

Four-component relativistic third-order algebraic diagrammatic construction theory for electron detachment, attachment, electronic excitation problem and calculation of first order transition properties

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Abstract

An efficient third-order algebraic diagrammatic construction (ADC) theory has been implemented to calculate ionisation potential, electron attachment and excitation energy (IP/EA/EE-ADC(3)) in a four-component relativistic framework. We have used polarisation propagator formulation for third-order perturbation theory to access the excitation energies (EE), and for IP/EA, a single-particle propagator has been used based on a non-Dyson formulation. The benchmarking calculations have been performed on various types of systems to test the accuracy of the four component ADC(3) scheme for the computation of IP, EA and EE. We have applied our IP-ADC(3) to demonstrate the computation of splitting in the IP states for halogen monoxides (XO, X = Cl, Br, I) due to spin-orbital coupling in the $^2\Pi$ ground state and compared it with experimental results. Next, we have studied the effect of relativity and the size of the basis set on the electron attachment calculations of halogen atoms (F, Cl, Br, I and At) using EA-ADC(3). As our next step, we have shown the efficiency of four component ADC(3) in computing excitation energies of triiodide ion and compared with relativistic equation of motion coupled cluster with singles and doubles (EOM-CCSD), intermediate Hamiltonian Fock space coupled cluster (IHFS-CC) and other EOM-CCSD schemes in which spin-orbit coupling is incorporated with different degrees of approximation. Finally, we have also investigated the excitation energies and transition dipole moments for the four excited states of Xe atom and compared them with our recent four-component EOM-CCSD implementation and relativistic finite field Fock space coupled cluster results, along with the experimental estimates.

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1. Introduction

The excited state energies and transition properties have vast applications in different fields of chemistry. Simulation of these properties plays a significant role in the field of spectroscopy, photochemistry, and photobiology. The fundamental challenge for excited state calculations is the development of theoretical methods which are accurate for all kinds of excited states and have low computational costs at the same time. The single reference wavefunction-based methods¹ are known to be a black box and systematically improvable. Within the framework of a wavefunction-based method, one can simulate excitation energy in two ways – I. “ Δ -based methods” or the separate and individual calculation of ground and excited states and taking the difference afterward and II. “direct difference of energy-based methods” or the methods involving single calculation on an initial ground state to generate the excitation energy as an eigenvalue to a secular Hamiltonian. While the former suffers problems like symmetry breaking, variational collapse etc., the latter one is free from these problems and more widely used. Moreover, the direct energy difference-based methods have an additional advantage over the former as they also provide access to the transition probability for each of the excited states. Out of the various direct difference based wave-function methods, the equation of motion coupled cluster (EOM-CC)²⁻⁵ theory has emerged as one of the most popular options for calculating excitation energy. The linear response coupled cluster (LR-CC)^{6,7} method gives identical results as the EOM-CC method for excitation energy, although both of them are derived from a very different theoretical point of view. However, due to the non-hermitian nature of the coupled cluster similarity transformed Hamiltonian, the calculation of transition properties in both LR-CC and EOM-CC methods requires significant additional effort over the energy calculation.

The Algebraic Diagrammatic Construction (ADC)⁸⁻¹⁴ theory, being Hermitian, has a great advantage in terms of property calculation compared to non-hermitian coupled cluster based excited state methods. In the non-hermitian formalism, both left and right eigenvectors need to be obtained in order to calculate the transition density. On the contrary, in the hermitian formalism like ADC, one needs to calculate only a single eigenvector for each excited state for property calculations, which reduces the computational cost nearly to half. The ADC theory was at first derived for the polarization propagator using diagrammatic perturbation expansion. Later on, Intermediate State Representation (ISR) became more popular due to its straightforward formalism, and easy access to the excited state wavefunction. The perturbative truncation in ADC based methods reduces its computational cost compared to the corresponding EOM-CC method. Mukherjee and Kutzelnigg¹⁵ has shown an alternative derivation to ADC using effective Liouvilian formalism and has been recently used in a work by Sokolov and coworkers.

For the simulation of excited states of heavy elements, one needs to include relativistic effect in the calculation. One of the most accurate way to include the relativistic effect, is to use a four-component Dirac Hamiltonian. The Dirac equation for the many electronic system is generally solved using the Dirac-Hartree-Fock (DHF) approximation. In the non-relativistic domain, a lot of work has been done in literature using the ADC schemes in recent times for both energy and property calculations¹⁶⁻²⁰. In the relativistic domain, second order and extended second order versions of ADC have been implemented by Pempfert et al^{21,22} for excitation energies and transition dipole moments. It has been evident that the second order ADC scheme often doesn't provide adequate accuracy and one needs to go at least third order in perturbation to get desired accuracy in the calculation²³. Extension of the fourth order ADC scheme has also been achieved in the literature²⁴. In this manuscript, we have presented the theory, implementation and benchmark of the ionized, electron-attached and the excited state energy and property within the third order algebraic diagrammatic construction scheme for the relativistic four component formalisms.

2. Theory

2.1 Relativistic Algebraic Diagrammatic Construction (ADC) Theory

Although the algebraic diagrammatic construction can be deduced from its initial occurrence in the context of propagator theory, we follow the intermediate state representation (ISR) derivation of ADC. In order to form the intermediate state basis, firstly, one needs to operate a linear excitation/ionization/electron-attachment operator on the reference state wave function to generate correlated excited states (CES)

$$|\psi_I^0\rangle = \hat{C}_I |\psi_0^N\rangle \quad (1)$$

The nature of the operator \hat{C}_I depends upon the desired target state

For ionization:

$$\{\hat{C}_I\} = \{\hat{c}_i, \hat{c}_a^\dagger \hat{c}_i \hat{c}_j, \hat{c}_b^\dagger \hat{c}_a^\dagger \hat{c}_i \hat{c}_j \hat{c}_k, \dots; i < j < k \dots, a < b < \dots\} \quad (2)$$

For excitation:

$$\{\hat{C}_I\} = \{\hat{c}_a^\dagger \hat{c}_i, \hat{c}_b^\dagger \hat{c}_a^\dagger \hat{c}_i \hat{c}_j, \hat{c}_c^\dagger \hat{c}_b^\dagger \hat{c}_a^\dagger \hat{c}_i \hat{c}_j \hat{c}_k, \dots; i < j < k \dots, a < b < c \dots\} \quad (3)$$

For electron-attachment:

$$\{\hat{C}_I\} = \{\hat{c}_a^\dagger, \hat{c}_b^\dagger \hat{c}_a^\dagger \hat{c}_i, \hat{c}_c^\dagger \hat{c}_b^\dagger \hat{c}_a^\dagger \hat{c}_i \hat{c}_j, \dots; i < j \dots, a < b < c \dots\} \quad (4)$$

These correlated excited states are generally not orthonormal, but they can be orthogonalized using Gram-Schmidt orthogonalization to form precursor states. These precursor states are then allowed to undergo a symmetric orthonormalization to form the intermediate state basis. In ISR, the ADC excited state wavefunction for the K^{th} state can be represented in terms of the intermediate state basis as follows

$$|\Psi_K^{ex}\rangle = \sum_I \mathbf{Y}_{IK} |\tilde{\Psi}_I\rangle \quad (5)$$

The coefficient matrix \mathbf{Y}_{IK} matrix and the eigenvalues Ω are obtained as the eigenvectors in the diagonalization of the secular matrix (\mathbf{M}_{IJ}) of the ADC Hamiltonian

$$\mathbf{M}\mathbf{Y} = \mathbf{Y}\Omega \quad (6)$$

where

$$\mathbf{M}_{IJ} = \langle \tilde{\psi}_I | \hat{H} - E_0^N | \tilde{\psi}_J \rangle \quad (7)$$

and

$$\mathbf{Y}_{IK} = \langle \tilde{\Psi}_I | \Psi_K \rangle; \mathbf{Y}^\dagger \mathbf{Y} = \mathbf{1} \quad (8)$$

In ADC, this secular matrix (\mathbf{M}_{IJ}) is expanded in the perturbation order as

$$\mathbf{M} = \mathbf{M}^{(0)} + \mathbf{M}^{(1)} + \mathbf{M}^{(2)} + \mathbf{M}^{(3)} + \dots \quad (9)$$

This series is truncated at perturbation order n for ADC(n) theory. Taking $n=2$ leads to ADC(2) method and $n=3$ leads to the ADC(3) method.

The four-component relativistic ADC method is generally based on the Dirac-Hartree-Fock mean-field wave function calculated using the Dirac-Coulomb Hamiltonian. For the molecular systems, the Dirac-Coulomb Hamiltonian (H_{DC}) can be written as,

$$H_{DC} = \sum_i^N \left[c\vec{\alpha}_i \cdot \vec{p}_i + \beta_i m_0 c^2 + \sum_A^{N_{mc}} V_{iA} \right] + \sum_{i < j}^N \frac{1}{r_{ij}} I_4 \quad (10)$$

Here, m_0 is the rest mass of the electron and c is the speed of light. \vec{p}_i and V_{iA} are the momentum and potential energy operators, respectively for the i^{th} electron in the field of the nucleus A . The α and β are Dirac

matrices and I_4 is 4×4 identity matrix. For many-body systems, the Dirac-Hartree-Fock (DHF) equation can be written in the matrix form as

$$\begin{bmatrix} \hat{V} + \hat{J} - \hat{K} & c(\sigma_{psm} \cdot \hat{p}) - \hat{K} \\ c(\sigma_{psm} \cdot \hat{p}) - \hat{K} & \hat{V} - 2m_0c^2 + \hat{J} - \hat{K} \end{bmatrix} \begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} = E \begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} \quad (11)$$

Here, $|\psi^L\rangle$ and $|\psi^S\rangle$ denote the large and the small components of the spinor $|\psi\rangle$ respectively, \hat{V} denote the electronuclear potential, \hat{J} and \hat{K} represent the Coulomb and the exchange operators respectively and σ_{psm} denotes Pauli spin matrices. After the solution of the DHF equation, the integrals on a molecular spinor basis are generated using the no-pair approximation. The ADC equations are generally solved using the Davidson iterative diagonalization procedure, where the trial vectors are multiplied with the dressed Hamiltonian to give the so-called ‘‘sigma’’ vectors. The programable expressions for the ADC(2) and ADC(3) methods for the ionization energy, electron attachment, and excitation energy have been provided in the supporting information. No Kramers restriction has been used in the present implementation to keep it independent of the framework used for the generation of the underlying DHF spinors.

2.2 Transition dipole moment and oscillator strength

The one-body reduced transition density matrices in the intermediate state representation can be evaluated as

$$\rho_{pq}^{K \leftarrow 0} = \langle \psi_K^{ex} | \hat{c}_p^\dagger \hat{c}_q | \psi_0^N \rangle = \sum_I \mathbf{Y}_{K,I}^\dagger \langle \tilde{\psi}_I | \hat{c}_p^\dagger \hat{c}_q | \psi_0^N \rangle \quad (12)$$

Using this transition density, one can obtain the transition properties $O^{K \leftarrow 0}$ corresponding to an operator (one-body) $\hat{O} = \sum_{pq} O_{pq} \hat{c}_p^\dagger \hat{c}_q$ as follows

$$O^{K \leftarrow 0} = \langle \psi_K^{ex} | O | \psi_0^N \rangle = \sum_{pq} O_{pq} \rho_{pq}^{K \leftarrow 0} \quad (13)$$

In the case of ADC, the computational advantage is that because of its Hermitian nature, one eigenvector per state needs to be calculated. One can obtain the square of the transition dipole moment as

$$|\mu^{K \leftarrow 0}|^2 = \sum_D |\mu_D^{K \leftarrow 0}|^2 \quad (14)$$

Subsequently, the oscillator strengths (observable) corresponding to each excited state are as follows.

$$f_{osc}^{K \leftarrow 0} = \frac{2}{3} \Omega^{K \leftarrow 0} |\mu^{K \leftarrow 0}|^2 \quad (15)$$

The transition properties in the ADC(3) method are calculated as a second-order intermediate state (ADC(3/2)) representation. Dreuw and co-workers have recently reported an intermediate state representation, which is complete up to third order in perturbation. However, it generally shows very a little improvement over ADC(3/2) method for property calculations.

3. Computational Details

All the calculations are performed using our in-house quantum chemistry software package BAGH²⁵. BAGH is currently interfaced with PySCF²⁶⁻²⁸, GAMESS-US²⁹ and DIRAC³⁰. The relativistic framework is interfaced with DIRAC and PySCF. The PySCF interface has been used to analyze the ionization potential of halogen oxides, electron attachment of halogen atoms, and transition energies of triiodide anion. The DIRAC interface has been used to generate the required integrals for the excitation energies and transition dipole moments for Xe. BAGH is primarily written in Python, with the computationally costly portions optimized with Cython and FORTRAN. The specific use of basis sets and truncation of correlation space at the canonical level is discussed in detail in the results and discussion section.

4. Results and Discussion

4.1 Ionization potential of Halogen monoxide anions

The ionization potential (IP) of halogen monoxide anions has grabbed special attention, especially in the field of atmospheric chemistry, for the last few decades. Algebraic Diagrammatic Construction theory can be a potential candidate to calculate the ionization potentials of these molecules. ADC has shown sufficiently accurate results for IP calculations. Table 1 presents the IP values corresponding to the first two ionized states of XO^- ($X=Cl, Br, \text{ and } I$), along with their splitting in IP-ADC(2) and IP-ADC(3) calculations. As one goes down the group, the relativistic effects become more prominent. One of the important consequences of these relativistic effects is the splitting in the ionization spectra due to spin-orbit coupling. In order to consider the spectroscopic splittings, one needs to go beyond the scalar relativistic effects and include spin-orbit coupling effects in the calculations. Considering these relativistic effects, we have calculated at the full four-component level. The splittings of states of halogen monoxide anions (XO^- ; $X=Cl, Br \text{ and } I$) have been calculated using dyall.av3z basis set for the halogen atom X and uncontracted aug-cc-pVTZ basis set has been used for the O atom. 26 occupied, 206 virtual spinors, and 44 occupied, 246 virtual spinors are considered in the correlation space of IP calculations of ClO^- and BrO^- ions respectively. For IO^- , 62 occupied and 248 virtual spinors are used in the electronically correlated level of calculations. All the IP results of Halogen monoxide anions provided here are calculated at experimental geometries of Halogen monoxides with a singlet DHF reference.

The splitting between $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states increases from Cl to I as the extent of spin-orbit coupling increases down the group. For all three systems, the calculated splittings using the ADC(2) method were underestimated while overestimated using ADC(3). The magnitudes of errors in both cases are comparable, and the maximum deviation in splittings is observed for IO^- with the magnitude of error being 0.13 eV, which is within the error bar.

4.2 Electron affinities of Halogen atoms

The theoretical investigation of electron affinity (EA) has remained fascinating for years. Unlike ionization potential, the electron affinity fails miserably at the Hartree-Fock level under Koopman's approximation, as orbital relaxation and correlation don't cancel out. In the case of halogen atoms,

the experimentally evident fact that they undergo electron attachment to attain a more stable configuration cannot be explained by calculating EA under Koopman's approximation. Thus, the effect of electron correlation plays an important role in the case of EA which determines whether the atom or molecule will be stable or not after electron attachment. Moreover, the study of electron attachment in systems containing heavy elements requires the consideration of relativistic effect into the calculation.

In literature, the study of EA for halogen atoms with explicit consideration of relativistic effect and electronic correlation is scarce. Hence, we have used EA-ADC(3) in the full four-component relativistic picture to investigate the vertical electron attachment energies of halogen atoms and compare them with the experimental values (see Table 2).

The study of electron attachment is highly dependent on the basis set used in the calculation³¹. Hence, we performed our calculations using different basis sets. For F, Cl, and Br we have used uncontracted Dunning's aug-cc-pVXZ(X=2,3,4) basis set and for I and At doubly augmented dyall's valance n zeta basis sets, i.e., d-aug-dyall.vnz (n=2,3,4) are used. Truncation of canonical virtual spinors based on energy reduces the cost of the calculation significantly and helps one to perform costly calculations with limited resources. No truncation in the canonical level was required for the calculations involving F, Cl, and Br atoms because of the smaller size of the basis set dimension. But in the case of I and At atoms, we truncated the virtual spinors at the canonical level. For At atom, 410 and 430 virtual spinors are taken into consideration in the correlation calculations for d-aug-dyall.v3z and d-aug-dyall.v4z basis set respectively, whereas for I, full canonical space is considered in d-aug-dyall.v3z basis set, but 380 virtual spinors are taken into account at d-aug-dyall.v4z basis set. The precedented outcome is observed along the basis set variation for all four halogen atoms. Quadruple zeta basis giving the best out of the three basis sets, shows higher accuracy with a mean absolute error (MAE) of 0.117 eV with respect to the experiment. The experimental trend of electron affinity shows the highest for Cl atom and the lowest for At atom. This is because the vacant d orbital of Cl atom creates an exception to the gradual decreasing downward trend otherwise. Although the quadruple zeta basis set is giving results with sufficient accuracy, but the trend is not followed here. This suggests that one needs to modify the basis set and switch to the one that describes the system sufficiently well. From Table 2, it can be seen that for all the halogen atoms ADC(3) results slightly underestimate the experimental EA values. The main reason behind this underestimation is due to the better description of the excited EA state in ADC(3) rather than the ground state, as already pointed out previously by Drew and coworkers. It is also evident from Table 2 that with an increase in the basis set, the correlation space increases and EA values are also increasing systematically. Moving towards a higher basis set improves the electron correlation treatment along with the orbital relaxation resulting in more accurate EA values, as demonstrated by MAE values. The MAE value decreases when moving to a bigger basis set and it is less than 0.2 eV at a quadruple zeta basis set with respect to the experiments.

4.3 Excitation energies of triiodide anion (I_3^-)

The accurate evaluation of excitation energy has gained much attention among theoretical chemists in recent years. Accurate simulation of excited states is indeed the primary focus of this manuscript. Our implementation of EE-ADC(3) in the full four-component relativistic framework enables us to perform excitation energy calculations along with the effect of relativity inherently incorporated.

Triiodide anion is indeed an important system to study the excitation energy. Previously, several studies have been performed on triiodide anion using Intermediate Hamiltonian Fock-Space Coupled Cluster (IHFS-CC), EOM-CCSD, CASPT2, MRCI, and TD-DFT in the relativistic framework. Also, in the non-relativistic picture, Z. Wang et al; approximated the SOC effect as a perturbation and added to the Hamiltonian in the post-Hartree-Fock level. They included the SOC only in the EOM-CCSD level because turning on the SOC effect in the ground state CCSD level would lead to 10 times more computational cost. Triiodide is an interesting system to study for many reasons. It is a molecule that does not follow the octet rule. It is an example of a closed-shell negatively charged molecule with an excited state having lower energy than its electron detachment energy. Several investigations have been performed for electronically excited states of triiodide in both gas and solution phases, focusing on the complicated dissociation dynamics in the excited state after excitation. The photofragment yield study by Neumark and coworkers in the gas phase exhibits two bands near 360 nm (3.4 eV) and 290 nm (4.3 eV). Previously semiempirical theoretical studies by Okada et al. also showed that these two bands are a combination of $1\pi_{0+u}$ and $3\sigma_{0+u}$ states, both of which are 0^+_{-u} states. We have compared our ADC(3) four-component implementation for excited states with previous relativistic calculations such as EE-EOM-CCSD, EE-IHFS, and CASPT2, as well as with the non-relativistic approximate perturbative SOC approach by Wang and co-workers. Results obtained from 4c-EE-ADC(3) are presented in Table 3, along with those obtained from the aforementioned methods. For a statistical comparison, we have calculated the mean absolute deviation (MAD) and standard deviation (STD). The MAD and STD for ADC(3) presented in Table 3 are calculated, taking DC^M-IHFS as the reference. It is evident that excitation energies obtained from ADC(3) are closer to IHFS values and surpass EOM-CCSD results in terms of MAD. Moreover, the STD of both ADC(3) and EOM-CCSD are comparable. Still, slightly better performance is observed in EOM-CCSD because of the systematic overestimation of excitation energies for all the states mentioned, whereas ADC(3) does not follow such a trend. However, individual excitation energies of all states are very close to the IHFS values compared to EOM-CCSD, demonstrating its efficiency. It should be noted that ADC(3) also predicted the excitation energies of two experimentally observed 0^+_{-u} states (12 and 15) with excellent accuracy. Wang and coworkers's non-relativistic Hamiltonian implementation with SOC as a perturbation in the post-Hartree Fock calculation obtained from effective core potential in a relativistic picture. When compared with the SOC-EOM-CCSD, the 4c-ADC(3) also shows better performance, demonstrating its reliability and efficiency in predicting the excited state of complicated anionic species, like triiodide anion.

4.4 Excitation energies and transition dipole moments of Xe atom

Our implementation of the relativistic four-component EE-ADC(3) method works for both molecules and atoms. The excitation energy and the corresponding transition moment are studied thoroughly for four states of the Xe atom, and the results are compared with the experimental ones in Table 4. The calculations are done in two different doubly augmented Dyall basis sets, namely d-aug-dyall.ae2z and d-aug-dyall.ae3z. For d-aug-dyall.ae2z all the occupied and virtual spinors are taken into consideration for correlation, whereas in case of d-aug-dyall.ae3z frozen core approximation is applied and all the virtual spinor more than 361 a.u. has been discarded, leading to 18 occupied and 364 virtual spinor in the correlation space. The deviation in excitation energy with respect to the

experiment decreases from double to triple zeta basis set. The maximum absolute deviation is observed for the state $5p^5(^2P_{3/2})6s^2[3/2]_1^o$ in both basis sets. In the double zeta basis set, the deviation in excitation energy is 2555 cm⁻¹, which is reduced to 2131 cm⁻¹ for the triple zeta one. The absolute deviations in excitation energy in the triple zeta basis set can become as minimal as 133 cm⁻¹ for the fourth state.

The transition dipole moments seem to be predictable for the former two states, while the deviations are comparatively high for the latter two states with respect to the experimental results. The transition dipole moments improve while going from the d-aug-dyall.ae2z to d-aug-dyall.ae3z basis set for all four states. The error in transition dipole moment is as minimal as 0.001 a.u. for the state $5p^5(^2P_{1/2})6s^2[1/2]_1^o$ in the d-aug-dyall.ae3z basis set. The excitation energies and the transition dipole moment results are also compared with our recent implementation of four component EOM-CCSD results³². Both the excitation energy and the transition dipole moments are minimal for the first state among the four states. The transition moments of these two methods are as close as 0.004 a.u. for the state $5p^5(^2P_{3/2})6s^2[3/2]_1^o$.

The primary advantage of using EE-ADC(3) for the transition dipole moment calculation is that ADC being a hermitian method, unlike a non-hermitian method, one needs to calculate only one eigenvector to get the transition properties which reduces the cost of that part by half. Prediction of comparable transition dipole moments with such minimal cost makes ADC theory appreciable.

5. Conclusions

We have showcased a robust and explicit 4 component implementation of ADC(3). Benchmarking calculation on three types of excitation problems shows its efficiency and versatility. The focus on the investigations of IP calculations for halogen monoxides reveals the importance of the consideration of spin-orbit coupling and relativistic effects. EA study also showed the failure of Koopman approximation, and one should consider electron correlation and relativistic effect simultaneously for accurate simulation of EA estimation, especially for heavier elements. The excitation energies of triiodide computed at 4c-EE-ADC(3) level anion demonstrated an excellent agreement with the IHFS results and underscores the results obtained at EE-EOM-CCSD level in a four component framework. Finally, in terms of properties, we benchmarked our implementation on the Xe atom by calculating transition dipole moments from the ground to four excited states. It has been shown that the transition dipole moment and oscillator strength calculated in the 4c-ADC(3) level provide almost similar numbers compared to the EOM-CCSD model. In contrast, the cost is nearly half of the EOM-CCSD calculation due to the Hermitian nature of the ADC Hamiltonian. In particular, ADC(3) showcases a balance between computational cost and accuracy, which is essential for practical applications. Further cost reduction and more efficient implementation to perform calculations on larger systems are necessary, especially in a relativistic framework, and work is in progress towards that direction.

Supplementary Material

Programmable expressions of IP/EA/EE-ADC(3).

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Table 1: The comparison of splittings of states in the IP values (in eV) calculated with ADC(2) and ADC(3) methods with respect to the experimental results (in eV) for halogen monoxide anions (XO^- ; $X=Cl, Br, I$) in the basis *dyall.av3z* for X atom and uncontracted *aug-cc-pVTZ* for O atom.

Molecule	Method	${}^2\Pi_{3/2}$	${}^2\Pi_{1/2}$	Splitting	Expt ³³ .	Error
ClO ⁻	4c-IP-ADC(2)	0.7779	0.8091	0.0312	0.0397	-0.0085
	4c-IP-ADC(3)	2.4158	2.4660	0.0503		0.0106
BrO ⁻	4c-IP-ADC(2)	0.8701	0.9462	0.0761	0.1270	-0.0509
	4c-IP-ADC(3)	2.5819	2.7470	0.1651		0.0381
IO ⁻	4c-IP-ADC(2)	0.9397	1.0697	0.1300	0.2593	-0.1293
	4c-IP-ADC(3)	2.5889	2.9760	0.3874		0.1281

Table 2: Electron affinity (in eV) of halogen atoms (F, Cl, Br, I and At) using 4c-EA-ADC(3) and a comparison with experimental values (eV). *unc-aug-cc-pVNZ(N=2,3,4)* is used for F, Cl, Br and *d-aug-dyall.vNz(N=2,3,4)* is used for I and At.

	2z	3z	4z	Expt.
F	2.862	2.959	3.011	3.401 ³⁴
Cl	3.364	3.419	3.575	3.613 ³⁵
Br	3.087	3.225	3.342	3.363 ³⁶
I	2.813	2.912	3.129	3.059 ³⁷
At	2.112	2.173	2.350	2.416 ³⁸
MAE	0.322	0.232	0.117	

Table 3: Vertical Excitation energy (eV) of Triiodide anion (I_3^-) using 4c-EE-ADC(3). The DC^M-EOM/IHFS, DCG^M-EOM/IHFS are taken from Shee et al³⁹.

State	Ω	DC ^M	DC ^M		DCG ^M		EOM ⁴⁰			CASPT2 ⁴¹
		ADC(3)	EOM	IHFS	EOM	IHFS	(a)	(b)	(c)	
1	2 _g	2.06	2.24	2.07	2.25	2.25	2.22	2.36	2.16	2.24
2	1 _g	2.19	2.37	2.20	2.38	2.21	2.35	2.50	2.29	2.32
3	0 _u ⁻	2.23	2.37	2.22	2.38	2.23	2.34	2.49	2.29	2.47
4	1 _u	2.23	2.38	2.23	2.38	2.24	2.34	2.47	2.30	2.47
5	0 _g ⁻	2.66	2.84	2.66	2.84	2.66	2.81	2.96	2.72	2.76
6	0 _g ⁺	2.71	2.89	2.71	2.89	2.71	2.86	2.99	2.75	2.82
7	1 _g	2.87	3.07	2.88	3.07	2.89	3.04	3.20	2.96	2.85
8	2 _u	3.13	3.32	3.19	3.33	3.20	3.30	3.47	3.25	3.10
9	1 _u	3.19	3.41	3.27	3.42	3.27	3.39	3.55	3.34	3.11
10	0 _u ⁺	3.43	3.66	3.51	3.67	3.52	3.65	3.79	3.56	3.52
11	2 _g	3.88	4.09	3.92	4.10	3.93	4.04	4.19	3.98	3.98
12	0 _u ⁻	3.89	4.08	3.93	4.08	3.93	4.05	4.18	3.91	3.79
13	1 _u	3.96	4.18	4.02	4.18	4.02	4.15	4.29	4.01	3.80
14	1 _g	3.99	4.21	4.03	4.22	4.04	4.17	4.32	4.10	4.06
15	0 _u ⁺	4.28	4.49	4.33	4.49	4.33	4.50	4.67	4.42	4.51
16	0 _g ⁻	4.49	4.69	4.51	4.69	4.51	4.65	4.76	4.51	4.51
17	0 _g ⁺	4.50	4.70	4.51	4.70	4.51	4.65	4.82	4.51	4.53
18	1 _g	4.85	4.90	4.71	4.90	4.71	4.86	4.99	4.73	4.60
MAD		0.04	0.17		0.17		0.13	0.28	0.05	0.11
STD		0.04	0.02		0.02		0.02	0.02	0.03	0.08

Table 4: Excitation energy (in cm^{-1}) and Transition Dipole Moments (TDM) (in a.u.) of Xe atom for the first four excited states using 4c-EE-ADC(3)

Excited state	d-aug-dyall.ae2z		d-aug-dyall.ae3z		Experiment ⁴²	
	EE	TDM	EE	TDM	EE	TDM
$5p^5(^2P_{3/2})6s^2[3/2]_1^o$	65,490	0.642	65,914	0.643	68,045	0.654
$5p^5(^2P_{1/2})6s^2[1/2]_1^o$	74,934	0.544	75,074	0.522	77,185	0.521
$5p^5(^2P_{3/2})5d^2[1/2]_1^o$	78,738	0.010	78,215	0.047	79,987	0.120
$5p^5(^2P_{3/2})5d^2[3/2]_1^o$	85,722	0.918	84,022	0.892	83,889	0.704

Supplementary Material: Four-component relativistic third-order algebraic diagrammatic construction theory for electronic excitation and transition dipole moment

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Contents

1. Programmable expressions
2. Comparison of EE-ADC(3) excitation energies (cm^{-1})s and transition moments (a.u.) with EE-EOM-CCSD ones in d-aug-dyall.ae3z basis set for Xe atom

Programmable expressions

IP-ADC

1h-1h block

$$\sigma_i^{(0)} = M_{ij}^{(0)} r_j$$

$$\sigma_i^{(2)} = M_{ij}^{(2)} r_j$$

$$\sigma_i^{(3)} = M_{ij}^{(3)} r_j$$

1h-2h1p block

$$\sigma_i^{(1)} = \frac{1}{\sqrt{2}} \langle ai || kj \rangle r_{jk}^a$$

$$\sigma_i^{(2)} = \frac{1}{\sqrt{2}} I_{jki}^{IP} r_{jk}^a$$

2h1p-1h block

$$\sigma_{ij}^{a(1)} = \frac{1}{\sqrt{2}} \langle ak || ji \rangle r_k$$

$$\sigma_{ij}^{a(2)} = \frac{1}{\sqrt{2}} I_{ijka}^{IP} r_k$$

2h1p-2h1p block

$$\sigma_{ij}^{a(0)} = f_{ab} r_{ij}^b - f_{ik} r_{kj}^a + f_{jk} r_{ki}^a$$

$$\sigma_{ij}^{a(1)} = \frac{1}{2} \langle kl || ij \rangle r_{kl}^a - \langle la || ic \rangle r_{ij}^c + \langle la || jc \rangle r_{li}^c$$

EA-ADC

1p-1p block

$$\sigma^{a(2)} = M_{ab}^{(2)} r^b$$

$$\sigma^{a(3)} = M_{ab}^{(3)} r^b$$

1p-2p1h block

$$\sigma^{a(1)} = -\frac{1}{2} \langle la || cd \rangle r_i^{cd}$$

$$\sigma^{a(2)} = -\frac{1}{2} I_{dcal}^{EA} r_l^{cd}$$

2p1h-1p block

$$\sigma_j^{ab(1)} = \langle jc || ba \rangle r^c$$

$$\sigma_j^{ab(1)} = I_{abcj}^{EA} r^c$$

2p1h-2p1h block

$$\sigma_j^{ab(0)} = f_{ac} r_j^{cb} - f_{bc} r_j^{ca} - f_{ij} r_l^{ab}$$

$$\sigma_j^{ab(1)} = \langle db || ca \rangle r_i^{ab} - \langle lb || jd \rangle r_i^{ad} + \langle la || jd \rangle r_i^{bd}$$

EE-ADC

1h1p-1h1p block

$$\sigma_i^{a(2)} = M_{ab}^{(2)} r_i^b + M_{ij}^{(2)} r_j^a + M_{iajb}^{(2)} r_j^b$$

$$\sigma_i^{a(3)} = M_{ab}^{(3)} r_i^b + M_{ij}^{(3)} r_j^a + M_{iajb}^{(3)} r_j^b$$

1h1p-2h2p block

$$\sigma_i^{a(1)} = I_{jkib}^{1(1)} r_{jk}^{ab} + I_{jabc}^{2(1)} r_{ij}^{bc}$$

$$\sigma_i^{a(2)} = I_{jkib}^{1(2)} r_{jk}^{ab} + I_{jabc}^{2(2)} r_{ij}^{bc} - \langle ic || ab \rangle t_{jk}^{bd(1)} r_{jk}^{cd} - \langle ak || ji \rangle t_{jl}^{bc(1)} r_{kl}^{bc}$$

2h2p-1h1p block

$$\sigma_{ij}^{ab(1)} = -\frac{1}{2} \mathcal{P}(ab) I_{ijka}^{1(1)} r_k^b + \frac{1}{2} \mathcal{P}(ij) I_{jcab}^{2(1)} r_i^c$$

$$\sigma_{ij}^{ab(2)} = -\frac{1}{2} \mathcal{P}(ab) I_{ijka}^{1(2)} r_k^b + \frac{1}{2} \mathcal{P}(ij) I_{jcab}^{2(2)} r_i^c - \frac{1}{2} \mathcal{P}(ab) \langle kb || cd \rangle t_{ij}^{ac(1)} r_k^d - \frac{1}{2} \mathcal{P}(ij) \langle ci || kl \rangle t_{jl}^{ab(1)} r_k^c$$

2h2p-2h2p block

$$\sigma_{ij}^{ab(0)} = \mathcal{P}(ab) f_{bc} r_{ij}^{ac} - \mathcal{P}(ab) f_{ik} r_{kj}^{ab}$$

$$\sigma_{ij}^{ab(1)} = \mathcal{P}(ij / ab) \langle kb || jc \rangle r_{ik}^{ac} + \frac{1}{2} \langle ij || kl \rangle r_{kl}^{ab} + \frac{1}{2} \langle ab || cd \rangle r_{ij}^{cd}$$

Intermediates

$$I_{ijka}^{IP} = \frac{1}{2} t_{ij}^{cd(1)} \langle ka || cd \rangle - t_{ii}^{ac(1)} \langle cl || jk \rangle + t_{jl}^{ac(1)} \langle ci || lk \rangle$$

$$I_{abei}^{EA} = -\frac{1}{2} t_{mn}^{ab(1)} \langle ei || nm \rangle - t_{mi}^{af(1)} \langle mb || ef \rangle + t_{mi}^{bf(1)} \langle ma || ef \rangle$$

$$I^{1(1)} = \langle ak || ji \rangle$$

$$I^{1(2)} = \mathcal{P}(ij) \langle bj || kl \rangle t_{ii}^{ab(1)} + \frac{1}{2} \langle ka || bc \rangle t_{ij}^{bc(1)}$$

$$I^{2(1)} = \langle ia || bc \rangle$$

$$I^{2(2)} = -\mathcal{P}(bc) \langle jc || ad \rangle t_{ij}^{bd(1)} + \frac{1}{2} \langle ai || kj \rangle t_{jk}^{bc(1)}$$

$$M_{ij}^{(0)} = -f_{ij}$$

$$M_{ij}^{(2)} = -\frac{1}{4} \mathcal{P}_+(ij) \langle jk || ab \rangle t_{ik}^{ab(1)}$$

$$M_{ij}^{(3)} = \mathcal{P}_+(ij) \left[\frac{1}{4} \langle jk || ab \rangle t_{ik}^{ab(2)} + \frac{1}{2} \mathcal{T}_{jkab}^1 t_{ik}^{ab(1)} + \langle aj || ik \rangle \mathcal{D}_{ka} \right] - \langle ik || jl \rangle \mathcal{D}_{kl} - \langle ia || jb \rangle \mathcal{D}_{ab}$$

$$\mathcal{T}_{ijab}^1 = -\langle kb || ic \rangle t_{jk}^{ac(1)} - \frac{1}{4} \langle ij || kl \rangle t_{kl}^{ab(1)}$$

$$M_{ab}^{(0)} = f_{ab}$$

$$M_{ab}^{(2)} = -\frac{1}{4} \mathcal{P}_+(ab) \langle ij || bc \rangle t_{ij}^{ac(1)}$$

$$M_{ab}^{(3)} = \mathcal{P}_+(ab) \left[\frac{1}{4} \langle ij || bc \rangle t_{ij}^{ac(2)} + \frac{1}{2} \mathcal{T}_{ijcb}^2 t_{ij}^{ac(1)} - \langle ia || bc \rangle \mathcal{D}_{ic} \right] + \langle ia || jb \rangle \mathcal{D}_{ij} + \langle ac || bd \rangle \mathcal{D}_{cd}$$

$$\mathcal{T}_{ijab}^2 = -\langle kb || ic \rangle t_{jk}^{ac(1)} + \frac{1}{4} \langle ab || cd \rangle t_{ij}^{cd(1)}$$

$$M_{iajb}^{(1)} = -\langle ja || ib \rangle$$

$$M_{iajb}^{(2)} = \mathcal{P}_+(ijab) \frac{1}{2} \langle jk || bc \rangle t_{ik}^{ac(1)}$$

$$M_{iajb}^{(3)} = \mathcal{P}_+(ijab) \left[-\frac{1}{2} \langle jk || bc \rangle t_{ik}^{ac(2)} - \frac{1}{2} t_{jk}^{bc(1)} \mathcal{T}_{ikac}^3 - \langle ib || kc \rangle \mathcal{T}_{kajc}^S \right. \\ \left. + \langle ib || ac \rangle \mathcal{D}_{jc} + \langle aj || ki \rangle \mathcal{D}_{kb} + \frac{1}{2} \langle ja || ic \rangle \mathcal{D}_{bc} - \frac{1}{2} \langle ja || kb \rangle \mathcal{D}_{ik} \right] \\ + \frac{1}{2} \langle ic || jd \rangle t_{kl}^{ac(1)} t_{kl}^{bd(1)} + \frac{1}{2} \langle ka || lb \rangle t_{ik}^{cd(1)} t_{jl}^{cd(1)} - \langle il || jk \rangle \mathcal{T}_{kalb}^S - \langle ac || bd \rangle \mathcal{T}_{idjc}^S$$

$$\mathcal{T}_{ijab}^3 = -\mathcal{P}_+(ijab) \langle kb || ic \rangle t_{jk}^{ac(1)} - \frac{1}{2} \langle ab || cd \rangle t_{ij}^{cd(1)} - \frac{1}{2} \langle ij || kl \rangle t_{kl}^{ab(1)}$$

$$\mathcal{Z}_{iajb}^S = t_{ik}^{ac(1)} t_{jk}^{bc(1)}$$

$$\mathcal{D}_{ij} = -\frac{1}{2} t_{ik}^{ab(1)} t_{jk}^{ab(1)}$$

$$\mathcal{D}_{ia} = \frac{\langle ja || bc \rangle t_{ij}^{bc(1)} + \langle bi || kj \rangle t_{jk}^{ab(1)}}{2(f_{ii} - f_{aa})}$$

$$\mathcal{D}_{ab} = \frac{1}{2} t_{ij}^{bc(1)} t_{ij}^{ac(1)}$$

$$t_{ij}^{ab(1)} = \frac{\langle ij || ab \rangle}{(f_{ii} + f_{jj} - f_{aa} - f_{bb})}$$

$$t_{ij}^{ab(2)} = \frac{\mathcal{P}(ij / ab) \langle kb || jc \rangle t_{ik}^{ac(1)} - \frac{1}{2} \langle ab || cd \rangle t_{ij}^{cd(1)} - \frac{1}{2} \langle ij || kl \rangle t_{kl}^{ab(1)}}{\frac{1}{2} \mathcal{P}_+(ij) (f_{ii} + f_{jj} - f_{aa} - f_{bb})}$$

$$\mathcal{P}(pq) f(p, q) = f(p, q) - f(q, p)$$

$$\mathcal{P}_+(pq) f(p, q) = f(p, q) + f(q, p)$$

$$\mathcal{P}(pq / rs) f(p, q, r, s) = f(p, q, r, s) - f(q, p, r, s) - f(p, q, s, r) + f(q, p, s, r)$$

$$\mathcal{P}_+(pqrs) f(p, q, r, s) = f(p, q, r, s) + f(q, p, s, r)$$

Table S1: Comparison of EE-ADC(3) excitation energies (cm^{-1})s and transition moments (a.u.) with EE-EOM-CCSD ones in *d-aug-dyall.ae3z* basis set for Xe atom

Excited state	EE-ADC(3)		EE-EOM-CCSD	
	EE	TDM	EE	TDM
$5p^5(^2P_{3/2})6s^2[3/2]_1^o$	65914	0.643	67886	0.647
$5p^5(^2P_{1/2})6s^2[1/2]_1^o$	75074	0.522	77166	0.535
$5p^5(^2P_{3/2})5d^2[1/2]_1^o$	78215	0.047	80368	0.201
$5p^5(^2P_{3/2})5d^2[3/2]_1^o$	84022	0.892	86328	0.949