



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



Himadri Pathak^{a,*}, Sudip Sasmal^{a,*}, Malaya K. Nayak^b, Nayana Vaval^a, Sourav Pal^c

^aElectronic Structure Theory Group, Physical Chemistry Division, CSIR-National Chemical Laboratory, Pune 411 008, India

^bBhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

^cDepartment of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India

ARTICLE INFO

Article history:

Received 5 October 2015

Received in revised form 12 December 2015

Accepted 13 December 2015

Available online 23 December 2015

Keywords:

Four-component

EOMCC

Electron affinity

X2C

ABSTRACT

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 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. Both four-component and exact two-component calculations are done for all the opted systems. Further, we have shown the effect of spin-orbit interaction considering the atomic systems. The results of our atomic calculations are compared with the values from the NIST database and the results are found to be very accurate (<1%).

© 2015 Elsevier B.V. All rights reserved.

1. 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 inappreciative 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 to 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. Thus, 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]. The attachment and detachment of an electron to a neutral species involves different forces. The attached extra electron to the neutral atom polarizes the electronic shell of the atom. As a result a dipolar electric field is generated which binds the extra electron with the other electrons. The charge distribution of the electron cloud, particularly the electron–electron correlation effects decides the stability of the negative ion. These interactions do not play much role in most of the neutral atoms as well as in positive ions where direct electrostatic force is the dominant factor for the stability of the neutral atom or the positive ion. On the other hand, these effects dominate in the negative ions. Therefore, the calculations of EA values of both atomic and molecular systems are challenging and is a real test for the performance of a many-body method. 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 of heavy atomic and molecular systems [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 relativity has a greater role towards the core orbitals and practically important for all the elements. The effects of relativity are incorporated in the electronic structure calculations by the

* Corresponding authors.

E-mail addresses: hmdrpthk@gmail.com (H. Pathak), sudipsasmal.chem@gmail.com (S. Sasmal).

choice of the Hamiltonian. The consideration of Dirac–Coulomb–Breit Hamiltonian without the quantum electrodynamics effects (QED) is sufficient for most of the relativistic electronic structure calculations using four-component wavefunction. However, in actual practice the Dirac–Coulomb Hamiltonian is most commonly used where two-body Coulomb interaction operator is added to the Dirac Hamiltonian (\hat{H}_D). Although, the form of the Coulomb operator is same as in the non-relativistic theory, however, the physical content is different as it takes care of the spin–same orbit interaction. This type of truncation in the two-body interaction does not effect much for most of the chemical purposes [17]. However, for very accurate studies of molecular spectra including fine structure, the inclusion of spin–other-orbit interaction and spin–spin interaction are required which can be done with the full inclusion of the Breit part of the two-body interaction. The relativistic calculations using four-component wavefunction are very expensive from the computational perspective. A lot of effort has been made to simplify the equations. The calculation of the small component of the wavefunction is the most challenging part of the computation. If a basis set is expressed in terms of contracted Gaussian functions, then the number of required primitive Gaussian functions for the small component is about twice the number of the large component with the imposition of the kinetic balance condition. On the other hand, the small component has a very minor contribution in the calculated values; therefore, it makes sense to look for an approximation. There are a number of Hamiltonians in between the scalar non-relativistic and four-component relativistic ones. However, the inclusion of the spin–orbit interaction requires at least a two-component description, though it will essentially increase the computational cost due to the appearance of complex algebra in place of real algebra. The electron correlation methods in the no-pair approximation require the transformation of the matrices from the atomic orbital (AO) basis to the molecular orbital (MO) basis. The spin coordinates of the electrons can be represented in terms of quaternion algebra in the four-index transformation step which helps to go from complex four-component to a two-component quaternion form. Therefore, the MO coefficients become quaternion and can be represented in terms of real matrices [18,19].

The generation of a two-component Hamiltonian from the parent four-component Hamiltonian is the most preferred choice for the purpose which includes the spin–orbit interaction with a lesser cost as compared to the four-component Hamiltonian. The central idea behind the generation of a two-component Hamiltonian is that it should reproduce the positive-energy spectrum of the parent Hamiltonian. Foldy and Wouthuysen proposed an idea to decouple the large and small component by a unitary transformation of the four-component Hamiltonian. Another well known approach is the elimination of the small component from the wavefunction. However, these two approaches can be shown to be equivalent [20]. The exact two-component approach (X2C) is one such approach to reduce the computational scaling which uses the elimination of the small component from the parent four-component Hamiltonian. The detailed description of the X2C approach including various other two-component methods can be found in Ref. [13,21,22].

Over the years, the equation-of-motion coupled-cluster (EOMCC) method gained popularity among correlation methods for the treatment of electron correlation due to its simplicity and elegance. The idea of EOMCC [23–31] is conceptually very simple and it is operationally a two step process: (i) solution of coupled cluster problem with the N electron closed-shell determinant as reference and (ii) construction and diagonalization of the effective Hamiltonian matrix for the Fock-space sector of interest in the configuration space. 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 wavefunction. Further, the relaxation effect, which has an important role in proper description of the eigenstates is also taken care. 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 [32]. The EOMCC is in close kinship with the coupled cluster linear response theory (CCLRT) [33,34] and symmetry adapted cluster expansion configuration interaction (SAC-CI) method [35,36]. It is worth to note that the transition energy calculated using CCLRT is identical with the EOMCC method for the one valence problem but the transition moments is identical only when it is represented as a energy derivative in EOMCC framework. Chaudhuri et al. [37,38] applied relativistic CCLRT for the ionization problem of atomic systems with spherical implementation. Beside these two methods, effective Hamiltonian variant of Fock-space multi-reference (FSMRCC) theory [39–44] always comes in the discussion on EOMCC since these two methods produce identical results for the one valence problem. The amplitudes of all the lower sector including the sector of interest are 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 approach eventually produces the same result for the one electron attachment or detachment problem. 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. There are ways in the FSMRCC framework to handle the problem of intruder such as the eigenvalue independent partitioning technique of Mukherjee (EIP-FSMRCC) [32,45] and the intermediate Hamiltonian variant of the FSMRCC (IH-FSMRCC) theory [46–48].

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 [49]. The implemented version of Blundell is applicable only for the purpose of atomic calculations as they have used the spherical implementation which allows the separation of radial and angular parts. Therefore, the 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. Such a separation is not possible in molecular systems due to the absence of spherical symmetry. The required one-body and two-body matrix elements are evaluated in the Cartesian coordinate system. The Cartesian coordinate system does not allow one to exploit the spherical symmetry to separate the matrix elements into radial and angular parts. Furthermore, the anti-symmetrized two-body matrix elements are used in this coordinate system calculations, which is not possible in the spherical implementations as angular factor will be different for the direct and exchange part of the two-body matrix element. Thus, our implemented version is a general one, applicable to both atoms as well as molecules starting from their closed-shell reference state configuration. It should be noted 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,

Download English Version:

<https://daneshyari.com/en/article/5393042>

Download Persian Version:

<https://daneshyari.com/article/5393042>

[Daneshyari.com](https://daneshyari.com)