Relativistic Effects From Coupled-Cluster Theory

Lan Cheng[1, a)]

Department of Chemistry, The Johns Hopkins University, Baltimore, MD 21218, USA

In this chapter we first discuss the theory and computational challenges of the relativistic coupled-cluster methods. Example calculations of heavy-atom-containing molecules are then presented to demonstrate the importance of scalar-relativistic, spin-orbit coupling, and electron-correlation effects on molecular properties as well as the applicability and usefulness of relativistic coupled-cluster methods in calculations aiming at high-accuracy results. A unique applicability of the spinor-based relativistic coupled-cluster methods is also highlighted using the calculations of open-shell actinide-containing small molecules. Finally, a summary is given together with an outlook into future developments.

[a)]Electronic mail: lcheng24@jhu.edu

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I. INTRODUCTION

The treatment of electron correlation plays an indispensable role in accurate quantum-chemical computations of molecular properties.[1,2] In a so-called "single-reference" electronic state, a Hartree-Fock (HF) wave function accounts for the majority of the total electronic wave function and the corresponding HF energy accounts for more than 99% of the total electronic energy. However, electron correlation, defined as the remaining correction to the HF model, contributes significantly to molecular properties of chemical relevance. A classic example is that the Hartree-Fock F-F bond energy in the simple fluorine molecule (F_2) takes a positive value. Namely, F_2 is unstable at the HF level.[3] It is mandatory to treat electron correlation to obtain chemically meaningful results in computational quantum chemistry. The coupled-cluster (CC) theory[4–6] has been established as an effective framework for treating electron-correlation effects in atoms and molecules.[7–11] Employing an exponential ansatz for the wave operator that transforms the HF wave function into the CC wave function[12,13], the CC theory provides size-extensive correlation energies. Namely, a CC correlation energy scales linearly with respect to the system size. This correct scaling is an important prerequisite for accurate calculations of atoms and molecules. The hierarchy of the CC methods with a variety of truncation schemes also offers systematic improvement of the computed energies and properties. The CC singles and doubles (CCSD) method[14] shows robust performance and provides qualitatively correct results. The CCSD augmented with a noniterative inclusion of triple excitations [CCSD(T)] method[15–17] often provides highly accurate results and is sometimes referred to as a "gold standard" in quantum chemistry. The CC methods with the inclusion of high-level correlation effects beyond CCSD(T), especially the full triples corrections and the quadruples contributions,[18–33] systematically approach the full

configuration interaction (FCI) limit and can provide results for many molecular applications that are essentially quantitative. Importantly, since the single excitations in the CC theory can take into account orbital rotation effectively,[34] the CC methods can handle complex systems with strong orbital-relaxation effects. This is particularly beneficial for treating metal-containing molecules, e.g., CC calculations of transition-metal-containing molecules involving large singles amplitudes have been shown to provide accurate results.[35–37]

The importance of electron correlation in the calculations of molecular properties is universal across the periodic table. It thus is necessary to treat relativistic effects[38–43] together with electron correlation accurately to obtain accurate computational results for heavy-atom-containing molecules. Scalar-relativistic effects induce significant contraction of s- and p-type orbitals in heavy atoms. This "direct" relativistic contraction of s- and p-type orbitals further induces "indirect" effects on the d- and f-type orbitals, resulting in the slight expansion of these orbitals. Furthermore, spin-orbit coupling can induce spatial contraction of p-type orbitals in heavy p-block elements. Namely, the $np_{1/2}$ component exhibits a significant spatial contraction compared with the $np_{3/2}$ component, which has spatial distribution similar to the corresponding scalar-relativistic np orbitals. Because special relativity has these pronounced effects on the orbitals, the coupling between relativistic and electron-correlation effects is expected to be important in the calculations of molecules containing heavy atoms. Therefore, relativistic electron-correlation calculations are required when aiming at high accuracy for heavy-atom-containing molecules.

We focus our discussion on the inclusion of relativistic effects in the CC calculations. A perturbational treatment is a natural option to include scalar-relativistic effects in CC calculations of energies and properties, when aiming at high accuracy for light-atom-containing molecules. The early development along this direction has been based on the Breit-Paul

Hamiltonian.[44] A scalar-relativistic correction to the electronic energy is obtained as the first derivative of the electronic energy by using the non-relativistic calculation as the zeroth-order treatment and the scalar-relativistic terms in the Breit-Paul Hamiltonian as the perturbation. This approach has been successfully used to include scalar-relativistic effects in high-accuracy model thermochemistries.[45,46] The scalar-relativistic corrections to nuclear gradients have been calculated as the analytic second derivatives of the electronic energy, enabling efficient geometry optimizations with the inclusion of the scalar-relativistic effects.[47] More recent developments of perturbational approaches[48–51] have been based on the direct perturbation theory (DPT).[52,53] While the use of the Breit-Pauli Hamiltonian is restricted to the leading-order perturbation theory, the DPT framework is compatible with the inclusion of higher-order contributions.

Meanwhile, the non-perturbative treatments of relativistic effects in the CC methods by combining the CC methods with relativistic four- and two-component Hamiltonians[43] in principle share the same CC formulations as in the non-relativistic theory, since the relativistic Hamiltonians in the occupation-number representation can be written in a same generic form as the non-relativistic Hamiltonian using molecular orbitals as the one-electron basis. Interestingly, a spin-free two-component calculation only requires the replacement of the non-relativistic one-electron Hamiltonian integrals with the scalar-relativistic two-component Hamiltonian integrals. The additional computational cost associated with this step is insignificant compared with the subsequent many-electron treatments. A spin-free four-component CC calculation has additional costs in the evaluation and transformation of the small-component integrals, but shares the same computational machinery as the non-relativistic one in the CC steps. Therefore, a spin-free two-component or four-component CC calculation is more efficient than a calculation of scalar-relativistic corrections as an energy

derivative of the non-relativistic CC energy. Scalar-relativistic CC calculations have been reported using the scalar-relativistic effective core potentials,[54] the spin-free Douglas-Kroll-Hess Hamiltonians,[55–57] the spin-free exact two-component theory[58–60] in its one-electron variant (the SFX2C-1e scheme),[61–63] the SFX2C theory in its mean-field variant,[64] and the spin-free Dirac-Coulomb (SFDC) approach.[65–67] Analytic gradient techniques have recently been developed for the SFX2C-1e- and SFDC-CC methods to expedite the calculations of molecular properties using these scalar-relativistic approaches at CC levels of theory.[63,67–71]

The CC methods with non-perturbative treatments of spin-orbit coupling, hereafter referred to as the "SO-CC" methods,[72–83] are the methods of choice for calculations aiming at high accuracy for atoms and molecules, in which either the magnitude of the spin-orbit coupling contributions is too large to be handled accurately using perturbation theory or a non-perturbative treatment of spin-orbit coupling enables more efficient calculations by focusing the treatments on fewer electronic states. In contrast to the ease of performing a spin-free two- or four-component CC calculation, a SO-CC calculation necessitates using the complex algebra and dealing with double group symmetry.[84] Consequently, more extensive modifications of the CC algorithms and implementations are required for performing SO-CC calculations. The SO-CC calculations are more expensive than the corresponding non-relativistic or scalar-relativistic calculations. For example, the floating point operation (FLOP) count for a CCSD calculation using spinors, i.e., orbitals with the inclusion of spin-orbit coupling, is around 20 times that of a non-relativistic or scalar-relativistic CCSD calculation.[73,85] Recent years have seen many efforts to extend the applicability of the SO-CC methods to larger molecules.[85–97] New algorithms have been developed to remove the major computational bottlenecks of the SO-CC calculations.[85–87] Analytic SO-CCSD(T) gradients[98,99] have been developed to enable efficient calculations of molecular properties.

Highly parallelized implementations[96,97] have also been reported.

We should mention that, because of the high cost of the SO-CC methods, perturbative treatments of spin-orbit coupling at the CC levels are computationally appealing. Perturbational treatments of spin-orbit coupling using the non-relativistic equation-of-motion CC (EOM-CC) wave functions[100–104] or state-specific multireference CC wave functions[105] as the zeroth-order wave functions have been reported to provide accurate spin-orbit splittings in light-atom-containing molecules. A perturbative treatment of spin-orbit coupling using the SFX2C-1e EOM-CC wave functions as the zeroth-order wave functions[106,107] can further provide accurate results for molecules containing heavy atoms, because the scalar-relativistic effects on both the unperturbed wave functions and the spin-orbit integrals have been accurately taken into account. We expect the SFX2C-1e-CC methods augmented with perturbative treatments of spin-orbit coupling to evolve into standard tools for accurate calculations of molecular energies and properties.

In this chapter, we first discuss the generalities of the CC theory in combination with various relativistic approaches, the computational challenges, and promising routes to extend the applicability to larger molecules. We then present example calculations to demonstrate the usefulness of the relativistic CC methods. We use the calculations of copper quadrupole-coupling constants as an example for the importance of scalar-relativistic effects and significance of the coupling between scalar-relativistic effects and electron correlation. Spinor-based relativistic CC calculations of bismuth quadrupole-coupling constants are then employed to show the importance of spin-orbit coupling effects on properties of molecules containing a 6p-block element. These examples involve calculations of electric-field gradients, a "core property" that samples the inner-shell electron density, for which the relativistic effects are very pronounced. Finally, relativistic CC calculations of thermochemical param-

eters for uranium-containing molecules are presented to demonstrate a unique applicability of spinor-based CC methods for calculations of heavy-atom-containing open-shell molecules.

II. THEORY

A. General aspects of relativistic coupled-cluster (CC) theory

In the CC theory, a single-determinant reference function is transformed into a CC wave function using an exponential wave operator $e^{\hat{T}}$[10,11]

$$|\Psi_{\rm CC}\rangle = e^{\hat{T}}|\Psi_{\rm ref}\rangle. \tag{1}$$

The cluster operator $\hat{T}$ is a linear combination of excitation operators weighted by the cluster amplitudes

$$\hat{T} = \sum_{ia} t_i^a a_a^\dagger a_i + \frac{1}{4}\sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i + \cdots, \tag{2}$$

in which t's are cluster amplitudes, i, j, $\cdots$ and a, b, $\cdots$ in the subscripts and superscripts refer to the occupied and virtual orbitals, respectively, $a^\dagger$ denotes a creation operator and a a destruction operator. For example, the action of $a_a^\dagger a_i$ or $a_a^\dagger a_b^\dagger a_j a_i$ on $|\Psi_{\rm ref}\rangle$ gives a singly excited determinant $|\Psi_i^a\rangle$ with an electron in the orbital i in the reference function promoted to an unoccupied orbital a or a doubly excited determinant $|\Psi_{ij}^{ab}\rangle$ with the electrons in i and j promoted to a and b,

$$|\Psi_i^a\rangle = a_a^\dagger a_i|\Psi_{\rm ref}\rangle \ , \ |\Psi_{ij}^{ab}\rangle = a_a^\dagger a_b^\dagger a_j a_i|\Psi_{\rm ref}\rangle. \tag{3}$$

Multiplying the time-independent Schrödinger equation

$$He^{\hat{T}}|\Psi_{\rm ref}\rangle = Ee^{\hat{T}}|\Psi_{\rm ref}\rangle \tag{4}$$

with $e^{-\hat{T}}$ from the left hand side leads to

$$\bar{H}|\Psi_{\rm ref}\rangle = E|\Psi_{\rm ref}\rangle, \tag{5}$$

with $\bar{H}$ being the CC similarity-transformed Hamiltonian

$$\bar{H} = e^{-\hat{T}} H e^{\hat{T}} = H + [H,\hat{T}] + \frac{1}{2}[[H,\hat{T}],\hat{T}] + \frac{1}{6}[[[H,\hat{T}],\hat{T}],\hat{T}] + \frac{1}{24}[[[[H,\hat{T}],\hat{T}],\hat{T}],\hat{T}]. \tag{6}$$

The commutator structure of $\bar{H}$ guarantees the connectivity of $\bar{H}$ and hence the size-extensivity of the CC theory. Note that the Baker-Campbell-Hausdorff expansion of $\bar{H}$ terminates at the quartic commutators, because $\hat{T}$ consists of excitation operators exclusively. This leads to a compact structure for the CC working equations. Projecting Eq. 5 onto the reference function and the excited determinants gives the CC energy equation

$$\langle\Psi_{\rm ref}|\bar{H}|\Psi_{\rm ref}\rangle = E, \tag{7}$$

and the CC amplitude equations

$$\langle\Psi_i^a|\bar{H}|\Psi_{\rm ref}\rangle = 0 \ , \ \langle\Psi_{ij}^{ab}|\bar{H}|\Psi_{\rm ref}\rangle = 0 \ , \ \cdots , \tag{8}$$

respectively. The reference function is the most often chosen as a Hartree-Fock (HF) wave function. On the other hand, since the single excitations in the CC theory take care of orbital rotation effectively, the CC results are relatively insensitive to the choice of the reference functions. The non-HF reference functions are often found very useful in applications.[108]

The Hamiltonian operator in Eq. 4 can be written in the occupation-number representation as[43]

$$H = \sum_{pq} f_{pq}\{a_p^\dagger a_q\} + \frac{1}{4}\sum_{pqrs} g_{pq,rs}\{a_p^\dagger a_q^\dagger a_s a_r\}, \tag{9}$$

$$f_{pq} = h_{pq} + \sum_i g_{pi,qi}. \tag{10}$$

In the non-relativistic theory and relativistic two-component theories, p, $q \cdots$ in the subscripts include all the molecular orbitals. The many-electron Hamiltonians in the four-component approaches employ the "no-pair" projection,[109] i.e., p, $q \cdots$ include the positive-energy-state (PES) orbitals and exclude all the negative-energy-state (NES) orbitals. h, g, and f represent the one-electron Hamiltonian matrix, the antisymmetrized two-electron interaction matrix, and the Fock matrix, respectively. In Eq. 9, $\{\cdots\}$ represents the normal ordering of the second-quantized operators with respect to the reference determinant $\Psi_{\rm ref}$ as the redefined vacuum. It should be emphasized that all the non-relativistic and relativistic electronic Hamiltonians share this generic form and differ in terms of the actual values of the one- and two-electron matrix elements f_{pq} and $g_{pq,rs}$. The non-relativistic theory as well as the two- and four-component relativistic approaches based on the Dirac-Coulomb Hamiltonian have the instantaneous Coulomb interaction as the two-electron interaction. The corresponding matrix elements are given by

$$g_{pq,rs} = \langle pq|rs\rangle - \langle pq|sr\rangle, \tag{11}$$

$$\langle pq|rs\rangle = \int \phi_p^\dagger(\vec{r}_1)\phi_r(\vec{r}_1)\frac{1}{|\vec{r}_1 - \vec{r}_2|}\phi_q^\dagger(\vec{r}_2)\phi_s(\vec{r}_2)d\vec{r}_1 d\vec{r}_2, \tag{12}$$

The Dirac-Coulomb-Gaunt (DCG) or Dirac-Coulomb-Breit (DCB) Hamiltonian includes additional contributions from the Gaunt or Breit term.

B. Relativistic approaches adopted in the present study

The example studies in the next section include CC calculations in combination with the non-relativistic theory, the SFX2C-1e scheme,[61,62] and the X2C Hamiltonian with atomic mean-field spin-orbit integrals (the X2CAMF scheme).[110,111] We take the differences between the SFX2C-1e scheme and the non-relativistic theory as the scalar-relativistic contributions.

The differences between the X2CAMF and SFX2C-1e results represent the spin-orbit contributions. In this subsection we briefly discuss these relativistic approaches, especially the structures of the corresponding wave functions, to facilitate the discussion in the next subsection on their applicability and efficiency in CC calculations.

The SFX2C-1e scheme performs an exact block-diagonlization for the spin-free one-electron Dirac Hamiltonian in its matrix representation with a single unitary transformation and then uses the resulting electronic block together with the untranformed two-electron Coulomb interaction in the many-electron treatments. The other spin-free two-component approaches, including the spin-free finite-order Douglas-Kroll-Hess (DKH) methods and[55,56,112] the spin-free zeroth-order regular approximation (ZORA) method,[113] are approximate variants of the SFX2C-1e scheme. The spin-free versions of an infinite-order DKH method[114–116] and and the infinite-order two-component method[117,118] can be viewed as more complicated versions of the SFX2C-1e scheme involving multiple transformations of the four-component Hamiltonian matrix. In the non-relativistic theory, the one-electron Hamiltonian consists of the non-relativistic kinetic energy and the nuclear attraction potential energy operators. The two-electron interaction is the instantaneous Coulomb interaction. Both these one- and two-electron Hamiltonian operators are spin-free. A molecular orbital ϕ_p has a single spin component, namely,

$$\phi_p = \begin{pmatrix} \phi_p^\alpha \\ \\ 0 \end{pmatrix} \text{ or } \phi_p = \begin{pmatrix} 0 \\ \\ \phi_p^\beta \end{pmatrix}, \tag{13}$$

and is real-valued. Both the one- and two-electron Hamiltonian matrix elements thus are spin-free and real-valued. The SFX2C-1e scheme differs from the non-relativistic theory only in the one-electron Hamiltonian matrix elements, i.e., the SFX2C-1e scheme replaces the non-relativistic one-electron Hamiltonian matrix with the SFX2C-1e Hamiltonian matrix,

which is still spin-free. The SFX2C-1e scheme thus preserves the spin symmetry. We should mention that the "no-pair" spin-free Dirac-Coulomb (SFDC) approach perhaps offers the most rigorous treatment of scalar-relativistic effects. The underlying approximation of the SFX2C-1e scheme, compared with the SFDC approach, lies in the neglect of the scalar two-electron picture-change effects. In other words, the transformation of the two-electron Coulomb interaction is neglected. It has been shown that the scalar two-electron picture-change corrections to molecular properties are in general small;[70,119] the SFX2C-1e scheme recovers the scalar-relativistic corrections to molecular properties very accurately. The SFDC approach also preserves the spin symmetry. A SFDC-CC calculation thus can also directly use the non-relativistic CC machineries in the CC steps. The SFDC positive-energy-state molecular orbitals ϕ_p's are spin-free four-component spinors

$$\phi_p = \begin{pmatrix} \phi_p^{\mathrm{L},\alpha} \\ 0 \\ \phi_p^{\mathrm{S},\alpha} \\ 0 \end{pmatrix} \text{ or } \phi_p = \begin{pmatrix} 0 \\ \phi_p^{\mathrm{L},\beta} \\ 0 \\ \phi_p^{\mathrm{S},\beta} \end{pmatrix}. \tag{14}$$

It thus is necessary to include the contributions from the small-component integrals in the evaluation of the molecular-orbital (MO) two-electron integral matrix. This renders the SFDC integral transformation significantly more expensive. The atomic-orbital (AO)-based algorithms are also less efficient for the SFDC approach than for the non-relativistic or SFX2C-1e scheme.

In contrast, the X2CAMF scheme works with complex-valued two-component spinors

$$\phi_p = \begin{pmatrix} \phi_p^{\alpha} \\ \phi_p^{\beta} \end{pmatrix}. \tag{15}$$

The corresponding relativistic one-electron Hamiltonian matrix is in general complex-valued

and does not have spin symmetry, i.e., the α and β spin components are coupled together. The two-electron Hamiltonian matrix elements also become spin-dependent and in general complex-valued. The X2CAMF scheme exploits the X2C transformation[58,62] and the atomic mean-field spin-orbit approach[120] to eliminate all molecular relativistic two-electron integrals to enhance the computational efficiency. The underlying approximations of the X2CAMF scheme compared with the four-component "no-pair" Dirac-Coulomb (DC) approach include the scalar two-electron picture-change effects and the atomic approximation for the two-electron spin-orbit contributions. These approximations have been shown to introduce only small errors in calculations of molecular energies and properties.[110,111] We mention that the inclusion of scalar-two-electron picture-change effects in the two-component calculations within the atomic approximation have been explored in density-functional theory calculations[121–123] and have recently been implemented for the Hartree-Fock reference function in combination with CC calculations.[123] It will be of interest for future study to assess the accuracy of the atomic approximation for the scalar two-electron picture-change effects in calculations of molecular properties. Finally, in the DC approach, a four-component spinor ϕ_p can be written as

$$\phi_p = \begin{pmatrix} \phi_p^{\mathrm{L},\alpha} \\ \phi_p^{\mathrm{L},\beta} \\ \phi_p^{\mathrm{S},\alpha} \\ \phi_p^{\mathrm{S},\beta} \end{pmatrix} . \tag{16}$$

While the two-electron integral matrix still takes the same compact form as in the two-component theory, the four-component two-electron integrals receive contributions from the small components of the four-spinors.

C. Computational challenges in relativistic CC calculations

The non-relativistic and relativistic CC calculations share the same formal computational scalings. The computationally most intensive steps in the solution of the CC singles and doubles (CCSD) amplitude equations are the calculations of the particle-particle ladder term $\frac{1}{2}\sum_{cd}\langle ab||cd\rangle t_{ij}^{cd}$ with a scaling of $\mathrm{O(N_{occ}^2N_{vir}^4)}$ and the ring terms $P_-(ij)P_-(ab)\sum_{me}\langle mb||ej\rangle t_{im}^{ae}$ and $P_-(ij)P_-(ab)\sum_{me}\langle mj||eb\rangle t_{im}^{ae}$ with a scaling of $\mathrm{O(N_{occ}^3N_{vir}^3)}$. In the following we compare the computational costs for these terms in a spin unrestricted non-relativistic or scalar-relativistic CCSD calculation with those in a Kramers unrestricted spinor-based relativistic CCSD calculation.

Because the non-relativistic Hamiltonian is spin-free, a non-relativistic unrestricted CCSD calculation involves three independent spin cases for the doubles amplitudes and the two-electron integrals, i.e., $t_{i^\alpha j^\alpha}^{a^\alpha b^\alpha}$, $t_{i^\beta j^\beta}^{a^\beta b^\beta}$, and $t_{i^\alpha j^\beta}^{a^\alpha b^\beta}$ for the amplitudes and $\langle p^\alpha q^\alpha||r^\alpha s^\alpha\rangle$, $\langle p^\beta q^\beta||r^\beta s^\beta\rangle$, and $\langle p^\alpha q^\beta||r^\alpha s^\beta\rangle$ for the integrals. Therefore, the evaluation of the particle-particle ladder term consists of three independent contributions $\frac{1}{2}\sum_{c^\alpha d^\alpha}\langle a^\alpha b^\alpha||c^\alpha d^\alpha\rangle t_{i^\alpha j^\alpha}^{c^\alpha d^\alpha}$, $\frac{1}{2}\sum_{c^\beta d^\beta}\langle a^\beta b^\beta||c^\beta d^\beta\rangle t_{i^\beta j^\beta}^{c^\beta d^\beta}$, and $\sum_{c^\alpha d^\beta}\langle a^\alpha b^\beta|c^\alpha d^\beta\rangle t_{i^\alpha j^\beta}^{c^\alpha d^\beta}$. The floating point operation (FLOP) count for this term thus is $\frac{1}{8}(N_{\mathrm{vir}}^\alpha)^4(N_{\mathrm{occ}}^\alpha)^2+\frac{1}{8}(N_{\mathrm{vir}}^\beta)^4(N_{\mathrm{occ}}^\beta)^2+(N_{\mathrm{vir}}^\alpha)^2(N_{\mathrm{occ}}^\alpha)(N_{\mathrm{vir}}^\beta)^2(N_{\mathrm{occ}}^\beta)$. Let us assume $N_{\mathrm{v}}=N_{\mathrm{vir}}^\alpha\approx N_{\mathrm{vir}}^\beta$ and $N_{\mathrm{o}}=N_{\mathrm{occ}}^\alpha\approx N_{\mathrm{occ}}^\beta$. The FLOP count is then rewritten as $\frac{5}{4}N_{\mathrm{vir}}^4N_{\mathrm{o}}^2$.[124] Similarly, a ring term can be decomposed into ten independent contributions and has a FLOP count of $10N_{\mathrm{vir}}^3N_{\mathrm{o}}^3$. We should emphasize that, since a spin-free two- or four-component Hamiltonian preserves the spin symmetry, a spin-free relativistic CCSD calculation shares the same FLOP count as the non-relativistic case and thus has exactly the same cost as a non-relativistic CCSD calculation. Actually, the spin-free relativistic CC calculations can directly use the non-relativistic CC machineries for the CC steps.

In contrast, the spinor-based CC calculations, i.e., CC calculations with the inclusion of spin-orbit coupling in the orbitals, are computationally more intensive than the corresponding non-relativistic or spin-free relativistic CC calculations.[73,83] They also require non-trivial extensions of the computational infrastructure. Because of the spin-symmetry breaking, the contributions to the CC amplitude equations cannot be factorized into separate spin components. Furthermore, the presence of spin-orbit coupling in the Hamiltonians necessitates using the complex algebra. Both factors increase the computational costs significantly, although the formal computational scaling for a given CC model remains unchanged. Let us compare the FLOP counts for the particle-particle ladder term and a ring term in a Kramers unrestricted spinor-based CCSD calculation with that in a non-relativistic spin-unrestricted CCSD calculation. The FLOP count for the evaluation of the particle-particle ladder term $\frac{1}{2}\sum_{cd}\langle ab||cd\rangle t_{ij}^{cd}$ in a spinor-based CCSD calculation amounts to $\frac{1}{8}N_{\mathrm{v,SO}}^4 N_{\mathrm{o,SO}}^2 \times 3$, in which the factor of three comes from the ratio between the FLOP of a complex matrix-matrix multiplication and that of a real matrix-matrix multiplication.[125] Since the total number of orbitals in a spinor-based calculation is equal to the sum of the α and β orbitals in the corresponding non-relativistic calculation, i.e., $N_{\mathrm{v,SO}} = N_{\mathrm{vir}}^{\alpha} + N_{\mathrm{vir}}^{\beta} \approx 2N_{\mathrm{v}}$ and $N_{\mathrm{o,SO}} = N_{\mathrm{occ}}^{\alpha} + N_{\mathrm{occ}}^{\beta} \approx 2N_{\mathrm{o}}$, the FLOP count for the ladder term in a spinor-based CCSD calculation becomes $\frac{3}{8}N_{\mathrm{v,SO}}^4 N_{\mathrm{o,SO}}^2 \approx 24N_{\mathrm{v}}^4 N_{\mathrm{o}}^2$, which is 19.2 times the value of $\frac{5}{4}N_{\mathrm{v}}^4 N_{\mathrm{o}}^2$ for a non-relativistic CCSD calculation. Similarly, the FLOP count for the evaluation of a ring term in a SO-CCSD calculation is $N_{\mathrm{v,SO}}^3 N_{\mathrm{o,SO}}^3 \times 3 \approx 192N_{\mathrm{v}}^3 N_{\mathrm{o}}^3$, with the factor of 3 again originating from the use of the complex algebra. This is also 19.2 times the value of $10N_{\mathrm{v}}^3 N_{\mathrm{o}}^3$ in the case of the non-relativistic calculation. Therefore, the FLOP of a SO-CCSD calculation is around 20 times that of a non-relativistic calculation. Since a CCSD calculation has a formal scaling of N^6, where N represents the system size, SO-CCSD should be able

to handle around half the system size that the non-relativistic CCSD method can. On the other hand, it is non-trivial to realize this potential of SO-CCSD, because of the additional challenge in dealing with large MO two-electron integral matrices.

The transformation of the two-electron integrals from the AO representation into the MO representation as well as the sorting of the MO two-electron integrals from the Mulliken notation to the Dirac notation have lower computational scalings than the solution of the CC equations. However, these steps are difficult to implement efficiently, and are often input/output (I/O) very intensive. They thus emerge as major bottlenecks in CC calculations. The size of the MO two-electron integral matrix $\langle pq||rs\rangle$ in a spin-unrestricted spin-free two-component or four-component calculation is the same as in a non-relativistic calculation. The independent MO two-electron integrals include three spin cases $\langle p^\alpha q^\alpha||r^\alpha s^\alpha\rangle$, $\langle p^\beta q^\beta||r^\beta s^\beta\rangle$, and $\langle p^\alpha q^\beta||r^\alpha s^\beta\rangle$, the sizes of which are $\frac{1}{4}(N_{\rm mo}^\alpha)^4$, $\frac{1}{4}(N_{\rm mo}^\beta)^4$, and $(N_{\rm mo}^\alpha)^2(N_{\rm mo}^\beta)^2$, respectively. Assuming $N_{\rm mo} = N_{\rm mo}^\alpha \approx N_{\rm mo}^\beta$, the total size of the integral matrix file is around $\frac{3}{2}N_{\rm mo}^4$. For comparison, a spinor-based Kramers unrestricted CC calculation works with MO two-electron integrals without spin symmetry. As a result, the size of the MO two-electron matrix is $\frac{1}{4}N_{\rm mo,\,SO}^4 \times 2$, with the factor of two coming from the use of the complex algebra. Since $N_{\rm mo,\,SO} \approx 2N_{\rm mo}$, the size of the MO two-electron integral matrix can be rewritten as $8N_{\rm mo}^4$, which is around 5 times the value of $\frac{3}{2}N_{\rm mo}^4$ for the non-relativistic case. This is a significant overhead. For example, for a CCSD calculation that correlates 100 electrons and 1000 virtual orbitals, the two-electron integral file in the spinor-based calculation is as large as 5 TB, to be compared with the size of around 1 TB in the non-relativistic or scalar-relativistic case. It is computationally challenging to handle integral matrices of such a size. It is difficult to implement the integral transformation efficiently, when the targeted MO integral matrices cannot be held in fast memory. Furthermore, the sorting of the integrals

from the Mulliken notation $(pq|rs)$ into the Dirac notation $\langle pq||rs\rangle$ with antisymmetrization is I/O very intensive. Consequently, although the integral transformation only scales as the fifth power of the system size and integral sorting step only as the fourth power, they are sometimes reported to be even more time-consuming than the CC steps in a spinor-based CC calculation[126].

D. Toward spinor-based relativistic CC calculations of larger molecules

The scalar-relativistic two-component CC calculations are as efficient as the non-relativistic CC calculations and hence share the same applicability. The spinor-based relativistic CC calculations, on the other hand, are significantly more expensive. A highly parallelized implementation of the spinor-based CCSD method has recently been reported to extend the applicability to larger molecules on supercomputers.[96,97] At the same time, since the computational overheads mainly come from the spin-symmetry breaking, an underlying idea for improving the efficiency of spinor-based CC calculations is the recovery of spin symmetry in the rate-determining steps of the calculations. One approach is to use AO-driven algorithms for the computationally demanding terms to enhance the computational efficiency,[83,85] hereby exploiting the spin-free nature of the instantaneous Coulomb interaction and the corresponding AO two-electron integrals. Note that the AO two-electron integrals in a spinor-based two-component CC calculation are the same as those in the corresponding non-relativistic or scalar-relativistic calculation. This partial recovery of the spin symmetry by using AO-based algorithms not only avoids the evaluation, sorting, and storage of large MO two-electron integral matrices, but also reduces the FLOP count for the particle-particle ladder term by a factor of 3-4. This AO-based algorithm has been implemented for the X2CAMF-CC method together with the corresponding analytic-gradient

techniques to expedite the calculations of molecular properties including structures and vibrational frequencies.[98,99]

An alternative scheme is to work with spin-free relativistic orbitals and to incorporate the spin-orbit coupling contributions into the Fock matrix in CC calculations[86,126–129]. In this case the MO two-electron integral matrix is the same as in the corresponding spin-free relativistic calculation. This thus alleviates the computational bottleneck due to large MO integral matrices. The remaining overhead comes from the coupling among different spin components of the CC equations due to spin-orbit coupling. Wang and collaborators have shown that such a SO-CCSD calculation is about 15 times more time-consuming than a corresponding non-relativistic or scalar-relativistic calculation.[86] Since single excitations in the CC theory can account for orbital rotation, the orbital relaxation due to spin-orbit coupling is effectively taken into account in this scheme. Benchmark calculations have shown that the use of scalar-relativistic orbitals in SO-CC calculations can provide accurate results for closed-shell[130] or nondegenerate open-shell molecules containing heavy atoms.[131] Analytic gradients[132] and hessians[133] have been implemented for this scheme to enable efficient geometry optimizations and calculations of vibrational frequencies.

III. EXAMPLE CALCULATIONS

In the section we present example calculations to demonstrate the usefulness of relativistic coupled-cluster methods for calculations of properties for heavy-atom-containing molecules. Relativistic coupled-cluster calculations have been widely used in high-accuracy calculations of small molecules containing heavy atoms. We refer the readers to Ref.[127,134–188] for an obviously incomplete account of interesting applications. Here we demonstrate the importance of scalar-relativistic effects and the coupling between scalar-relativistic and electron-correlation

effects using the calculations of nuclear quadrupole-coupling constants for copper-containing molecules. The calculations of bismuth quadrupole-coupling constants are used to discuss the significance of spin-orbit contributions and the coupling between the spin-orbit coupling and electron-correlation effects. Furthermore, we present the calculations of thermochemical parameters for uranium-containing atomic and molecular species to show a unique applicability of spinor-based relativistic coupled-cluster methods for calculations of heavy-atom-containing open-shell species. The SFX2C-1e scheme and the X2CAMF scheme as implemented in the CFOUR program package[63,94,110,111,189] have been used for all the calculations presented here.

A. Scalar-relativistic and correlation effects on Cu quadrupole-coupling constants

A nuclear quadrupole-coupling tensor χ represents the interaction between the electric-field gradients q at the position of the target nucleus and the nuclear electric quadrupole moment Q

$$\chi = eQq. \tag{17}$$

A tensor component χ_{uv} in MHz takes the value of

$$\chi_{uv} = \kappa Q q_{uv}, \tag{18}$$

in which Q is the value of the nuclear electric quadrupole moment in millibarn (mb), q_{uv} is the value of the corresponding electric-field gradient component in a.u., the elementary charge "e" takes a value of unity in a.u., and the conversion factor κ take a value of 1/0.2349647 for the units chosen here. Since electric-field gradient involves an operator localized at the targeted nucleus, nuclear quadrupole-coupling constants sample the electron density in the

TABLE I. Copper quadrupole-coupling constants (MHz).[190] The uncontracted ANO-RCC basis sets[192–194] have been used in all the calculations with all the electrons correlated. The differences between the SFX2C-1e and non-relativistic (Nonrel) results represent the scalar-relativistic corrections (ΔSR).

	HF-SCF			CCSD(T)			
	Nonrel	ΔSR	SFX2C-1e	Nonrel	ΔSR	SFX2C-1e	Experiment
CuF	67.1	-3.0	64.1	32.6	-9.6	23.0	21.9562(24)[195]
CuCl	45.3	-1.3	43.9	21.2	-5.7	15.5	16.16908(72)[196]
CuCN	62.4	-1.6	60.8	30.2	-6.2	24.0	24.523(17)[197]
CuCCH	58.5	-2.5	56.0	22.1	-7.0	15.1	16.391(21)[197]
$CuCH_3$	37.6	-4.1	33.5	-0.1	-7.5	-7.6	-3.797(47)[197]

vicinity of the nucleus and exhibit strong relativistic effects. In Table I, we summarize the computed Cu quadrupole-coupling constants for several representative molecules at the non-relativistic and SFX2C-1e-HF and CCSD(T) levels of theory taken from Ref.[190]. Here we have computed the electric-field gradients at the position of the Cu atoms and then used a value of -220(15) mb for the Cu electric quadrupole moment[191] to convert the computed electric field gradients into the Cu quadrupole-coupling constants. The differences between the SFX2C-1e and non-relativistic results represent scalar-relativistic corrections and are denoted as ΔSR in Table I.

Electron correlation plays a central role in accurate calculations of Cu quadrupole-coupling constants in these molecules. The HF values obtained from both non-relativistic and SFX2C-1e calculations grossly overestimate the values of the Cu quadrupole-coupling constants. Importantly, the coupling between scalar-relativistic and electron-correlation ef-

fects is significant. The CCSD(T) scalar-relativistic contributions (ΔSR in Table I) are several times larger than the HF values. It thus is necessary to treat scalar-relativistic and electron-correlation effects consistently to obtain accurate results. Spin-orbit contributions and scalar two-electron picture-change effects have been shown to be insignificant for Cu quadrupole-coupling constants.[70] The SFX2C-1e-CCSD(T) results thus compare favorably with the experimental data. We should emphasize that a SFX2C-1e-CC calculation is as efficient as the corresponding non-relativistic CC calculation. Therefore, the SFX2C-1e CC methods are clearly the methods of choice for these calculations.

B. Spin-orbit and correlation effects on Bi quadrupole-coupling constants

Heavy p-block elements, especially the 6p- and 7p-block elements, exhibit extraordinarily large spin-orbit effects. Spin-orbit coupling not only induces large energy splittings for the valence p orbitals in these elements, but also significantly affects the shape of the orbitals and hence can be strongly coupled with electron correlation. Here we use the calculations of bismuth quadrupole-coupling constants to demonstrate the importance of the spin-orbit contributions. The Bi quadrupole-coupling constants in Table II have been obtained by using the computed electric field gradients at the positions of the Bi atoms taken from Ref.[110] and the recent recommended value of 422(3) mb for the Bi nuclear electric quadrupole moment.[198] We mention that the Bi electric quadrupole moment has been determined by using the computed electric-field gradients and the measured Bi quadrupole-coupling constants in the Bi atom or bismuth-containing small molecules.[90,110,198–200] The differences between the X2CAMF and SFX2C-1e results in Table II represent the spin-orbit contributions. We have given the HF values, the correlation contributions at the CCSD(T) level, and the total CCSD(T) values obtained from the SFX2C-1e and X2CAMF calculations for comparison.

TABLE II. Bismuth quadrupole-coupling constants (MHz).[110] The contracted ANO-RCC basis sets have been used in all the calculations. The Bi 5p5d6s6p electrons as well as the valence electrons in N, P, F, Cl, I have been correlated in the CC calculations. The electron correlation have been treated at the CCSD(T) level of theory. The differences between the X2CAMF and SFX2C-1e results represent the spin-orbit contributions.

	SFX2C-1e			X2CAMF			
	HF	correlation	total	HF	correlation	total	Experiment
BiN	1270	-277	993	569	350	919	894.5607(69)[201]
BiP	1309	-341	968	973	-53	920	898.2172(46)[201]
BiF	-1128	132	-996	-1323	175	-1148	-1148.08(10)[202]
BiCl	-992	97	-894	-1182	148	-1034	-1027.0(120)[203]
BiI	-802	45	758	-1051	124	-927	-909.5(20)[204]

The computed Bi quadrupole-coupling constants exhibit significant spin-orbit contributions. At the HF level, the spin-orbit contributions reduce the values by 30-50% in the cases of BiN and BiP, and increase the absolute magnitude of the computed values by 20-30% in the cases of BiF, BiCl, and BiI. The electron-correlation contributions for BiN and BiP obtained in the SFX2C-1e calculations differ dramatically from those from X2CAMF calculations. The SFX2C-1e electron-correlation contributions amount to -277 and -341 MHz, respectively, to be compared with the X2CAMF values of 350 and -53 MHz. This is consistent with the observation in Ref.[90]. In the calculations for BiF, BiCl, and BiI, the coupling between the spin-orbit and electron-correlation contributions is also significant. The X2CAMF electron-correlation contributions amount to 175, 149, and 124 MHz, significantly higher than the corresponding SFX2C-1e values of 132, 97, and 45 MHz. The remaining

corrections to the X2CAMF scheme, including the scalar two-electron picture-change effects and the multiple-center two-electron spin-orbit contributions have been shown to be small for Bi quadrupole-coupling constants.[110] Therefore, as shown in Table II, the X2CAMF-CCSD(T) results are in good agreement with the experimental values.

C. Spinor-based relativistic CC calculations of uranium thermochemistry

We present a unique applicability of spinor-based relativistic coupled-cluster theory in calculations of heavy-atom-containing open-shell atoms and molecules.[205] The parameters targeted here include the ionization energies of U, UO, and UO_2 as well as the bond energies of UO and UO_2. The electronic states involved here include the electronic ground states for U, U^+, UO, UO^+, UO_2 and UO_2^+. All these electronic states are dominated by single determinants in the spinor representation. The high-spin analogue of the ground state $^5L_6$ of the uranium atom is dominated by $[\mathrm{Rn}][5f_{5/2,5/2}]^1\ [5f_{5/2,3/2}]^1\ [5f_{5/2,1/2}]^1\ [6d_{3/2,3/2}]^1\ [7s_{1/2,1/2}]^1\ [7s_{1/2,-1/2}]^1$, while that of the $^4I_{9/2}$ state of U^+ is dominated by $[\mathrm{Rn}][5f_{5/2,5/2}]^1\ [5f_{5/2,3/2}]^1\ [5f_{5/2,1/2}]^1\ [7s_{1/2,1/2}]^1\ [7s_{1/2,-1/2}]^1$. The leading valence configurations of UO with $\Omega = 4$ and UO^+ with $\Omega = 4.5$ are $[5f_{5/2,5/2}]^1\ [5f_{5/2,3/2}]^1\ [5f_{5/2,1/2}]^1\ [7s_{1/2,-1/2}]^1$ and $[5f_{5/2,5/2}]^1\ [5f_{5/2,3/2}]^1\ [5f_{5/2,1/2}]^1$, respectively. The electronic ground state of UO_2 and UO_2^+ take valence electron configurations $[5f_{5/2,5/2}]^1\ [7s_{1/2,-1/2}]^1$ and $[5f_{5/2,5/2}]^1$.

On the other hand, we should mention that the open-shell species with more than one open-shell 5f-electrons, including U, U^+, UO, and UO^+, have multideterminantal wave functions in scalar-relativistic calculations using real-valued wave functions. For example, the leading configuration of UO^+, $[5f_{m_l=3,m_s=1/2}]^1\ [5f_{m_l=2,m_s=1/2}]^1\ [5f_{m_l=1,m_s=1/2}]^1$, is a single complex-valued determinant. Either the real or the imaginary part is a linear combination of four real-valued determinants. Therefore, a calculation of such a state using a standard

TABLE III. Ionization energies (IEs) for U, UO, and UO_2, and equilibrium dissociation energies (D_e's for UO and UO_2 computed at the CCSD(T) level of theory (in kJ/mol) using triple-zeta basis sets with valence electrons correlated.[205] "X2C-1e" represents the exact two-component approach in its one-electron variant, "$\Delta_{\text{2e-SO}}$" respresents the two-electron spin-orbit contributions obtained as the differences between the X2CAMF and X2C-1e results, and "Δ_{Breit}" represents the contributions from the Breit term obtained by including the Breit term in the X2CAMF scheme.

kJ/mol	X2C-1e	$\Delta_{\text{2e-SO}}$	Δ_{Breit}
IE(U)	599.9	-3.2	0.2
IE(UO)	573.7	1.5	-1.6
IE(UO_2)	585.0	0.0	-2.3
D_e(UO)	718.1	11.4	0.1
D_e(UO_2)	700.9	29.8	-4.6

quantum-chemistry program packages with real-valued wave functions requires the use of multireference methodologies. It is a unique applicability of spinor-based representation to enable single-reference CC calculations of such open-shell systems with high-level treatments of dynamical correlation.

As shown in Table III, the two-electron spin-orbit (2e-SO) interactions make significant contributions to the computed thermochemical parameters in general, e.g, the 2e-SO contributions to the dissociation energies of UO and UO_2 amount to 11 kJ/mol and 30 kJ/mol, respectively. The smallness of the 2e-SO contributions to the ionization energies of UO and UO_2 is due to that the ionized electrons are in the 7s orbitals. Furthermore, it is necessary to take into account the Breit term when aiming at chemical accuracy in these calculations. One should be aware of the potential importance of quantum electro-

TABLE IV. Ionization energies (IEs) for U, UO, and UO_2 as well as equilibrium dissociation energies (D_e's) for UO and UO_2 computed using the X2CAMF scheme for treating relativistic effects (in kJ/mol).[205]

kJ/mol	HF	CCSD	CCSD(T)	$CCSD(T)_\Lambda$	Experiment
IE(U)	577.1 (-20.5)	596.1 (-1.5)	598.5 (0.9)	594.8 (-2.8)	597.6[208]
IE(UO)	515.5 (-66.0)	569.8 (-11.7)	578.1 (-3.4)	577.6 (-3.9)	581.5[209]
$IE(UO_2)$	519.3 (-71.0)	577.1 (-13.2)	587.8 (-2.5)	588.2 (-2.1)	590.3[210]
$D_e(UO)$	403.6 (-353/-354)	714.6 (-42/-43)	752.7 (-4/-5)	761.1 (4/3)	757±13[211]/758±10[212]
$D_e(UO_2)$	347.1 (-406/-388)	671.1 (-82/-64)	729.7 (-23/-5)	739.7 (-13/5)	753±14[211]/735±15[212]

dynamics (QED) contributions as well. The QED contribution to the U ionization energy has been shown to be around 1 kJ/mol.[206] On the other hand, at the present stage, the treatments of electron correlation with accurate inclusion of relativistic effects remain the central challenge in accurate calculations of thermochemical parameters. The spinor representation enables single-determinantal description of these electronic states and the use of coupled-cluster methods to treat dynamic correlation effects accurately. Table IV shows systematic improvement of computed results with the inclusion of the CCSD correlation contributions and the triples corrections obtained from CCSD(T)[15] or $CCSD(T)_\Lambda$[207] calculations. The X2CAMF-CCSD(T) and $CCSD(T)_\Lambda$ results in general compare favorably with the measured values.

It should be noted that the triples corrections calculated using the two perturbative triples approaches are significant. They amount to more than 35 kJ/mol in the case of $D_e(UO)$ and more than 50 kJ/mol for $D_e(UO_2)$. Furthermore, the CCSD(T) and $CCSD(T)_\Lambda$ results differ by around 10 kJ/mol. The study of high-level correlation effects, including the full

triples corrections and the quadruples contributions, will be important to provide more accurate results. The difference between the four-component Dirac-Coulomb results and the X2CAMF results has been shown to be rather small. On the other hand, it will still be useful to study the accuracy of the atomic approximation for the Breit term in the X2CAMF scheme, by comparing the X2CAMF results with full Dirac-Coulomb-Breit calculations. Finally, it would be very helpful to have reference values with reduced uncertainties to benchmark the calculations. The current reference values show relatively large uncertainties for $D_e(UO)$ and $D_e(UO_2)$; as listed in Table IV, the two latest reference values for $D_e(UO_2)$ differ from each other by around 18 kJ/mol.

IV. SUMMARY AND OUTLOOK

Relativistic coupled-cluster methods provide high-level treatments of electron-correlation effects for heavy-atom-containing molecules, provided that the wave function is dominated by a single determinant. This chapter reviews the general aspects of relativistic coupled-cluster theory, with an emphasis on the computational considerations. The usefulness of relativistic coupled-cluster methods is demonstrated using example calculations of molecular properties, in which scalar-relativistic effects and spin-orbit coupling exhibit strong coupling with electron correlation. A unique applicability of the spinor representation is also discussed using spinor-based relativistic coupled-cluster calculations of open-shell uranium-containing atomic and molecular species.

The scalar-relativistic two-component CC theory has essentially the same applicability as the non-relativistic CC theory. In contrast, the spinor-based relativistic CC methods are computationally more expensive. Highly parallelized implementations of spinor-based relativistic coupled-cluster methods are expected to significantly extend the applicability

of these methods to larger molecules on supercomputers. Meanwhile, the recent development of new algorithms to improve the computational efficiency through partial recovery of spin symmetry will enable calculations of larger molecules. With the ongoing developments of analytic-gradient techniques and the implementation of low-scaling computational techniques for spinor-based relativistic coupled-cluster methods, we expect significantly enhanced capabilities for practical applications to heavy-element chemistry and spectroscopy.

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