

Reappraisal of Nuclear Quadrupole Moments of Atomic Halogens via Relativistic Coupled Cluster Linear Response Theory for the Ionization Process

Rajat K. Chaudhuri*

Indian Institute of Astrophysics, Bangalore 560034, India

Sudip Chattopadhyay*

Department of Chemistry, Bengal Engineering and Science University, Shibpur, Howrah 711103, India

Uttam Sinha Mahapatra

Department of Physics, Maulana Azad College, 8 Rafi Ahmed Kidwai Road, Kolkata 700 013, India

ABSTRACT: The coupled cluster based linear response theory (CCLRT) with four-component relativistic spinors is employed to compute the electric field gradients (EFG) of ^{35}Cl , ^{79}Br , and ^{127}I nuclei. The EFGs resulting from these calculations are combined with experimental nuclear quadrupole coupling constants (NQCC) to determine the nuclear quadrupole moments (NQM), Q of the halide nuclei. Our estimated NQMs [$^{35}\text{Cl} = -81.12$ mb, $^{79}\text{Br} = 307.98$ mb, and $^{127}\text{I} = -688.22$ mb] agree well with the new atomic values [$^{35}\text{Cl} = -81.1(1.2)$, $^{79}\text{Br} = 302(5)$, and $^{127}\text{I} = -680(10)$ mb] obtained via Fock space multireference coupled cluster method with the Dirac–Coulomb–Breit Hamiltonian. Although our estimated $Q(^{79}\text{Br})$ value deviates from the accepted reference value of 313(3) mb, it agrees well with the recently recommended value, $Q(^{79}\text{Br}) = 308.7(20)$ mb. Good agreement with current reference data indicates the accuracy of the proposed value for these halogen nuclei and lends credence to the results obtained via CCLRT approach. The electron affinities yielded by this method with no extra cost are also in good agreement with experimental values, which bolster our belief that the NQMs values for halogen nuclei derived here are reliable.

$$Q[\text{b}] = \frac{-B[\text{MHz}]}{234.9674 \times q[\text{a.u.}]}$$

I. INTRODUCTION

The relativistic quantum chemical methodology finds one of its most important domain of applications in the evaluation of molecular properties.^{1–4} The analytic evaluation of molecular response properties calls for the analytic derivatives of the molecular energy, and in this regard, the generation of analytic energy gradients (and Hessians) are considered to be one of the esteemed ways for reaching molecular properties within the domain of traditional many-body approaches.⁵ It has become quite popular and standard to perform quantum chemical calculations of electric response properties with nonrelativistic methods.⁵ However, quite contrary to this, the study of the domain of systems involving heavy elements is comparatively less explored, because such systems warrant a truly relativistic description.^{1–4} The formal complexity and extensively involved numerical implementation of complete four-component relativistic many-body formulations restrict the applicability of such methods to small systems only⁶ and motivates one to look for simple but accurate computational strategies.

The nuclear quadrupole moment (NQM) that emerges due to the nonspherical distribution of the nuclear charge plays an important role in atomic, molecular, and solid state spectroscopy^{7–18} besides the direct interest in nuclear physics, where its

determination can be used to check nuclear models. Moreover, investigations of molecular dynamics require the information of Q in systems where NQM values determine the spin–lattice relaxation time. The information of NQM (assigned here as Q) is also useful in the evaluation of the nuclear magnetic resonance measurements in biological systems. Currently, the nuclear quadrupole moment Q of an atom is determined by exploiting the following relation⁹

$$Q[\text{b}] = \frac{-B[\text{MHz}]}{234.9647 \times q[\text{a.u.}]} \quad (1)$$

where q is the electric field gradient (EFG) and B is the nuclear quadrupole coupling constant (NQCC). As the nuclear quadrupole coupling constant can be determined experimentally with high precision,^{19–23} the accuracy of the nuclear quadrupole moment Q derived from eq 1 solely relies on the accuracy of the computed EFG, q . Therefore, the error associated with Q can be attributed to the uncertainty in the computation of EFG value. The EFG tensor at the location of

Received: August 29, 2013

Revised: October 25, 2013

Published: October 30, 2013

an atomic nucleus in a molecule is determined by the total environment of electric charges, stemming from both electrons and other nuclei. It can be calculated directly from high-level correlated molecular wave functions as a one-electron expectation value or by finite field approaches. Experimentally, the EFG is manifested through its interaction with the electric nuclear quadrupole moment which is usually described in terms of NQCC attainable by both experiment and theory. This situation offers the possibility for interpretation and understanding of highly resolved experimental spectra. Thus, the computed EFGs are of interest for a number of contemporary questions in the theory of atomic structure, high resolution spectroscopy, and so on. We should mention that EFG at an atomic nucleus is a sensitive property, indicating the local environment because it depends on the nonspherical electron density distribution of the atom. The determination of the EFG tensor as the expectation value of a well-known EFG operator is nontrivial in one-(scalar) or two-component relativistic calculations.

Traditionally, EFGs were determined from the magnetic hyperfine structure by invoking ad hoc corrections to the quadrupole shielding (Sternheimer's formulation²⁴). However, in recent times, the EFGs are computed by ab initio methods without any further corrections which significantly improve the NQMs.⁹ For example, Yakobi et al.²⁵ applied the finite field approach to compute the EFG of Cl, Br, and I atoms at the Fock-space multireference coupled cluster (FS-MRCC) level of theory^{26–37} [for a review on the FS-MRCC approach, see refs 38–40 with four-component Dirac–Coulomb–Briet Hamiltonian [see refs 41 and 42 for details of relativistic FS-MRCC applications]]. In the finite difference approach (a nonanalytical or numerically oriented static response approach), the effect of a small external field on the energy functional of the perturbed correlated state is monitored numerically and the response properties are extracted by finite difference approximations to the various derivatives.⁵ From a computational point of view, the finite difference method (numerical energy gradient procedure) is the simplest approach for computing the energy gradients (and hence the properties of interest) as the expression of the energy gradient is independent of the methodology. On the other hand, sufficient care has to be taken to maintain the precision of the calculation as well as the linearity of the perturbation throughout the calculations. Moreover, the numerical gradient approaches are too expensive and cumbersome to apply to systems described by more than few geometrical degrees of freedom. Thus, despite its conceptual and computational simplicity, the numerical response approach is neither convenient nor useful for general applications.

The above-mentioned problems can be circumvented by an analytic differentiation technique based on the analytical expressions of the response functions to compute the required derivatives. The analytical gradient technique is formally exact at a given level of theory, where the accuracy and the linearity of the energy gradient are independent of the field strength. More importantly, this procedure preserves the symmetry of the system, which eases the computation of higher order derivatives. Nevertheless, computation of the derivatives via analytic approaches increases the accuracy and reduces the computational cost considerably. Therefore, analytic derivatives are now-a-days used as standard techniques in quantum chemistry.⁴³ The *state-of-the-art* Z-vector technique of Handy and Schaefer⁴⁴ arguably the most important scheme available to

the computational chemist for studying analytic gradient calculations for correlated wave functions. In an important subsequent paper, Salter et al.⁴⁵ applied this technique to the problem of analytic derivative expressions in the *single reference* coupled cluster (SRCC)^{46–50} theory (usually termed as Λ -operator method). The key to all CC-based gradients has been the recognition of how the interchange theorem of Dalgarno and Stewart⁵¹ can be used to avoid computing the response of the ground state cluster amplitudes to each perturbation.

The generalization of the Z-vector technique and effective CC density matrices for multireference (MR) CC theories was initiated by Szalay.⁵² Considerable efforts have been made by Pal and co-workers^{53,54} in extending the SRCC based analytic gradient approach to FS-MRCC for arbitrary valence-sector, who have also reported its Hilbert-space version.⁵⁵ Using the constrained variation approach (CVA),^{56–58} Pal and co-workers have extended their FS-MRCC gradient method for higher order derivatives.⁵⁹ Although FS-MRCC formalism ensures the size-extensivity³⁹ of the computed properties for arbitrary valence sector, the computation of energy gradients via FS-MRCC is tedious and expensive, as two sets of CC equations have to be solved for each valence sector in a hierarchical fashion. In other words, the FS-MRCC equations have to be solved by invoking the so-called “sub-system embedding conditions” (SEC).³⁹ The FS-MRCC based expectation value approach has also been used to compute the one-electron properties of atomic systems.⁶⁰ Recently, the FS-MRCC method with four-component relativistic spinors has emerged as a method of choice for interpretation of the spectral properties of various relativistic systems.^{41,42,61–66} Though the properties resulting from this approach are found to be quite reasonable, the method suffers from intrinsic uncertainties as the numerator and the denominator appearing in the expression of property are nonterminating by construction.

The methods free from some of the above-mentioned problems are the coupled cluster based linear response theory (CCLRT)^{67–71} and equation-of-motion coupled cluster (EOMCC) method.^{72–76} The CCLRT (and EOM-CC) can be viewed as an alternative strategy in lieu of the FS-MRCC method that has the simplicity of the SR formalism to describe complex multiconfigurational wave functions as excitations from a judiciously chosen well-behaved reference state or function. The CCLRT and EOMCC are now considered to be the most powerful and effective tools for accurate description of the many-electron systems. These methods are specially designed for the high precision calculations of excitation/ionization energies of many-electron systems.^{77–88} In this context, we also refer to recent review articles.^{89–93} The greatest premise of these methods (CCLRT and EOM-CC) is that they are *direct* methods for energy difference calculations. In addition, the computed energies are size-extensive (at least for one-valence problem), a property that is crucial for the accurate determination of energy differences. The symmetry adapted cluster configuration interaction (SAC-CI) approach^{94,95} of Nakatsuji and co-workers is also closely related to EOMCC and CCLRT. The EOMCC based analytic energy derivative was made available by Stanton and co-workers,^{96–99} who have also applied this procedure to compute various molecular properties of excited/ionized states.

The EOM-CC and CCLRT analytic energy derivatives at the nonrelativistic level have been available in almost all quantum chemistry packages over several years and are routinely used to compute the transition dipole moments, oscillator strengths,

etc. of small to large molecular systems. On the other hand, despite tremendous methodological developments and associated computational advancements, the CCLRT method, CCLRT-IP (where IP stands for ionization potential) in particular, is hardly applied for relativistic systems.^{100,101} Thus, our modest aim in this paper is to extend this formalism to the relativistic regime. In particular, we shall apply the CCLRT for ionization process (IP) to compute the nuclear quadrupole moment Q for the isotopes of Cl, Br, and I within the framework of the four-component Dirac–Coulomb (DC) Hamiltonian. It is generally accepted that the incorporation of relativistic effects in union with the electron correlation is crucial for the theoretical description of such type of nuclei. The hyperfine constants for the halogen nuclei are particularly well suited and these nuclei are the prime objects in the realm of nuclear quadrupole resonance studies.^{25,60,102–109}

It is pertinent to note that the calculation of properties of an N -electron system benefits from the study of $N - 1$ or $N + 1$ electron systems, when N is a closed shell and $N - 1$ or $N + 1$ is the system of interest. For example, in the case of the halogens (X), whose electronic configuration is ns^2np^5 , it is convenient to start with the closed shell configuration ns^2np^6 (X^-) and remove an electron ($N - 1$) to arrive at the neutral configuration. This procedure is simple and computationally convenient though the orbitals used in this procedure are either more contracted (for $N + 1$ case) or diffused (for $N - 1$ case) than the neutral one. An advantage of such a scheme is that the wave function for the target state with one fewer or one more electron is a pure spin state when a closed-shell state is chosen as reference. Although the direct approach is more appealing from a computational standpoint and from the aspect of the orbitals, its implementation for arbitrary open-shell is nontrivial.

The organization of the paper is as follows: in section II the CCLRT method has been delineated in brief along with computational details. The results calculated via the state-of-art relativistic calculations are presented and compared with other methods in the subsequent section, section III. Finally, summarizing remarks have been assembled in section IV.

II. COUPLED CLUSTER LINEAR RESPONSE THEORY (CCLRT): A BRIEF RESUMÉ

The method has been described in detail elsewhere [see refs 67–76], and only a brief outline is given here. A major theoretical advantage of the CCLRT (and EOM-CC) method lies in the representation of the excited state in terms of the ground state. As a result, this description automatically incorporates the components of the correlation contribution from the ground state that remains more or less unvaried and which largely prevails in the low lying excited or ionized state(s) correlation. The differential correlations and the additional correlations concomitant with ionization or excitation can then be included in a systematic manner in the linear response function which endows it with flexibility to include the differential correlation and additional correlation effects on top of the ground state correlation components. The common correlation terms then drop out in the energy differences. Consequently, the CCLRT (and EOM-CC) method provides a description of the ionization or excitation energies in a more balanced and accurate manner than the traditional methods.

In CCLRT/EOM-CC method, energy differences with respect to the initial state are computed directly by diagonalizing the similarity transformed Hamiltonian \mathcal{H} ,

$$\begin{aligned}\mathcal{H} &= \exp(-T)H\exp(T) \\ &= H + [H, T] + \frac{1}{2}[[H, T], T] + \dots\end{aligned}\quad (2)$$

where H is the bare electron Hamiltonian and T is the cluster operator that defines the single reference ground state wave function and its energy (E_{ref}) via the coupled cluster ansatz

$$|\Psi_0\rangle = \exp(T)|\Phi_0\rangle \quad (3)$$

and

$$E_{\text{ref}} = \langle \Phi_0 | \mathcal{H} | \Phi_0 \rangle \quad (4)$$

in which $|\Phi_0\rangle$ is the single reference unperturbed ground/reference state wave function. The cluster operators T appearing in eqs 2 and 3 are given by

$$T = \sum_n T_n = \sum_{p,\alpha} t_{\alpha p}^p a_p^\dagger a_\alpha + \frac{1}{4} \sum_{p,q,\alpha,\beta} t_{\alpha\beta}^{pq} a_p^\dagger a_\alpha^\dagger a_q a_\beta + \dots \quad (5)$$

Conceptually, CCLRT (and EOM-CC) is very similar to configuration interaction (CI). When \mathcal{H} is diagonalized in the complete many-electron basis, CCLRT (and EOM-CC) is identical to the full CI (FCI). However, in the more practical situation of a truncated basis, the CCLRT (and EOM-CC) model is numerically better in comparison with the corresponding truncated CI one because correlation effects are “folded in” in the transformed Hamiltonian. The simpler structure of the formalism also facilitates implementation of analytic gradients and properties calculations.^{75,96–99} The CI-like form of the CCLRT (and EOM-CC) excitation/ionization operator enables access to multiconfigurational open-shell wave functions, exactly and nearly degenerate states, as well as interacting states of different character.⁹³ In that sense, the CCLRT (and also EOM-CC) can be viewed as a multistate approach; that is, multiple electronic states are obtained in a single calculation and are described on the same footing.

The similarity transformed Hamiltonian \mathcal{H} appearing in eq 2 is non-Hermitian as the cluster wave operator $\exp(T)$ is not unitary. Therefore, the target states are represented by a biorthogonal set of bra and ket functions parametrized by T , where the left and right eigenfunctions for the k th state satisfy

$$\langle \tilde{\Psi}_k | = \langle \Phi_0 | \mathcal{L}_k \exp(-T) \quad (6)$$

$$\langle \Phi_0 | \mathcal{L}_k \mathcal{H} = \langle \Phi_0 | \mathcal{L}_k \Delta E_k \quad (7)$$

and

$$|\Psi_k\rangle = \mathcal{R}_k \exp(T) |\Phi_0\rangle \quad (8)$$

$$\mathcal{H} \mathcal{R}_k |\Phi_0\rangle = \Delta E_k \mathcal{R}_k |\Phi_0\rangle \quad (9)$$

respectively. Thus, the CCLRT/EOM-CC equation for the k th state energy can be expressed in a functional form as

$$\Delta E_k = \langle \Phi_0 | \mathcal{L}_k \mathcal{H} \mathcal{R}_k | \Phi_0 \rangle \quad (10)$$

It is worth mentioning that the excitation level in T , \mathcal{L} , and \mathcal{R} defines a particular CCLRT (and EOM-CC) model and determines its accuracy in conjunction with computational cost. The excitation and de-excitation operators \mathcal{R} and \mathcal{L} are completely specified in the second quantization by a set of amplitudes and hole–particle creation-annihilation operators, which for ionization process (i.e., CCLRT-IP/EOMCC-IP) are given by

$$\mathcal{R} = \sum_n \mathcal{R}_n = \sum_\alpha \tau_\alpha a_\alpha + \frac{1}{2} \sum_{p,\alpha,\beta} \tau_{\beta\alpha}^p a_p^\dagger a_\beta a_\alpha + \dots \quad (11)$$

and

$$\mathcal{L} = \sum_n \mathcal{L}_n = \sum_\alpha l_\alpha^\dagger a_\alpha^\dagger + \frac{1}{2} \sum_{p,\alpha,\beta} l_p^{\beta\alpha} a_p^\dagger a_\beta a_\alpha^\dagger + \dots \quad (12)$$

respectively. In this way, all of FS (the space with any number of electrons) is accessible to the CCLRT equations, which amount to just a non-Hermitian matrix diagonalization. The eigenspectrum resulting from the untruncated diagonalization space is exact. Apart from the basis set approximation, to this point, this is an exact formalism and gives the same results (and costs as much) as FCI. Of course, for practical applications, truncation must be introduced to limit the size of T and the dimension of the diagonalization space (i.e., \mathcal{L} and \mathcal{R}). Therefore, an approximate CCLRT (and EOM-CC) method is characterized by two parameters: the orders of T and \mathcal{L} , and or \mathcal{R} . The most practical realization for ground state and excited/ionized state CC is the singles and double (SD) excitations (CCSD). In this work, T , \mathcal{L} and \mathcal{R} are truncated at the two-hole-two-particle (2h-2p), two-hole-one-particle (2h-1p), and two-hole-one-particle (2h-1p) levels, respectively. In other words, the expansions of T , \mathcal{L} , and \mathcal{R} in eqs 5, 11, and 12 are truncated at $n = 2$.

Once the left and right eigenvectors are known, the one-electron properties can be computed via the following relation

$$\langle \Psi_k | O | \Psi_l \rangle = \sum_{i,j} \rho_j^i O_i^j \quad (13)$$

in which O_p^q is the one-electron matrix element for the property of interest and

$$\rho_j^i = \langle \Phi_0 | \mathcal{L}_k \exp(-T) a_i^\dagger a_j \exp(T) \mathcal{R}_l | \Phi_0 \rangle \quad (14)$$

Following the Einstein summation convention, the one-particle density matrix elements in spin-orbital basis for hole-hole, particle-particle, hole-particle, and particle-hole blocks can be written as

$$\rho_\alpha^\beta = -l_\alpha^\alpha \tau_\beta - l_p^{\gamma\alpha} \tau_{\gamma\beta}^p - l_p^{\alpha\gamma} \tau_{\gamma\beta}^p$$

$$\rho_q^p = \frac{1}{2} l_q^{\gamma\beta} \tau_{\beta\gamma}^p + l_q^{\gamma\beta} \tau_{\gamma}^p t_\beta^p$$

$$\rho_p^\alpha = l_p^{\alpha\beta} \tau_\beta$$

and

$$\begin{aligned} \rho_\alpha^p &= l_\alpha^\beta \tau_{\alpha\beta}^p - l_\alpha^\beta \tau_\alpha t_\beta^p + l^{\beta\gamma} \tau_{\gamma}^p t_{\alpha\beta}^p - l^{\beta\gamma} \tau_{\gamma}^p t_\beta^p t_\alpha^q - \frac{1}{2} l_q^{\beta\gamma} \tau_\alpha t_{\beta\gamma}^{qp} \\ &+ t_\alpha^p - \frac{1}{2} l_q^{\beta\gamma} \tau_{\gamma}^p t_{\beta\alpha}^q - l_q^{\beta\gamma} \tau_{\beta\alpha}^q t_\gamma^p \end{aligned}$$

respectively. It is evident from the above expressions of ρ that these single-particle reduced matrix elements are non-Hermitian.

The computation of transition energies and one-electron properties via CCLRT (and/or EOM-CC) begins with the computation of one- and two-electron integrals in the atomic orbital (AO) basis. These AO integrals are subsequently used to construct the zeroth-order ground state Slater determinant ($|\Phi_0\rangle$) by solving the self-consistent field equations. The AO integrals are then transformed to the molecular orbital (MO).

The coupled cluster equations for the ground state are next solved to determine the cluster amplitudes t and the ground/reference state energy E_{ref} . The one- and two-body integrals of the similarity transformed Hamiltonian \mathcal{H} is constructed to compute the excited/ionized state energies. In a CCLRT or EOM-CC calculation, excited/ionized states are mutually biorthogonal. The left and right eigenvectors of \mathcal{H} (\mathcal{L} and \mathcal{R}) are computed for the desired root. The one-particle reduced density matrix elements ρ are subsequently evaluated to compute the property under study.

Equations 6–14 provide a complete description of the CCLRT theory for the ionization process. The steps involved in the computation of transition energies and related properties via CCLRT for electron attached and excited states (CCLRT-EA and CCLRT-EE) are essentially same as those of CCLRT-IP procedure. On the other hand, the property calculation via analytic gradient at the FS-MRCC level involves the computation of (a) cluster amplitudes t for ground/reference state, (b) cluster amplitudes s for excited/ionized state, (c) externally perturbed cluster amplitudes \tilde{s} for the excited/ionized state, and (d) externally perturbed cluster cluster amplitudes \tilde{t} for ground/reference state. Again, from the operational point of view, the CCLRT theory is the more viable and user-friendly alternative over the FS-MRCC method.

In passing, we reiterate that although the FS-MRCC theory is size-extensive with respect to core-core, core-valence, and valence-valence interactions, the CCLRT (and also EOM-CC) energy is size-extensive with respect to core-core and core-valence interactions. As a result of this, unlike FS-MRCC, CCLRT (and also EOMCC) fails in size-extensivity for charge-transfer excitations owing to the linear ansatz in CCLRT (and EOM-CC).^{87,88} Other troubles can occur in practical applications of the conventional FS-MRCC method, and they emerge from the so-called intruder states and multiplicity of the solutions^{110,111} that invites numerical divergence during the calculation of the properties. These are often so severe that they frequently prohibit obtaining any solution of the FS-MRCC equations. The accuracy as well as convergence of the method rely significantly on the partitioning of the function space into the model space and the virtual space. To improve the convergence behavior of the FS-MRCC method, various methodologies have been developed and implemented.^{112–117} Unlike FS-MRCC, being an eigenvalue equation, CCLRT (and EOM-CC) does not suffer from convergence problem. Another important issue in favor of the CCLRT (and EOM-CC) method is that unlike the FS-MRCC, the CCLRT is a straightforward scheme as it does not require the knowledge of the other valence sector cluster amplitudes except the 0-hole-0-particle valence sector (i.e., reference/ground state amplitudes of cluster operator T). It has long been known that although the FS-MRCC approach is derived from quite different assumptions than the CCLRT (and EOM-CC) method, the principal IPs and EAs obtained by CCLRT (and EOM-CC) and FS-MRCC are precisely the same.^{77,78} The detailed interconnection between the two approaches has been discerned.^{87,88} The sector-wise partitioning of the FS and the structural regimentation of the cluster operators and equations are noteworthy features, as has already been known. Evaluation of IPs and EAs calls for the solutions associated with the ground state, or the (0, 0) sector, and in this regard, one can suitably bypass the problems associated to the effective Hamiltonian or the Bloch equation approach by recognizing the fact that the equations that are being solved for the one-

valence sector are linear in the unknown S amplitudes [with the (0, 0) sector being the only exception]. At this juncture it is worth mentioning that the principal idea of the FS-MRCC approach is to solve the eigenvalue equation for the effective Hamiltonian operator to obtain only a few eigenvalues out of the whole spectrum to avoid the diagonalization of the Hamiltonian operator in the large configurational space. Therefore, one may trace out an alternative route to formulate the eigenvalue problem for the linear case by invoking the method of direct diagonalization of the appropriately formed Hamiltonian matrix. This enjoys a dual benefit by directly yielding the CCLRT (or the EOM-CC) method and simultaneously provides the identical eigenvalues for the main IPs and EAs as the one-valence segment of the FS. Thus, one achieves an easy handle to substitute the computationally expensive iterative solution of the Bloch equation by a direct diagonalization procedure by intuitively formulating the FS-MRCC methods in the one-valence sector. Unfortunately, the CCLRT (and EOM-CC) with SD scheme performance deteriorates for electronic states with large contributions of double excitations as, for example, some valence states of radicals. Moreover, the CCLRT (or EOM-CC) accuracy degrades when the reference wave function is spin-contaminated. We conclude this discussion by stating that because both FS-MRCC and CCLRT have their inherent benefits and limitations, the choice of the method should stem out from the nature of the problem that one deals with.

III. RESULTS AND DISCUSSION

In this work, the closed-shell negative ions of the halogen atoms are exploited as reference states. The Dirac–Hartree–Fock functions are first obtained in the framework of the four-component Dirac–Coulomb Hamiltonian:

$$H = \sum_i h_D(i) + \sum_{i<j} e^2/r_{ij} \quad (15)$$

where h_D is the one-electron Dirac Hamiltonian. Here, the nuclei are described by the Fermi nucleus model to capture the effect arising from finite-size nuclear correction.

The calculations for Cl atom have been carried out with uncontracted universal Gaussian basis set,¹¹⁸ whereas a well-tempered basis set¹¹⁹ has been used for bromine and iodine atoms. The EFGs of Cl, Br, and I atoms are computed with a minimum (maximum) basis set of 21s16p13d7f (23s17p14d8f3g2h), 26s22p16d10f (26s23p17d12f10g4h2i), and 28s23p21d10f8g (28s24p22d12f10g4h2i), respectively. Here, it is worth noting that accurate calculation of EFGs requires large basis sets to describe the core and valence polarization. The computations have been performed with increasing s, p, d, f, g, and h to access the contribution and convergence behavior of EFG. Though all the core orbitals are kept active in the post Dirac–Fock calculations, virtual orbitals with single particle orbital energies greater than 450.00 au for s, p and 130 au for d, f, g, h, i are discarded in the CC calculations as their contributions are negligible.

The first ab initio study on the NQM of ^{35,37}Cl was carried out by Sundholm and Olsen¹⁰² at the multiconfiguration Hartree–Fock (MCHF) theory, who predicted the NQM of ³⁵Cl to be −81.65 mb.¹⁰² Alonso et al.¹⁰³ obtained a value of −85.5(1.1) mb from the ab initio full-potential linear-augmented plane-wave method. Their solid state-based value for ³⁵Cl was later revised to −85.0(1.1) mb.⁹ The calculated

$Q(^{35}\text{Cl})$ due to Kellö and Sadleir¹⁰⁵ is −81.6 mb. In their calculation, the electron correlation contribution has been taken into account at the level of the CCSD(T) theory with four component relativistic spinors. A full blown relativistic Fock-space MRCC calculation on the NQM of ³⁵Cl was later carried out by Yakobi et al.,²⁵ who employed the finite field approach to compute the EFG at the ³⁵Cl nucleus. Their best estimated $Q(^{35}\text{Cl})$ after incorporating the Gaunt corrections (main part of the Breit interaction) is −81.1 (1.2) mb. This value is accepted as the new standard value for $Q(^{35}\text{Cl})$.⁹ Therefore, atomic $Q(^{35}\text{Cl})$ value due to Sundholm and Olsen¹⁰² has been further validated by the atomic calculations of Yakobi et al.²⁵ Recently, Carette et al.¹²⁰ reexamined these two systems using the multireference configuration interaction (MRCI) method with nonrelativistic spinors in which the relativistic corrections were incorporated via Pauli approximation. With this scheme, they obtained a value of −81.764 mb for the NQM of ³⁵Cl. On the other hand, the FS-MRCC yields a value of −79.5 mb for this system, in which the EFG at the ³⁵Cl nucleus was determined via expectation value approach.¹²¹ It is worth mentioning that for nonvariational ab initio methods, the energy gradient and the expectation value of the Hamiltonian response are not identical because the gradient additionally contains “relaxation” terms accounting for the response of the nonvariational wave function parameters. In particular, for CC-based methods, the gradient scheme for property calculations is generally more preferable than the expectation value scheme because the latter approach does not have a simple natural truncation.

The EFG and NQM values of Cl obtained from CCLRT-IP method have been compared with previously published data in Table 1. From the table it is found that our new $Q(^{35}\text{Cl})$ value,

Table 1. Calculated Electric Field Gradient (q) and Nuclear Quadrupole Moment (Q) of the ³⁵Cl Atom for Different Basis Sets along with Other Previously Published Results

method		q (au)	Q (mb)
present work	21s16p13d7f2g	2.86799	−81.43
	22s17p13d7f2g	2.86799	−81.43
	23s17p14d8f3g	2.89636	−81.12
	23s17p14d8f3g2h	2.87873	−81.12
Sundholm et al. ¹⁰²			−81.65(80)
Kellö et al. ¹⁰⁵			−81.6
Haas et al. ¹⁰⁶			−81.9(11)
Alonso et al. ¹⁰⁴			−85.0(11)
Yakobi et al. ²⁵			−81.1(1.2)
Carette et al. ¹²⁰			−81.76
Das et al. ⁶⁰			−79.5

−81.12 mb, is quantitatively supported by the very accurate value of −81.1(1.2) mb by Yakobi et al.²⁵ It is worth stressing here, the Gaunt contribution in the case of $Q(^{35}\text{Cl})$ has been found to be −0.13 mb.²⁵ The very close agreement between CCLRT and FS-MRCC (with Breit contribution) results is highly encouraging as (a) the biorthogonal scheme does not suffer from truncation error and (b) FS-MRCC is formally equivalent to CCLRT/EOMCC-IP for the one-valence problem. The NQM and EFG displayed in Table 1 show that the NQM value remains the same (−81.43 mb) for 21s16p13d7f2g to 22s17p13d7f2g and −81.12 mb for 23s17p14d8f3g to 23s17p14d8f3g2h basis sets. Our calculations further show that the inclusion of an additional d, f, and g functions to 22s17p13d7f2g increases (decreases) the NQM

(EFG) by 0.3 mb (0.02 au). It is also evident from Table 1 that the addition of an s function to 21s17p13d7f2g basis and an h function to 23s17p14d8f3g barely changes the NQM and EFG values.

A lot of work has been reported in the literature concerning the nuclear quadrupole moments for ^{79}Br [Table 1 in ref 109 gives an overview on the values available in the literature and illustrates their spread around 300 mb]. Table 2 summarizes

Table 2. Comparison of CCLRT Calculated Electric Field Gradient (q) and Nuclear Quadrupole Moment (Q) of ^{79}Br Atom for Different Basis Sets along with Other Previously Published Results

method		q (au)	Q (mb)
present work	26s22p16d10f	5.22873	313.23
	26s22p16d10f8g	5.27700	310.40
	26s22p16d10f8g2h	5.31049	308.44
	26s23p17d11f8g2h	5.31062	308.44
	26s23p17d11f9g3h	5.31329	308.28
	26s23p17d12f10g4h2i	5.31844	307.98
Kellö et al. ¹⁰⁵			298.9
Haas et al. ¹⁰⁶			305(5)
Bierón et al. ¹⁰⁷			313(3)
Alonso et al. ¹⁰⁴			318(5)
Yakobi et al. ²⁵			302(5)
Pyykkö ⁹			313(3)
Stopkowicz et al. ¹⁰⁹			308.7(20)

our computational results for ^{79}Br which demonstrates the importance of the extent of electron-correlation effects in conjunction with size of basis sets used. Bierón et al.¹⁰⁷ have reported the present best value of 313(3) mb for the ^{79}Br nuclide.⁸ An experimentally obtained quadrupole coupling of $-384.878(8)$ MHz for the ^{79}Br atom along with the values for the EFG from numerical MCSCF calculations suitably complemented by relativistic and Breit corrections contribute to this value. A slightly different value of 302(5) mb has been reported by Yakobi et al.²⁵ from a four-component FS-MRCC calculation within the SD approximation scheme. Considering recent investigations as the most reliable, the values reported for the ^{79}Br quadrupole moment vary from 293 to 331 mb, thus leading to a remaining uncertainty of about 10% or even more. This uncertainty in the values of bromine quadrupole moment generates serious differences in the predicted values of the bromine quadrupole coupling constants, because the calculation of the later is intricately dependent upon the values of the former. As that of Yakobi et al.,²⁵ just recent calculations due to Stopkowicz et al.¹⁰⁹ also suggest that the long-time recommended tabular values should be adjusted downward.⁸

Stopkowicz et al.¹⁰⁹ have very recently reported a value of 308.7(20) mb for the bromine quadrupole moment based on the analysis of the experimental NQCC for the bromine atom and the HBr molecule and high-accuracy calculations for the corresponding EFGs. Use of the higher order CC corrections to treat electron correlation, coupled with the implementation of large atomic orbital basis sets and a balanced accounting of the relativistic effects together leads to a betterment of the calculated values. Alonso et al.¹⁰³ produced a less accurate value of 330 mb. Their solid state based value for Br was later modified. The revised value of Alonso et al.¹⁰⁴ is 318 mb which is far from the reference value of 313(3) mb due to Pyykkö.¹⁰⁷ Kellö and Sadlej¹⁰⁵ performed a reanalysis of the previous

atomic data (304.5 mb) for $Q(^{79}\text{Br})$. The reanalyzed Q value for bromine of 298.9 mb deviates remarkably from the reference value of 313(3) mb.¹⁰⁷ The NQM reported by Haas and Petrilli¹⁰⁶ for ^{79}Br is 305 mb and is found to be reasonably close to our present estimates as well as with the new “atomic” value of 302(5) mb by Yakobi et al.²⁵ The four-component Dirac–Coulomb Hamiltonian serves as the framework, all electrons correlated by the FS-MRCCSD in addition with the Gaunt term (main part of the Breit interaction) have been included in the calculations of Yakobi et al.²⁵ According to their calculations, the Gaunt correction is 1.7 mb. In this context, we should mention that Haas and Petrilli have reanalyzed the Q value for bromine and found it to be 308.7 mb,¹⁰⁷ which is remarkably close to ours. The biorthogonal procedure with smallest 26s22p16d10f and largest 26s23p17d12f10g4h2i uncontracted well-tempered basis yield the EFG (NQM) value of the ^{79}Br atom to be 5.22873 au (313.23 mb) and 5.31844 au (307.98 mb), respectively (Table 2). The NQM determined by our present calculation with 26s23p17d12f10g4h2i basis departs by 7 mb from the numerical gradient based FS-MRCCSD estimate of 300 mb²⁵ (without Gaunt corrections). The NQM values reported in Table 2 show that the inclusion of additional p, d, f, g, and h functions to 26s22p16d10f8g basis set increases the Q value by 2 mb. It further shows that the effect of i orbital to Q and q is negligibly small. A comparison with the values for the bromine quadrupole moment given earlier in the literature shows that the value given by Bierón et al. is about 5 mb larger, whereas the one by Yakobi et al.²⁵ is by about 6 mb smaller than our present value. Here, we should mention that the average deviation of our Q value for ^{79}Br with respect to very currently published revised values obtained via high-level CC calculations including an adequate treatment of scalar-relativistic effects by Stopkowicz et al.¹⁰⁹ is around 0.7 mb, indicating the accuracy of our revised Q value for ^{79}Br . As our present value deviates from the one given in recent compilations of nuclear quadrupole moments by Pyykkö,⁹ we seek a revision by replacing the current reference value of 313(3) mb by the one computed in the present work in conjunction with the new value for the bromine quadrupole moment due to Stopkowicz et al.¹⁰⁹

The rather large quadrupole moment and its monoisotopic nature would make ^{127}I a good candidate for a direct measurement of the nuclear quadrupole moment by the muonic or pionic X-ray methods. The previous standard value for $Q(^{127}\text{I})$ was considered to be $-710(10)$ mb.¹⁰⁷ It was subsequently revised to $-696(12)$ mb by van Stralen and Visscher¹⁰⁸ and $-680(10)$ mb by Yakobi et al.²⁵ This huge deviation in Q value (-722 mb of Alonso et al.¹⁰⁴ to $-680(10)$ of Yakobi et al.²⁵) mainly arises due to the methodology and basis sets used in the computation of EFG. Although the two values are within each other's error limits, the method and basis used by Yakobi et al. in their calculation of EFG is certainly more sophisticated than those used by Alonso et al.,¹⁰⁴ and hence, their reported value is considered to be more accurate. In ref 107, Pyykkö stated that the atomic value of Yakobi et al.²⁵ would be further lower. In this present work, the EFG calculations at the ^{127}I nucleus are performed with 28s24p21d10f8g2h, 28s24p22d11f8g2h, 28s24p22d11f9g3h, and 28s24p22d12f10g4h2i well-tempered Gaussian basis sets. The EFGs resulting from the CCLRT-IP calculations when combined with the NQCC of ^{127}I yield the $Q(^{127}\text{I})$ to be -699.88 and -688.22 mb for the 28s24p21d10f8g2h and 28s24p22d12f10g4h2i basis sets, respectively (Table 3). These

Table 3. Calculated Electric Field Gradient (q) and Nuclear Quadrupole Moment (Q) of the ^{127}I Atom for Different Basis Sets along with Other Previously Published Results

method		q (au)	Q (mb)
present work	28s24p22d10f8g2h	6.97095	−699.88
	28s24p22d11f8g2h	7.05485	−691.56
	28s24p22d11f9g3h	7.06147	−690.91
	28s24p22d12f10g4h2i	7.08904	−688.22
Pyykkö ⁹			−696(12)
Haas et al. ¹⁰⁶			−689(15)
Bierón et al. ¹⁰⁷			−710(10)
van Stralen et al. ¹⁰⁸			−696(12)
Alonso et al. ¹⁰⁴			−722(21)
Yakobi et al. ²⁵			−680(10)

values may be compared with the current reference values¹⁰⁷ of ^{127}I . In our present calculation, a somewhat larger difference appears in ^{127}I , which is ~ 22 mb lower than the reference value.¹⁰⁷ It is worth noting that the Gaunt correction contributes about 5 mb²⁵ toward $Q(^{127}\text{I})$. The NQM value of ^{127}I obtained via relativistic FS-MRCCSD calculation without Breit interaction due to Yakobi et al.²⁵ is 675.8 mb. It is found that adding the Gaunt corrections gives a NQM of 680.2 mb for ^{127}I , which is 30 mb lower than the reference value. Molecular calculations due to van Stralen and Visscher¹⁰⁸ also demonstrates a qualitatively similar trend of deviation. From the present works, it is suggested that the generally accepted value for the $Q(^{127}\text{I})$ should be slightly corrected. One envisages the fact that a judicious accounting of the relativistic and electron correlation effects in conjunction with appropriate large basis yields higher EFG values and, as a consequence, lower values of the quadrupole moments. We experience this trend in our present work, where we observe that improved basis sets, more electrons correlated, and the implementation of more virtual orbitals lead to lower values of Q .

The spread of the NQMs for atomic halogens (Tables 1–3) calculated from the corresponding NQCCs gives an indication of the quality of the theoretical method used to compute the required EFGs, and it is interesting to see how well different quantum chemical methods perform to provide NQMs. Systematic studies of basis set convergence of the EFG on halogen nucleus show that use of a sufficiently large all-electron basis set is mandatory. Electron correlation is as crucial as relativity in the calculation of EFGs. The results and analysis presented above clearly illustrate that state-of-the-art calculations of EFGs at nuclei can provide high quality data for the nuclear quadrupole moment which is confirmed by their close agreement with the currently accepted reference values, indicating the applicability and usefulness of our recently developed relativistic CCLRT code. Our results along with the values reported by recent calculations^{25,109} might suggest that the current recommended standard data for the NQMs of ^{35}Cl , ^{79}Br , and ^{127}I nuclei need to be reconsidered and updated. However, we point out that the NQM values derived here has more room for further modification through the incorporation of full-blown nonperturbative triples along with the Breit term, which will be computationally demanding. One may hope that future fully relativistic all-electron CC calculations will give us more accurate NQMs of the halogen atoms considered here.

To prove the usefulness of the present code, we have also carried out the computation of the EAs for Cl, Br, and I, which help to illustrate the accuracy of the calculations for NQMs.

The EA of X (X = Cl, Br, and I) is the negative of the ionization potential of X^- , and this is a byproduct of the CCLRT-IP method. We have presented the EAs to demonstrate the accuracy of the CCLRT-IP method. Note that there is no experimental value of NQM to compare. EA is an important atomic property for the estimation of the reactivity of an element. The knowledge of EA helps in calculating its chemical potential or electronegativity, which are guiding values for chemists for chemical identification. Electron affinities have traditionally been regarded as one of the hardest atomic or molecular properties to reproduce in an ab initio quantum mechanical calculation. EAs involve a change in the number of valence electrons correlated in the system in conjunction with a pronounced change in the spatial extent of the wave function (and hence very demanding in terms of the basis set as well). Therefore, to get accurate computation of EAs, the theory needs to describe both dynamical and nondynamical correlation effects accurately, which are of the same order of magnitude as EA itself. The calculated electron affinities (which in this case are determined by removing an electron from the closed negative ion via CCLRT-IP) of Cl, Br, and I have been assembled and compared with experimental values¹²² in Table 4. For convenience, we report the EAs from the largest basis set

Table 4. Electron Affinities (kJ/mol) at the CCLRT Level for Chlorine, Bromine, and Iodine Atoms with 23s17p14d8f3g2h, 26s23p17d12f10g4h2i, and 28s24p22d12f10g4h2i Basis Sets along with Previously Published Theoretical and Experimental Estimates^a

atom	electron affinity		
	CCLRT-IP	MCDF ¹²³	experiment ¹²²
Cl	352.4 (3.65)	317.92 (3.30)	349.0 (3.61)
Br	334.0 (3.46)	295.73 (3.06)	324.6 (3.36)
I	305.9 (3.17)	269.58 (2.79)	295.2 (3.06)

^aThe entries in parentheses indicate the results in electronvolts.

calculations. We further emphasize that the electron affinities converge faster than the EFGs. The computed EA results are compared with the available values in the literature¹²³ and experimental estimates.¹²² CC theory nowadays is the preferred choice, but the MCDF treatment of Chang et al. might be competitive as long as the active space is chosen large enough. Experimental EAs of group XVII support the trend appearing in Table 4. The EAs obtained at the CCLRT level are in excellent agreement with experimental data.¹²² Comparing the calculated results and available experimental data,¹²² one can find that the discrepancies are 3.0 kJ/mol (0.04 eV), 9.4 kJ/mol (0.10 eV), and 10.7 kJ/mol (0.11 eV) for Cl, Br, and I, respectively. As the CCLRT-IP reproduces the electron affinities with a maximum deviation of 10.7 kJ/mol or 0.11 eV (3%), we have reason to believe that the NQM values reported here should be reliable. The gap between the computed and reference values can be removed or at least reduced by incorporating higher order electron correlation in the calculations and we intend to look into this matter further in a later work. They can also be reduced by the inclusion of Breit interaction in our calculations. In passing, we mention that Hughes and Kaldor¹²⁴ employed the FS-MRCCSD theory for the evaluation of electron affinities of halogen atoms. They incorporated valence and core correlations in addition to the relativistic effects and found an average error of 3.9 kJ/mol (0.05 eV) in the EA values of Cl, Br, and I, which can be qualified as highly accurate. We should

mentioned that the EAs emerging as byproduct of our CCLRT calculations complemented with relativistic effect are in good agreement with experimental data provided an adequate basis set is used.

The spread of the NQMs for atomic halogens [such as ^{35}Cl , ^{79}Br , and ^{127}I] as reported in the literature indicate that the values should be checked by highly correlated ab initio relativistic calculations. This is the focus of our present work. Here, we do not claim that CCLRT with four-component spinors in the frame of analytical gradient scheme is a superior method for general use; rather, it is a powerful and flexible electronic structure tool capable of accurate estimation of EFG, electron affinity (EA), and other properties of spectroscopic interest without facing any numerical divergence problem. Very close agreement of our results with the estimation of relativistic FS-MRCC suggest the smaller NQMs for ^{35}Cl , ^{79}Br , and ^{127}I than those given in ref 8. Finally, we conclude that, although accurate, the relativistic CCLRT method used here cannot be routinely applied to very large chemical systems. However, its usefulness and reliability in the description of the excited/ionized states of spectroscopic interest of small relativistic system opens an important field of possible applications, especially as these states are more difficult to access experimentally. The values computed here may be used to calculate revised numbers for all other isotopes of the halogens by simply multiplying the experimentally determined ratios of the quadrupole coupling constant values.

IV. SUMMARY AND CONCLUSION

A lot of computational work has been reported in the literature of electronic structure theory regarding the nuclear quadrupole moments (denoted in the present paper as Q) of the halogens the reliability of which depends on two factors, namely, the reliability and accuracy of both the used experimental quadrupole coupling constants and the theoretical electric field gradient (EFG) values. Although the high accuracy of quadrupole coupling constants is usually ensured by starting from atomic data, an accurate computation of EFGs is challenging.

EFGs at the nuclei of halogen atoms [^{35}Cl , ^{79}Br , and ^{127}I] are calculated using an analytical gradient approach. For investigations of the quadrupole interaction (results from the coupling between nuclear electric quadrupole moment and the EFG at the nuclear site) the halogen nuclei (Cl, Br, and I) are particularly well suited. They are the prime objects of nuclear quadrupole resonance studies. A very abundant data material is therefore available in the literature. The coupled cluster linear response theory (CCLRT) for the ionized states (defined as CCLRT-IP) with the four-component Dirac–Coulomb Hamiltonian in conjunction with very large basis sets [e.g., 28s24p22d12f10g4h2i Gaussian-type functions for I] serve as the computational method. Response theory provides equations defining spectroscopic observable quantities. CCLRT is a reliable, robust, and accurate method, and it is relatively cost-effective. In our computation, the Breit interaction is excluded. If all the leading target configurations originate from single excitations from the reference, one can invoke the CCLRT method to describe a plethora of multiconfiguration wave functions and encompass both the dynamical and non-dynamical correlation effects through a single computational step. In CCLRT, all advantages of the CC description of the corresponding reference state are kept and hence it has evolved to be the method of choice for the treatment of properties of

spectroscopically interest within the CC framework as it provides equations defining spectroscopic observable quantities.

On the basis of the experimental nuclear quadrupole coupling constants in connection with the computed EFGs, we have estimated the nuclear quadrupole moments (NQM) of ^{35}Cl , ^{79}Br , and ^{127}I that are in good agreement (both the magnitudes and trends) with current generation estimates. Therefore, theory for analytic energy derivatives of electronic states described by the CCLRT method has been generalized to estimate the NQMs and hence we have extended the applicability spectrum of the CCLRT method. Our recommended value for the NQMs (in mb) of ^{35}Cl , ^{79}Br , and ^{127}I are -81.12 , $+307.98$, and -688.22 , respectively. The accuracy of our derived NQMs has been confirmed by their close agreement (differ by $\sim 1\text{--}2\%$) with the current generation reference values [$^{35}\text{Cl} = -81.1(1.2)$, $^{79}\text{Br} = 302(5)$, and $^{127}\text{I} = -680(10)$ mb, respectively] obtained by four component Dirac–Coulomb Fock-space multireference coupled cluster calculations with the main part of the Breit interaction in combination with the very large basis sets due to Kaldor and co-workers. The present study also confirms the reliability of analytical gradient scheme within the frame of the CCLRT method. At this juncture, we should mention that the finite field approach has been used by Kaldor and co-workers to calculate the EFGs at the Cl, Br, and I nuclei. There is a general consensus that the analytic technique is more efficient and more precise than the numeric differentiation or finite field one. Although it is comprehensible that the energy landscape can be scrutinized through numerical differentiation approach, it is quite inefficient and only applicable for small systems owing to the computational cost. In conjunction with recent computations,^{25,109} present NQMs for ^{35}Cl , ^{79}Br , and ^{127}I nuclei indicate that the previous standard values [$^{35}\text{Cl} = -81.65(80)$, $^{79}\text{Br} = 313(3)$, and $^{127}\text{I} = -710(10)$ mb] may be revised. Therefore, the present results call for additional full-blown relativistic all-electron correlated investigations.

In the present paper, we also reported EAs of atomic halogens obtained as a byproduct of calculation. It is worth stressing that accurate calculation of EA has posed a significant challenge for CC approaches. The trend of our estimated EAs is in accord with the overall behavior of the group 17 elements. The EAs of elements in the group, shown in Table 4, go down monotonically. The converged exhaustive computations for elements and the very good agreement of our computed EAs of Cl, Br, and I with experiment bolster our belief that our estimated NQMs are quite reliable. Although the numerical performance of our analytical gradient scheme in the frame of relativistic CCLRT method for the systems studied by us is encouraging, further studies for systems with arbitrary complexity are called for. More extensive applications of our newly developed relativistic CCLRT code are under way and will be reported in our forthcoming publications.

The calculations done for smaller systems demonstrate that our newly developed code is capable of reproducing experimental (whenever available) and state-of-the-art current generation theoretical reference data with high accuracy provided a basis set of adequate size is used. Finally, high level theoretical implementation presented here can be used to reveal the relationship between the electronic structure and the measured nuclear quadrupole interaction by means of which one can interpret the experimental spectroscopic estimates.

■ AUTHOR INFORMATION

Corresponding Authors

*R. K. Chaudhuri: e-mail, rkchaudh@iiap.res.in.

*S. Chattopadhyay: e-mail, sudip_chattopadhyay@rediffmail.com.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work has been supported by DST (India) under Grant No. SR/S1/PC-61/2009. S.C. acknowledges the infrastructural facility created in his department through UGC-SAP program.

■ DEDICATION

We dedicate this paper to Professor Deb Shankar Ray (IACS, Kolkata) on the happy occasion of his reaching 60, in appreciation of his many seminal contributions to non-equilibrium Statistical Mechanics.

■ REFERENCES

- (1) Hirao, K.; Ishikawa, Y. *Recent Advances in Relativistic Molecular Theory*; World Scientific Publishing: Singapore, 2004.
- (2) Grant, I. P. *Relativistic quantum theory of atoms and molecules. Theory and computation*; Springer: New York, 2007.
- (3) Dyall, K. G.; Fægri, K. *Introduction to Relativistic Quantum Chemistry*; Oxford University Press: Oxford, U.K., 2007.
- (4) Peng, D.; Reiher, M. Exact Decoupling of the Relativistic Fock Operator. *Theor. Chem. Acc.* **2012**, *131*, 1081 (1–20).
- (5) Yamaguchi, Y.; Goddard, J. D.; Osamura, Y.; Schaefer, H. F. *New Dimension to Quantum Chemistry: Analytic Derivative Methods in Ab Initio Molecular Electronic Structure Theory*; Oxford University Press: Oxford, U.K., 1994.
- (6) Dyall, K. G.; Enevoldsen, T. Interfacing Relativistic and Nonrelativistic Methods. III. Atomic 4-Spinor Expansions and Integral Approximations. *J. Chem. Phys.* **1999**, *111*, 10000–10007.
- (7) Pyykkö, P. The Nuclear Quadrupole Moments of the 20 First Elements: High-precision Calculations on Atoms and Small Molecules. *Z. Naturforsch.* **1992**, *47a*, 189–196.
- (8) Pyykkö, P. Spectroscopic Nuclear Quadrupole Moments. *Mol. Phys.* **2001**, *99*, 1617–1629.
- (9) Pyykkö, P. Nuclear Quadrupole Moments. *Mol. Phys.* **2008**, *106*, 1965–1974 and references therein.
- (10) Kellö, V.; Sadlej, A. J. Nuclear Quadrupole Moments from Molecular Microwave Data: The Quadrupole Moment of ^{85}Rb and ^{87}Rb Nuclei and Survey of Molecular Data for Alkali-Metal Nuclei. *Phys. Rev. A* **1999**, *60*, 3575–3585.
- (11) Kellö, V.; Sadlej, A. J.; Pyykkö, P.; Sundholm, D.; Tokman, M. Electric Quadrupole Moment of the ^{27}Al Nucleus: Converging Results from the AlF and AlCl Molecules and the Al Atom. *Chem. Phys. Lett.* **1999**, *304*, 414–422.
- (12) Schwerdtfeger, P.; Pernpointner, M.; Nazarewicz, W. In *Calculation of NMR and EPR Parameters. Theory and Applications*; Kaupp, M.; Bühl, M.; Malkin, V. G., Eds.; Wiley-VCH: Weinheim, 2004; pp 279–291.
- (13) Kellö, V.; Sadlej, A. J.; Pyykkö, P. The Nuclear Quadrupole Moment of ^{45}Sc . *Chem. Phys. Lett.* **2000**, *329*, 112.
- (14) Belpassi, L.; Tarantelli, F.; Sgamellotti, A.; Quiney, H. M.; van Stralen, J. N. P.; Visscher, L. Nuclear Electric Quadrupole Moment of Gold. *J. Chem. Phys.* **2007**, *126*, 064314(1–7).
- (15) Pyykkö, P. Relativistic Effects in Chemistry: More Common Than You Thought. *Annu. Rev. Phys. Chem.* **2012**, *63*, 45–64.
- (16) Pyykkö, P. The Physics behind Chemistry and the Periodic Table. *Chem. Rev.* **2012**, *112*, 371–384.
- (17) Zou, W.; Filatov, M.; Cremer, D. Development, Implementation, and Application of an Analytic Second Derivative Formalism for the Normalized Elimination of the Small Component Method. *J. Chem. Theory Comput.* **2012**, *8*, 2617–2629.
- (18) Tu, Z.; Wang, F.; Li, X. Equation-of-Motion Coupled-Cluster Method for Ionized States with Spin-Orbit Coupling. *J. Chem. Phys.* **2012**, *136*, 174102(1–10).
- (19) Davis, L.; Feld, B. T.; Zabel, C. W.; Zacharias, J. R. The Hyperfine Structure and Nuclear Moments of the Stable Chlorine Isotopes. *Phys. Rev.* **1949**, *76*, 1076–1085.
- (20) Jaccarino, V.; King, J. G. On the Ratio of the Nuclear Magnetic and Electric Quadrupole Interactions for Atomic Cl^{35} and Cl^{37} . *Phys. Rev.* **1951**, *83*, 471–472.
- (21) King, J. G.; Jaccarino, V. Hyperfine Structure and Nuclear Moments of the Stable Bromine Isotopes. *Phys. Rev.* **1954**, *94*, 1610–1616.
- (22) Jaccarino, V.; King, J. G.; Satten, R. A.; Stroke, H. H. Hyperfine Structure of ^{127}I . Nuclear Magnetic Octupole Moment. *Phys. Rev.* **1954**, *94*, 1798–1799.
- (23) Fuller, G. H. Nuclear Spins and Moments. *J. Phys. Chem. Ref. Data* **1976**, *5*, 835–1092.
- (24) Sternheimer, R. M. Shielding and Antishielding of Nuclear Quadrupole Moments. *Z. Naturforsch. A* **1986**, *41a*, 24–36.
- (25) Yakobi, H.; Eliav, E.; Visscher, L.; Kaldor, U. High-Accuracy Calculation of Nuclear Quadrupole Moments of Atomic Halogens. *J. Chem. Phys.* **2007**, *126*, 054301(1–4).
- (26) Mukherjee, D.; Moitra, R. K.; Mukhopadhyay, A. Correlation Problem in Open-shell Atoms and Molecules A Non-perturbative Linked Cluster Formulation. *Mol. Phys.* **1975**, *30*, 1861–1888.
- (27) Applications of a Non-perturbative Many-body Formalism to General Open-shell Atomic and Molecular Problems: Calculation of the Ground and the Lowest π - π^* Singlet and Triplet Energies and the First Ionization Potential of Trans-Butadiene. *Mol. Phys.* **1977**, *33*, 955–969.
- (28) Lindgren, I. A Coupled-Cluster Approach to the Many-body Perturbation Theory for Open-shell Systems. *Int. J. Quantum Chem.* **1978**, *S12*, 33–58.
- (29) Haque, A.; Mukherjee, D. Application of Cluster Expansion Techniques to Open Shells: Calculation of Difference Energies. *J. Chem. Phys.* **1984**, *80*, 5058–5069.
- (30) Kutzelnig, W. Quantum chemistry in Fock space. I. The Universal Wave and Energy Operators. *J. Chem. Phys.* **1982**, *77*, 3081–3097.
- (31) Kutzelnig, W.; Mukherjee, D.; Koch, S. Connected-diagram Expansions of Effective Hamiltonians in Incomplete Model Spaces. I. Quasicomplete and Isolated Incomplete Model Spaces. *J. Chem. Phys.* **1987**, *87*, 5902–5910.
- (32) Sinha, D.; Mukhopadhyay, S. K.; Mukherjee, D. A Note on the Direct Calculation of Excitation Energies by Quasi-Degenerate MBPT and Coupled-Cluster Theory. *Chem. Phys. Lett.* **1986**, *129*, 369–374.
- (33) Mukhopadhyay, S. K.; Chaudhuri, R.; Mukhopadhyay, D.; Mukherjee, D. A Comparative Study of Core-Extensive and Core-Valence-Extensive Coupled-Cluster Theories for Energy Differences: Excitation Energies. *Chem. Phys. Lett.* **1990**, *173*, 181–186.
- (34) Musiał, M.; Bartlett, R. J. Fock Space Multireference Coupled Cluster Method with Full Inclusion of Connected Triples for Excitation Energies. *J. Chem. Phys.* **2004**, *121*, 1670–1675.
- (35) Barnholdt, D. E.; Bartlett, R. J. A Critical Assessment of Multireference-Fock Space CCSD and Perturbative Third-Order Triples Approximations for Photoelectron Spectra and Quasidegenerate Potential Energy Surfaces. *Adv. Quantum Chem.* **1999**, *34*, 271–293.
- (36) Haque, A.; Kaldor, U. Three-Electron Excitation in Open-Shell Coupled-Cluster Theory. *Chem. Phys. Lett.* **1985**, *120*, 261–265.
- (37) Pal, S.; Rittby, M.; Bartlett, R. J. Multi-Reference Coupled-Cluster Methods for Ionization Potentials with Partial Inclusion of Triple Excitations. *Chem. Phys. Lett.* **1989**, *160*, 212–218.
- (38) Lindgren, I.; Mukherjee, D. On the Connectivity Criteria in the Open-shell Coupled-Cluster Theory for General Model Spaces. *Phys. Rep.* **1987**, *151*, 93–127.

- (39) Mukherjee, D.; Pal, S. Use of Cluster Expansion Methods in the Open-Shell Correlation Problem. *Adv. Quantum Chem.* **1989**, *20*, 291–373.
- (40) Kaldor, U. The Fock Space Coupled Cluster Method: Theory and Application. *Theor. Chim. Acta* **1991**, *80*, 427–439.
- (41) Eliav, E.; Kaldor, U.; Ishikawa, Y. Open-Shell Relativistic Coupled-Cluster Method with Dirac-Fock-Breit Wave Functions: Energies of the Gold Atom and its Cation. *Phys. Rev. A* **1994**, *49*, 1724–1729.
- (42) Kaldor, U.; Eliav, E. Four-Component Electronic Structure Methods. In *Relativistic Methods for Chemists: Challenges and Advances in Computational Chemistry and Physics*, 10; Barysz, M.; Ishikawa, Y., Eds.; Springer: Dordrecht, Netherlands, 2010; pp 279–349.
- (43) Puzzarini, C.; Stanton, J. F.; Gauss, J. Quantum-Chemical Calculation of Spectroscopic Parameters for Rotational Spectroscopy. *Int. Rev. Phys. Chem.* **2010**, *29*, 273–367.
- (44) Handy, N. C.; Schaefer, H. F., III. On the Evaluation of Analytic Energy Derivatives for Correlated Wave Functions. *J. Chem. Phys.* **1984**, *81*, 5031–5033.
- (45) Salter, E. A.; Trucks, G. E.; Bartlett, R. J. Analytic Energy Derivatives in Many-Body Methods. I. First Derivatives. *J. Chem. Phys.* **1989**, *90*, 1752–1766 and reference therein.
- (46) Bartlett, R. J. Many-Body Perturbation Theory and Coupled Cluster Theory for Electron Correlation in Molecules. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359–401.
- (47) Gauss, J. *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R.; Allinger, N. L.; Clark, T.; Gasteiger, J.; Kollman, P. A.; Schaefer, H. F., III; Schreiner, P. R., Eds.; Wiley: Chichester, U.K., 1998; Vol. 1, pp 615–636.
- (48) Paldus, J.; Li, X. A Critical Assessment of Coupled Cluster Method in Quantum Chemistry. *Adv. Chem. Phys.* **1999**, *110*, 1–175.
- (49) Crawford, T. D.; Schaefer, T. D. An Introduction to Coupled Cluster Theory for Computational Chemists. *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; Wiley-VCH: New York, USA, 2000; pp 33–136.
- (50) Shiozaki, T.; Valeev, E. F.; Hirata, S. Explicitly Correlated Coupled-Cluster Methods. *Annu. Rep. Comput. Chem.* **2009**, *5*, 131–148.
- (51) Dalgarno, A.; Stewart, A. L. A Perturbation Calculation of Properties of the Helium Iso-Electronic Sequence. *Proc. R. Soc. London, Ser. A* **1958**, *247*, 245–259.
- (52) Szalay, P. Analytic Energy Derivatives for Coupled-Cluster Methods Describing Excited States: General Formulas and Comparison of Computational Costs. *Int. J. Quantum Chem.* **1995**, *55*, 151–163.
- (53) Pal, S. Fock Space Multireference Coupled-Cluster Method for Energies and Energy Derivatives. *Mol. Phys.* **2010**, *108*, 3033–3042.
- (54) Shamasundar, K. R.; Pal, S. A constrained Variational Approach for Energy Derivatives in Fock-Space Multireference Coupled-Cluster Theory. *J. Chem. Phys.* **2004**, *120*, 6381–6398.
- (55) Shamasundar, K. R.; Pal, S. Development of an Efficient Linear Response Approach to the Hilbert Space Multi-Reference Coupled-Cluster Theory. *J. Chem. Phys.* **2001**, *114*, 1981–1988.
- (56) Helgaker, T.; Jørgensen, P. Analytical Calculation of Geometrical Derivatives in Molecular Electronic Structure Theory. *Adv. Quantum Chem.* **1988**, *19*, 183–245.
- (57) Koch, H.; Jensen, H. J. A.; Jørgensen, P.; Helgaker, T.; Scuseria, G. E.; Schaefer, H. F., III. Coupled Cluster Energy Derivatives. Analytic Hessian for the Closed-Shell Coupled Cluster Singles and Doubles Wave Function: Theory and Applications. *J. Chem. Phys.* **1990**, *92*, 4924–4940.
- (58) Helgaker, T.; Olsen, J.; Jørgensen, P. In *Molecular Electronic-Structure Theory*; Wiley: Chichester, U.K., 2000.
- (59) Shamasundar, K. R.; Pal, S. Higher Energy Derivatives in Hilbert Space Multi-Reference Coupled Cluster Theory: A Constrained Variational Approach. *Int. J. Mol. Sci.* **2002**, *3*, 710–732.
- (60) Das, M.; Chaudhuri, R. K.; Chattopadhyaya, S.; Mahapatra, U. S. Fock-Space Multireference Coupled-Cluster Calculations of the Hyperfine Structure of Isoelectronic ^{33}S and $^{35,37}\text{Cl}$. *Phys. Rev. A* **2011**, *84*, 042512(1–7).
- (61) Eliav, E.; Kaldor, U.; Ishikawa, Y.; Pyykkö, P. Element 118: The First Rare Gas with an Electron Affinity. *Phys. Rev. Lett.* **1996**, *77*, 5350–5352.
- (62) Yakobi, H.; Eliav, E.; Kaldor, U. Nuclear Quadrupole Moment of ^{197}Au from High-Accuracy Atomic Calculations. *J. Chem. Phys.* **2007**, *126*, 184305(1–4).
- (63) Chaudhuri, R. K.; Sahoo, B. K.; Das, B. P.; Merlitz, H.; Mahapatra, U. S.; Mukherjee, D. Relativistic Coupled Cluster Calculations of the Energies for Rubidium and Cesium Atoms. *J. Chem. Phys.* **2003**, *119*, 10633–10637.
- (64) Nayak, M. K.; Chaudhuri, R. K. Relativistic Coupled Cluster Method. *Eur. Phys. J. D* **2006**, *37*, 171–176.
- (65) Sur, C.; Chaudhuri, R. K. Relativistic Multireference Fock-Space Coupled-Cluster Calculation of the Forbidden $6s^2\ ^1S_0 \rightarrow 6s5d\ ^3D_1$ Magnetic-Dipole Transition in Ytterbium. *Phys. Rev. A* **2007**, *76*, 012509(1–7).
- (66) Chaudhuri, R. K.; Chattopadhyaya, S. K.; Mahapatra, U. S. Taming the Electronic Structure of Lead and Eka-lead (Flerovium) by the Relativistic Coupled Cluster Method. *J. Phys. Chem. A* **2013**, *117*, 8555–8567.
- (67) Monkhorst, H. J. Calculation of Properties with the Coupled-Cluster Method. *Int. J. Quantum Chem. Symp.* **1977**, *11*, 421–432.
- (68) Mukherjee, D.; Mukherjee, P. K. A Response-Function Approach to The Direct Calculation of The Transition-Energy in a Multiple-Cluster Expansion Formalism. *Chem. Phys.* **1979**, *39*, 325–335.
- (69) Datta, B.; Sen, P.; Mukherjee, D. Coupled-Cluster Based Linear Response Approach to Property Calculations: Dynamic Polarizability and Its Static Limit. *J. Phys. Chem.* **1995**, *99*, 6441–6451.
- (70) Herman, M. F.; Freed, K. F.; Yeager, D. L. Analysis and Evaluation of Ionization Potentials, Electron Affinities, and Excitation Energies by the Equations of Motion Green's Function Method. *Adv. Chem. Phys.* **1981**, *48*, 1–69.
- (71) Dalggaard, E.; Monkhorst, H. J. Some Aspects of The Time-Dependent Coupled-Cluster Approach to Dynamic Response Functions. *Phys. Rev. A* **1983**, *28*, 1217–1222.
- (72) Sekino, H.; Bartlett, R. J. A Linear Response, Coupled-Cluster Theory for Excitation Energy. *Int. J. Quantum Chem.* **1984**, *S18*, 255–265.
- (73) Piecuch, P.; Bartlett, R. J. Eomcc: A New Coupled-Cluster Method for Electronic Excited States. *Adv. Quantum Chem.* **1999**, *34*, 295–380 and references therein..
- (74) Koch, H.; Jørgensen, P. Coupled Cluster Response Functions. *J. Chem. Phys.* **1990**, *93*, 3333–3344.
- (75) Stanton, J. F.; Bartlett, R. J. The Equation of Motion Coupled-Cluster Method. A Systematic Biorthogonal Approach to Molecular Excitation Energies, Transition Probabilities, and Excited State Properties. *J. Chem. Phys.* **1993**, *98*, 7029–7039.
- (76) Shavitt, I.; Bartlett, R. J. In *Many-Body Methods in Chemistry and Physics: MBPT and Coupled Cluster Theory*; Cambridge University Press: Cambridge, U.K., 2009.
- (77) Datta, B.; Chaudhuri, R.; Mukherjee, D. Method of Intermediate Hamiltonians via Eigenvalue-independent Partitioning: Application to Theoretical spectroscopy. *J. Mol. Struct. (THEOCHEM)* **1996**, *361*, 21–31.
- (78) Chaudhuri, R.; Datta, B.; Das, K.; Mukherjee, D. A Spin-adapted Coupled-Cluster Based Linear Response Theory for Double Ionization Potentials. *Int. J. Quantum Chem.* **1996**, *60*, 347–358.
- (79) Dutta, B.; Sen, P.; Mukherjee, D. Coupled-Cluster Based Linear Response Approach to Property Calculations: Dynamic Polarizability and Its Static Limit. *J. Phys. Chem.* **1995**, *99*, 6441–6451.
- (80) Watts, J. D.; Bartlett, R. J. The Inclusion of Connected Triple Excitations in the Equation-of-Motion Coupled-Cluster Method. *J. Chem. Phys.* **1994**, *101*, 3073–3078.
- (81) Szalay, P. G.; Gauss, J. Spin-restricted Open-Shell Coupled-Cluster Theory for Excited States. *J. Chem. Phys.* **2000**, *112*, 4027–4036.

- (82) Kucharski, S. A.; Wloch, M.; Musiał, M.; Bartlett, R. J. Coupled-Cluster Theory for Excited Electronic States: The Full Equation-of-Motion Coupled-Cluster Single, Double, and Triple excitation method. *J. Chem. Phys.* **2001**, *115*, 8263–8266.
- (83) Hirata, S. Higher-Order Equation-of-Motion Coupled-Cluster Methods. *J. Chem. Phys.* **2004**, *121*, 51–59.
- (84) Smith, C. E.; King, R. A.; Crawford, T. D. Coupled Cluster Methods including Triple Excitations For Excited States of Radicals. *J. Chem. Phys.* **2005**, *122*, 054110(1–8).
- (85) Piecuch, P.; Kowalski, K.; Pimienta, I.; Fan, P.; Lodriguito, M.; McGuire, M.; Kucharski, S. A.; Kus, T.; Musiał, M. Method of Moments of Coupled-Cluster Equations: A New Formalism for Designing Accurate Electronic Structure Methods for Ground and Excited States. *Theor. Chim. Acta* **2004**, *112*, 349–393.
- (86) Shen, J.; Piecuch, P. Doubly Electron-attached and Doubly Ionized Equation-of-Motion Coupled-Cluster Methods with 4-Particle-2-Hole and 4-Hole-2-Particle Excitations and Their Active-Space Extensions. *J. Chem. Phys.* **2013**, *138*, 194102(1–16).
- (87) Mukhopadhyay, D.; Mukhopadhyay, S.; Chaudhuri, R.; Mukherjee, D. Aspects of Separability in the Coupled Cluster Based Direct Methods for Energy Differences. *Theor. Chim. Acta* **1991**, *80*, 441–467.
- (88) Musiał, M.; Bartlett, R. J. Multireference Fock-Space Coupled-Cluster and Equation-of-Motion Coupled-Cluster Theories: The Detailed Interconnections. *J. Chem. Phys.* **2008**, *129*, 134105(1–12).
- (89) Bartlett, R. J.; Musiał, M. Coupled-Cluster Theory in Quantum Chemistry. *Rev. Mod. Phys.* **2007**, *79*, 291–352.
- (90) Bartlett, R. J. Coupled-Cluster Theory and Its Equation-of-Motion Extensions. *WIREs: Comput. Mol. Sci.* **2012**, *2*, 126–138.
- (91) Watts, J. D. An Introduction to Equation-of-Motion and Linear-Response Coupled-Cluster Methods For Electronically Excited States of Molecules. In *Radiation Induced Molecular Phenomena in Nucleic Acids: Challenges and Advances In Computational Chemistry and Physics Vol. 5*; Shukla, M. K., Leszczynski, J., Eds.; Springer: Dordrecht, Netherlands, 2008; pp 65–92.
- (92) Crawford, T. D.; Sekino, H. On the Performance of a Size-Extensive Variant of Equation-of-Motion Coupled Cluster Theory for Optical Rotation in Chiral Molecules. in *Advances in the Theory of Atomic and Molecular Systems, Progress in Theoretical Chemistry and Physics* 19; Piecuch, P., et al., Eds.; Springer Science: Dordrecht, Netherlands, 2009; pp:225–239.
- (93) Reisler, H.; Krylov, A. I. Interacting Rydberg and Valence States in Radicals and Molecules: Experimental and Theoretical Studies. *Int. Rev. Phys. Chem.* **2009**, *28*, 267–308.
- (94) Nakatsuji, H.; Hirao, K. Cluster Expansion of the Wavefunction. Pseudo-orbital Theory Applied to Spin Correlation. *Chem. Phys. Lett.* **1977**, *47*, 569–571.
- (95) Ehara, M.; Hasegawa, J.; Nakatsuji, H. In *Theory and Applications of Computational Chemistry*; Dykstra, C., Frenking, G., Kim, K., Scuseria, G., Eds.; Elsevier: New York, 2005.
- (96) Stanton, J. F. Many-Body Methods for Excited State Potential Energy Surfaces. I. General Theory of Energy Gradients for the Equation-of-Motion Coupled-Cluster Method. *J. Chem. Phys.* **1993**, *99*, 8840–8847.
- (97) Stanton, J. F.; Gauss, J. Analytic Energy Gradients for the Equation-of-Motion Coupled-Cluster Method: Implementation and Application to the HCN/HNC System. *J. Chem. Phys.* **1994**, *100*, 4695–4698.
- (98) Stanton, J. F.; Gauss, J. Analytic Energy Derivatives for Ionized States Described by the Equation-of-Motion Coupled Cluster Method. *J. Chem. Phys.* **1994**, *101*, 8938–8944.
- (99) Stanton, J. F.; Gauss, J. Analytic Energy Derivatives for the Equation-of-Motion Coupled-Cluster Method: Algebraic Expressions, Implementation and Application to the S1 State of HFCO. *Theor. Chim. Acta* **1995**, *91*, 267–289.
- (100) Das, M.; Chaudhuri, R. K.; Chattopadhyay, S.; Sinha Mahapatra, U.; Mukherjee, P. K. Application of Relativistic Coupled Cluster Linear Response Theory to Helium-like Ions Embedded in Plasma Environment. *J. Phys. B* **2011**, *44*, 165701(1–9).
- (101) Chaudhuri, R. K.; Panda, P. K.; Das, B. P.; Mahapatra, U. S.; Mukherjee, D. Relativistic Coupled-Cluster-Based Linear Response Theory for Ionization Potentials of Alkali-Metal and Alkaline-Earth-Metal Atoms. *Phys. Rev. A* **1999**, *60*, 246–252.
- (102) Sundholm, D.; Olsen, J. Finite Element Multiconfiguration Hartree-Fock Determination of the Nuclear Quadrupole Moments of Chlorine, Potassium, and Calcium Isotopes. *J. Chem. Phys.* **1993**, *98*, 7152–7158.
- (103) Alonso, R. E.; Svane, A.; Rodríguez, C. O.; Christensen, N. E. Nuclear Quadrupole Moment Determination of ^{35}Cl , ^{79}Br , and ^{127}I . *Phys. Rev. B* **2004**, *69*, 125101(1–6).
- (104) Alonso, R. E.; Svane, A.; Rodríguez, C. O.; Christensen, N. E. Erratum: Nuclear Quadrupole Moment Determination of ^{35}Cl , ^{79}Br , and ^{127}I [*Phys. Rev. B* **2004**, *69*, 125101 (1–6)]. *Phys. Rev. B* **2004**, *70*, 119901(1–1).
- (105) Kellö, V.; Sadlej, A. J. Determination of the Quadrupole Moment of the Halogen Nuclei (Cl, Br, I) from molecular data. *Mol. Phys.* **1996**, *89*, 127–137.
- (106) Haas, H.; Petrilli, H. M. Quadrupole Moments of the Halogen Nuclei. *Phys. Rev. B* **2000**, *61*, 13588–13592.
- (107) Bieroń, J.; Pykkö, P.; Sundholm, D.; Kellö, V.; Sadlej, A. J. Nuclear Quadrupole Moments of Bromine and Iodine from Combined Atomic and Molecular Data. *Phys. Rev. A* **2001**, *64*, 052507(1–12).
- (108) van Stralen, J. N. P.; Visscher, L. Molecular Relativistic Electric Field Gradient Calculations Suggest Revision of the Value of the Nuclear Electric Quadrupole Moment of ^{127}I . *Mol. Phys.* **2003**, *101*, 2115–2124.
- (109) Stopkiewicz, S.; Cheng, L.; Harding, M. E.; Puzzarini, C.; Gauss, J. The Bromine Nuclear Quadrupole Moment Revisited. *Mol. Phys.* **2013**, *111*, 1382–1389.
- (110) Kaldor, U. Intruder States and Incomplete Model Spaces in Multireference Coupled-Cluster Theory: The $2p^2$ State of Be. *Phys. Rev. A* **1988**, *38*, 6013–6016.
- (111) Kowalski, K.; Piecuch, P. Complete Set of Solutions of Multireference Coupled-Cluster Equations: The State-Universal Formalism. *Phys. Rev. A* **2000**, *61*, 052506(1–8).
- (112) Sinha, D.; Mukhopadhyay, S. K.; Chaudhuri, R. K.; Mukherjee, D. The Eigenvalue-Independent Partitioning Technique in Fock Space: An Alternative Route to Open-Shell Coupled-Cluster Theory for Incomplete Model Spaces. *Chem. Phys. Lett.* **1989**, *154*, 544–549.
- (113) Mukhopadhyay, D.; Datta, B.; Mukherjee, D. The Construction of a Size-extensive Intermediate Hamiltonian in a Coupled-Cluster Framework. *Chem. Phys. Lett.* **1992**, *197*, 236–242.
- (114) Meissner, L.; Bartlett, R. J. A Dressing for the Matrix Elements of the Singles and Doubles Equation-of-Motion Coupled-Cluster Method that Recovers Additive Separability of Excitation Energies. *J. Chem. Phys.* **1995**, *102*, 7490–7498.
- (115) Landau, A.; Eliav, E.; Kaldor, U. Relativistic Coupled Cluster Method. *Adv. Quantum Chem.* **2001**, *39*, 171–176.
- (116) Chattopadhyay, S.; Mitra, A.; Sinha, D. Explicitly Intruder-Free Valence-Universal Multireference Coupled Cluster Theory as Applied to Ionization Spectroscopy. *J. Chem. Phys.* **2006**, *125*, 244111(1–17).
- (117) Musiał, M.; Bartlett, R. J. Intermediate Hamiltonian Fock-space Multireference Coupled-Cluster Method with Full Triples for Calculation of Excitation Energies. *J. Chem. Phys.* **2008**, *129*, 044101(1–10).
- (118) Malli, G. L.; Da Silva, A. B. F.; Ishikawa, Y. Universal Gaussian Basis Set for Accurate ab initio IP Relativistic Dirac-Fock Calculations. *Phys. Rev. A* **1993**, *47*, 143–146.
- (119) Huzinaga, S.; Klobukowski, M. Well-tempered Gaussian Basis Sets for the Calculation of Matrix Hartree-Fock Wavefunctions. *Chem. Phys. Lett.* **1993**, *212*, 260–264.
- (120) Carette, T.; Godefroid, M. R. Ab initio Calculations of the $^{33}\text{S}3p^43p_1$ and $^{33}\text{S}/^{37,35}\text{Cl}3p^52p_1^0$ Hyperfine Structures. *J. Phys. B* **2011**, *44*, 105001(1–10).
- (121) In FS-MRCC expectation value based approach, the property O is computed via the following expression: $O = ((\langle\Phi_0|a_\alpha^\dagger(1 + S^\dagger)\exp(T^\dagger)O\exp(T)(1 + S)a_\alpha|\Phi_0\rangle))/(\langle\Phi_0|a_\alpha^\dagger(1 + S^\dagger)\exp(T^\dagger)\exp(T)(1$

$+ S)a_a|\Phi_0\rangle) = N/D$. The numerator (N) and the denominator (D) appearing in this expression are nonterminating, and hence, N and D are truncated at some power of T .

(122) Ralchenko, Y.; Kramida, A. E.; Reader, J. NIST ASD Team (2008) In *NIST Atomic Spectra Database (Version 3.1.5)*; National Institute of Standards and Technology: Gaithersburg, MD, April 2008 (<http://physics.nist.gov/asd3>).

(123) Chang, Z.; Li, J.; Dong, C. Ionization Potentials, Electron Affinities, Resonance Excitation Energies, Oscillator Strengths, and Ionic Radii of Element Uus ($Z = 117$) and Astatine. *J. Phys. Chem. A* **2010**, *114*, 13388–133894.

(124) Hughes, S. R.; Kaldor, U. The Fock-Space Coupled-Cluster Method: Electron Affinities of the Five Halogen Elements with Consideration of Triple Excitations. *J. Chem. Phys.* **1993**, *99*, 6773–6776.