Relativistic equation-of-motion coupled-cluster method for the electron attachment problem

Himadri Pathak, Sudip Sasmal, Malaya K. Nayak, Nayana Vaval and Sourav Pal

Electronic Structure Theory Group, Physical Chemistry Division, CSIR-National Chemical Laboratory, Pune, 411008, India and Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India

The article considers the successful implementation of relativistic equation-of-motion coupled cluster method for the electron attachment problem (EA-EOMCC) at the level of single- and double-excitation approximation. The Dirac-Coulomb Hamiltonian is used to generate the single particle orbitals and two-body matrix elements. The implemented relativistic EA-EOMCC method is employed to calculate ionization potential values of alkali metal atoms (Li, Na, K, Rb, Cs, Fr) and the vertical electron affinity values of LiX (X=H, F, Cl, Br), NaY (Y=H, F, Cl) starting from their closed-shell configuration. We have taken C_2 as an example to understand what should be the nature of the basis and cut off in the orbital energies that can be used for the correlation calculations without loosing a considerable amount of accuracy in the computed values. Both four-component and X2C calculations are done for all the opted systems to understand the effect of relativity in our calculations as well as to justify the fact that the relativistic effects and electron correlation are intertwined. To test the performance of the newly implemented EA-EOMCC method, we have compared our atomic results with the values from the NIST database and our results are found to be well within 0.6% with the standard NIST values. Therefore, by looking at the accuracy in the atomic results, we can conclude that the accuracy in the molecular calculations will also be fair enough and these computed values can be used as a reliable standard to benchmark the capability of other theoretical methods.

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I. INTRODUCTION

A considerable growing interest is noticed in recent years in the study of negative ions as negative ions have significance in many areas of physics like in astrophysics, plasma physics and surface physics [1–4]. The electron affinity (EA) is an important quantity of these ions. The precise measurement of EA of atomic or molecular systems is always a challenge as the resulting negative ion is difficult to handle. Despite of the complexity in the measurement, there have been significant advances in the experimental techniques like laser photodetachment electron spectroscopy (LPES), laser photodetachment threshold spectroscopy (LPTS), accelerator mass spectroscopy (AMS) and photodetachment microscopy, et cetera are capable of precise measurements of EA of an atomic system [5–8]. However, the situation is appreciative in achieving such an extent of accuracy in the molecular systems due to the possibility of structural change on attachment of an extra electron. Therefore, it is an outstanding challenge for the computational physicists to complement these atomic measurements as well as for new predictions for the future purpose.

The computational prediction of EA is difficult due to the absence of long-range Coulomb field outside of a neutral precursor. Therefore, an extra electron is solely bound through correlation with other electrons [9–10]. Moreover, most of the theoretical calculations are based on the quantum chemical basis set methods, the finite size of the basis and unbalanced treatment of electron correlation in the atomic or molecular system and in the resulting ion are the sources of error [11–12]. It is an established fact that not only the electron correlation but also the effect of relativity play a definite role in accurate description of the eigenstates [13]. It is, therefore, in such a case a highly correlated many-body method, capable of simultaneous treatment of relativity and electron correlation is required due to the intricate coupling between these two effects [14–16].

The four-component relativistic equation-of-motion coupled cluster (EOMCC) method is an elegant choice to fulfill the purpose. The performance of the fully four-component EOMCC has already been established for both atomic and molecular systems for the single ionization and double ionization problem [17–19]. The idea of EOMCC [20–26] is conceptually very simple and it is operationally a two step process: (i) solution of the N electron closed-shell determinant and (ii) construction and diagonalization of the effective Hamiltonian matrix for the Fock-space sector of interest in the configuration space. The simultaneous treatment of two Hilbert space (N and N+1 electron determinantal space in the case of EA problem) ensures the inclusion of relaxation effects, which also have an important role in proper description of the eigenstates. It takes into account of both the dynamic and non dynamic part of the electron correlation. The exponential structure of the coupled cluster operator takes care of the dynamic part of the electron correlation and...
non dynamic part is included by means of diagonalization of the effective Hamiltonian matrix in the configurational space. The diagonalization of effective Hamiltonian, by and large is associated with the multi-reference theories, whereas EOMCC works within a single reference description to tackle the complex multi-configurational wave function. The multiple roots can be addressed in a single calculation and each of the states are treated with equal weightage. The EOMCC method behaves properly at the non-interacting limit but not rigorously extensive (only for the core-core and core-valence interactions) due to the linear structure of the EOM operator [27].

The EOMCC is in close kinship with the coupled cluster linear response theory (CCLRT) [28, 29] and symmetry adapted cluster expansion configuration interaction (SAC-CI) method [31, 31]. Besides these two methods, effective Hamiltonian variant of Fock space multi-reference (FSMRCC) theory [32-37] always comes in the discussion on EOMCC as these two methods produce identical results for the one valence problem. The amplitudes of all the lower sector including the sector of interest is involved in the FSMRCC theory. On the other hand, EOMCC deals with the amplitudes of the (0,0) sector and the sector of interest. Therefore, both the approaches are eventually the same for the one electron attachment or detachment problem. The superiority of EOMCC over FSMRCC is the capability in addressing the shake-up states [35]. The EOMCC is free from the problem of intruder due to its CI (configuration interaction method) like structure, which is associated with the effective Hamiltonian variant of the FSMRCC theory.

Recently, Blundell implemented relativistic EOMCC method for the electron affinity problem and applied to calculate fine-structure splittings in high-lying states of rubidium atom [39]. The implemented version of Blundell is applicable only for the atomic calculations. Ours is a general one, applicable to both atoms as well as molecules starting from their closed-shell ground state configuration. The spherical implementation, which is very common in atomic systems allows the separation of radial and angular parts. Therefore, evaluation of radial integrals is only required and the angular part will add up to it as a multiplier. The radial integrals can be evaluated numerically. A separation of that kind is not possible in the molecular case since evaluation of two-body matrix elements for molecular calculations are done in Cartesian coordinate system due to the absence of spherical symmetry. Furthermore, the anti-symmetrized two-body matrix elements are used in molecular relativistic calculations, which is not possible in the atomic calculations as angular factor will be different for the direct and exchange part of the two body matrix element. It appears that the spherical implementation is much more complex than that of the molecular calculations, but it is favorable from the computational point of view as it requires only the solution of radial integrals. Therefore, atomic calculations are computationally easy, which allows to correlate more number of electrons and amenable to use

large basis for the correlation calculation to achieve better accuracy.

In this article, we report the implementation of relativistic EOMCC method for the electron affinity problem applicable to both atomic and molecular systems. The implemented EA-EOMCC method is employed to calculate ionization potential of open-shell atomic systems starting from their singly positive closed-shell configuration. Further, the vertical EA values of molecular systems are also calculated. Both four-component and exact two component (X2C) calculations are done for all the considered systems to understand the effect of relativity in the calculated values and to justify the fact that the relativistic and correlation effects are non-additive in nature.

The manuscript is organized as follows. The EOMCC theory in regard to the electron attachment problem is briefly described in Sec. II and the computational details of our calculations are presented in Sec. III. We have discussed our results in Sec. IV and finally made concluding remarks in Sec. V. We are consistent with the atomic unit if not stated explicitly.

II. THEORY

In the EOMCC method the kth target excited state of single electron attached state is defined as

\[ |\Psi_k \rangle = R_k^{N+1} |\Psi_0 \rangle, \quad k = 1, 2, \ldots \]  

Here, the \( R_k^{N+1} \) is a linear operator, which on acting on the single reference coupled cluster (SRC) ground state wave function \( |\Psi_0 \rangle \), generates the \( k \) th excited state wave function \( |\Psi_k \rangle \). The \( R_k^{N+1} \) operator takes the form in the coupled cluster single-double (CCSD) approximation as

\[ R_k^{N+1} = R_1 + R_2 \]

\[ = \sum_a r^{a} a^\dagger_a + \sum_{b<a} \sum_j s^{ba}_j a^\dagger_a a^\dagger_j a_j \]  

The \( R_1 \) and \( R_2 \) operator are diagrammatically represented in Fig. 1. The \( R_1 \) is a one particle (1p) creation operator and \( R_2 \) is a two-particle and one-hole (2p-1h) creation operator. The circled arrow is just to represent that overall it is a one electron attachment process.

![FIG. 1: Diagrammatic representation of \( R_1 \) and \( R_2 \) operator.](image)

The Schrödinger equation for the ground state (k=0) is

\[ H_N |\Psi_0 \rangle = \Delta E_0 |\Psi_0 \rangle, \]  

where \( H_N \) is the effective Hamiltonian matrix in the configurational space. The diagonalization of effective Hamiltonian matrix is obtained by means of configuration interaction (CI) method [31, 31].
The electron attached states (k=1,2, . . . ) is written as
\[ H_N R_k |\Psi_0\rangle = \Delta E_k R_k |\Psi_0\rangle \] (5)

The above equation on multiplication with a non-singular operator e^{-T} (where T is the coupled cluster excitation operator) in the course it is assumed that R_k commute with T (as strings of same quasi-particle creation operator) with some mathematical manipulation leads to equation of motion with respect to the R_k operator,
\[ [\hat{H}_N, R_k] |\Phi_0\rangle = \Delta E_k R_k |\Phi_0\rangle \quad \forall k. \] (6)

In the above equation, \( \Delta E_k \) is the energy change associated with the electron attachment process and \( \hat{H}_N = e^{-T} H e^{T} - (|\Phi_0\rangle e^{-T} H e^{T} |\Phi_0\rangle) \) is the similarity transformed normal ordered effective Hamiltonian. In our case it is the Dirac-Coulomb Hamiltonian, which is given by
\[ \hat{H}_{DC} = \sum_A \sum_i [c(\vec{\alpha}_i \cdot \vec{p}_i) + (\beta - 1/4)c^2 + V_{iA}] \]
\[ + \sum_{i>j} \frac{1}{r_{ij}} \hat{\mathbb{I}}_{4}, \] (7)

where \( \alpha_i \) and \( \beta \) are the usual Dirac matrices, \( V_{iA} \) is the nuclear potential and \( \frac{1}{r_{ij}} \) is the electron-electron repulsion potential. The orbital energies are scaled with respect to the free electron rest mass energy (\( c^2 \)), which is zero in the non-relativistic case. We have chosen a correlated determinant space of \( |\Phi^a\rangle \) and \( |\Phi^{ab}\rangle \) (1p and 2p-1h) with respect to the Dirac-Hartree-Fock determinant \( (|\Phi_0\rangle) \) to project the above equation to get the desired electron affinity values, \( \Delta E_k \).
\[ \langle \Phi^a | [\hat{H}_N, R_k] |\Phi_0\rangle = \Delta E_k R^a, \] (8)

The matrix form of the above equations is as \( \hat{H} R_k = R_k \Delta E_k \). The effective Hamiltonian matrix is constructed in 1p and 2p-1h space and diagonalized only in the 1p space. In Figs. 2 and 3, the contributing diagrams for the 1p and 2p-1h space is presented, respectively. The evaluation of these diagrams requires the solution of the coupled-cluster amplitude equations. The converged \( T_1 \) and \( T_2 \) amplitudes are contracted with the two-body matrix elements of the Hamiltonian matrix to construct one body, two body and three body intermediate diagrams. The intermediate diagrams are categorized into \( f_{pp} \), \( f_{hp} \), \( f_{hh} \), \( V_{hpp} \), \( V_{ppp} \), \( V_{php} \), and \( W \). Here \( f \)’s, \( V \)’s and \( W \) stands for one-body, two-body, and three-body intermediates, respectively. We have followed a recursive intermediate factorization scheme as described in Ref. 10 to evaluate these intermediate diagrams. The factorization scheme in the construction of intermediate diagrams saves enormous computational resources. The matrix elements corresponding to the three-body intermediate diagram are not stored rather computed on the fly. The programmable algebraic expression for the diagrams corresponding to 1p block and 2p-1h block are presented in Eq. 10 and 11 respectively. We have used the standard notation \( (f_{\text{out}, \text{in}}) \) and \( (V \text{ left out, right out, left in, right in}) \) for one-body and two-body intermediate matrix element. In Eqs. 10 and 11 \( i, j, \ldots (a, b, \ldots) \) stands for hole (particle) index. \( \hat{P} \) is a permutation operator and any odd permutation introduces a negative sign. The constructed effective Hamiltonian matrix is iteratively diagonalized using Davidson algorithm [41] to get the desired set of eigenvalues and eigenvectors.

\[ \Delta E_k R^a = \sum_b \bar{f}_{pp}(a, b)r^{ab} + \sum_{j, b} \bar{f}_{hp}(j, b)r^{ja} + 0.5 \sum_{j, b, c} \bar{V}_{hpp}(j, a, b, c)r_{j}^{bc} \quad \forall a \] (10)
\[ \Delta E_k R^{ba}_j = \bar{P}(ab) \sum_c \bar{f}_{pp}(b, c)r_{j}^{ca} - \sum_j \bar{f}_{hh}(j, i)r_{j}^{ja} + 0.5 \sum_{c, d} \bar{V}_{ppp}(a, b, c, d)r_{j}^{dc} - \bar{P}(ab) \sum_{c, k} \bar{V}_{php}(a, k, c, i)r_{k}^{hc} \]
\[ + \sum_c \bar{V}_{ppp}(a, b, c, j)r_{j}^{ca} - 0.5 \sum_{k, l, c, d} \bar{V}_{hhp}(k, l, c, d)r_{k}^{al} \quad \forall (i, b < a) \] (11)

### III. COMPUTATIONAL DETAILS

The DIRAC program package [42, 43] is used to evaluate the required one-body and two-body matrix elements for the correlation calculation. In the implemented version of X2C SCF in DIRAC program package, the nature of the basis is uncontracted in nature. Therefore, all the four-component calculations are also done using uncontracted basis to generate same determinantal space. The finite atomic basis is consists of scalar real gaussian functions. The small component of the basis is linked with the large component of the basis through the restricted kinetic balance (RKB) condition. The RKB condition represents the kinetic energy properly in the non-relativistic limit and avoids the variational collapse [44]. This is achieved by pre-projecting in scalar basis and un-
TABLE I: SCF ($E_{\text{HF}}^0$) and correlation energy from MBPT(2) and CCSD of alkali metal ions.

| Atom | X2C SCF | MBPT(2) | CCSD | 4C SCF | MBPT(2) | CCSD |
|------|---------|---------|------|--------|---------|------|
| Li$^+$ | $-7.23704549$ | $-0.03852045$ | $-0.04231370$ | $-7.23717432$ | $-0.03849060$ | $-0.04228408$ |
| Na$^+$ | $-161.88587136$ | $-0.35207268$ | $-0.35582452$ | $-161.89563722$ | $-0.35150440$ | $-0.35525894$ |
| K$^+$ | $-601.31791575$ | $-0.65537110$ | $-0.66965441$ | $-601.37819785$ | $-0.65413264$ | $-0.66841936$ |
| Rb$^+$ | $-2979.12536975$ | $-1.60387768$ | $-1.54495385$ | $-2979.69321719$ | $-1.60053355$ | $-1.54166739$ |
| Cs$^+$ | $-7784.57978591$ | $-1.74620488$ | $-1.65455691$ | $-7786.64351172$ | $-1.74003797$ | $-1.64856937$ |
| Fr$^+$ | $-24296.91067142$ | $-1.63529104$ | $-1.46831264$ | $-24308.06150516$ | $-1.63476824$ | $-1.46778303$ |

TABLE II: Bond length (in Å), SCF ($E_{\text{HF}}^0$) and correlation energy from MBPT(2) and CCSD of LiX(X=H, F, Cl, Br) and NaY(H, F, Cl).

| Molecule | Bond Length [Å] | SCF | MBPT(2) | CCSD | SCF | MBPT(2) | CCSD |
|----------|-----------------|------|---------|------|------|---------|------|
| LiH      | 1.5957          | $-7.98779458$ | $-0.06922346$ | $-0.08095520$ | $-7.98792880$ | $-0.06919119$ | $-0.08092337$ |
| LiF      | 1.5939          | $-107.07888706$ | $-0.40034142$ | $-0.39917108$ | $-107.08402402$ | $-0.40009740$ | $-0.39897226$ |
| LiCl     | 2.0207          | $-468.46973809$ | $-0.60601695$ | $-0.62223553$ | $-468.51153946$ | $-0.60551567$ | $-0.62173813$ |
| LiBr     | 2.1704          | $-2621.13492411$ | $-1.45099947$ | $-1.4092724$ | $-2621.60399340$ | $-1.46372185$ | $-1.40358587$ |
| NaH      | 1.8874          | $-162.60217640$ | $-0.35882176$ | $-0.39792504$ | $-162.61952555$ | $-0.38525166$ | $-0.39735770$ |
| NaF      | 1.9259          | $-261.67902123$ | $-0.69445654$ | $-0.69149995$ | $-261.69167076$ | $-0.69401168$ | $-0.6910812$ |
| NaCl     | 2.3608          | $-623.07791354$ | $-0.84612827$ | $-0.86181591$ | $-623.12953435$ | $-0.84548828$ | $-0.86117973$ |

![Diagrams contributing to the 1p block.](image)

FIG. 2: Diagrams contributing to the 1p block.

Physical solutions are removed by diagonalizing the free particle Hamiltonian. The RKB condition generates the positron solution and electronic solution in 1:1 manner. The DIRAC program package uses Gaussian distribution nuclear model to take care of the finite size of the nucleus. The used nuclear parameters are taken as default values from DIRAC package [45]. We adopted aug-cc-pCVQZ basis for Li$^+$ [46] and Na$^+$ [48] atom and all the generated orbitals are taken into consideration for the correlation calculations. Dyall.cv4z [49] basis is opted for K$^+$ and Rb$^+$. We have neglected the virtual orbitals those energy is more than 500 a.u. for the K$^+$ and Rb$^+$ atom. The Cs$^+$ and Fr$^+$ are calculated using dyall.cv3z basis [49]. The cutoff used for Cs$^+$ atom is 1000 a.u. whereas for Fr$^+$ atom, we have taken the orbitals having energy in between −25 a.u. to 100 a.u. in our correlation calculations. In the molecular calculations of LiF, LiCl, LiBr, we have chosen aug-cc-pCVTZ basis for Li atom [46] and cutoff of 100 a.u. for the virtual orbitals. The calculations of F and Cl are done using aug-cc-pCVQZ [46, 48] basis and for Br, dyall.cv4z [50] basis is used. In LiH we have chosen aug-cc-pCVQZ basis [46] for the H atom and none of the electrons are frozen for the correlation calculations. Aug-cc-pCVTZ basis is opted for both Na [48] and Cl [47] in the calculations of NaCl and a cutoff of 100 a.u. is used for the virtual orbitals. The single particle orbitals and two-body matrix elements are generated by taking account of C$_{2v}$ symmetry. Both X2C and four-component calculations of Rb and LiBr are done with the DIRAC14 version and rest of the calculations are done using DIRAC10. The implemented version of X2C SCF [51] in DIRAC10 is capable of taking up to g harmonics but the opted basis for Rb and LiBr require up to h harmonics to express the
FIG. 3: Diagrams contributing to the 2p-1h block.

TABLE III: Convergence pattern of electron affinity (in eV) of the C\(_2\) (R=1.243 Å, Ref \[52\]) as a function of basis set.

| Basis            | Spinor | Electron affinity | Expt. \[53\] |
|------------------|--------|-------------------|--------------|
| cc-pVDZ          | 88     | 2.649364          |              |
| cc-pCVDZ         | 104    | 2.664512          |              |
| aug-cc-pVDZ      | 124    | 3.189648          |              |
| aug-cc-pCVDZ     | 140    | 3.194913          |              |
| cc-pVTZ          | 152    | 3.114016          |              |
| cc-pCVTZ         | 192    | 3.128478          |              |
| aug-cc-pVTZ      | 216    | 3.331555          | 3.30±0.1     |
| cc-pVQZ          | 252    | 3.274313          |              |
| aug-cc-pCVTZ     | 256    | 3.341214          |              |
| cc-pCVQZ         | 316    | 3.285105          |              |
| aug-cc-pCVQZ     | 416    | 3.384036          |              |
| aug-cc-pCVQZ\(^a\)| 488    | 3.385261          |              |

\(^a\) All the virtual orbitals are used for the EOMCC calculation.

large component of the wave function. Therefore, these two calculations are done using DIRAC14 version. We have fixed a cutoff of 10\(^{-12}\) to store the matrix elements for the intermediate diagrams as two-body matrix elements contributed negligibly beyond this limit. The convergence of 10\(^{-10}\) is fixed for the solution of SRCC amplitude equations and 10\(^{-5}\) for the Davidson algorithm in the EOMCC part. A direct inversion in the iterative subspace (DIIS) of 6 is used in the solution of ground state amplitudes for all the calculations. The newly implemented relativistic EOMCC code is tested by comparing EA-EOMCC results with the (1,0) sector FSMRCC code implemented in the DIRAC package as these two theories are supposed to produce identical results for one electron attachment process. The MBPT(2) correlation energy is identical whereas CCSD correlation energy and the EA value are matching up to ten-digit and eight-digit, respectively. The test is performed with identical convergence cut off, equal number of DIIS space and without any cutoff in the intermediate diagrams. We have done the test over a series of atoms and molecules with various basis sets and successful in achieving similar agreement for all the considered system, independent of the choice of basis set.

IV. RESULTS AND DISCUSSION

We have reserved this section of our manuscript to present numerical results of our calculations and to interpret the outcome of these calculations. The four-component and exact two component (X2C) EOMCC calculations are performed for all the considered atomic and molecular systems starting from their closed-shell configuration. These results will help us to understand the effect of relativity in a correlation calculation using EOMCC method and to show that the relativistic effects and the electron correlation are non-additive in nature.

In Tables \[I\] and \[II\] we present numerical results of our SCF and correlation energy from MBPT(2) and CCSD calculation of singly positive alkali metal atomic systems (Li\(^+\), Na\(^+\), K\(^+\), Rb\(^+\), Cs\(^+\), Fr\(^+\)) and molecular systems (LiX (X=H, F, Cl, Br) and NaY (Y=H, F, Cl)) in their closed-shell configuration. The bond length of the molecular systems is also compiled in Table \[II\]. Both X2C and four-component calculation are done for all these systems to understand how the effect of relativity plays a role and to show the intertwined nature of the relativistic and electron correlation effect. For atomic systems (Table \[I\]), we noticed that the difference between X2C and four-component SCF is in the fourth digit after the decimal place for Li\(^+\), whereas the difference is about 2 a.u. for Cs\(^+\) and 8 a.u. for Fr\(^+\). The difference between SCF energy in X2C and four-component keep on increasing as we go down the group. In the X2C approach \[52\], the electronic and positronic states are decoupled by the elimination of small component from the relativistic wave function and thus the SCF wave function is two compo-
nent in nature. Therefore, the effect of relativity is not as comprehensive as in four-component wave function. Fr$^+$ is a very heavy system where effect of relativity have much more significant role than in the other considered systems. This corresponds to the large difference in SCF energy between X2C and four-component calculations for the Fr$^+$. On the other hand, Cs$^+$ is a moderate heavy system, therefore the difference is less as compared to Fr$^+$ ion.

The molecular systems (in Table III) follow the same trend also; i.e., the difference between the X2C and four-component SCF values increases as the system became heavier. This trend is expected as relativistic effect has a major role in the heavier systems. The molecular systems considered in our calculations are of moderate size. Therefore, the difference is not that much what we observed in the atomic case specially in Cs$^+$ and Fr$^+$.

As the generated determinantal space for correlation calculations of both X2C and four-component calculations is same, the difference in the SCF energy of both atomic and molecular systems should reflect in the correlation energy values as a difference, if and only if, these two effects are additive. But the outcomes of Table I and III clearly suggest otherwise; i.e., the difference in SCF energy and the difference in correlation energy between X2C and four-component calculations are not same. Therefore, it can be inferred that the effect of relativity and electron correlation are not additive rather these two effects are coupled to each other. The effect is more prominent for the heavier systems, which is evident from the computed values in Fr$^+$.

We have done a series of calculations to understand how the electron affinity value changes with the nature of basis set and cutoff in the orbital energies can be used without losing considerable amount of accuracy as EOMCC calculations for the EA problem are computationally costly. We have chosen C\textsubscript{2} as an example system for which experimental vertical EA value is reported in the literature. We have started our calculation with cc-pVDZ, which is a very small basis as it generates only 88 spinor for the beyond SCF calculations using a cutoff of 100 a.u. for the virtual orbitals. A few more calculations are also done by improving the nature of the basis functions. The EA value as well as the number of generated spinor in different basis are tabulated in Table III. We have taken 1.243 Å as bond length for the C\textsubscript{2} molecule, which is the experimentally reported bond length. The reported experimental value is 3.30±0.1 eV, whereas our calculation yields 3.384036 eV for aug-cc-pCVQZ basis with a cutoff of 100 a.u. in the virtual orbital energy. On the other hand, without using any cut off, the result is 3.385261 eV. Therefore, a cutoff of 100 a.u. for virtual orbital energies and similar basis set can be used without losing much accuracy for all other calculations to achieve a good agreement with the experiment. It will save enormous computational time without losing a significant amount of accuracy as contribution from the high energy virtual orbitals is very less in the correlation calculations. The reported experimental uncertainty is in the first digit after the decimal point. Therefore, it is hard to comment on the accuracy of our calculated results. It can be said that our results is also spanning same range starting from a reasonable basis.

In Table IV we report the calculated ionization potential values of atomic systems using both X2C and four-component EA-EOMCC method. We have started our calculations from singly positive alkali metal ions and applied EA-EOMCC method. The negative of the computed values are reported as ionization potential values of the open-shell atomic systems. These computed ionization potential values are compared with the values from the National Institute of Standards and Technology (NIST) database. A nice agreement with NIST values is achieved for all the considered systems. The maximum deviation is obtained for the Na atom, which is also in the accuracy of ~ 0.6% with the NIST value. The difference between the X2C with four-component results is in the fifth digit after the decimal for Li atom whereas the difference is about 0.01 eV for Fr atom. The Dirac-Hartee-Fock method is the best possible way to include the effect of relativity in a single determinantal theory within a four-component description. In X2C approach the wave function is consist of only with the large component of the wave function. Therefore, the X2C wave function is not capable to treating effect of relativity comprehensively as compared to the four-component wave function. In heavier systems effect of relativity is a prominent player in describing the eigenstates properly. As a result of which, ionization potential values of Fr atom differing about 0.01 eV in X2C and four-component approach.

In Table V we present the results of our calculations of vertical EA of molecular systems using both X2C EA-EOMCC and four-component EA-EOMCC method. Further, we have compared our result with the theoretical results calculated by Gutsev et al 56. They also employed EA-EOMCC method for correlation treatment to calculate the vertical EA values of the molecular systems. In their calculation, Gutsev et al misses the effect of relativity, which is included in our calculation in its four-component formalism. We have achieved a nice agreement for the atomic results and also for the vertical EA value of C\textsubscript{2} molecule. Therefore, it can be said that

| Molecule | X2C   | 4C    | Others [56] |
|----------|-------|-------|-------------|
| LiH      | 0.290759 | 0.290757 | 0.247       |
| LiF      | 0.354954 | 0.354964 | 0.340       |
| LiCl     | 0.552586 | 0.552595 | 0.551       |
| LiBr     | 0.614757 | 0.614773 |             |
| NaH      | 0.321751 | 0.321740 | 0.319       |
| NaF      | 0.484822 | 0.484863 | 0.485       |
| NaCl     | 0.672601 | 0.672653 | 0.672       |
our calculated results for the molecular systems are also quite accurate though there is no reliable experimental data or any other values calculated using any variant of relativistic coupled cluster theory to compare with. However, the accuracy of the molecular calculations will not be that much accurate as compared to the atomic results. The reason behind this is due to the possibility of structural change on attachment of an extra electron to the neutral molecule depending on the polarity of the molecule.

V. CONCLUSION

The relativistic EOMCC method for the electron attachment problem applicable to both atomic and molecular systems is successfully implemented. To test the performance of the EA-EOMCC method, we applied to calculate ionization potential values of alkali metal atoms starting from closed-shell configuration. We have compared our calculated ionization potential values with the values from NIST database. We are successful in achieving about 0.6% agreement with the NIST values. We have also presented molecular EA values of LiX (X=H, F, Cl, Br) and NaY (Y=H, F, Cl) using our relativistic EOMCC methods. Both four-component and X2C EOMCC calculations are performed for all the considered system to understand the role of relativity in proper description of eigenstates. The outcome clearly suggests that effect of relativity play a significant role in proper description of electron attached states and these two effects are intertwined.

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[1] M Larsson, W D Geppert and G Nyman, Reports on Progress in Physics 75, 066901 (2012).
[2] David J Pegg, Reports on Progress in Physics 67, 857 (2004).
[3] A. A. Mamuna and P. K. Shukla, Physics of Plasmas 10, 1518 (2003).
[4] E. Stoffels, W. W. Stoffels and G. M. W. Kroesen, Plasma Sources Sci. Technol. 10, 311 (2001).
[5] V. T. Davis, J. Thompson and A. Covington, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 241, 118 (2005).
[6] C. W. Walter, N. D. Gibson, C. M. Janczak, K. A. Starr, A. P. Sneden, R. L. Field III, and P. Andersson, Phys. Rev. A 76, 052702 (2007).
[7] D. Berkovits, E. Boaretto, S. Ghelberg, O. Heber, and M. Paul, Phys. Rev. Lett. 75, 414 (1995).
[8] M. Vandezande, C. Drag, and C. Blondel, Phys. Rev. A 85, 015401 (2012).
[9] T. Andersen, Physics Reports 394, 157 (2004).
[10] Sten Salomonson, HÅkan Warston, and Ingvar Lindgren, Phys. Rev. Lett. 76, 3092 (1996).
[11] R. A. Kendall, T. H. Dunning Jr and R. J. Harrison, J. Chem. Phys. 96, 6796 (1992).
[12] T. Noro, M. Yoshimine, M. Sekiya and F. Sasaki, Phys. Rev. Lett. 66, 1157 (1991).
[13] Wenjian Liu, Molecular Physics. 108, 1679 (2010).
[14] I. P. Grant, *Relativistic Quantum Theory of Atoms and Molecules: Theory and Computation* (Springer, New York, 2010).
[15] I. Lindgren and J. Morrison, *Atomic Many-Body Theory* (Springer-Verlag, New York,1985).
[16] R. J. Bartlett and M. Musial, Rev. Mod. Phys. 79, 291 (2007).
[17] H. Pathak, B. K. Sahoo, B. P. Das, N. Vaval, and S. Pal, Phys. Rev. A 89, 042510 (2014).
[18] H. Pathak, A. Ghosh, B. K. Sahoo, B. P. Das, N. Vaval, and S. Pal, Phys. Rev. A 90, 010501(R) (2014).
[19] H. Pathak, S. Sasma, M. K. Nayak, N. Vaval, and S. Pal, Phys. Rev. A 90, 062501 (2014).
[20] H. Sekino and R. J. Bartlett, Int. J. Quantum Chem. 26, 255 (1984).
[21] J. F. Stanton and R. J. Bartlett, J. Chem. Phys. 98, 7029 (1993).
[22] R. J. Bartlett, Comput. Mol. Sci. 2, 126 (2012).
[23] Anna I. Krylov, Ann. Rev. Phys. Chem. 59, 433 (2008).
[24] M. Musial, and R. J. Bartlett, J. Chem. Phys. 119, 1901 (2003).
[25] S. Hirata, T. Yanai, R. J. Harrison, M. Kamiya, and Peng-Dong Fan, J. Chem. Phys. 126, 024104 (2007).
[26] M. Nooijen and R. J. Bartlett, J. Chem. Phys. 102, 3629 (1995).
[27] D. Sinha, S. K. Mukhopadhyay, R. Chaudhuri, and D.Mukherjee, Chem. Phys. Lett. 154, 544 (1989).
[28] E. Dalgaard, H. J. Monkhorst, Phys. Rev. A. 28, 1217 (1983).
[29] D. Mukherjee and P. K. Mukherjee, Chem. Phys. 39, 325 (1979).
[30] H. Nakatsuji Chem. Phys. Lett. 59, 362 (1978).
[31] H. Nakatsuji, K. Hirao J. Chem. Phys. 68, 2053 (1978).
[32] E. Ilyabaev and U. Kaldor, J. Chem. Phys. 97, 8455 (1992).
[33] L. Visscher, E. Eliav, and U. Kaldor J. Chem. Phys. 115, 9720 (2001).
[34] I. Lindgren, Int. J. Quantum Chem. 14, 33 (1978).
[35] M. Haque and D. Mukherjee, J. Chem. Phys. 80, 5058 (1984).
[36] D. Mukherjee and I. Lindgren, Phys. Rep. 151, 93 (1987).
[37] S. Pal, M. Rittby, R. J. Bartlett, D. Sinha, and D. Mukherjee, J. Chem. Phys. 88, 4357 (1988).
[38] J. H. D. Eland, M. Tashiro, P. Linusson, M. Ehara, K. Ueda, and R. Feifel, Phys. Rev. Lett. 105, 213005 (2010).
[39] S. A. Blundell, Phys. Rev. A. 90, 042514 (2014).
[40] I. Shavitt and R. J. Bartlett, Many-body methods in chemistry and physics. (Cambridge University Press, 2009).
[41] E. R. Davidson, J. Comput. Phys. 17, 87 (1975).
[42] DIRAC, a relativistic ab initio electronic structure program, Release DIRAC10 (2010), written by T. Saue, L. Visscher and H. J. Aa. Jensen, with contributions from R. Bast, K. G. Dyall, U. Ekström, E. Eliav, T. Enevoldsen, T. Fleig, A. S. P. Gomes, J. Henriksen, M. Ilias, Ch. R. Jacob, S. Knecht, H. S. Nataraj, P. Norman, J. Olsen, M. Pernpointner, K. Ruud, B. Schimmelpfennig, J. Sikkema, A. Thorvaldsen, J. Thyssen, S. Villaume, and S. Yamamoto. (see http://dirac.chem.vu.nl).
[43] DIRAC, a relativistic ab initio electronic structure program, Release DIRAC14 (2014), written by T. Saue, L. Visscher, H. J. Aa. Jensen, and R. Bast, with contributions from V. Bakken, K. G. Dyall, S. Dubillard, U. Ekstroem, E. Eliav, T. Enevoldsen, E. Fasshauer, T. Fleig, O. Fossgaard, A. S. P. Gomes, T. Helgaker, J. K. Laerdal, Y. S. Lee, J. Henriksen, M. Ilias, Ch. R. Jacob, S. Knecht, S. Komorovsky, O. Kullie, C. V. Larsen, H. S. Nataraj, P. Norman, O. Olejniczak, J. Olsen, Y. C. Park, J. K. Pedersen, M. Pernpointner, R. Di Remigio, K. Ruud, P. Salek, B. Schimmelpfennig, J. Sikkema, A. J. Thorvaldsen, J. Thyssen, J. van Stralen, S. Villaume, O. Visser, T. Winther, and S. Yamamoto (see http://www.diracprogram.org)]
[44] K. G. Dyall and K. Faegri, Jr., Introduction to Relativistic Quantum Chemistry (Oxford University Press, New York, 2006).
[45] L. Visscher and K. G. Dyall, At. Data Nucl. Data Tabl. 67, 207 (1997).
[46] T.H. Dunning, Jr. J. Chem. Phys. 90, 1007 (1989).
[47] D. E. Woon and T.H. Dunning, Jr. J. Chem. Phys. 98, 1358 (1993).
[48] D.E. Woon and T.H. Dunning, Jr. (to be published)
[49] K.G. Dyall, J. Phys. Chem. A. 113, 12638 (2009).
[50] K.G. Dyall, Theor. Chem. Acc. 115, 441 (2006).
[51] M. Ilias and T. Saue, J. Chem. Phys., 126, 064102 (2007).
[52] K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure: Constants of Diatomic Molecules (Van Nostrand Reinhold, New York, 1979).
[53] S. Yang, K. J. Taylor, M. J. Craycraft, J. Conceicao, C. L. Pettiette, O. Cheshnovsky, and R. E. Smalley, Chem. Phys. Lett. 144, 431 (1988).
[54] http://physics.nist.gov/PhysRefData/ASD/ionEnergy.html
[55] K. G. Dyall, J. Chem. Phys. 106, 9618 (1997).
[56] G. L. Gustev, M. Nooijen, and R. J. Bartlett, Chem. Phys. Lett. 276, 13 (1997).