

Inclusion of orbital relaxation and correlation through the unitary group adapted open shell coupled cluster theory using non-relativistic and scalar relativistic Hamiltonians to study the core ionization potential of molecules containing light to medium-heavy elements

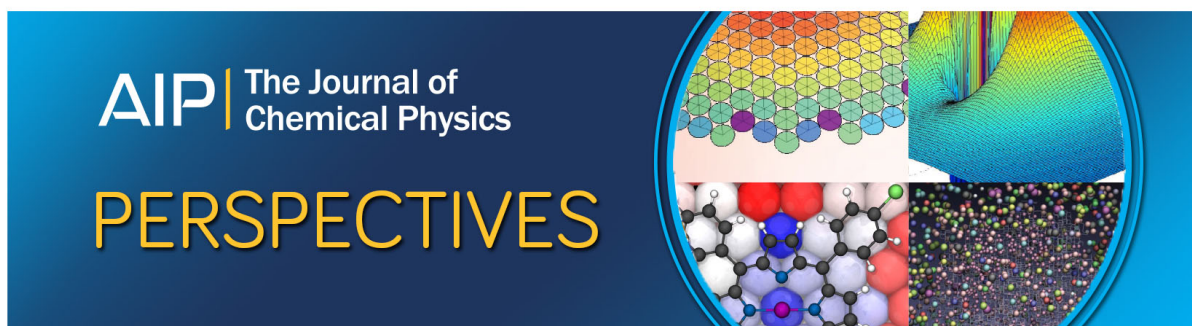
Sangita Sen, Avijit Shee, and Debashis Mukherjee

Citation: *The Journal of Chemical Physics* **148**, 054107 (2018);

View online: <https://doi.org/10.1063/1.5018086>

View Table of Contents: <http://aip.scitation.org/toc/jcp/148/5>

Published by the *American Institute of Physics*



Inclusion of orbital relaxation and correlation through the unitary group adapted open shell coupled cluster theory using non-relativistic and scalar relativistic Hamiltonians to study the core ionization potential of molecules containing light to medium-heavy elements

Sangita Sen,^{1,a),b)} Avijit Shee,^{2,a),c)} and Debashis Mukherjee^{3,d)}

¹*Hylleraas Centre for Quantum Molecular Sciences, University of Oslo, Oslo, Norway*

²*Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109, USA*

³*Raman Center for Atomic, Molecular and Optical Sciences, Indian Association for the Cultivation of Science, Kolkata, India*

(Received 3 December 2017; accepted 18 January 2018; published online 6 February 2018)

The orbital relaxation attendant on ionization is particularly important for the core electron ionization potential (core IP) of molecules. The Unitary Group Adapted State Universal Coupled Cluster (UGA-SUMRCC) theory, recently formulated and implemented by Sen *et al.* [J. Chem. Phys. **137**, 074104 (2012)], is very effective in capturing orbital relaxation accompanying ionization or excitation of both the core and the valence electrons [S. Sen *et al.*, Mol. Phys. **111**, 2625 (2013); A. Shee *et al.*, J. Chem. Theory Comput. **9**, 2573 (2013)] while preserving the spin-symmetry of the target states and using the neutral closed-shell spatial orbitals of the ground state. Our Ansatz invokes a normal-ordered exponential representation of spin-free cluster-operators. The orbital relaxation induced by a specific set of cluster operators in our Ansatz is good enough to eliminate the need for different sets of orbitals for the ground and the core-ionized states. We call the single configuration state function (CSF) limit of this theory the Unitary Group Adapted Open-Shell Coupled Cluster (UGA-OSCC) theory. The aim of this paper is to comprehensively explore the efficacy of our Ansatz to describe orbital relaxation, using both theoretical analysis and numerical performance. Whenever warranted, we also make appropriate comparisons with other coupled-cluster theories. A physically motivated truncation of the chains of spin-free T-operators is also made possible by the normal-ordering, and the operational resemblance to single reference coupled-cluster theory allows easy implementation. Our test case is the prediction of the 1s core IP of molecules containing a single light- to medium-heavy nucleus and thus, in addition to demonstrating the orbital relaxation, we have addressed the scalar relativistic effects on the accuracy of the IPs by using a hierarchy of spin-free Hamiltonians in conjunction with our theory. Additionally, the contribution of the spin-free component of the two-electron Gaunt term, not usually taken into consideration, has been estimated at the Self-Consistent Field (Δ SCF) level and is found to become increasingly important and eventually quite prominent for molecules with third period atoms and below. The accuracies of the IPs computed using UGA-OSCC are found to be of the same order as the Coupled Cluster Singles Doubles (Δ CCSD) values while being free from spin contamination. Since the UGA-OSCC uses a common set of orbitals for the ground state and the ion, it obviates the need of two N^5 AO to MO transformation in contrast to the Δ CCSD method. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5018086>

I. INTRODUCTION

Theoretical prediction of the core ionization potential (IP) poses a special challenge to any high level correlated theory. The magnitude of the core IP is shaped not only by the magnitude of differential correlation accompanying the core ionization process relative to the ground state correlation but also by the attendant large orbital relaxation. Thus a precise description of the core ionization phenomenon requires proper

quantitative modeling of not only differential correlation but also of the orbital relaxation.

Often the Self-Consistent Field (Δ SCF) method is considered good enough for core IP as the orbital relaxation for the ionized state is taken care of at the mean field level, and the difference in the correlation energies for the two states, each with their corresponding optimized orbitals, is easily swamped by the large orbital relaxation for core processes.¹ This is, however, the outcome of partial error cancellation and cannot be relied on for high accuracy computations. Moreover, its scope is limited for other types of core processes such as electron excitation and shake up phenomena,² notwithstanding the obvious limitation of its inability to handle processes sensitive to static and dynamic electron correlation.^{3–5} Recently, advances in electron

^{a)}S. Sen and A. Shee contributed equally to this work.

^{b)}Electronic mail: sangita.sen310187@gmail.com

^{c)}Electronic mail: ashee@umich.edu

^{d)}Electronic mail: pcdemu@gmail.com

correlation theories have made the accurate prediction of X-ray ionization and excitation spectra viable.^{6–9} A high level correlation theory should, in principle, take care of correlation and orbital relaxation in a generic situation involving energy differences of the ground and ionized, electron attached, or excited states. However, for core IP in particular, a proper correlation theory must also accurately capture not only a partial cancellation of dynamic correlation between the states but also take account of the large orbital relaxation in an explicit manner. We will study in this paper a fairly general non-perturbative method applicable for core processes which, as we shall show, adequately demonstrates these two requirements when applied to the computation of core IPs.

One can broadly classify correlated theories for energy differences such as IP into two categories: (A) separate computations for the ground states (GSs) and the ionized state each with their corresponding optimized orbitals and (B) the same set of orbitals for computation of the energies of the ground and the ionized states.

The possible advantage of the methods belonging to category A in offering a more complete account of orbital relaxation is however quite offset by the disadvantage stemming from the necessity for separate transformation of two-electron integrals from AO to MO basis for the two states, i.e., two N^5 scaling computations, and the difficulty of computing transition properties due to non-orthogonal orbitals. The Static Exchange (STEX)¹⁰ approach, Open-shell Reference Symmetry Adapted Cluster (OR-SAC),¹¹ and Coupled Cluster Singles Doubles (Δ CCSD) methods¹² belong to this category of correlation methods. The calculation of core excited states using orbitals of the core ionized state has also been attempted.¹³ However, the UHF- or ROHF-based CC computations for the doublet state would lead to a spin contaminated wave function.

The methods belonging to category B are clearly advantageous on two counts: they provide a natural way of cancellation of common terms in the energy differences and only one N^5 transformation. These theories include Equation Of Motion Coupled Cluster (EOMCC),^{13–22} Coupled Cluster Linear Response Theory (CC-LRT),^{8,23–32} Similarity-Transformed EOMCC (STEOMCC),^{33–36} Symmetry Adapted Cluster Configuration Interaction (SAC-CI),^{37–39} propagator methods with orbital relaxation,⁴⁰ Algebraic Diagrammatic Construction (ADC),^{41,42} and other response-based theories. In almost all these methods, the orbitals used are those for the closed shell ground state. Then, the linear Ansatz in response approaches results in poor orbital relaxation unless three and higher rank excitations are included.⁴³ This difficulty may be largely resolved by formulating a theory for describing the core-ionized state with GS orbitals but adopting a suitable cluster expansion Ansatz for describing correlation and orbital relaxations—the latter in the spirit of the Thouless theorem.⁴⁴ For core IP, a spin-free open shell coupled cluster theory with spin-free cluster operators using only ground state orbitals seems clearly to be such a viable theory which would simultaneously prevent spin contamination.

We have recently formulated Unitary Group Adapted (UGA) Multi-Reference Coupled Cluster (MRCC) theories of the state-specific (UGA-SSMRCC)⁴⁵ and the state-universal

(UGA-SUMRCC)⁴⁶ variants for studying a specific state or a set of states which are capable of handling multi-reference effects. By their very construction, they are spin adapted in nature and may be looked upon as the spin adapted versions of spinorbital-based SSMRCC^{47–50} and SUMRCC,⁵¹ respectively. For an overview of these developments, we quote Ref. 52. The literature covering the diverse MRCC theories is vast, and we mention only certain representative ones of relevance to us.^{47–51,53–64} We also refer the readers to a set of comprehensive review articles on the latest general developments.^{65,66}

The Ansatz for the wave operator of the UGA-MRCC theories, suggested by us, is strongly reminiscent of the one suggested by Jeziorski and Monkhorst⁵¹ except that in our spin-free formulation, the spin-free cluster operators are non-commuting in general but whose structural complexity we avoid by positing a normal ordered exponential representation of each component of the wave operator, $\Omega_\mu = \{e^{T_\mu}\}$, acting on a model function ϕ_μ . ϕ_μ is a spin-adapted Gel'fand state.^{67,68} Unlike in the UGA formulations suggested by Li and Paldus,⁵⁶ where they used an ordinary exponential representation of the wave operator which leads to rather unwieldy expressions for a class of terms in their working equations, our formulation using normal ordered exponential leads to much more compact expressions. The UGA-SSMRCC was found to be very successful in the study of potential energy surfaces of molecules in various electronic states, all leading to proper fragmentation, while the UGA-SUMRCC was used for studying ionized or excited states. The deepest lying core-orbital of molecules which contain only one heavy nucleus is generally well separated from the others. The molecules investigated in this paper all belong to this category. There is thus only one core-ionized model function for the deepest core-ionized state and it is clear that they can be studied with the single open-shell CSF limit of both the UGA-SUMRCC and UGA-SSMRCC (since they are equivalent) and we want to call this the Unitary Group Adapted Open-Shell Coupled Cluster (UGA-OSCC) theory.

It is well-known that the ordinary Thouless parameterization involves an ordinary exponential⁴⁴ of a one-body excitation operator inducing orbital relaxation. Due to the presence of the normal ordering in our Ansatz, we will refer to our analog as a generalized Thouless parametrization. The orbital relaxing spin-free cluster operators in the generalized Thouless parametrization are not, however, necessarily one-body. In our paper, we will analyze in some detail the relaxation mechanism in UGA-OSCC in order to have a comparison of the orbital relaxation brought out by the generalized Thouless parametrization, *vis-à-vis*, the standard Thouless parametrization. In our earlier publications,^{46,69,70} we had used a sufficiency condition to arrive at our working equations. However, recent developments by us indicate that the theory can be rigorously derived and the sufficiency condition used by us^{46,69,70} amounts to a first approximation. In this paper, we will use the final rigorous equation to help us explain the relaxation mechanism. We will also adduce theoretical reasons to rationalize why the sufficiency condition was physically motivated. Thus, while we use our earlier equations to compute numbers, we invoke the rigorous equation to analyze the relaxation

mechanism. Our pilot applications published earlier⁷⁰ bear out the merit of this approximation clearly. In this paper, we shall present a more systematic study with more challenging test cases. This analysis will not only help us in discerning certain key aspects of the relaxation mechanism in the UGA-OSCC theory but also shed light on that of the parent UGA-SUMRCC/UGA-SSMRCC theories where the coupling term poses certain non-trivial issues.

Formalisms related to ours include the Open-Shell Coupled Cluster (OSCC) of Paldus *et al.*^{55,58,59,71,72} and the Combinatoric Open-Shell Coupled Cluster of Datta and Mukherjee.^{73,74} Both these theories also incorporate a high degree of orbital relaxation, but there are important structural differences with our formalism. The OSCC theory of Paldus^{55,58,59,71,72} uses an ordinary exponential parameterization for their spin-free wave operator and, because of the non-commutativity in the cluster operators in their Ansatz, the formalism is both algebraically and implementationally more complicated than ours. The COS-CC of Datta and Mukherjee involves selective contractions of the active orbitals in the orbital-relaxing terms—as one obtains in a Fock-space formulation of the MRCC methods.^{53,54} In COS-CC, all the cluster operators of the ionized state involve spectator excitations labeled by the active orbitals (which are ionized) and they are contracted with each other in the various terms. Our formulation bypasses most of the active orbital contractions.

For an accurate description of the core IP of molecules containing one medium-heavy atom, the scalar relativistic effect tends to become important and in the series of example molecules of the general formula $[XH_n]$ with X as the non hydrogen atom, we will present results using both non-relativistic (NR) and spin-free Dirac-Coulomb Hamiltonians. Since for the core IP, the orbital from which the electron is ionized is almost entirely of s-character, the spin-orbit effects are negligible. The spin-free DC Hamiltonian has been studied in both a four-component^{75–79} and a two-component framework.^{80,81} The most widely accepted approach for the two-component theories is the eXact two-component one-electron (X2C-1e) Hamiltonian,^{82–86} and the spin-free version of the X2C-1e Hamiltonian, the so-called SF-X2C-1e Hamiltonian, has also been extensively studied.^{80,81} The “picture change error”⁸⁷ arising from not transforming the two-electron part of the Hamiltonian when going from a four-component to a two-component representation has also been studied in this paper in the context of core IPs. The spin-free 4-component Hamiltonian and the SF-X2C-1e Hamiltonian will, respectively, be called the SF-4C and the SF-2C Hamiltonian in the rest of this paper. In our work, the use of explicitly spin-free coupled cluster theories enables us to have a unified treatment for both NR and the SF-4C/2C Hamiltonians. The effects of correlation and relativity are not additive, and non-perturbative theories are ideally suited for handling them together. We should also mention that this is not only true for core IP processes but also for more complex processes^{9,88–93} leading all the way to multi-reference theories with relativistic Hamiltonians which are being actively investigated.^{94–101}

We have also assessed the lowest order Quantum Electrodynamics (QED) correction to the core IP. It has been

shown previously by Indelicato *et al.*¹⁰² and others,¹⁰³ in the context of atomic core ionizations and also valence ionizations,¹⁰⁴ that QED effects could be vitally important. We have estimated the importance of the spin-free part of the Gaunt term at the mean field level, i.e., the Δ SCF level, which contains the current-current interaction. We have also assessed the contribution of the spin-dependent part of the Gaunt term at the Δ SCF level and found it to be much smaller than the spin-free part.

This paper is organized as follows. Section II gives a brief derivation of the UGA-OSCC theory and puts our earlier derivations^{46,69} involving a sufficiency condition in the context of an exact derivation. Section III discusses the nature of orbital relaxation as induced by a generalized Thouless parameterization. Section III A clarifies that the generalized Thouless parametrization does not lose any physical component inducing orbital relaxation despite the use of a normal ordered exponential. There are several subtle issues which are outlined in this section. Section III B motivates towards the actual truncation scheme used in this paper which is the same as the single configuration state function (CSF) limit of the UGA-SUMRCC presented earlier⁴⁶ as well. In Sec. IV, we discuss the spin-free relativistic Hamiltonians which we have used in our study. Section V contains molecular applications in which Sec. V A discusses the computational details, and Sec. V B presents our findings. Finally, in Sec. VI we summarize our work and comment on future prospects.

II. THE UGA-OSCC FORMALISM

As emphasized in Sec. I, the UGA-OSCC theory is the single CSF limit of the UGA-SUMRCC⁴⁶ or UGA-SSMRCC.⁴⁵ In the UGA-OSCC, which we will use to describe the core ionized state, we choose one ϕ_μ which represents the core ionized model function and write the correlated ionized state as

$$|\Psi\rangle = \Omega_\mu |\phi_\mu\rangle. \quad (1)$$

The index “ μ ” is superfluous but we carry it to indicate that the amplitudes of the cluster operators will be determined for the open-shell state itself and not for some underlying vacuum function (or ground state) with subsequent corrections (as in the Fock-space coupled cluster formalism, for instance). In the spin-free formulation, one represents Ω_μ in terms of spin free cluster operators T_μ whose various components are written in terms of spin-free excitation operators which are generators of the unitary group.

The spin-free Hamiltonian we will be using can be expressed entirely in terms of matrix elements involving orbitals. We will use the labels i, j, \dots , etc., for the doubly occupied inactive orbitals or holes; a, b, c, \dots , etc., for the inactive virtual orbitals or particles; and the labels (I, J, \dots) and (A, B, \dots) for the active holes and the active particles, respectively. In the extant case, the function ϕ_μ is a 1-hole (1h) state, where the core orbital, I , is singly occupied. In this situation, it is possible for various components of T_μ to excite both from and into I , which results in the non-commutativity of the T_μ s. This is generally the case that the spin-free generators in T_μ involving singly occupied orbitals will introduce the problem of non-commutativity of certain components of these

operators. With an exponential Ansatz for Ω_μ , i.e., e^{T_μ} , the Baker-Campbell-Hausdorff (BCH) expansion would not have terminated at the quartic power. This problem is overcome by an additional normal ordering over the full Ansatz denoted by $\{\}$ in the following equation:

$$\Omega_\mu = \{e^{T_\mu}\}. \quad (2)$$

Here the normal ordering is taken with respect to a suitable closed shell determinant, chosen as the vacuum. In our present formulation, we choose as our vacuum, the Hartree-Fock function, ϕ_0 , of the neutral ground state.

Since the operators of T_μ are spin-free, they cannot change the spin of the function they act upon. The action of products of the operators also, thus, does not affect the spin state leading to the spin-free nature of the full exponential Ansatz or any approximation thereof. In general, our choice for the spin-adapted Configuration State Function (CSF), ϕ_μ , is a Gel'fand state.^{67,68,72} However, for the doublets we deal with in this paper, the functions are unique and no specific choice for the spin and the spatial part is necessary. We treat the doublet ionized states as described by the 1-hole (1h) sector model and virtual functions, with the ground-state Hartree-Fock function taken as the vacuum.

The excited functions in our formulation are generated by the action of linearly independent spin-free generators of the unitary group ($\{\epsilon_\mu^l\}$), acting on ϕ_μ ,

$$|\chi_\mu^l\rangle = \{\epsilon_\mu^l\}|\phi_\mu\rangle, \quad (3)$$

where $\{\epsilon_\mu^l\}$ s are in normal order with respect to $|\phi_0\rangle$. The functions χ_μ^l are CSFs but they are neither Gel'fand states nor the SU2 adapted CSFs of Li and Paldus.⁵⁷ $\{\epsilon_\mu^l\}$ s are linearly independent specific combinations of spatial orbital replacement operators, $\{E_\mu^l\}$, which are generators of the unitary group. For further details of the operators chosen, we refer the readers to our earlier publication.⁶⁹ The final working equations involve matrix elements between ϕ_μ s wherein reduced density matrices (RDMs) labeled by active orbitals (I in the present case of core-ionized states) appear which incorporate the spin information of the model function ϕ_μ and hence how we choose the excited CSFs does not play an important role.

Using this Ansatz in the Schrödinger equation, we have

$$\{H\}\{e^{T_\mu}\}|\phi_\mu\rangle = E_\mu\{e^{T_\mu}\}|\phi_\mu\rangle \quad (4)$$

Introducing an operator, $W_{\mu\mu}$, defined by

$$W_{\mu\mu}|\phi_\mu\rangle = |\phi_\mu\rangle E_\mu \quad (5)$$

and using Wick's theorem on both sides of Eq. (4), we have

$$\begin{aligned} \{e^{T_\mu}\overline{H}e^{T_\mu}\}|\phi_\mu\rangle &= \{e^{T_\mu}\overline{e^{T_\mu}W_{\mu\mu}}\}|\phi_\mu\rangle, \\ \{e^{T_\mu}\overline{H}_\mu\}|\phi_\mu\rangle &= \{e^{T_\mu}Y_{\mu\mu}\}|\phi_\mu\rangle, \end{aligned} \quad (6)$$

where \overline{H}_μ is a compact notation of an operator in normal order defined by the series,

$$\overline{H}_\mu = \{\overline{He^{T_\mu}}\} = \{H + \overline{HT_\mu} + \frac{1}{2}\overline{HT_\mu T_\mu} + \dots\}, \quad (7)$$

and the operator $Y_{\mu\mu}$ has a similar structure of the form

$$Y_{\mu\mu} = \{\overline{e^{T_\mu}W_{\mu\mu}}\}. \quad (8)$$

Let us note that in Eqs. (7) and (8), the contribution of the unit operator coming from $\{e^{T_\mu}\}$ is also included.

In our earlier publications,^{46,69,70} we had used a sufficiency condition at this point in Eq. (6) to suggest the following equation:

$$\{\overline{H}_\mu\}|\phi_\mu\rangle = \{Y_{\mu\mu}\}|\phi_\mu\rangle. \quad (9)$$

As already indicated in Sec. I, we have recently found that it is possible to arrive rigorously at a connected working equation, which on a first approximation yields our earlier equations. In this paper, we will present the rigorous equation as Eq. (10) and indicate, in Sec. III B, the approximations necessary to arrive at Eq. (9), for establishment of the sufficiency condition. We will present the full derivation and analysis in a forthcoming publication. The detailed derivation and analysis open the way for a systematic hierarchy of approximations and warrants a detailed study. In this paper, we have used the older version of the working equation, and the current level of numerical accuracy already appears to be quite good. The theoretical basis for the success of this approximation is analyzed in Sec. III B.

The rigorous equation most recently derived by us for the UGA-OSCC takes the form

$$[\{\overline{H}_\mu + \tilde{e}(\theta_\mu)\overline{H}_\mu\} - \{Y_{\mu\mu} + \tilde{e}(\theta_\mu)Y_{\mu\mu}\}]|\phi_\mu\rangle \equiv \{G_\mu\}|\phi_\mu\rangle = 0, \quad (10)$$

where

$$\theta_\mu = \{-T_\mu + \overline{T_\mu T_\mu} - \overline{T_\mu T_\mu T_\mu} + \dots\} \quad (11)$$

and $\tilde{e}(\theta_\mu)$ is $(\{e^{\theta_\mu}\} - 1)$.

Thus,

$$\{G_\mu\} = \{\overline{H}_\mu + \tilde{e}(\theta_\mu)\overline{H}_\mu\} - \{Y_{\mu\mu} + \tilde{e}(\theta_\mu)Y_{\mu\mu}\}. \quad (12)$$

The first term in $\{G_\mu\}$ [Eq. (12)] is called the “*direct term*” and the second is the so-called “*coupling term*” (or rather, “*folded term*” for our single CSF case).

We note that any many-body operator can be decomposed into an excitation part, A_{ex} , and a closed part, A_{cl} , depending on their action on the model function, ϕ_μ . A_{ex} acting on ϕ_μ produces virtual functions only, while A_{cl} leads only to ϕ_μ . We make this separation as and when required.

To get the final working equations for determining the cluster amplitudes of T_μ , Eq. (10) is simply projected by the excited functions to yield Eq. (13) which are called projection equations,

$$R_{\mu,ex}^l = \langle \chi_\mu^l | \{G_\mu\}_{ex} | \phi_\mu \rangle = 0. \quad (13)$$

Equation (13) is to be solved iteratively till the residual goes below a pre-assigned convergence threshold. In Eq. (13), only the excitation part of $\{G_\mu\}$ contributes, which is why we have used the sub-script “*ex*.”

Analogous to Eq. (13), we get the expression for the energy of the correlated ϕ_u as

$$E_\mu = \langle \phi_\mu | \{G_\mu\}_{cl} | \phi_\mu \rangle. \quad (14)$$

Using the expression of $\{G_{\mu}\}_{cl}$ from Eq. (12), we find that

$$W_{uu} = \{\overline{H}_u\}_{cl}. \quad (15)$$

III. TREATMENT OF ORBITAL RELAXATION THROUGH A GENERALIZED THOULESS PARAMETRIZATION

We arrive now to one of the major theoretical ramifications of the formalism expounded in Sec. II: the mechanism of orbital relaxation in our UGA-OSCC. As mentioned before, in our UGA-OSCC theory, the T_μ operators are defined in spatial orbitals and the resulting problem of non-commutativity of the components of T_μ s involving singly occupied active orbitals is alleviated by an additional normal-ordering of the Ansatz with respect to a common closed shell vacuum. A problem with such an approach is that the orbitals to be used could very well be optimized for the function ϕ_0 . Thus the orbitals may not be optimal for the model functions, making it essential to have a mechanism for correction of orbitals to be induced by the wave operator Ansatz. The normal ordered exponential Ansatz in the UGA-OSCC theory takes care of the orbital relaxation both due to ionization and due to correlation. These two effects are, however, intermingled and cannot be separated out numerically. One may, however, separately analyze the mechanism by which they are introduced.

Before we embark on this analysis, we may point out that in conventional coupled-cluster theory, the wave operator with the Thouless parameterization, e^{T_1} , acts only on the ket function—the bra function remains unrelaxed. A fuller parametrization for relaxation of both the bra and the ket functions would have been a unitary transformation of the orbitals via e^σ where σ is an anti-Hermitian operator. However, σ is a combination of excitation and de-excitation operators, $\sigma = T_1 - T_1^\dagger$, making them non-commuting. This makes such a theory unwieldy due to the occurrence of a non-terminating series of operators. This is useful only when orbital relaxations to a given order under some external perturbation need to be evaluated, such as during the solution of the Coupled Perturbed Hartree-Fock (CPHF) equations for computation of molecular properties. In what follows, we compare the orbital relaxation achieved in the UGA-OSCC theory, which uses the ground-state spatial orbitals, with ordinary open-shell CC which uses the spinorbitals of the ground-state. Our results will indicate the fruitfulness of the UGA-OSCC theory. For

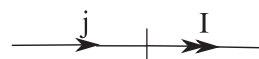


FIG. 1. Spin-free T_j^I when I is a singly occupied active hole orbital with a closed-shell core as vacuum.

for a clearer perspective of the results, we will present numbers from the Δ CCSD approach as well, where the explicit use of the optimized orbitals for the ground and ionized states is made.

A. Extent of clustering in our UGA-OSCC Ansatz

Since in our UGA-OSSC, Ω_μ is in normal order, the one-body *inactive* excitations will have exactly the same form for the orbital relaxation as in an ordinary exponential wave operator, e^{T_μ} , that is, $T_{\mu I}^a$. On the other hand, the one-body excitations involving the singly occupied *active* orbitals (I, in our case) can have I appearing in both the destruction and the creation component of T_μ . In addition to the single excitation from I, $T_{\mu I}^a$, we will also have excitations into I, like $T_{\mu j}^I$. Moreover, we have a rank 2 excitation of the type $T_{\mu j I}^{Ia}$ (involving the spectator excitation of I in the exchange mode) which excites j to a and we therefore call it a pseudo-two-body excitation. *Unlike in the spinorbital-based description, both the one-body and the pseudo-two-body cluster operators induce orbital relaxation.* Without going into the details here, we can show that the pseudo-two-body excitation leads to spin-flipping of the orbital I. This introduces the major non-trivial difference between the spin-free Thouless parametrization and the conventional spinorbital-based ordinary Thouless parametrization. On the other hand, the normal ordering in our Ω_μ will prevent possible contractions between different components of T_μ in which the active hole I is created in one and destroyed in the other. Then, for the one active hole problem, the quadratic and higher powers of the cluster operators which destroy I (T_j^I , shown in Fig. 1, for example), will annihilate ϕ_μ . Thus, it may appear that there would be incomplete clustering of these T_μ s.

Some reflection shows that higher powers of T_j^I appear to contribute to the CC equations for an ordinary exponential Ansatz only because the function ϕ_μ is itself taken as the vacuum for normal-ordering the cluster operators (denoted by $\{\dots\}_\mu$) and T_μ is written in the spinorbital basis (as opposed to writing it in spin-free form). These diagrams will be of the Exclusion Principle Violating (EPV) type with the same spinorbital I_\uparrow appearing twice in a quadratic term as in Fig. 2.

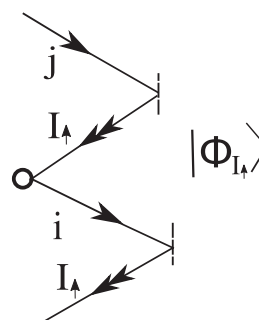


FIG. 2. $H-T_1^2$ term in spinorbital OSCC with ϕ_μ as vacuum.

Here, the vacuum is ϕ_μ itself with a hole I_\uparrow obtained by destroying an electron in the spinorbital I_\uparrow in ϕ_0 : $\phi_\mu \equiv \phi_{I_\uparrow} \equiv a_{I_\uparrow} \phi_0$. Thus, I_\uparrow is a particle and I_\downarrow is a hole spinorbital. We note that this EPV diagram appears because one has used the BCH expansion of $e^{-T_\mu} \text{He} T_\mu$ first and then let it act on ϕ_μ as shown in Fig. 2. Clearly, in the exponential parameterization of Ω_μ

with commuting T_μ s in the spinorbital basis, there are no cluster operators on the left of H indicating that the correlation and relaxation processes are all happening on the ket, $|\rangle$.

From the terms in $\{G_\mu\}_{ex}$ containing θ_μ and W in Eq. (13), with only the linear power of T_μ retained on the left of \bar{H}_μ and $W_{\mu\mu}$, we get the expression

$$\{G_\mu\}_{ex} \Rightarrow \{\bar{H}_\mu\}_{ex} + \{\theta_\mu(\bar{H}_\mu)_{ex}\} + \{\theta_\mu(\bar{H}_\mu)_{cl}\} - \{W_{\mu\mu}\} - \{T_\mu W_{\mu\mu}\} - \{\theta_\mu Y_{\mu\mu}\} \quad (16)$$

$$\Rightarrow \{\bar{H}_\mu\}_{ex} - \{T_\mu(\bar{H}_\mu)_{ex}\} - \{T_\mu(\bar{H}_\mu)_{cl}\} - \{W_{\mu\mu}\} - \{T_\mu W_{\mu\mu}\} + \{T_\mu W_{\mu\mu}\} \quad (17)$$

$$\Rightarrow \{\bar{H}_\mu\}_{ex} - \{T_\mu(\bar{H}_\mu)_{ex}\} - \{W_{\mu\mu}\} - \{T_\mu W_{\mu\mu}\}. \quad (18)$$

Remember that $W_{\mu\mu} \equiv \bar{H}_{\mu cl}$. The entity analogous to the one in Fig. 2 comes from the fourth term of Eq. (18). The spin-free analog of Fig. 2 is shown in Fig. 3, when it acts on $a_{I_\uparrow} \phi_0$. Note that the negative sign from the series expansion of θ_μ [Eq. (11)] takes care of the fact that this operator contracts from the left as opposed to from the right in spinorbital-based OSCC. The composite, to be eventually contracted with the destruction operator a_{I_\uparrow} acting on ϕ_0 , is spin-free, but the action on ϕ_0 filters out the up-spin part only. Interestingly, Fig. 3 does not look like an EPV diagram at all, as T_i^l and T_j^l appear on either side of the Hamiltonian vertex.

In the examples chosen by us above, only one-body operators with the active label I occur but the same arguments hold for analogous quadratic terms containing orbital-relaxing pseudo-two-body operators with active destruction labels, T_{il}^{la} , for example. The rest of the operators involving I are responsible for correlation. The observation that T_μ s appear both on the left and the right of the Hamiltonian is a diagrammatic possibility for our Ansatz with no analog in the spinorbital formulation.

We conclude this subsection with another interesting feature of our Ansatz. Let us consider two T -operators, $t_j^l\{E_j^l\}$ and $t_j^b\{E_j^b\}$. The quadratic term from $\{e^{T_\mu}\}$ will be $t_j^l t_j^b \{E_j^l E_j^b\}$ where the T s are never contracted among themselves. This is analogous to the spinorbital-based quadratic term, $t_j^l\{e_j^l\}_\mu \times t_j^b\{e_j^b\}_\mu$. On the other hand, had we used an ordinary exponential with spin-free T_μ s, we would have obtained an additional contracted composite like the one shown in Fig. 4, which lacks a clear physical interpretation.

We must emphasize, however, that the normal-ordered, spin-free, exponential Ansatz is by no means equivalent to the spinorbital exponential Ansatz and one must not expect a one-to-one correspondence of all the terms because there will

be counter-terms in the spin-free Ansatz which would prevent the occurrence of spin-contamination inherent to the spinorbital formulation.

Summarizing the novel features of the normal-ordered, spin-free, exponential Ansatz, we may comment that (a) it does not miss any clustering warranted by the exponential Ansatz in a spinorbital basis, (b) the normal-ordering avoids some unwarranted T_μ - T_μ contractions, and (c) spin-contaminating terms are eliminated without the loss of relaxation and correlation.

B. Approximations used in our applications and their implications on orbital relaxation

We have approximated $e^{\theta_\mu \bar{H}_{\mu ex}}$ by $\bar{H}_{\mu ex}$ only; $\bar{H}_{\mu ex}$ is an order of magnitude smaller than $\bar{H}_{\mu cl}$, and removing all powers of θ_μ in $e^{\theta_\mu \bar{H}_{\mu ex}}$ is a good approximation. On the other hand, our approximation for e^{θ_μ} is $1 - T_\mu$ for terms involving $\bar{H}_{\mu cl}$. From Eq. (18), we can see that a linear approximation for e^{θ_μ} results in mutual cancellation of the contributions from the direct and the folded terms which involve $\bar{H}_{\mu cl}$. Hence, $\{G_\mu\}_{ex}$ in our implementation is

$$\{G_\mu\}_{ex} = \{\bar{H}_\mu\}_{ex} - \{e^{T_\mu} W_{\mu\mu}\}, \quad (19)$$

which indicates that, operationally speaking, we have simply neglected all the terms containing θ_μ .

With these approximations on e^{θ_μ} , we recover the single CSF limit of the UGA-SUMRCC presented earlier.⁴⁶ Equation (19) is identical to that used in our earlier publications^{46,69,70} where the derivation involved the use of a sufficiency condition rather than an exact derivation with e^{θ_μ} followed by an approximation, as presented here.

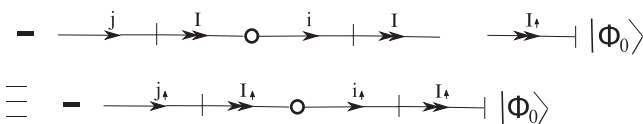


FIG. 3. H - T_1^2 term in UGA-OSCC with ϕ_0 as vacuum. Analog of Fig. 2.

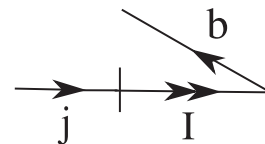


FIG. 4. T_μ - T_μ contraction occurring in an OSCC with a spin-free e^{T_μ} Ansatz but absent in the UGA-OSCC which uses a $\{e^{T_\mu}\}$ Ansatz.

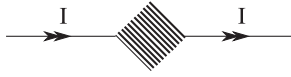
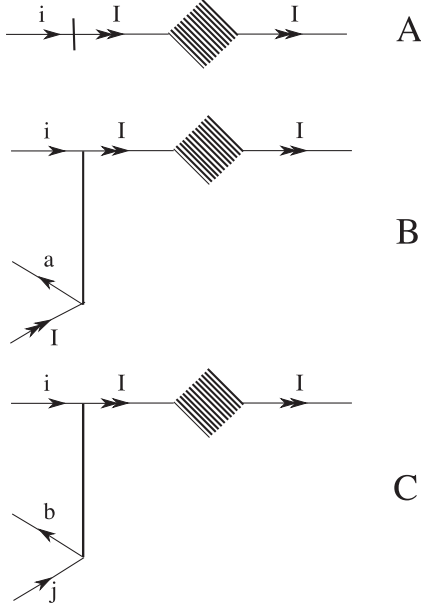
FIG. 5. $W_{\mu\mu}$ for the 1-hole sector.

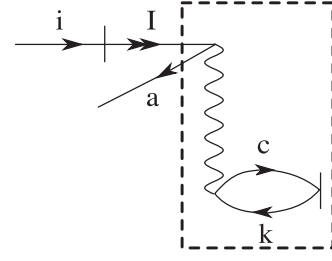
FIG. 6. Possible structures of the folded terms.

We note that the direct term in $\{G_{\mu}\}_{ex}$ in Eq. (19) will now necessarily truncate at quartic power in all situations. However, the termination of the folded term will depend on the rank of the valence sector under consideration. In the extant case, this will be at the quadratic term.

Since E_i^a and E_{il}^a are proportional when they act on ϕ_{μ} , contributions from the composites G_i^a and G_{il}^a are added together and the sum contributes to the equation for T_i^a . No cluster amplitudes of the type t_{il}^{al} are considered. Non-linear terms involving operators like T_i^l , T_{il}^{la} , and T_{ij}^{lb} are missing from the direct term but the *folded terms* of Eq. (19) reintroduce higher powers of these operators when the terms contain the operator $W_{\mu\mu} \equiv \overline{H}_{\mu c l}$. Thus, some measure of $T_{\mu}-T_{\mu}$ contraction is also introduced in our equations. In the following paragraphs, we enumerate the powers of the T_i^l , T_{il}^{la} , and T_{ij}^{lb} operators that we can retain in UGA-OSCC under our approximation.

For the 1h sector, $W_{\mu\mu}$ has the structure in Fig. 5. Terms where T_{μ} s are contracted via the active hole destruction, a_I , can only arise from the folded term. As shown in Fig. 6, the quadratic powers of T_i^l , T_{il}^{la} , and T_{ij}^{lb} are recovered in the folded term as $W_{\mu\mu}$ can contain up to one of these active destructing operators. The class of terms absent in our approximated UGA-OSCC are like those in Figs. 7 and 8. The missed terms in $(G_{1b})_{ex}$ and $(G_{2b})_{ex}$ are responsible for the relaxation of the virtual functions responsible for correlation and are thus less important than those contributing to the R_i^l and R_{il}^{la} residues which are responsible for the orbital relaxation of ϕ_{μ} and spin-polarization, respectively.

In our implementation, we have confined ourselves to cluster operators up to rank two and G_{μ} up to rank three. The

FIG. 7. Example of a missing 1-body term when $e^{\theta_{\mu}}$ is approximated in the UGA-OSCC formalism. The boxed structure is a component of $\overline{H}_{\mu ex}$.

three-body G_{μ} s are all pseudo-triples which have 2 inactive hole and 2 inactive particle labels with I appearing in direct and exchange spectator modes. They are as follows:

$$G_{ijl}^{abl}, G_{ijl}^{bal}, G_{ijl}^{alb}, G_{ijl}^{bla}, G_{ijl}^{lab}, G_{ijl}^{lba} \rightarrow \text{pseudo-triples}.$$

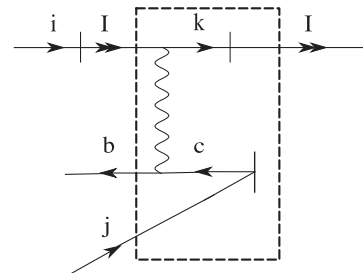
We would like to point out that the terms in our theory in its current form do not simply form a subset of the spinorbital OSCC. Due to the use of projection equations, certain three-body structures of the spin-flip type (e.g., G_{ijl}^{alb}) are present which are absent from the singles-doubles truncated spinorbital OSCC. Moreover, as mentioned before, spin-contaminating contributions are absent.

We conclude by summarizing the major features of the UGA-OSCC as implemented by us from the leading approximation of the exact formulation.

1. The closed term is unaffected by approximations in $e^{\theta_{\mu}}$.
2. Among the terms contributing to $(G_{1b})_{ex}$ and $(G_{2b})_{ex}$, terms like Figs. 7 and 8 which cannot be represented by a T contracting with a closed one-body $W_{\mu\mu}$ from the left are missing.
3. $(G_{3b})_{ex}$ misses all terms containing more than one active destruction containing operator (i.e., EPV terms) since no folded three-body term is possible.

IV. THE SCALAR RELATIVISTIC HAMILTONIAN

As mentioned in Sec. I, the parent relativistic Hamiltonian used in our investigation consists of the one-electron Dirac Hamiltonian, H^D , in the Born-Oppenheimer approximation and a two-electron operator H_{2-el} containing one term of order c^0 and some selected terms of order c^{-2} as derived from QED. In the Coulomb gauge, the leading two-electron term is the Coulomb interaction, V^C , of order c^0 ,

FIG. 8. Example of a missing 2-body term when $e^{\theta_{\mu}}$ is approximated in UGA-OSCC. The boxed structure is a component of $\overline{H}_{\mu ex}$.

with the Breit term, V^B , of order c^{-2} —being the first order QED correction

$$H^D = \sum_i c(\alpha \cdot \mathbf{p}(i)) + \beta c^2 + v(i), \quad (20)$$

where $v(i) = -\phi(i)$, $\phi(i)$ being the potential due to frozen nuclei, and α and β are (4×4) Dirac matrices, which give a 4-component structure to the equation. V^C is given by

$$V^C = \frac{1}{2} \sum_{i \neq j} \frac{I_4 \cdot I_4}{r_{ij}}. \quad (21)$$

The Breit interaction, V^B , consists of two terms—the first term is called the Gaunt term, V^G , which can be interpreted as a current-current interaction, and the second one is the gauge-dependent entity V^{gauge} ,

$$V^B = V^G + V^{gauge}, \quad (22)$$

with

$$V^G = -\frac{1}{2} \sum_{i \neq j} \frac{1}{c^2} \frac{(\mathbf{c}\alpha_i) \cdot (\mathbf{c}\alpha_j)}{r_{ij}} \quad (23)$$

and

$$V^{gauge} = -\frac{1}{2} \sum_{i \neq j} \frac{1}{c^2} \frac{(\mathbf{c}\alpha_i r_{ij}) \cdot (\mathbf{c}\alpha_j r_{ij})}{r_{ij}^3}. \quad (24)$$

In our applications, we will entirely neglect the gauge-dependent term in the Breit interaction and will consider the Gaunt term only. Our parent Dirac-Coulomb-Gaunt (DCG) Hamiltonian will thus have the form

$$H = H^D + V^C + V^G. \quad (25)$$

As emphasized in Sec. I, since our goal is to describe molecules with up to only medium-heavy elements, a consideration of the spin-free part of H above should suffice. This separation is not unique¹⁰⁵ and can be attained in various ways.

Dyall proposed⁷⁵ a separation of the spin-dependent terms by expressing the small-component of the wave-function, Ψ_S , in terms of a pseudo-large component ϕ_L : $2c\Psi_S = (\boldsymbol{\sigma} \cdot \mathbf{p})\phi_L$, where ϕ_L has the same symmetry properties as Ψ_L . This change of representation yields the so-called modified-Dirac Hamiltonian (H^{MD}), and the subsequent spin separation is carried out by using the Dirac identity. In another approach by Visscher and Saue,⁷⁶ one writes a more compact representation of H^{MD} using quaternions and sets to zero all the quaternion-imaginary terms. The two-body part of the Hamiltonian, H_{2-el} , is also subjected to a similar treatment. The difference between the approach by Dyall and that by Visscher and Saue is that in the former, the spin-separation is done at the operator level, which is effectively for each Ψ_S basis, while in the latter, the

real part of the full Hamiltonian integrals in their quaternionic form is separated out after applying the metric transformation of Dyall to the wave function. In numerical terms, the differences in the energies computed are very small although it increases as the nuclei get heavier. In our applications, we have used the DIRAC program package and hence have adopted the second approach. The approach by Dyall is implemented in CFOUR,^{78,97,98,106,107} for example, and results can be slightly different from DIRAC as far as the spin-free Hamiltonian is concerned.

Under the “no pair” approximation,¹⁰⁸ the second-quantized representation of our spin-free relativistic Hamiltonian may be written as

$$H = \sum_{pq} \langle p | H^D | q \rangle_{SF} E_q^p + \frac{1}{2} \sum_{pqrs} \langle pq | (V^C + V^G) | rs \rangle_{SF} E_{rs}^{pq}, \quad (26)$$

where p, q, r , and s are general orbital indices belonging to the positive energy solution and E_q^p and E_{rs}^{pq} are the generators of the unitary group introduced in Sec. II. $\langle p | \hat{O} | q \rangle_{SF}$ is a generic notation to denote the real part of the integral in quaternionic form. We note that the relativistic Hamiltonians under the “no pair” approximation resemble non-relativistic Hamiltonians in structure—only the Hamiltonian operators involved are relativistic.

The spin-free DC Hamiltonian has been very well studied in several contexts,^{75,78,80,97,98} but similar studies including the spin-free Gaunt term are scarce although some studies of the full Gaunt term on atoms have been carried out.^{94,109,110} When the spin-separation is carried out on the Gaunt term following Dyall, we get a scalar part, a spin-orbit part, and a spin-spin part, among which only the scalar part is kept giving us the SF-DCG Hamiltonian. The scalar part has a Darwin-like term and a part of the orbit-orbit contribution. In practice, we generate the spin-free matrix elements of $\langle pq | V^G | rs \rangle$ by setting to zero all the quaternionic imaginary components of the integrals following Visscher and Saue.⁷⁶ In our applications, in this paper, only the SF-4C Hamiltonian is used at the correlated level. The effect of the spin-free Gaunt term is estimated at the Δ SCF level and added to the correlated IP values computed using UGA-OSCC with the SF-4C Dirac-Coulomb Hamiltonian. We refer to this approach as the SF-4C+G.

We now provide a succinct qualitative discussion of the reduction of a four-component relativistic theory to a two-component theory. This was always considered useful in view of the fact that in most of the chemical applications, the negative energy part is not so important. To generate the SF-2C working equations, a unitary transformation is applied to the SF-4C equations to block-diagonalize H^{MD} and decouple the equations for the large and the pseudo-large components of the wave-function. V_{SF}^C and V_{SF}^G , the two-electronic parts of the Hamiltonian, are not transformed, rather the large-large components are simply retained. This is called the SF-X2C-1e approach in the literature.^{78,80,81} As a result of this approximation, the Hamiltonian is no longer equivalent to the SF-4C and a so-called “picture change error”⁸⁷ is introduced. In this paper, we investigate how significant the “picture change error” is, when we are probing the core electrons.

V. MOLECULAR APPLICATIONS

A. Computational details

We have chosen the hydrides of elements from groups 14-17 and periods 2-4 for our study. The vertical IP of the 1s electron of the heavy atom is computed in each case. For the non-relativistic calculations, we have used the cc-pCVTZ basis sets for the molecules from periods 2 and 3 and the uncontracted dyall.cv3z basis set for those from period 4. For the relativistic calculations, the uncontracted dyall.cv3z basis set was used in all cases. The ground-state molecular geometries were taken from the NIST database¹¹¹ and are listed in the [supplementary material](#). The experimental values are used as benchmarks for assessing the accuracy of the computed IPs with different Hamiltonians and wave-function Ansätze although no special effort is made to mimic experimental conditions such as inclusion of vibrational effects, geometry relaxations, etc. Our conclusions are only with regard to trends, the role of different terms in the Hamiltonian and the level of accuracy of the wave-function Ansatz in approaching the experimental IP. We shall see that the magnitude of the changes is sufficient for us to be conclusive without further polishing our computations, although this is eminently possible, if required. For some of the molecules containing atoms of periods 3 and 4, the experimental values available are atomic, but for the core IP of hydrides these are known to be very close to the corresponding molecular values.¹¹² When more than one experimental value is reported, we have used the average of these values to compute differences with our results.

The DIRAC quantum chemistry package¹¹³ is interfaced to our in-house UGA-OSCC code where DIRAC has been used for generating the Hamiltonian integrals in the molecular orbital basis. The Δ SCF and Δ CCSD computations have been computed entirely within DIRAC. We have used the Gaussian nucleus model for the relativistic Hamiltonians and a point nucleus model for the non-relativistic one. For the post-SCF coupled-cluster computations, energy cutoffs were used for the virtual orbitals in order to discard very high energy unphysical orbitals which are often generated when using uncontracted basis sets. A rough estimate of the energy of physically relevant virtual orbitals was made from the binding energy of the innermost electron. The same cutoff was used for the GS and the ionized state CCSD and UGA-OSCC computations. These cutoffs are provided in Table I of the [supplementary material](#). Default convergence thresholds in DIRAC were used in all cases, while for the UGA-OSCC, the convergence threshold of the CCSD residual was 10^{-8} for all molecules except H_2O (10^{-5}).

B. Results and discussions

In this paper, we have studied a series of spin-free relativistic Hamiltonians with and without the incorporation of electron correlation and have addressed five main issues:

- Whether the orbital relaxation captured by our UGA-OSCC theory is adequate to describe the core ionization process.
- The role of electron correlation, both with and without inclusion of relativity, in the accuracy of the core IP.

- The role of the spin-free Dirac-Coulomb (SF-DC) terms in the Hamiltonian in determining the accuracy of the core IP for light to medium heavy elements.
- The accuracy of the SF-2C Hamiltonian vis-a-vis the SF-4C.
- The contribution of the spin-free Gaunt (SF-4C+G) terms to the core IP.

In this paper, we have explored two pathways for computing the core IP when including both orbital relaxation and correlation effects. The correlated GS, in all cases, is treated with the ordinary closed shell CCSD. For the ion, the first, more straightforward path is to compute the Hartree-Fock state via an average of configuration¹¹⁴ calculations followed by a spinor/spinorbital-based open-shell coupled-cluster computation. The open-shell is kept at the core region via a maximum overlap technique at every iterative step of the orbital optimization. The first step thus incorporates the full orbital relaxation on ionization of the core-electron. The coupled-cluster computation then includes the electron correlation, albeit with some accompanying spin-contamination. This is called the Δ CCSD method for IPs. In this procedure we can, thus, easily identify the effect of orbital relaxation and correlation on the state energies and IPs. We call this approach A.

The second path for computation of the IP is by calculating the difference of the closed-shell coupled-cluster GS energy and the energy of the ionized state with coupled-cluster but using the GS orbitals. Thus, the CC Ansatz is responsible for both the orbital relaxation and the electron correlation. The CC computation may be done with the spinor/spinorbital OSCC which we call CCSD (GS orb) or with our UGA-OSCC. The degree of correlation in the CCSD (GS orb) and the UGA-OSCC ionized state is not exactly the same and not transparent enough to establish theoretically (as explained in Sec. II). Thus, we wish to establish the degree of incorporation of orbital relaxation and correlation in the UGA-OSCC theory through a numerical comparison of CCSD (GS orb) and UGA-OSCC with Δ CCSD as the reference value. We call this approach B.

When approach A is adopted, the relaxation contribution comes from SCF optimization of the ion and this is tabulated in Table I. The orbital relaxation shown in Table I is very high and roughly similar for NR and SF-4C/SF-2C computations. The quantity is very sensitive to the central heavy atom and increases rapidly across a period and even faster down a group. For the lightest molecule in group 14, CH_4 , orbital relaxation is roughly 0.517/0.519/0.519H (NR/SF-2C/SF-4C) and for the heaviest, GeH_4 , it is 1.863/1.913/1.908H. Comparing with GeH_4 , the leftmost molecule in period 4, the rightmost, i.e., HBr , shows orbital relaxation of 1.931/1.996/1.989H. We also note that SF-2C gives the same orbital relaxation contribution to energy for the lighter molecules and slightly overestimates it for the heavier ones.

The correlation energies for the ground states are tabulated in Table II and the correlation contribution from Δ CCSD and CCSD (GS orb) to the core IPs of elements of period 4 is presented in Table III. From Tables II and III, one can notice that the correlation energy with relativistic and non-relativistic Hamiltonians is different. This establishes the fact

TABLE I. Orbital Relaxation contribution to the core IP in Hartrees. This is the difference between the ΔSCF and Koopmans' IPs.

Theory	XH ₄		XH ₃		XH ₂		XH	
	X	IP _{orb-relax}	X	IP _{orb-relax}	X	IP _{orb-relax}	X	IP _{orb-relax}
NR SCF	C	-0.517	N	-0.637	O	-0.742	F	-0.812
	Si	-1.015	P	-1.069	S	-1.116	Cl	-1.152
	Ge	-1.863	As	-1.889	Se	-1.914	Br	-1.931
SF-2C SCF	C	-0.519	N	-0.646	O	-0.755	F	-0.826
	Si	-1.026	P	-1.083	S	-1.134	Cl	-1.172
	Ge	-1.913	As	-1.944	Se	-1.974	Br	-1.996
SF-4C SCF	C	-0.519	N	-0.646	O	-0.755	F	-0.826
	Si	-1.026	P	-1.082	S	-1.133	Cl	-1.171
	Ge	-1.908	As	-1.939	Se	-1.968	Br	-1.989

that correlation and relativity are not additive. Moreover, the difference is not the same for the ground and the ionized states.

The correlation energy in approach B for UGA-OSCC and CCSD (GS orb) is roughly estimated by taking a difference with the SCF energy of the ion. A simple difference of the correlated energy of the ion and the ground state CCSD energy would give both relaxation and correlation. The correlation energies of the ionic states of the full set of molecules, computed using UGA-OSCC, are presented in Table IV. For our test set of molecules, the number of electrons is the same for each period. The differences in the correlation energies are thus related to the difference in the chemical environment. While the absolute value of the correlation energy for both the GS (Table II) and the ion (Table IV) is very large, ranging from a few hundred millihartrees (mH) for period 2 to more than a Hartree for period 4, the difference between them (i.e., the effect on the IP) is quite small (10-20 mH for period 4). This is expected as the GS and the ion only differ by one electron. We can thus anticipate that to describe IPs accurately with a correlated theory, the level of correlation of the ground and ionized states must be at par. We can conclude that it is probably better to not have correlation at all than in an unbalanced fashion. CC linear response methods are not suitable on this ground.

TABLE II. Correlation energies in Hartrees of the ground state using various Hamiltonians.

Theory	XH ₄		XH ₃		XH ₂		XH	
	X	E _{corr} ^{GS}	X	E _{corr} ^{GS}	X	E _{corr} ^{GS}	X	E _{corr} ^{GS}
NR CCSD	C	-0.269	N	-0.301	O	-0.325	F	-0.282
	Si	-0.445	P	-0.509	S	-0.531	Cl	-0.546
	Ge	-1.294	As	-1.355	Se	-1.360	Br	-1.383
SF-2C CCSD	C	-0.256	N	-0.304	O	-0.289	F	-0.339
	Si	-0.489	P	-0.523	S	-0.539	Cl	-0.555
	Ge	-1.310	As	-1.364	Se	-1.381	Br	-1.401
SF-4C CCSD	C	-0.256	N	-0.304	O	-0.296	F	-0.339
	Si	-0.489	P	-0.523	S	-0.539	Cl	-0.554
	Ge	-1.309	As	-1.362	Se	-1.379	Br	-1.398

TABLE III. Comparison of correlation energies of the ion in Hartrees computed using CCSD, CCSD (GS orb), and UGA-CCSD for the molecules of period 4.

GeH ₄			
	NR	SF-2C	SF-4C
CCSD	-1.297	-1.306	-1.303
CCSD (GS orb)	-1.227	-1.292	-1.226
UGA-CCSD	-1.287	-1.282	-1.282
AsH ₃			
	NR	SF-2C	SF-4C
CCSD	-1.395	-1.357	-1.354
CCSD (GS orb)	-1.391	-1.357	-1.322
UGA-CCSD	-1.408	-1.409	-1.408
H ₂ Se			
	NR	SF-2C	SF-4C
CCSD	-1.363	-1.370	-1.368
CCSD (GS orb)	-1.336	-1.337	-1.336
UGA-CCSD	-1.332	-1.333	-1.332
HBr			
	NR	SF-2C	SF-4C
CCSD	-1.370	-1.388	-1.385
CCSD (GS orb)	-1.342	-1.375	-1.373
UGA-CCSD	-1.339	-1.372	-1.370

The correlation energies for the ionized state using CCSD (GS orb) and UGA-OSCC differ at most by a few milli-Hartrees (mH) from each other and by tens of mH from $\Delta CCSD$ (see Table III). Two notable exceptions were GeH₄ and AsH₃ which we investigated further. In the case of GeH₄, UGA-OSCC is 22mH away from $\Delta CCSD$, while CCSD (GS orb) is 77mH away leading to a large difference of 55mH between them. On increasing the cutoff energy of the virtual orbitals, this difference reduces to 49mH. In the case of AsH₃, UGA-OSCC places the ion 54mH below the $\Delta CCSD$ value and CCSD (GS orb) places it 33mH above, leading to a massive difference of 86mH. On increasing the virtual space by 1 orbital,

TABLE IV. Correlation energies in Hartrees of the ion computed with UGA-OSCC using various Hamiltonians.

Theory	XH ₄		XH ₃		XH ₂		XH	
	X	E _{corr} ^{Ion}	X	E _{corr} ^{Ion}	X	E _{corr} ^{Ion}	X	E _{corr} ^{Ion}
NR UGA-OSCC	C	-0.279	N	-0.306	O	-0.319	F	-0.238
	Si	-0.361	P	-0.488	S	-0.505	Cl	-0.518
	Ge	-1.287	As	-1.408	Se	-1.332	Br	-1.339
SF-2C UGA-OSCC	C	-0.277	N	-0.304	O	-0.299	F	-0.313
	Si	-0.481	P	-0.516	S	-0.509	Cl	-0.522
	Ge	-1.282	As	-1.409	Se	-1.333	Br	-1.372
SF-4C UGA-OSCC	C	-0.276	N	-0.304	O	-0.299	F	-0.313
	Si	-0.481	P	-0.516	S	-0.509	Cl	-0.522
	Ge	-1.282	As	-1.408	Se	-1.332	Br	-1.370

TABLE V. IP of 1s electron (core IP) of the central atom in eV.

Molecule	State	Basis	Hamiltonian	UGA-OSCC	Experiment
CH ₄	C 1s-1	cc-pCVTZ	NR	290.56	290.86 ¹¹⁵
		dyall.cv3z	SF-2C	290.33	
		dyall.cv3z	SF-4C	290.36	
SiH ₄	Si 1s-1	cc-pCVTZ	NR	1 846.12	1 847.1 ¹¹⁶
		dyall.cv3z	SF-2C	1 848.18	
		dyall.cv3z	SF-4C	1 848.64	
GeH ₄	Ge 1s-1	dyall.cv3z	NR	10 976.06	11 103.1 ^{a 117}
		dyall.cv3z	SF-2C	11 127.60	
		dyall.cv3z	SF-4C	11 134.07	
NH ₃	N 1s-1	cc-pCVTZ	NR	405.22	405.6 ¹¹⁵
		dyall.cv3z	SF-2C	405.53	
		dyall.cv3z	SF-4C	405.57	
PH ₃	P 1s-1	cc-pCVTZ	NR	2 146.90	2 150.88 ¹¹⁸
		dyall.cv3z	SF-2C	2 152.14	
		dyall.cv3z	SF-4C	2 152.72	
AsH ₃	As 1s-1	dyall.cv3z	NR	11 718.05	11 866.7 ^{a 117}
		dyall.cv3z	SF-2C	11 890.19	
		dyall.cv3z	SF-4C	11 897.34	
H ₂ O	O 1s-1	cc-pCVTZ	NR	539.38	539.78 ¹¹⁵
		dyall.cv3z	SF-2C	539.26	
		dyall.cv3z	SF-4C	539.52	
H ₂ S	S 1s-1	cc-pCVTZ	NR	2 472.76	2 478.91 ¹¹⁹
		dyall.cv3z	SF-2C	2 480.35	
		dyall.cv3z	SF-4C	2 481.06	
H ₂ Se	Se 1s-1	dyall.cv3z	NR	12 488.83	12 657.8 ^{a 117}
		dyall.cv3z	SF-2C	12 684.43	
		dyall.cv3z	SF-4C	12 692.29	
HF	F 1s-1	cc-pCVTZ	NR	694.38	694.01 ¹¹⁵
		dyall.cv3z	SF-2C	694.40	
		dyall.cv3z	SF-4C	694.51	
HCl	Cl 1s-1	cc-pCVTZ	NR	2 822.44	2 822.4 ^{a 117}
		dyall.cv3z	SF-2C	2 832.31	
		dyall.cv3z	SF-4C	2 833.17	
HBr	Br 1s-1	dyall.cv3z	NR	13 283.24	13 473.7 ^{a 117}
		dyall.cv3z	SF-2C	13 503.35	
		dyall.cv3z	SF-4C	13 512.00	

^a Atomic core IP.

CCSD (GS orb) gains a correlation energy of 20mH and the energy of the ion comes to lie 13mH above the Δ CCSD value. This orbital is found to have a large Rydberg-like s-character which results in a high contribution to the energy of the 1s ionized state. Unfortunately, we were unable to converge our UGA-OSCC computation in this increased space but we may surmise that a large change in correlation energy would result from the inclusion of this virtual orbital which may act to bring the ion energies from CCSD (GS orb) and UGA-OSCC closer. The virtual orbital cutoff, although essential, must thus be chosen carefully. Overall, our results indicate that UGA-OSCC is very effective at not only balancing out the correlation of the GS and ion but also achieving a correlation energy comparable to the Δ CCSD and CCSD (GS orb). For example, the 1s

TABLE VI. SF-4C and SF-2C relativistic contributions to the core IP in eV computed using UGA-OSCC.

Hamiltonian	X	XH ₄		XH ₃		XH ₂		XH	
		IP _{Rel} -IP _{NR}		IP _{Rel} -IP _{NR}		IP _{Rel} -IP _{NR}		IP _{Rel} -IP _{NR}	
SF-4C	C	-0.200	N	0.354	O	0.141	F	0.129	
	Si	2.524	P	5.826	S	8.303	Cl	10.728	
	Ge	158.012	As	179.286	Se	202.062	Br	228.765	
SF-2C	C	-0.231	N	0.306	O	-0.118	F	0.018	
	Si	2.055	P	5.242	S	7.590	Cl	9.863	
	Ge	151.539	As	172.139	Se	194.202	Br	220.113	
SF-4C-SF-2C	C	-0.031	N	-0.048	O	-0.259	F	-0.111	
	Si	-0.469	P	-0.584	S	-0.713	Cl	-0.865	
	Ge	-6.473	As	-7.147	Se	-7.860	Br	-8.652	

IP of HBr with an SF-4C Hamiltonian computed with UGA-OSCC and Δ CCSD differs by only 0.4 eV, while UGA-OSCC and CCSD (GS orb) differ by only 0.09 eV. The difference in the correlation energy of the ion captured by UGA-OSCC and Δ CCSD is about 15 mH ($\sim 1\%$ of the correlation energy). With CCSD (GS orb), the difference is only 3 mH. This indicates that the loss of clustering arising from our approximations on e^{θ_μ} in the working equation is not significant enough to affect the accuracy of the computed IPs. The primary motivation for the UGA-OSCC method continues to be the avoidance of spin-contamination which is inherent in the Δ CCSD and CCSD (GS orb) methods. Moreover, Δ CCSD incurs the cost of two integral transformations—one with the GS orbitals and one with the ionic orbitals.

A comparison of the core IPs computed by us, using the UGA-OSCC theory and various Hamiltonians, with the experimental values is presented in Table V. We first focus our

TABLE VII. Errors in the core IP in eV relative to the experimental value with various Hamiltonians.

GeH ₄					
Diff. with expt. in eV	NR	SF-2C	SF-4C	SF-4C+G	DCG
Koopmans' IP	-76.55	75.80	82.17	66.60	66.28
Δ SCF	-127.37	23.74	30.24	14.10	13.76
AsH ₃					
Diff. with expt. in eV	NR	SF-2C	SF-4C	SF-4C+G	DCG
Koopmans' IP	-95.93	77.61	84.63	67.42	67.04
Δ SCF	-147.38	24.70	31.88	14.04	13.65
H ₂ Se					
Diff. with expt. in eV	NR	SF-2C	SF-4C	SF-4C+G	DCG
Koopmans' IP	-114.34	82.34	90.08	71.09	70.65
Δ SCF	-166.62	28.63	36.52	16.87	16.40
HBr					
Diff. with expt. in eV	NR	SF-2C	SF-4C	SF-4C+G	DCG
Koopmans' IP	-139.12	83.17	91.66	70.78	70.25
Δ SCF	-191.67	28.86	37.52	15.92	15.38

TABLE VIII: Best estimates for the computed core IPs of the elements of period 4. The IP computed with an SF-4C Hamiltonian at the correlated level is corrected with an estimate of the Gaunt contribution to the IP calculated at the SCF level (i.e., the difference in the Δ SCF IP values with and without the spin-free Gaunt term in the Hamiltonian).

GeH ₄		
	IP in eV	Diff. with expt. in eV
UGA-CCSD(SF-4C)+SCF Gaunt	11 117.93	14.83
Δ CCSD(SF-4C)+SCF Gaunt	11 117.34	14.24
Experimental IP	11 103.1	
AsH ₃		
	IP in eV	Diff. with expt. in eV
UGA-CCSD(SF-4C)+SCF Gaunt	11 879.50	12.80
Δ CCSD(SF-4C)+SCF Gaunt	11 880.96	14.26
Experimental IP	11 866.7	
H ₂ Se		
	IP in eV	Diff. with expt. in eV
UGA-CCSD(SF-4C)+SCF Gaunt	12 672.63	18.13
Δ CCSD(SF-4C)+SCF Gaunt	12 671.68	17.18
Experimental IP	12 654.5	
HBr		
	IP in eV	Diff. with expt. in eV
UGA-CCSD(SF-4C)+SCF Gaunt	13 490.40	16.70
Δ CCSD(SF-4C)+SCF Gaunt	13 489.99	16.29
Experimental IP	13 473.7 \pm 0.4	

attention on the effect of relativistic corrections, at the SF-4C level against the spin-free NR Hamiltonian, with the UGA-OSCC theory as the correlation model. Our observations bear out the expectation that the relativistic contributions increase with the weight of the nucleus. As evident from Table VI, for the elements of period 2, the relativistic contribution to the IP is a few tenths of an eV which is of the order of experimental accuracy but the sign of the correction as well as the variation from the left to right of the periodic table is not smooth. Periods 3 and 4 are well-behaved. In period 3, for example, the core IP of Si in SiH₄ is shifted by 2.5 eV from the NR value by the SF-4C relativistic contribution. Period 4 shows the same trends as period 3 albeit with the magnitudes of the relativistic contributions increased by an order of magnitude. For example, the relativistic contribution to the core IP of Ge in GeH₄ is 158 eV.

The loss in going from SF-4C to SF-2C is about 0.03–0.12 eV for period 2 (well below experimental accuracy), 0.4–0.9 eV for period 3, and 6–9 eV for period 4 making the 2C theories more and more unreliable for heavier elements. This is certainly a fallout of the ‘picture change’ error resulting from not transforming the two-electron part of the Hamiltonian.⁸⁷

Within the limits of the spin-free approximation, the most accurate Hamiltonian we have used is the SF-DCG. The spin-free Gaunt correction to the SF-4C IP is calculated at the Δ SCF

level and added to the SF-4C IP computed at the UGA-OSCC level (SF-4C+G). Compared to the SF-4C+G, the SF-4C overestimates the relativistic contribution, as does the SF-2C (viz. Table VII) by about 16–22 eV for the elements of period 4 indicating that the Gaunt term is absolutely essential. For example, the relativistic contribution to the core IP of Ge in GeH₄ is 142 eV at the SF-4C+G, 158 eV at the SF-4C, and 152 eV at the SF-2C level. The relativistic contributions increase as we move to the right of the period, as expected, and for the heaviest atom in our test set, Br, the SF-4C+G contribution is 207 eV. The computed core IP for HBr is still away from the experimental value by 16 eV at both the correlated and the uncorrelated levels. We have investigated further by including the spin-dependent terms in the Hamiltonian, that is, with the full DCG Hamiltonian at the Δ SCF level. In the particular case of the 1s ionization, we have observed that the role of the spin-dependent terms is negligible. For instance, we have observed an improvement of only ~ 0.5 eV for HBr with the full DCG Hamiltonian over the corresponding spin-free approximation. Therefore, even the inclusion of Gaunt terms into the Hamiltonian is not good enough to approach experimental accuracy. Even higher order QED corrections must thus be important in these cases. The best estimates of the IPs for the period 4 molecules are presented in Table VIII.

VI. SUMMARY AND FUTURE PERSPECTIVE

With regard to the efficacy of our UGA-OSCC theory, we have concluded the following: (a) The accuracy of the computed IPs is of the same order as the CCSD (GS orb) and the Δ CCSD theory without the problem of spin-contamination or different non-orthogonal orbitals. Therefore the UGA-OSCC method is perfectly suited for the calculation of transition properties. (b) The orbital relaxation mechanism of the wavefunction Ansatz in UGA-OSCC is sufficiently good to take care of very high energy processes such as the ionization of the 1s electron from medium-heavy atoms without unmanageable convergence difficulties. This particular aspect is important in the multi-reference version of this theory since in a multi-reference calculation, we typically utilize the same set of orbitals for all the states, and the present approach is capable of incorporating adequate orbital relaxation for each of them separately. (c) The correlation energy for the ground and ionized states are treated in a balanced way in spite of the lack of full exponentiation in the approximated equation for the ionized state.

Through this study, we have made three primary observations with regard to the relativistic effects on the core IP: (a) The relativistic contribution of the spin-free terms to the core IP is of the order of experimental error margins (usually tenths of an eV) even for elements of period 2 and increases by a factor of 10 when going down the group in the periodic table. (b) To approach experimental accuracy, the Gaunt terms in the Hamiltonian are necessary from period 3 onwards. This is evident even at the Δ SCF level. (c) The difference between the spin-free two-component theories and the spin-free four-component theories is about one order of magnitude less than that between the non-relativistic and spin-free four-component

theories but is still more than experimental accuracy from period 3 onwards.

An obvious future line of exploration would be to study satellite peaks and near-edge X-ray peaks by expanding our formalism to the UGA-SUMRCC, which has the capability of handling multi-reference ionized states. Another avenue worth exploring is to study core-ionization processes for molecules which have just one non-singlet CSF as their ground-states. Core-excitations are currently being investigated and will form the subject matter of a future publication.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for the geometries of all the molecules studied and the energy cutoffs for the virtual orbitals.

ACKNOWLEDGMENTS

We thank Trond Saue, Lan Cheng, and Dibyajyoti Chakravarti for stimulating discussions. We also thank the referees for their comments and especially for noticing a discrepancy in the numbers which helped us to find a data handling error. D.M. thanks the SERB, India for the Distinguished Fellowship conferred on him, the CEFIPRA bilateral project (Grant No. 4705-3) and the institute research grant. S.S. thanks the CEFIPRA (Grant No. 4705-3) for travel support and the Research Council of Norway (Grant No. 240674) for her fellowship. This work was also partially supported by the Research Council of Norway through its Centres of Excellence scheme, project number 262695. A.S. thanks the CEFIPRA (Grant No. 4705-3) for the financial support of his Ph.D.

- ¹C. South, A. Shee, D. Mukherjee, A. K. Wilson, and T. Saue, *Phys. Chem. Chem. Phys.* **18**, 21010 (2016).
- ²P. S. Bagus, *Phys. Rev.* **139**, A619 (1965).
- ³H. Nakatsuji and T. Yonezawa, *Chem. Phys. Lett.* **87**, 426 (1982).
- ⁴H. Wasada and K. Hirao, *Chem. Phys.* **138**, 277 (1989).
- ⁵B. Datta, R. Chaudhuri, and D. Mukherjee, *J. Mol. Struct.: THEOCHEM* **361**, 21 (1996).
- ⁶M. Ilias, V. Kello, and M. Urban, *Acta Phys. Slovaca. Rev. Tutorials* **60**, 259 (2010).
- ⁷S. Coriani, O. Christiansen, T. Fransson, and P. Norman, *Phys. Rev. A* **85**, 022507 (2012).
- ⁸S. Coriani, T. Fransson, O. Christiansen, and P. Norman, *J. Chem. Theory Comput.* **8**, 1616 (2012).
- ⁹T. Fransson, D. Burdakova, and P. Norman, *Phys. Chem. Chem. Phys.* **18**, 13591 (2016).
- ¹⁰U. Ekström, P. Norman, and V. Carravetta, *Phys. Rev. A* **73**, 022501 (2006).
- ¹¹Y. Ohtsuka and H. Nakatsuji, *J. Chem. Phys.* **124**, 054110 (2006).
- ¹²J. D. Watts and R. J. Bartlett, *J. Chem. Phys.* **93**, 6104 (1990).
- ¹³M. Nooijen and R. J. Bartlett, *J. Chem. Phys.* **102**, 6735 (1995).
- ¹⁴H. Sekino and R. J. Bartlett, *Int. J. Quantum Chem.* **26**, 255 (1984).
- ¹⁵J. Geertsen, M. Rittby, and R. J. Bartlett, *Chem. Phys. Lett.* **164**, 57 (1989).
- ¹⁶J. F. Stanton and R. J. Bartlett, *J. Chem. Phys.* **98**, 7029 (1993).
- ¹⁷R. J. Bartlett, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2**, 126 (2012).
- ¹⁸M. Musial, S. A. Kucharski, and R. J. Bartlett, *J. Chem. Phys.* **118**, 1128 (2003).
- ¹⁹J. D. Watts, *Radiat. Induc. Mol. Phenom. Nucleic Acids* **5**, 65 (2008).
- ²⁰A. I. Krylov, *Annu. Rev. Phys. Chem.* **59**, 433 (2008).
- ²¹N. A. Besley, *Chem. Phys. Lett.* **542**, 42 (2012).
- ²²B. Peng, P. J. LeStrange, J. J. Goings, M. Caricato, and X. Li, *J. Chem. Theory Comput.* **11**, 4146 (2015).
- ²³H. J. Monkhorst, *Int. J. Quantum Chem.* **12**, 421 (1977).
- ²⁴D. Mukherjee and P. Mukherjee, *Chem. Phys.* **39**, 325 (1979).
- ²⁵S. Ghosh, D. Mukherjee, and S. Bhattacharyya, *Mol. Phys.* **43**, 173 (1981).

- ²⁶H. Koch and P. Jørgensen, *J. Chem. Phys.* **93**, 3333 (1990).
- ²⁷H. Koch, H. J. A. Jensen, P. Jørgensen, T. Helgaker, G. E. Scuseria, and H. F. Schaefer, *J. Chem. Phys.* **92**, 4924 (1990).
- ²⁸H. Koch, H. J. A. Jensen, P. Jørgensen, and T. Helgaker, *J. Chem. Phys.* **93**, 3345 (1990).
- ²⁹B. Datta, P. Sen, and D. Mukherjee, *J. Phys. Chem.* **99**, 6441 (1995).
- ³⁰O. Christiansen, P. Jørgensen, and C. Hättig, *Int. J. Quantum Chem.* **68**, 1 (1998).
- ³¹S. Coriani and H. Koch, *J. Chem. Phys.* **143**, 181103 (2015).
- ³²S. Coriani and H. Koch, *J. Chem. Phys.* **145**, 149901 (2016).
- ³³M. Nooijen and R. J. Bartlett, *J. Chem. Phys.* **106**, 6449 (1997).
- ³⁴M. Nooijen and R. J. Bartlett, *J. Chem. Phys.* **107**, 6812 (1997).
- ³⁵A. Landau, *J. Chem. Phys.* **139**, 014110 (2013).
- ³⁶J. Sous, P. Goel, and M. Nooijen, *Mol. Phys.* **112**, 616 (2014).
- ³⁷H. Nakatsuji and K. Hirao, *J. Chem. Phys.* **68**, 2053 (1978).
- ³⁸H. Nakatsuji, *Chem. Phys. Lett.* **67**, 329 (1979).
- ³⁹H. Nakatsuji, *Chem. Phys. Lett.* **67**, 334 (1979).
- ⁴⁰L. S. Cederbaum, W. Domcke, and J. Schirmer, *Phys. Rev. A* **22**, 206 (1980).
- ⁴¹J. Schirmer and A. Thiel, *J. Chem. Phys.* **115**, 10621 (2001).
- ⁴²A. Dreuw and M. Wormit, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **5**, 82 (2015), and references therein.
- ⁴³M. Ehara and H. Nakatsuji, *Collect. Czech. Chem. Commun.* **73**, 771 (2008).
- ⁴⁴D. Thouless, *Nucl. Phys.* **21**, 225 (1960).
- ⁴⁵R. Maitra, D. Sinha, and D. Mukherjee, *J. Chem. Phys.* **137**, 024105 (2012).
- ⁴⁶S. Sen, A. Shee, and D. Mukherjee, *J. Chem. Phys.* **137**, 074104 (2012).
- ⁴⁷U. S. Mahapatra, B. Datta, and D. Mukherjee, *J. Chem. Phys.* **110**, 6171 (1999).
- ⁴⁸U. S. Mahapatra, B. Datta, and D. Mukherjee, *Mol. Phys.* **94**, 157 (1998).
- ⁴⁹F. A. Evangelista, W. D. Allen, and H. F. Schaefer, *J. Chem. Phys.* **125**, 154113 (2006).
- ⁵⁰F. A. Evangelista, W. D. Allen, and H. F. Schaefer, *J. Chem. Phys.* **127**, 024102 (2007).
- ⁵¹B. Jeziorski and H. Monkhorst, *Phys. Rev. A* **24**, 1668 (1981).
- ⁵²R. Maitra, D. Sinha, S. Sen, A. Shee, and D. Mukherjee, *AIP Conf. Proc.* **1456**, 81 (2012).
- ⁵³D. Mukherjee, R. K. Moitra, and A. Mukhopadhyay, *Mol. Phys.* **33**, 955 (1977).
- ⁵⁴I. Lindgren, *Int. J. Quantum Chem.* **14**, 33 (1978).
- ⁵⁵X. Li and J. Paldus, *Int. J. Quantum Chem.* **48**, 269 (1993).
- ⁵⁶X. Li and J. Paldus, *J. Chem. Phys.* **102**, 2013 (1995).
- ⁵⁷X. Li and J. Paldus, *J. Chem. Phys.* **101**, 8812 (1994).
- ⁵⁸P. Piecuch, R. Tobola, and J. Paldus, *Chem. Phys. Lett.* **210**, 243 (1993).
- ⁵⁹X. Li and J. Paldus, *J. Chem. Phys.* **103**, 6536 (1995).
- ⁶⁰P. Piecuch and K. Kowalski, *Int. J. Mol. Sci.* **3**, 676 (2002).
- ⁶¹U. S. Mahapatra, B. Datta, B. Bandyopadhyay, and D. Mukherjee, *Adv. Quantum Chem.* **30**, 163 (1998).
- ⁶²F. A. Evangelista and J. Gauss, *J. Chem. Phys.* **134**, 114102 (2011).
- ⁶³M. Hanauer and A. Köhn, *J. Chem. Phys.* **134**, 204111 (2011).
- ⁶⁴Y. Garniron, E. Giner, J.-P. Malrieu, and A. Scemama, *J. Chem. Phys.* **146**, 154107 (2017).
- ⁶⁵P. Pyykkö and J. F. Stanton, *Chem. Rev.* **112**, 1 (2012), all the articles therein.
- ⁶⁶A. Köhn, M. Hanauer, L. A. Mück, T.-C. Jagau, and J. Gauss, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **3**, 176 (2013).
- ⁶⁷J. Paldus, *J. Chem. Phys.* **61**, 5321 (1974).
- ⁶⁸I. Shavitt, *Int. J. Quantum Chem.* **14**, 5 (1978).
- ⁶⁹A. Shee, S. Sen, and D. Mukherjee, *J. Chem. Theory Comput.* **9**, 2573 (2013).
- ⁷⁰S. Sen, A. Shee, and D. Mukherjee, *Mol. Phys.* **111**, 2625 (2013).
- ⁷¹J. Paldus and X. Li, *Symmetries in Science VI* (Springer US, Boston, MA, 1993), pp. 573–591.
- ⁷²B. Jeziorski, J. Paldus, and P. Jankowski, *Int. J. Quantum Chem.* **56**, 129 (1995).
- ⁷³D. Datta and D. Mukherjee, *J. Chem. Phys.* **131**, 044124 (2009).
- ⁷⁴D. Datta and D. Mukherjee, *J. Chem. Phys.* **134**, 054122 (2011).
- ⁷⁵K. G. Dyall, *J. Chem. Phys.* **100**, 2118 (1994).
- ⁷⁶L. Visscher and T. Saue, *J. Chem. Phys.* **113**, 3996 (2000).
- ⁷⁷T. Fleig and L. Visscher, *Chem. Phys.* **311**, 113 (2005).
- ⁷⁸L. Cheng and J. Gauss, *J. Chem. Phys.* **134**, 244112 (2011).
- ⁷⁹L. Cheng, J. Gauss, B. Ruscic, P. B. Armentrout, and J. F. Stanton, *J. Chem. Theory Comput.* **13**, 1044 (2017).

- ⁸⁰L. Cheng and J. Gauss, *J. Chem. Phys.* **135**, 084114 (2011).
- ⁸¹W. Zou, M. Filatov, and D. Cremer, *J. Chem. Phys.* **134**, 244117 (2011).
- ⁸²W. Kutzelnigg and W. Liu, *Mol. Phys.* **104**, 2225 (2006).
- ⁸³W. Liu and W. Kutzelnigg, *J. Chem. Phys.* **126**, 114107 (2007).
- ⁸⁴W. Liu and D. Peng, *J. Chem. Phys.* **131**, 031104 (2009).
- ⁸⁵T. Saue, *Chem. Phys. Chem.* **12**, 3077 (2011).
- ⁸⁶M. Iliaš and T. Saue, *J. Chem. Phys.* **126**, 064102 (2007).
- ⁸⁷J. Sikkema, L. Visscher, T. Saue, and M. Iliaš, *J. Chem. Phys.* **131**, 124116 (2009).
- ⁸⁸O. Visser, L. Visscher, P. J. C. Aerts, and W. C. Nieuwpoort, *J. Chem. Phys.* **96**, 2910 (1992).
- ⁸⁹M. Vijayakumar and M. S. Gopinathan, *J. Chem. Phys.* **103**, 6576 (1995).
- ⁹⁰S. DeBeer George, T. Petrenko, and F. Neese, *Inorg. Chim. Acta* **361**, 965 (2008).
- ⁹¹H. Pathak, S. Sasmal, M. K. Nayak, N. Vaval, and S. Pal, *Phys. Rev. A* **90**, 062501 (2014).
- ⁹²H. Pathak, S. Sasmal, M. K. Nayak, N. Vaval, and S. Pal, *J. Chem. Phys.* **145**, 074110 (2016).
- ⁹³H. Pathak, S. Sasmal, M. K. Nayak, N. Vaval, and S. Pal, *Comput. Theor. Chem.* **1076**, 94 (2016).
- ⁹⁴E. Eliav, U. Kaldor, and Y. Ishikawa, *Phys. Rev. A* **49**, 1724 (1994).
- ⁹⁵I. Infante, E. Eliav, M. J. Vilkas, Y. Ishikawa, U. Kaldor, and L. Visscher, *J. Chem. Phys.* **127**, 124308 (2007).
- ⁹⁶L. Visscher, E. Eliav, U. Kaldor, T. J. Lee, and K. G. Dyall, *J. Chem. Phys.* **115**, 8769 (2001).
- ⁹⁷F. Lipparini and J. Gauss, *J. Chem. Theory Comput.* **12**, 4284 (2016).
- ⁹⁸F. Lipparini, T. Kirsch, A. Köhn, and J. Gauss, *J. Chem. Theory Comput.* **13**, 3171 (2017).
- ⁹⁹A. Ghosh, R. K. Chaudhuri, S. Chattopadhyay, and U. S. Mahapatra, *J. Comput. Chem.* **36**, 1954 (2015).
- ¹⁰⁰A. Ghosh, R. K. Chaudhuri, and S. Chattopadhyay, *J. Chem. Phys.* **145**, 124303 (2016).
- ¹⁰¹A. Ghosh, S. Sinha Ray, R. K. Chaudhuri, and S. Chattopadhyay, *J. Phys. Chem. A* **121**, 1487 (2017).
- ¹⁰²T. Mooney, E. Lindroth, P. Indelicato, E. G. Kessler, and R. D. Deslattes, *Phys. Rev. A* **45**, 1531 (1992).
- ¹⁰³J. Niskanen, P. Norman, H. Aksela, and H. Ågren, *J. Chem. Phys.* **135**, 054310 (2011).
- ¹⁰⁴L. F. Pašteka, E. Eliav, A. Borschevsky, U. Kaldor, and P. Schwerdtfeger, *Phys. Rev. Lett.* **118**, 023002 (2017).
- ¹⁰⁵L. Visscher and E. van Lenthe, *Chem. Phys. Lett.* **306**, 357 (1999).
- ¹⁰⁶J. Stanton, J. Gauss, M. Harding, P. Szalay, A. Auer, R. Bartlett, U. Benedikt, C. Berger, D. Bernholdt, Y. Bomble, L. Cheng, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W. Lauderdale, D. Matthews, T. Metzroth, L. Mück, D. O'Neill, D. Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffrmann, W. Schwalbach, C. Simmons, S. Stopkowitz, A. Tajti, J. Vázquez, F. Wang, J. Watts, J. Almlöf, P. Taylor, T. Helgaker, H. A. Jensen, P. Jørgensen, J. Olsen, A. V. Mitin, and C. van Wüllen, CFOUR, a quantum chemical program package.
- ¹⁰⁷L. Cheng, S. Stopkowitz, J. F. Stanton, and J. Gauss, *J. Chem. Phys.* **137**, 224302 (2012).
- ¹⁰⁸J. Sucher, *Phys. Rev. A* **22**, 348 (1980).
- ¹⁰⁹C. Thierfelder and P. Schwerdtfeger, *Phys. Rev. A* **82**, 062503 (2010).
- ¹¹⁰N. N. Dutta and S. Majumder, *Phys. Rev. A* **85**, 032512 (2012).
- ¹¹¹R. D. Johnson III, NIST Computational Chemistry Comparison and Benchmark Database NIST Standard Reference Database Number 101 Release 18, 2016.
- ¹¹²P. D'Angelo, A. Di Cicco, A. Filippini, and N. V. Pavel, *Phys. Rev. A* **47**, 2055 (1993).
- ¹¹³L. Visscher, H. J. A. Jensen, R. Bast, and T. Saue, with contributions from, V. Bakken, K. G. Dyall, S. Dubillard, U. Ekström, E. Eliav, T. Enevoldsen, E. Faßhauer, T. Fleig, O. Fossgaard, A. S. P. Gomes, T. Helgaker, J. K. Lærdahl, Y. S. Lee, J. Henrikss, and S. Yamamoto, DIRAC, a relativistic *ab initio* electronic structure program, Release DIRAC13, 2013.
- ¹¹⁴J. Thyssen, "Development and applications of methods for correlated calculations of molecular properties," Ph.D. dissertation (Department of Chemistry, University of Southern Denmark, 2001), available at <http://diracprogram.org>.
- ¹¹⁵A. A. Bakke, H.-W. Chen, and W. L. Jolly, *J. Electron Spectrosc. Relat. Phenom.* **20**, 333 (1980).
- ¹¹⁶A. Potts, H. Fhadil, J. Benson, and I. Hillier, *Chem. Phys. Lett.* **230**, 543 (1994).
- ¹¹⁷J. A. Bearden and A. F. Burr, *Rev. Mod. Phys.* **39**, 125 (1967).
- ¹¹⁸R. N. Sodhi and R. G. Cavell, *J. Electron Spectrosc. Relat. Phenom.* **32**, 283 (1983).
- ¹¹⁹R. N. Sodhi and R. G. Cavell, *J. Electron Spectrosc. Relat. Phenom.* **41**, 1 (1986).