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Relativistic equation-of-motion coupled-cluster method for the ionization problem: Application to molecules

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We report the implementation of the four-component spinor relativistic equation-of-motion (EOM) coupled-cluster method within the single- and double-excitation approximation to calculate the ionization potential of molecules. We have applied this method to calculate vertical ionization potentials of the molecules XH ($X =$ F, Cl, Br, I) along with Cl_2 and Br_2 in their closed-shell configuration. We have also presented intermediate results using the second-order many-body perturbation-theory level in the EOM framework to understand the role of electron correlation. All the calculated values are compared with the available experimental results. Our results are found to be in good agreement with sophisticated experiments, and relative deviation of less than 1% is achieved for all the considered systems.

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I. INTRODUCTION

It is always a hard task for the theoretical physicist to come up with a method that can depict atomic and molecular spectroscopic properties very precisely. The effects of electron correlations as well as relativistic effects have to be taken into consideration simultaneously, as they are intertwined [1]. The Dirac–Hartree-Fock method in its four-component formalism is the best possible way to include the effects of the relativity within a single determinantal description. On the other hand, coupled-cluster theory is known to be the most elegant to effectuate the electron correlation [2,3]. It is, therefore, the combination of these two methods that will surely be the solution to the problem.

The first step put forward in this direction is by Kaldor and coworkers. They implemented the relativistic counterpart of the Fock-space multireference coupled-cluster theory (FSMRCC) for the cause and applied it extensively to both atomic and molecular systems [4–8]. The original idea of FSMRCC theory is based on the construction of an effective Hamiltonian using the Bloch-Lindgren equation to extricate some of the roots of the Hamiltonian matrix from the set of the entire eigenspectrum [9–15]. The effective Hamiltonian variant of FSMRCC theory works within a reduced dimensional space, called model space, which is the part of the correlation space chosen to construct the effective Hamiltonian, and the rest of the space is known as orthogonal space. The linear combination of suitably chosen active configurations based on energetic criteria is used to construct the model space. An operator, called wave operator is defined through which the contribution of orthogonal space included, is the tool to construct the effective Hamiltonian. Finally, the diagonalization of the effective Hamiltonian matrix includes the correlation contribution of the model space and results to the set of desired eigenvalues. The problem associated with a reduced dimensional effective Hamiltonian is the problem of an intruder state, which leads to the failure in convergence. It appears that the effective Hamiltonian formalism of the FSMRCC theory is not straightforward and is conceptually difficult, and lot of complication is associated with it.

An alternative elegant approach to tackle the problem is to use the equation-of-motion variant of the coupled-cluster theory (EOMCC) [16–21]. The EOMCC is operationally a two step process: (i) solution of the coupled-cluster equation for the N electron determinant and (ii) construction and diagonalization of the effective Hamiltonian matrix in the $(N-1)$ electron determinantal space to get the desired set of eigenvectors and eigenvalues. As EOMCC simultaneously treats two Hilbert spaces (N and $N-1$ electron space) in a single problem; the effect of relaxation is also taken into consideration, which plays a key role in the accurate description of the electronic states. The dynamic part of the electron correlation is taken care of by the exponential structure of the CC operator, whereas the nondynamical part comes through the diagonalization of the effective Hamiltonian in the configuration space. We must admit that the EOMCC for the single ionization problem is equivalent to the (0,1) sector FSMRCC theory and produces identical results for the principal peaks [22,23]. The superiority of the EOMCC method over FSMRCC theory is that the numerical instability due to the problem of intruder states in FSMRCC does not arise in EOMCC, as it is an eigenvalue problem. The EOMCC is capable of giving shake-up states, which play important roles in explaining various photoionization spectra [24].

The EOMCC can be viewed as a multistate approach where multiple states are obtained in a single calculation and are treated on equal footing. It works within a single reference description to describe the complex multiconfigurational wave function. It is pertinent to say that EOMCC behaves properly at the noninteracting limit but is not rigorously size extensive [25,26]. The error due to the size extensivity is reduced due to the presence of a higher-order block. Furthermore, the eigenstates in the EOMCC method are obtained directly in contrast to the propagator approaches, though both the methods are of EOM structure [27,28].

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Recently, we stepped into the domain of fully four-component relativistic EOMCC and employed it to calculate single-ionization and double-ionization potentials, but that was for the atomic systems in their closed-shell configuration [29–31]. The molecular relativistic calculations are always more tedious than the atomic ones. The spherical symmetry can be exploited in the atomic case, which allows the separation of the radial and angular part to use the reduced matrix elements. The evaluation of radial integrals can be done using numerical integration. This reduces computational scaling. However, the method is less straightforward, as each of the radial integrals has to be multiplied by the corresponding angular factor. The use of antisymmetrized quantities (two-body matrix elements) is common in molecular calculations, but is not suitable for the spherical implementation in the atomic case, as different angular factors will arise for the direct and exchange parts of the radial integrals. The complexity associated with the atomic calculations is more than compensated for by the need to solve only for the radial equations. This allows the use of a very large basis set and correlation of more electrons with numerically evaluated radial integrals to achieve better accuracy of results.

The relativistic effective core potential (RECP) is routinely used in molecular relativistic calculations [32]. In RECP, only valence and some outer-core electrons are treated explicitly, and the rest of the electrons are replaced by an effective RECP operator. This includes the simulating interaction of explicitly treated electrons with those which are excluded from the RECP calculation. There are a variety of RECPs depending on how the RECPs are optimized [33]. Among the various RECPs, the RECP with spin-orbit (SO) interaction is the most popular one. This is generally done on the basis of separation of the electrons into core and valence and between the scalar and spin-orbit relativistic effects according to the energy. It allows exclusion of a large number of chemically inert electrons from the self-consistent field (SCF) calculations, which eventually reduces the computational costs for the correlation calculation as compared to the all electron two-component and four-component calculation. The problem associated with this approach is the lack of control over accuracy.

Hirata *et al.* was first to implement relativistic EOMCC for the purpose of molecular calculations [34]. They combined different electron correlation methods, basis set, and relativistic treatment to make a composite method. The dynamic part of the electron correlation is taken care of with a low rank method including the scalar relativistic effect and employed various basis sets to enable complete basis set extrapolation. The nondynamical correlation is treated using the EOMCC method with a small basis set. Finally, the SO effect is added as the energy difference between the RECP+SO with RECP calculated using a low rank correlated method. This approach cancels some of the errors associated with the RECP methods. We would rather call Hirata *et al.*'s treatment a good compromise of the different many-body effects to get reasonable results. This approach does not address the complex interplay between the relativistic and correlation effects, which has been taken into account using the four-component single-particle wave function, and the Dirac-Coulomb Hamiltonian along with the correlation treatment are done by the EOM-CCSD method.

In this paper, we consider the implementation of the fully four-component relativistic EOMCC method to calculate ionization potentials of molecular systems within the single- and double-excitation approximation (the EOM-CCSD method). Pilot calculations of molecular ionization potential using the EOM-CCSD method are presented. We have also presented results by constructing the ground-state wave function at the first-order perturbation-theory level, which corresponds to the second-order perturbation energy as the ground-state energy. We call this EOM-MBPT(2). These results are compared with the EOM-CCSD results to understand the role of electron correlation. To justify the fact that the relativistic and electron correlation effects are nonadditive, we have chosen HF as an example system. Both exact two-component (X2C) and four-component EOMCC calculations are performed on it.

The paper is organized as follows. A brief description of the EOMCC theory in the context of ionization potential is given in Sec. II, and the computational details are presented in Sec. III. We present and discuss results in Sec. IV, before making our final remarks in Sec. V. Atomic units are used unless stated otherwise.

II. THEORY

The starting point for the EOMCC calculation for the ionization problem is the solution of the reference wave function, which is the N electron CC closed-shell ground-state wave function. The ground-state wave function in the CC method is defined as

$$|\Psi_0\rangle = e^{\hat{T}}|\Phi_0\rangle, \tag{1}$$

where $|\Phi_0\rangle$ is the single slater determinant, which is the closed-shell N electron Dirac–Hartree-Fock reference determinant in our case. $\hat{T}$ is the cluster operator, which within the CCSD approximation is represented as

$$\begin{aligned} T &= T_1 + T_2 \\ &= \sum_{i,a} t_i^a a_a^\dagger a_i + \sum_{\substack{a<b\\ i<j}} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i. \end{aligned} \tag{2}$$

$i,j(a,b)$ are the indices for the occupied (virtual) spinors. The cluster operators are solved by the following simultaneous nonlinear algebraic equations:

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

where $|\Phi_i^a\rangle$ and $|\Phi_{ij}^{ab}\rangle$ are the singly and doubly excited determinant with reference to the N electron closed-shell Dirac–Hartree-Fock determinant. Finally, the ground-state energy is obtained by solving the equation for the energy:

$$E_{\text{CCSD}} = \langle\Phi_0|e^{-T}\hat{H}e^{T}|\Phi_0\rangle, \tag{4}$$

where $\hat{H}$ is the Dirac-Coulomb Hamiltonian, which is

$$\hat{H}_{\text{DC}} = \sum_A \sum_i [c(\vec{\alpha}\cdot\vec{p})_i + \beta_i m_0 c^2 + V_{iA}] + \sum_{i>j} \frac{1}{r_{ij}} \mathbb{1}_4. \tag{5}$$

α and β are the usual Dirac matrices. V_{iA} stands for the potential-energy operator for the ith electron in the field of

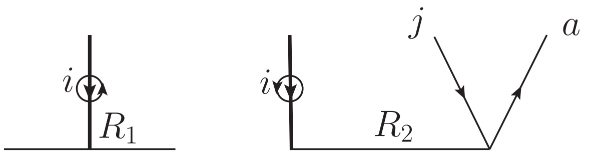

FIG. 1. Diagrammatic representation of R_1 and R_2 operators.

nucleus A. m_0c^2 is the free-electron rest mass energy, where c is the speed of light.

In the EOMCC approach for the single electron ionization problem, the wave function for the kth target state is created by the action of a linear operator $R(k)$ on the single reference coupled-cluster wave function $|\Psi_0\rangle$:

$$|\Psi_k\rangle = R(k)|\Psi_0\rangle. \tag{6}$$

Within the CCSD approximation, $R(k)$ is also approximated to

$$\begin{aligned} R(k) &= R_1 + R_2 \\ &= \sum_i r_i a_i + \sum_{\substack{a \\ i<j}} r_{ij}^a a_a^\dagger a_j a_i. \end{aligned} \tag{7}$$

The diagrammatic representations of the R_1 and R_2 operator are presented in Fig. 1 and are one rank higher than the CC operators.

The energy of the kth ionized state is determined by the equation

$$e^{-T} H R e^T |\Phi_0\rangle = e^{-T} H e^T R |\Phi_0\rangle = \bar{H} R |\Phi_0\rangle = E R |\Phi_0\rangle. \tag{8}$$

It is assumed that e^T and R commute, as they are the strings of the same quasiparticle creation operator. Here, $\bar{H} = e^{-T} H e^T$ is the effective Hamiltonian and E, which is the energy of the ionized state, is the sum of E_{CCSD} and the corresponding ionization potential. Subtraction of E_{CCSD} from Eq. (8) takes the form of

$$[\bar{H}, \hat{R}(k)]|\Phi_0\rangle = \Delta E_k \hat{R}(k)|\Phi_0\rangle, \quad \forall k. \tag{9}$$

That is why this approach is called EOMCC in analogy to Heisenberg's equation of motion for the excitation operator $R(k)$. A correlated determinantal space of $|\phi_i\rangle$ and $|\phi_{ij}^a\rangle$ ($1h$ and $2h-1p$) with respect to $|\Phi_0\rangle$ is chosen to project the above equation to get the desired ionization potential values, ΔE_k:

$$\langle \phi_i [\bar{H}, R(k)] |\phi_0\rangle = \Delta E_k R_i, \tag{10}$$

$$\left\langle \phi_{ij}^a [\bar{H}, R(k)] |\phi_0\right\rangle = \Delta E_k R_{ij}^a. \tag{11}$$

The above equations can be represented in the matrix form as $\bar{H}R = R\Delta E_k$. The antisymmetrized diagrams contributing to the $1h$ and $2h-1p$ blocks are presented in Figs. 2 and 3, respectively. The evaluation of these diagrams is done by constructing one-body, two-body, and three-body intermediate diagrams. This requires the solution of the coupled-cluster ground-state amplitude equations. With the converged T_1 and T_2 amplitudes from CC ground-state calculations, these intermediate diagrams are constructed by contracting one-body and two-body parts of the effective Hamiltonian matrix elements.

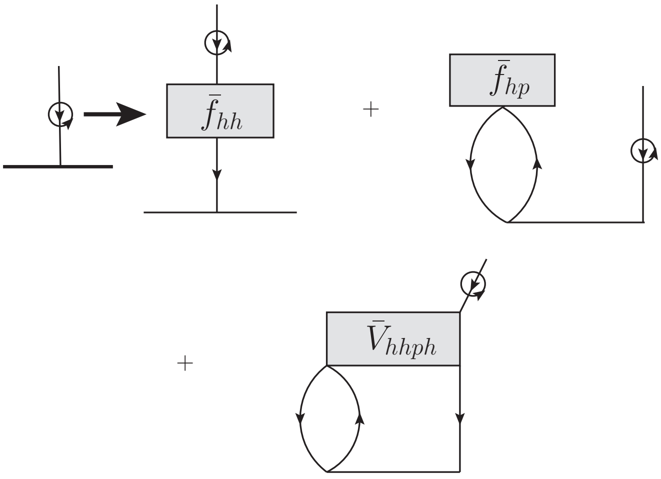

FIG. 2. Diagrams contributing to the $1h$ block.

There are three distinct types (three one-body, four two-body and one three-body) of intermediate diagrams, which are required for the calculation of the ionization potential using the EOM-CCSD method. We denote these as $\bar{f}_{hh}$, $\bar{f}_{pp}$, $\bar{f}_{hp}$, $\bar{v}_{hphh}$, $\bar{v}_{hhhh}$, $\bar{v}_{hhph}$, $\bar{v}_{hphp}$, and $\bar{W}$. Here $\bar{f}$, $\bar{v}$, and $\bar{W}$ stand for one-body, two-body, and three-body intermediates, respectively. The algebraic expression as well as diagrammatic of the intermediate diagrams can be found in Ref. [35]. All these intermediate diagrams are inserted in-between the diagrams contributing to the $1h$ and $2h-1p$ blocks. A circled arrow represents a detached occupied orbital.

The dimension of the $\bar{H}$ matrix is quite large $(nh + nh^2np, nh + nh^2np)$ for the relativistic calculations in a reasonable basis. Therefore, following a full diagonalization scheme is not at all a good idea. Here nh and np represent the number of holes and particles, respectively. The Davidson algorithm [36], which is an iterative diagonalization scheme, is implemented for the diagonalization purpose of $\bar{H}$ to get the desired set of eigenvalues ΔE_k and the corresponding eigenvectors. This avoids computation, storage, and diagonalization of the full matrix. The EOMCC can be re-

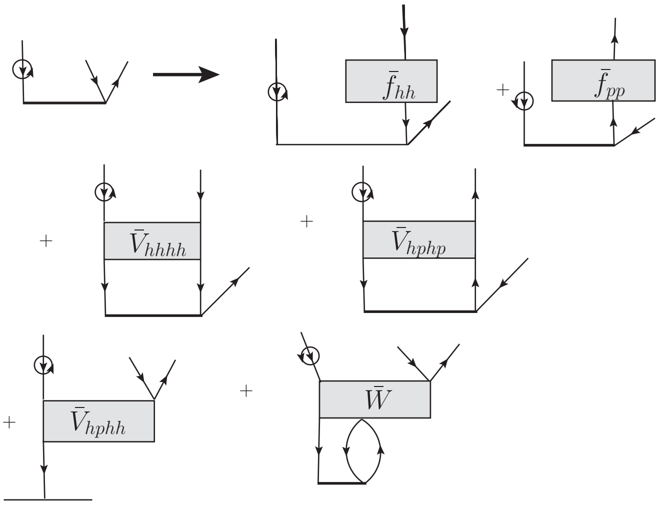

FIG. 3. Diagrams contributing to the $2h$-$1p$ block.

TABLE I. Comparison of correlation energy from MBPT(2) [$E_{\mathrm{corr}}^{(2)}$] and CCSD [$E_{\mathrm{corr}}^{(\mathrm{CCSD})}$] of HF as a function of the number of basis functions. All energies are in atomic units.

	X2C-EOMCC		4C-EOMCC	
No. of orbitals	$E_{\mathrm{corr}}^{(2)}$	$E_{\mathrm{corr}}^{(\mathrm{CCSD})}$	$E_{\mathrm{corr}}^{(2)}$	$E_{\mathrm{corr}}^{(\mathrm{CCSD})}$
200	−0.2921	−0.2930	−0.2921	−0.2929
220	−0.3176	−0.3167	−0.3175	−0.3166
250	−0.3482	−0.3477	−0.3480	−0.3475
280	−0.3619	−0.3615	−0.3615	−0.3612
308	−0.3659	−0.3655	−0.3655	−0.3651

garded as the diagonalization of the coupled-cluster similarity transformed Hamiltonian in the configuration space. This makes the EOMCC a hybrid method of coupled cluster and configuration interaction.

III. COMPUTATIONAL DETAILS

The one-body and two-body matrix elements are generated with the help of the DIRAC10 program package [37]. The finite atomic orbital basis consists of scalar real Gaussian functions. The large components of the basis set are contracted, and the small components are uncontracted except for the Br_2 molecule, where both the large and small components are uncontracted in nature. The small component of the basis set is generated by imposing a restricted kinetic balance (RKB) condition with the large components. This RKB is done by the preprojection in the scalar basis, and the unphysical solutions are removed by diagonalizing the free particle Hamiltonian. The DIRAC10 uses Gaussian charge distribution for the nuclear potential. The nuclear parameters used in our calculations are all default values. We adopted the cc-pVQZ basis set [38] for the H atom in all the calculations. In the calculation of HF and HCl molecules, the basis set chosen both for the F and Cl atom is aug-cc-pCVQZ [39,40]. The dyall.acv4z [41] basis is chosen for Br and I for the calculations of HBr and HI. The basis sets chosen for Cl and Br atoms are aug-cc-pCVQZ [40] and dyall.cv3z [41], respectively, in the calculation of Cl_2 and Br_2. We have taken into account C_{2v} symmetry to generate the single-particle orbitals and two-body matrix elements in all the calculations, and none of the electrons are frozen for the correlation calculations. In the implemented version of X2C SCF in DIRAC10, the large component of the basis is uncontracted in nature. Therefore, to compare the four-component calculations with X2C-EOMCC, both the large and small components of the basis are also taken as uncontracted to generate the same determinantal space. The matrix elements of the intermediate diagrams are stored setting a cutoff of 10^{-12} to save storage requirements, as the contribution of the matrix elements beyond 12 decimal places is much less. To debug our newly implemented relativistic EOM-CCSD code, we benchmarked our results with the Fock-space MRCC code of DIRAC10 for the ionization problem with the same basis, same convergence criteria, and equal amount of direct inversion in the iterative subspace (DIIS), as these two methods in principle are supposed to produce identical results. We have achieved identical results for the MBPT(2) correlation energy, ten-digit agreement for the CCSD correlation energy, and eight-digit agreement for ionization potential values. This agreement is achieved independently of the choice of molecules as well as of the basis sets. The discrepancy beyond this limit could be due to the different convergence algorithm and the use of a cutoff in the construction of the intermediate diagrams. The experimental bond lengths used in our calculations are taken from [42]. In our calculations we have used 10^{-6} as a convergence cutoff for the Davidson algorithm and 10^{-10} for the ground-state coupled-cluster equations. The numerical labeling of the ionized states is done from the inner to the outer.

IV. RESULTS AND DISCUSSION

We present numerical results of our calculations using the four-component EOM-CCSD method developed by us for the calculation of ionization potentials of molecular systems by removing an electron from their closed-shell configuration. We also present results using an intermediate scheme, EOM-MBPT(2), which uses a first-order perturbed wave function for the construction of a ground-state wave function. We applied both these methods to HF, HCl, HBr, HI, Cl_2, and Br_2 molecules. Comparison has been done between the X2C-EOMCC and four-component EOMCC to justify the fact that the relativistic and correlation effects are nonadditive in nature, taking as an example of the HF molecule.

In Table I, we present the correlation energies from MBPT(2) [$E_{\mathrm{corr}}^{(2)}$] and CCSD [$E_{\mathrm{corr}}^{(\mathrm{CCSD})}$] methods as a function of the number of basis functions for both the X2C-EOMCC and four-component EOMCC of the HF molecule. The SCF energy for the four-component calculation is −100.161280, whereas it is −100.156272 for the X2C calculations. In both the calculations the basis functions are used in an

TABLE II. Variation of ionization potential (in eV) as a function of the basis function of the HF molecule.

	X2C-EOMCC					4C-EOMCC				
No. of orbitals	5Π	4Π	3Π	2Σ	1Σ	5Π	4Π	3Π	2Σ	1Σ
200	16.0432	16.0862	19.9960	39.4931	696.7720	16.0433	16.0859	19.9961	39.4968	696.8845
220	16.1150	16.1549	20.0505	39.5434	696.1626	16.1150	16.1546	20.0506	39.5472	696.2763
250	16.1366	16.1780	20.0648	39.5638	696.1292	16.1365	16.1777	20.0649	39.5675	696.2421
280	16.1400	16.1800	20.0677	39.5727	696.3374	16.1399	16.1798	20.0677	39.5763	696.4479
308	16.1398	16.1798	20.0681	39.5765	696.4326	16.1397	16.1796	20.0682	39.5800	696.5410

uncontracted fashion. We have started our calculation with 200 active orbitals for the calculation of correlation energies using MBPT(2) and CCSD and keep on increasing up to 308, which is the maximum number of orbitals possible to generate for the opted basis. In correlation calculation the determinantal space is identical for both the X2C and four-component calculations; therefore, in principle correlation energy must be the same but the values obtained are not identical. The difference in the SCF energy is on the order of 0.01 a.u. The same difference should be reflected in the correlation energy calculations if these two effects are additive. The outcome is clearly because of the nonadditivity of the relativity and electron correlation. The difference between the two schemes is less for the calculation using 200 active orbitals and increases with increase in the correlation space. The deviation between the X2C-EOMCC and four-component EOMCC calculations is expected to be more for the molecules containing heavier atoms, as the effect of relativity is the dominant factor for the heavy atoms.

In Table II, the results of variation of the ionization potential as a function of the basis function for both the X2C-EOMCC and four-component EOMCC of the HF molecule with different numbers of active orbitals are presented. The difference between the X2C-EOMCC and four-component EOMCC is negligible for the outer orbitals but more for the inner orbitals. The deviation is in the fourth digit for the valence orbitals, whereas the difference is in the first digit for the inner core orbitals after the decimal. The deviation increases toward the core orbitals as the effect of relativity increases. It is expected that the difference will be more for the inner orbitals, as the effect of relativity is dominant near the nucleus. The effect will be prominent for the heavier systems, as the effect of relativity plays a more decisive role in those systems. The results further justify the argument of nonadditivity of relativity and electron correlation.

In Table III, we present the equilibrium bond length used in the calculations of considered diatomic molecules and also the SCF energy (E^0_{DF}), correlation energy from the second-order perturbation theory [$E^{(2)}_{\text{corr}}$], and CCSD method [$E^{(\text{CCSD})}_{\text{corr}}$]. The reported SCF results are calculated using DIRAC10, and correlation calculations are done with the relativistic code developed by us for the purpose of ground-state energy calculations within the single- and double-excitation approximation.

In Table IV, we present results of the vertical ionization potential of diatomic molecules using EOM-CCSD and EOM-MBPT(2) methods. The results of our calculation of ionization potentials are compared with the available experimental values. Our EOM-CCSD results for the valence orbitals show good agreement with the experimental values, and the difference is less than 0.1 eV. The difference is slightly more for the inner orbitals; it is expected that the extent of accuracy will definitely be less as compared to the valence orbitals, as we have used the Dirac-Coulomb Hamiltonian in our calculations. The higher-order relativistic effects, especially the Breit interactions for the neutral molecules, make a significant contribution to the inner orbitals. On the other hand, the deviation for the EOM-MBPT(2) is more, as a dominant part of the dynamic correlation is missing in the scheme. We present the deviation of valence ionization calculations as $\delta\%$ in Fig. 4. In all the calculated systems we have achieved an accuracy of less than 1% with the standard values. The maximum deviation is for the Br_2 molecule, which is 0.77%,

TABLE III. Bond length (in A^0), SCF energy (E^0_{DF}), and correlation energies from the MBPT(2) [$E^{(2)}_{\text{corr}}$] and CCSD [$E^{(\text{CCSD})}_{\text{corr}}$] methods for different systems. Energies are in a.u.

Molecule	Bond length [42]	E^0_{DF}	$E^{(2)}_{\text{corr}}$	$E^{(\text{CCSD})}_{\text{corr}}$
HF	0.9168	−100.1604	−0.3649	−0.3646
HCl	1.2750	−461.5644	−0.6228	−0.6382
HBr	1.4140	−2605.6330	−1.6500	−1.5873
HI	1.6090	−7116.3860	−2.0049	−1.9134
Cl_2	1.9870	−921.9144	−1.2180	−1.2404
Br_2	2.2810	−5210.0830	−2.9822	−2.8543

TABLE IV. Vertical IPs (in eV) of XH (X = F, Cl, Br, I), Cl_2, and Br_2 using EOM-CCSD methods.

Molecule	Ionizing state	EOM-MBPT(2)	EOM-CCSD	Experiment
HF	5 Π	16.1709	16.1380	16.1200[43]
	4 Π	16.2109	16.1777	
	3 Σ	20.0648	20.0667	19.8900[43]
	2 Σ	39.5239	39.5802	39.6500[43]
	1 Σ	697.0884	696.6777	694.0000[43]
HCl	9 Π	12.8248	12.8079	12.7450[44]
	8 Π	12.9090	12.8917	12.8300[44]
	7 Σ	16.8321	16.8230	
	6 Σ	25.8646	25.8799	
HBr	18 Π	11.8294	11.6977	11.6450[45]
	17 Π	12.1693	12.0343	11.9800[45]
	16 Σ	15.9093	15.8169	15.6500 [45]
HI	27 Π	10.6763	10.4229	10.3880 [46]
	26 Π	11.3628	11.0998	11.047 [46]
Cl_2	17 Π	11.6842	11.6679	11.5900 [47]
	16 Π	11.7774	11.7604	
	15 Π	14.6353	14.4969	14.4000 [47]
	14 Π	14.7138	14.5751	
Br_2	35 Π	10.5681	10.4370	10.5180 [48]
	34 Π	10.9252	10.7897	10.8670 [48]

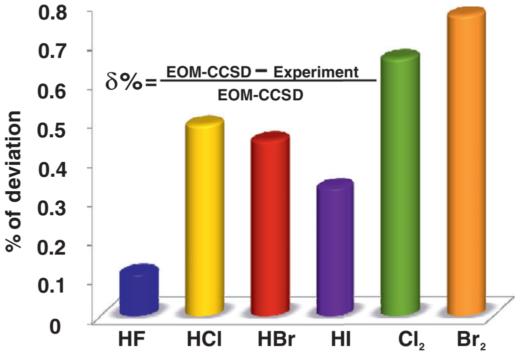

FIG. 4. (Color online) Relative deviations in % from the experimental values.

and the minimum is for HF, which is 0.11%. One possible reason for the deviation in the Br_2 molecule could be that the basis employed is not adequate for the exact description of the ionized states.

V. CONCLUSION

We have successfully implemented the four-component relativistic equation-of-motion coupled-cluster method (EOM-CCSD) to calculate the ionization potential of a molecular system in closed-shell configuration. We presented numerical results of our calculation using both EOM-CCSD and EOM-MBPT(2) methods. Our results are found to be in excellent agreement with the experimental values.

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