charged ions. The atomic relativistic calculations enjoy the exploitation of the spherical symmetry, which permits separate computation of the radial and angular part to work with the numerically evaluated reduced matrix elements. On the other hand, in the spherical atomic implementation, the use of the antisymmetrized two-body matrix elements is not feasible due to the appearance of the different angular factors for the direct and exchange part of the two-body matrix elements. Thus, this non-separability of radial and angular part in the non-spherical case makes molecular relativistic calculations onerous. The EOMCC methods for the calculations of ionization potentials, and electron affinities of molecular systems considering both four-component, as well as exact two-component (X2C) formalism have been implemented and shed light on the non-additivity of the relativistic effects and electron correlation effects through calculations. Further, we have implemented the open-shell reference four-component EOMCC method and applied to calculate ionization potential of super-heavy atomic and molecular systems using DC Hamiltonian. Recently, Shee et al. used Dirac-Coulomb-Gaunt Hamiltonian in their implementation of the EOMCC method.

The simultaneous removal of two electrons is a serious multireference problem. The EOMCC method for double ionization potentials (DIPs) and double electron affinities (DEAs) has been developed to deal with the complex multireference problem within a single-reference description. However, those works are in the non-relativistic framework. Further, we have implemented four-component relativistic DI-EOMCC method for closed-shell atomic systems and employed to calculate valence DIP values of alkaline earth metal atoms where valence electrons are well separated from the other inner electrons.

In this work, we extend the four-component DI-EOMCC method using DC Hamiltonian based on antisymmetrized actual two-body matrix elements applicable to both atomic and molecular systems starting from their closed-shell configuration. We have employed to calculate a few low-lying doubly-ionized states of noble gas atoms (Ar, Kr, Xe, Rn) and molecular systems (Cl2, Br2, HBr, and HI).

The ground state reference wavefunction is defined at the coupled-cluster single- and double- excitation level (CCSD) and the EOM matrix constructed in the 2h and 3h-1p space. Further, two intermediate schemes have been designed to analyse the roles of correlation contributions; one uses the ground state description of the second-order many-body perturbation theory [MBPT(2)], and in the later the EOM matrix is constructed only in the 2h space.

The outline of this paper is as follows. A brief description of the DI-EOMCC method is presented in Sec. II, Sec. III and Sec. IV are allocated for details of the computational parameters and about the discussion of the obtained results in our calculations, respectively. Finally, we convey our concluding thoughts in Sec. V. Atomic units are consistently used unless otherwise stated.

II. METHOD

The wavefunction in the EOMCC method is defined as $\text{Re}^T|\Phi_0\rangle$, where $e^T|\Phi_0\rangle$ is the coupled-cluster ground state wavefunction and $|\Phi_0\rangle$ is the restricted closed-shell reference determinant. $T$ is the usual cluster operator and the $R$ is a linear-operator. The $R$ operator acts upon the coupled-cluster ground state wavefunction and generates the excited state configurations. The second-
quantization form of the cluster-operator $T$ and the EOM operator $R$ is as follows,

$$T = T_1 + T_2 + \ldots = \sum_{i,a} t_{ia} a_i^\dagger a_i + \sum_{a,b \atop i<j} t_{ij} a_i^\dagger a_j + \ldots \tag{1}$$

$$R = R_2 + R_3 + \ldots = \sum_{i<j} r_{ij} a_i a_j + \sum_{i<j<k} r_{ijk} a_i^\dagger a_k a_j a_i + \ldots \tag{2}$$

$i, j, k \ldots (a, b, c, \ldots)$ are hole (particle) indices that are occupied and unoccupied in the reference determinant, respectively. We have restricted our DI-EOMCC implementation up to $T = T_1 + T_2$ and $R = R_2 + R_3$ excitation level. The first step for the EOMCC calculation is the solution of the cluster amplitudes in Eq. 1. These amplitudes are obtained by iterative solution of the following nonlinear-simultaneous equations,

$$\langle \Psi_i^a | e^{-T} H e^T | \Phi_0 \rangle = 0, \quad \langle \Psi_i^{ab} | e^{-T} H e^T | \Phi_0 \rangle = 0 \tag{3}$$

where $| \Psi_i^a \rangle$ and $| \Psi_i^{ab} \rangle$ are the single and double excited configurations with respect to the reference determinant. The ground-state energy obtained by solving equation for the energy,

$$E = \langle \Phi_0 | e^{-T} H e^T | \Phi_0 \rangle \tag{4}$$

Here, $H$ is the Dirac-Coulomb Hamiltonian and is of the following form,

$$H_{DC} = \sum_A \sum_i [c(\vec{\alpha} \cdot \vec{p})_i + (\beta - 1) m_0 c^2 + V_{iA}] + \sum_{i>j} \frac{1}{r_{ij}} \tag{5}$$

$\alpha$ and $\beta$ are the usual Dirac matrices. $V_{iA}$ is the potential energy operator for the $i^{th}$ electron in the field of nucleus $A$. $m_0 c^2$ is the rest mass energy of the free electron, where $c$ stands for the speed of light. The energy as well as the $R$ operator is determined by solving the following equation:

$$\hat{H} R | \Phi_0 \rangle = E R | \Phi_0 \rangle \tag{6}$$

where $\hat{H} = e^{-T} H e^T$ and $E$ is the energy of the doubly ionized state.

The above equation is projected onto the set of excited determinants $(| \Psi_{ij} \rangle)$ and $(| \Psi_{ij}^{ab} \rangle)$ to obtain the following equations,

$$\langle \Psi_{ji} | [\hat{H}, R_{\nu}] | \Phi_0 \rangle = \Delta E_{\nu} r_{ji}, \tag{7}$$

$$\langle \Psi_{kji}^{ab} | [\hat{H}, R_{\nu}] | \Phi_0 \rangle = \Delta E_{\nu} r_{kji}^{ab}, \tag{8}$$

Where $\Delta E_{\nu}$ is the amount of energy required to expel two electrons simultaneously from any given reference configuration. The commutative property of the $T$ and $R$ is assumed in deriving the above equations. The algebraic expression of the left hand sides of Eq. 7 and Eq. 8 are as follows,

$$\Delta E_{\nu} r_{ji} = -\hat{P}(ij) \sum_k \hat{f}_{ij} r_{ki} + 0.5 \sum_{l,k} \hat{V}_{lj} r_{lk} + \sum_k \hat{f}_{ji} r_{kj} - 0.5 \hat{P}(ij) \sum_{l,k,a} \hat{V}_{ljk} r_{lk} \quad \forall \ j < i \tag{9}$$

$$\Delta E_{\nu} r_{kji}^{ab} = -\hat{P}(i|jk) \sum_l \hat{V}_{lk}^a r_{li} - \hat{P}(ij|k) \sum_l \hat{V}_{lk}^b r_{li} + 0.5 \hat{P}(i|jk) \sum_{l,m} \hat{V}_{lm}^a r_{li} \quad \forall \ (a, k < j < i) \tag{10}$$

Here $\hat{f}$, $\hat{V}$ and $t_{lkm}^a V_{lm}^{bc}$ stand for one-body, two-body and three-body intermediate matrix elements constructed by contracting appropriate one-body and two-body Hamiltonian matrix elements and the converged amplitudes from the coupled-cluster ground-state calculation as described in the Ref. $\hat{P}(i|j|\ldots|j|\ldots)$ stands for the cyclic permutation operator. The above equations can be expressed in the matrix form as $\hat{H} R = R \Delta E_{\nu}$. The size of the $\hat{H}$ matrix is large enough ($nh^2 + nb^2 np, nh^2 + nb^3 np, nh$ and $np$ stand for the number of holes and particles, respectively) to follow a full diagonalization algorithm in a reasonable basis. Therefore, we have used David-son diagonalization algorithm for the diagonalization of the non-Hermitian matrix. The DI-EOMCC method is prone to slow convergence. Therefore, to obtain a smooth and faster convergence, we have used eigenvectors obtained from the full diagonalization of 2h block as an initial guess for the iterative procedure. The intermediate scheme MBPT(2) approximates CCSD ground state wavefunction at the second-order many-body perturbation theory level and for the 2h scheme, the dimension of the EOM matrix is reduced to $(nh^2, nh^2)$, by ignoring contribution from the $3h - 1p$ block.
TABLE III. Experimental and theoretical DIP values (in eV) in EOMCC approximation

| System | State | Ref. | MBPT(2) | 2h | CCSD | NIST |
|--------|-------|------|---------|----|------|------|
| Ar     | $^3P_2$ | 43.481 | 48.955 | 43.448 | 43.389 |
|        | $^3P_1$ | 43.629 | 49.129 | 43.596 | 43.527 |
|        | $^3P_0$ | 43.690 | 49.191 | 43.657 | 43.584 |
|        | $^1D_2$ | 45.307 | 50.710 | 45.241 | 45.126 |
|        | $^1S_0$ | 47.793 | 51.771 | 47.694 | 47.514 |
| Kr     | $^3P_2$ | 38.657 | 42.880 | 38.421 | 38.359 |
|        | $^3P_1$ | 39.211 | 43.572 | 39.123 | 39.028 |
|        | $^3P_0$ | 39.308 | 43.552 | 39.135 | 39.018 |
|        | $^1D_2$ | 40.466 | 44.835 | 40.218 | 40.175 |
|        | $^1S_0$ | 42.791 | 46.127 | 42.566 | 42.461 |
| Xe     | $^3P_2$ | 33.406 | 36.742 | 33.016 | 33.105 |
|        | $^3P_1$ | 34.597 | 38.202 | 34.268 | 34.319 |
|        | $^3P_0$ | 34.413 | 37.586 | 34.065 | 34.133 |
|        | $^1D_2$ | 35.516 | 39.187 | 35.222 | 35.225 |
|        | $^1S_0$ | 37.897 | 41.017 | 37.659 | 37.581 |
| Rn     | $^3P_2$ | 29.972 | 33.070 | 29.837 | 32.149 |
|        | $^3P_1$ | 33.814 | 37.900 | 33.887 | 33.941 |
|        | $^3P_0$ | 31.329 | 34.077 | 31.215 | 31.215 |
|        | $^1D_2$ | 34.573 | 38.578 | 34.641 | 34.641 |
|        | $^1S_0$ | 39.276 | 43.773 | 39.557 | 39.557 |

III. COMPUTATIONAL CONSIDERATIONS

The SCF solution using DC Hamiltonian and the required one-body and two-body matrix elements for the correlation calculations are obtained from the DIRAC14 program package.\textsuperscript{111} Consideration of finite size nuclear model is most suited for the relativistic electronic structure calculations. Therefore, the Gaussian charge density distribution nuclear model is taken into account to mimic the effects of the finite size nucleus. All the parameters for this model are taken as default.\textsuperscript{112} The contribution from the high-lying orbitals in a correlation calculation is inconsequential due to their large energy values. Therefore, we have restricted the number of virtual orbitals on the basis of energy criteria. The orbitals above a threshold value are discarded from the correlation calculations. The details of the basis set, threshold energy cutoff for the virtual orbitals including the number of occupied and virtual spinors are reported in Tab. I. The two-body matrix elements below 10\textsuperscript{−12} are neglected in all our calculations due to their negligible contribution in the correlation calculations. SCF calculations are performed with a cutoff of 10\textsuperscript{−7} for the norm of the error vector. The ground state coupled-cluster calculations uses convergence cutoff of 10\textsuperscript{−9} and a DIIS space of 6. The DI-EOMCC method uses convergence threshold of 10\textsuperscript{−5}. Scalar real Gaussian functions constitute the finite atomic orbital basis and are used in our calculations in an uncontracted fashion. Dyall.cv3z\textsuperscript{36} basis is chosen for Ar. We opted Dyall.acv3z\textsuperscript{37} for Kr and Xe and dyall.acv4z\textsuperscript{37} basis for the Rn atom. For the molecular systems, dyall.acv3z\textsuperscript{36} basis is chosen for Cl in Cl\textsubscript{2}, and dyall.cv3z\textsuperscript{37} basis is for Br atom in Br\textsubscript{2}. aug-cc-pVTZ\textsuperscript{38} basis is chosen for the H atom in both HBr and HI. Dyall.av3z\textsuperscript{37} basis is used for Br in HBr and dyall.ae3z\textsuperscript{37} basis has opted for I in HI. We have used experimental bond-length of 1.9870\,\textmu A, 2.2810\,\textmu A, 1.4140\,\textmu A, and 1.6090\,\textmu A for Cl\textsubscript{2}, Br\textsubscript{2}, HBr, and HI respectively and these values are taken from the Ref.\textsuperscript{113}

IV. RESULTS AND DISCUSSION

The correlation energies from MBPT(2) and CCSD calculations are reported in Tab. I. The obtained correlation energies are compared with the values from the DIRAC14\textsuperscript{111} to test the correctness of the implementation of the ground state calculations. Our results from the correlation calculations match with the DIRAC14 values up to 8-digit after the decimal point. We have carried out several calculations and found that the agreement is irrespective of the chemical systems or basis sets. The discrepancy beyond this limit is due to the use of different convergence algorithm or the cutoff used in the storage of the two-body matrix elements.

In Tab. II, we reported results with various basis sets, and Hamiltonian and taken Kr as an example for comparison. A two-component description is needed.
Such treatment of the SOC operator database. It is in the EOMCC approximation.

| System | State | MBPT(2) | 2h | CCSD | Expt. |
|--------|-------|---------|----|------|-------|
| Cl₂    | \(^3\Sigma^-\) | 31.310  | 35.902 | 31.397 | 31.13₁¹¹⁴ |
|        | \(^1\Delta\)   | 31.827  | 36.293 | 31.907 | 31.74₁¹¹⁴ |
|        | \(^1\Sigma^+\) | 33.210  | 36.475 | 32.294 | 32.12₁¹¹⁴ |
|        | \(^1\Sigma^-\) | 33.217  | 37.418 | 33.319 | 32.97₁¹¹⁴ |
| Br₂    | \(^3\Sigma^-\) | 28.752  | 32.380 | 28.473 | 28.53₁¹¹⁵ |
|        | \(^1\Delta\)   | 29.327  | 32.935 | 29.041 | 28.91₁¹¹⁵ |
|        | \(^1\Sigma^+\) | 29.801  | 33.346 | 29.519 | 29.38₁¹¹⁵ |
|        | \(^1\Sigma^-\) | 30.058  | 33.421 | 29.794 | 30.30₁¹¹⁵ |
| HBr    | \(^3\Sigma^\alpha\) | 32.688  | 36.859 | 32.757 | 32.62₁¹¹⁶ |
|        | \(^1\Delta\)   | 34.109  | 38.245 | 34.143 | 33.95₁¹¹⁶ |
|        | \(^1\Sigma^+\) | 35.400  | 38.942 | 35.429 | 35.19₁¹¹⁶ |
| HI     | \(^3\Sigma^\alpha\) | 29.596  | 33.010 | 29.174 | 29.15₁¹¹⁷ |
|        | \(^1\Delta\)   | 29.837  | 33.399 | 29.412 | 29.37₁¹¹⁷ |
|        | \(^1\Sigma^\alpha\) | 30.931  | 34.458 | 30.481 | 30.39₁¹¹⁷ |
|        | \(^1\Sigma^\alpha^\prime\) | 32.238  | 35.367 | 31.801 | 31.64₁¹¹⁷ |

The numerical results of the lowest five double-ionized states calculated using the four-component relativistic DI-EOMCC method by simultaneously removing two-electrons from the closed-shell configuration are presented in Tab. III. Further, the results from the intermediate calculations using MBPT(2) and the 2h schemes are also compiled in the same table. All these methods are employed to noble gas atoms (Ar, Kr, Xe, and Rn). We have compared our results with the values from DI-EOMCC calculations with SOC effects. Finally, all these values are tested against the NIST database. It is observed that both MBPT(2) and the 2h scheme tend to overestimate DI-EOMCC results; however, the deviation is larger for the 2h scheme. 2h scheme lacks the contributions of the 3h – 1p block which is a major source of non-dynamical electron correlation. The ground state defined at the MBPT(2) level is rather a better approximation than the 2h scheme. The DI-EOMCC results are found to be very accurate in comparison to the NIST database for Ar, Kr, and Xe atoms, and there is a clear improvement over the DI-EOMCC results with SOC effects. The employed virtual subspace for the chosen basis set for the Rn atom is rather small and gives results similar to the values reported by Wang et al. In their work, the SOC effect is treated perturbatively for the post SCF part using a scalar-relativistic Hamiltonian. The RECPs are used for taking care of the relativistic effects, and the one-electron SOC operator is taken from the RECP operator. However, they disregarded the two-electron part of the SOC operator. Such treatment of the SOC operator leads to a gross overestimation of spin-orbit effects. There is a large deviation (2.4 eV) from the experimental value reported in the NIST database. We take note of the experimental value, which is reported with an uncertainty of 1.9 eV.

Further, we employed all the three schemes in the DI-EOMCC framework to molecular systems (Cl₂, Br₂, HBr, and HI) and compared with the available experimental values. These results are tabulated in Tab. IV. The reported values for all the states computed using DI-EOMCC scheme with CCSD as a reference wavefunction are found to be very accurate and relative deviation is well within 2.0% from the experimental values. The deviation of the MBPT(2) results are less in comparison to the 2h approximation from the experimental values. Therefore, MBPT(2) is a better approximation than the 2h method in the EOMCC framework.

V. CONCLUSION

We have successfully implemented the relativistic DI-EOMCC method using four-component Dirac spinors for the calculation of double-ionization spectra. The implementation is a general one based on anti-symmetrized ac-

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Note: The table contains experimental and theoretical DIP values for various systems, comparing different calculations and methods. The text elaborates on the methods used, the results obtained, and the conclusions drawn from these analyses.
tual two-body matrix elements. It supports both atomic and molecular systems starting from their closed-shell configuration. The implemented method is employed to compute a few low-lying doubly-ionized states of both atoms and molecules. The results of our relativistic DI-EOMCC method found to be very accurate in comparison to the available experimental values. The outcome of our computation suggests that the MBPT(2)-EOMCC method is a better approximation than the 2h-EOMCC scheme.

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