Coupled cluster Green’s function: Past, Present, and Future

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Coupled cluster Green’s function (CCGF) approach has drawn much attention in recent years for targeting the molecular and material electronic structure problems from a many-body perspective in a systematically improvable way. Here, we will present a brief review of the history of how the Green’s function method evolved with the wavefunction, early and recent development of CCGF theory, and more recently scalable CCGF software development. We will highlight some of the recent applications of CCGF approach and propose some potential applications that would emerge in the near future.

Keywords: Green’s function, coupled cluster, scalable simulation

CONTENTS

I. Introduction 11
   A. Quantum Green’s function method and its convolution with the wavefunction 11
   B. Coupled cluster Green’s function, early work and recent development 12

II. Theoretical foundation and Numerical approaches 13
   A. CCGF theory 13
   B. Numerical approaches for computing CCGF 14
   C. The state-of-the-art implementation and software development towards scalable simulations 16

III. Recent applications 17

IV. Potential future applications 18
   A. Quantum transport 18
   B. Double ionization and double electron attachment 18
   C. Fingerprint spectroscopy 19

V. Conclusion 20

VI. Acknowledgement 20

I. INTRODUCTION

A. Quantum Green’s function method and its convolution with the wavefunction

In his seminal work, “An essay on the application of mathematical analysis to the theories of electricity and magnetism” (1828), George Green (1793–1841), an English miller, physicist, and (possibly) self-taught mathematician, introduced what has been known today as the Green’s function, and developed a theory for solving the partial differential equations with general boundary conditions. This work was first self-published by Green himself and only circulated around family members and friends. Green’s seminal work was rediscovered and recognized by Lord Kelvin, Sturm, Liouville, Dirichlet, Riemann, Neumann, Maxwell, and many other mathematicians and physicists. Since then, the Green’s function method has been greatly developed and well established as a powerful mathematical tool for solving inhomogeneous differential equations and has been widely used in the quantum many-body theory.

Formally, the Green’s function was developed as auxiliary functions for solving a linear differential equation with a Dirac delta inhomogeneous source and homogeneous boundary conditions. Loosely speaking, suppose we would like to solve a partial linear inhomogeneous differential equation

\[ \mathcal{L}p(x) = q(x) \]  

with \( \mathcal{L} \) being a linear differential operator, and \( p(x) \) and \( q(x) \neq 0 \) the solution and inhomogeneity source, respectively. Utilizing the Green’s function \( G(x, x') \), defined as the solution of similar linear differential equation with a delta inhomogeneity

\[ \mathcal{L}G(x, x') = \delta(x - x') = \begin{cases} \infty, & x = x' \\ 0, & x \neq x' \end{cases} \]

a solution of \( p(x) \) can then be formally found through

\[ p(x) = \int G(x, x')q(x')dx'. \]

Since it was born, the Green’s function method had played a key role in solving the boundary-value problems in acoustics, hydrodynamics, thermodynamics, and electromagnetism during the second half of the 19th century. By the beginning of the 20th century, the Green’s function technique had paved the foundation for the whole theory of the partial differential equation and the development of functional analysis. In particular, it was generalized to linear operator theory and applied to second-order linear differential equations. With the
emergence of quantum mechanics during the same time, the Green’s function manifested its power for dealing with the Schrödinger equation by converting the differential equation into integral operator problems. In this context, the time-dependent Schrödinger equation (TDSE) is viewed as a linear partial differential equation that is of first-order in time,

\[
\left[i\hbar \frac{\partial}{\partial t} + \frac{\hbar^2}{2m} \nabla^2\right] \Psi(r, t) = V(r, t)\Psi(r, t),
\]

where \( \Psi(r, t) \) represents the time evolution of the wavefunction, \( \frac{\hbar^2}{2m} \nabla^2 \) is the kinetic energy operator with the momentum operator \( p = -i\hbar \nabla \), and \( V(r, t) \) is the external potential term. To apply the Green’s function method, one can first transform Eq. \( \ref{eq:tdse} \) to an inhomogeneous problem with Green’s function being defined as its solution,

\[
\left[i\hbar \frac{\partial}{\partial t} + \frac{\hbar^2}{2m} \nabla^2\right] G(r, t; r', t') = \delta(r - r')\delta(t - t').
\]

The inhomogeneous solution \( \Psi(r, t) \) may then be obtained through

\[
\Psi(r, t) = \int G(r, t; r', t')\Psi(r', t')d\mathbf{r}'.
\]

Eq. \( \ref{eq:inhomogeneous} \) can also be interpreted as the time evolution of the wavefunction from a given time and position \((r', t')\) to another time and position \((r, t)\).

Note that the wavefunction \( \Psi(r, t) \) in the Schrödinger picture can be rewritten as time propagation of state vectors in the position representation, i.e.

\[
\Psi(r, t) = \langle r'|\Psi(t)\rangle = \langle r'|U(t, t')\Psi(t')\rangle \\
= \int \langle r'|U(t, t')|\mathbf{r}'\rangle\langle \mathbf{r}'|\Psi(t')\rangle d\mathbf{r}' \\
= \int \langle r'|U(t, t')|\mathbf{r}'\rangle\Psi(\mathbf{r}', t') d\mathbf{r}',
\]

where the closure relation \( \int \langle r'|r\rangle d\mathbf{r}' = 1 \) is applied, and the time evolution operation \( U(t, t') = e^{-\frac{i\hbar}{\hbar}H(t-t')} \) in the Schrödinger picture evolves the wavefunction \( \Psi(r', t') \) to \( \Psi(r, t) \) in infinitesimal time intervals. Comparing Eq. \( \ref{eq:position} \) with Eq. \( \ref{eq:inhomogeneous} \), we can then write

\[
G(r, t; r', t') = \langle r'|U(t, t')|r\rangle = \langle r, t|r', t'\rangle,
\]

which associates the Green’s function to the probability amplitude of finding the particle in a state \( |r, t\rangle \) given its initial state \( |r', t'\rangle \). Since the Hamiltonian can be represented as \( H = \sum_n E_n|n\rangle\langle n| \) with \( \langle E_n, |n\rangle \)'s being its eigenpairs, and the eigenstates, \( |n\rangle \)'s, form a complete set, i.e. \( \sum_n |n\rangle\langle n| = 1 \), we can further rewrite Eq. \( \ref{eq:green} \) as

\[
G(r, t; r', t') = \sum_n \langle r'|e^{-\frac{i\hbar}{\hbar}H(t-t')}|n\rangle\langle n|r\rangle \\
= \sum_n \langle r|n\rangle\langle n|r'\rangle e^{-\frac{i\hbar}{\hbar}E_n(t-t')} \\
= \sum_n \psi_n(r)\psi_n^*(r') e^{-\frac{i\hbar}{\hbar}E_n(t-t')} ,
\]

whose Fourier transform then gives the spectral expansion

\[
G(r, r'; E) = \sum_n \frac{\psi_n(r)\psi_n^*(r')}{E - E_n}.
\]

Here \( \psi_n(r) \) defines the projection \( \langle r|n\rangle \).

In the mid 20th century, the quantum Green’s functions were further developed as being introduced as quantum propagators in the quantum field theory by Feynman and Schwinger for the complete development of a path-integral formulation that interprets the wavefunction, i.e. Eq. \( \ref{eq:path_integral} \), as the sum of the probabilities of the particle taking different quantum-mechanically possible trajectories. In particular, Feynman generalized the Green’s function \( G(r, t; r', t') \) as a new quantum field propagator by accounting for the forward and backward propagation in space-time and causal time orderings. Martin and Schwinger also realized the importance of Green’s function in quantum field theory and applied many-body Green’s function in the condensed-matter physics to evaluate particle currents and spectral amplitudes. Furthermore, thermodynamic many-particle Green’s function using a grand-canonical ensemble average was also developed during this time by Kadanoff and Baym.

Since then, the quantum many-body Green’s function that connects different positions and times has stated to manifest its power in particle scattering, non-equilibrium and finite-temperature physics, quantum transport, and many other fields. In these studies, often time the solution of the problem is obtained for an effective single-particle wavefunction which is only exact for non-interacting system, and becomes approximate in interacting system. For example, the Landauer–Büttiker method applied for the study of coherent quantum transport is usually not enough to describe electron-electron and electron-vibron interactions. When a single-particle picture no longer holds, explicit consideration of the wavefunction in the full many-body Hilbert space becomes necessary.

B. Coupled cluster Green’s function, early work and recent development

Among the well-developed explicit wavefunction approaches, the coupled cluster (CC) approach is one
of the most successful and efficient approaches that handle the many-body effect in a systematically improvable way. The marriage of the coupled cluster approach with the Green’s function method, or namely the coupled cluster Green’s function (CCGF) approach, dates back to the early 1990s when Nooijen and Suijnders first showed in their seminal works that CCGF can be directly computed rather than being obtained through solving Dyson’s equation with approximate self-energy. In the CCGF framework, the systematically improvable CC parametrization of the correlated wavefunction helps improve the computation of the Green’s function in a systematically improvable manner. Also, due to the connection between the CCGF approach and the equation-of-motion coupled cluster (EOM-CC) approach, the pole positions in the CCGF structure representing ionization potentials or electron affinities can be exactly reproduced by the eigenvalues of the similarity transformed Hamiltonian in normal product form in \((N \pm 1)\)-particle Hilbert space. However, due to the high-order polynomial scaling of the CCGF approach with respect to the system size (e.g. for CCGF with singles and doubles, i.e. CCSDGTGF, the scaling is \(O(n^6)\) with \(n\) being the number of basis functions representing the system size. For CCSRFGF, i.e. CCGF with singles, doubles, and triples, the scaling becomes \(O(n^9)\)) and limitation of computing software and hardware, early CCGF practice was subject to only resolving limited ionized states of small molecules described by small basis sets.

During the last 30 years, one has witnessed the rapid development of high-performance computing software and hardware that boosts size limit and time scale in quantum simulations. In recent years, CCGF starts to regain attention in molecular and material quantum chemical calculations. For example, for quantum systems described by <500 basis functions, one can now routinely employ CCSDGF approach to compute the corresponding many-body electronic structures, and the spectral function calculations have been reported for systems ranging from uniform electron gas,\(^{22}\) light atoms,\(^{23}\) heavy metal atoms,\(^{24}\) and simple 1-D periodic systems\(^{22,23}\) to a bunch of small and medium-size molecular systems.\(^{25,27}\) More recently, the CCGF impurity solver has been reported for computing the electronic structure of complex materials in the embedding computing framework.\(^{28,31}\) However, large CCGF calculations with more than 1000 basis functions are still challenging today, and one would need to introduce further approximations that might compromise the accuracy or employ supercomputing facility to perform “hero” runs. For example, with the aid of Oakridge leadership computing facility and deeply optimized numerical library specializing CCGF calculations, Peng et al. reported the CCSDGF calculations for deciphering the valence band electronic structures of C60 molecules and a series of large DNA fragments described with as many as \(~1200\) basis functions.\(^{33}\)

In the following, we will first review the theoretical foundation of the CCGF approach. After that, we will give a discussion about the numerical approach and the development of relevant software. Then we will elaborate on some recent applications employing the CCGF approach. At last, we will conclude by proposing and outlook some potential theoretical developments and applications in this area in the future.

II. THEORETICAL FOUNDATION AND NUMERICAL APPROACHES

A. CCGF theory

In the following, we give a brief introduction of the CCGF theory. For a detailed review of the GFCC method employed in this work, we refer the readers to Refs. \(^{21,22}\)\(^{25,26}\)\(^{28,29}\)\(^{30,31}\) Following Eq. (9), the analytical time-dependent Green’s function of an \(N\)-electron system that is governed by Hamiltonian \(H\) at the frequency \(\omega\) can be expressed as

\[
G_{pq}(t) = \langle \Psi | a_p e^{+ i 2 \pi (H - E_0) t} a_q^T | \Psi \rangle + \langle \Psi | a_q^T e^{- i 2 \pi (H - E_0) t} a_p | \Psi \rangle. \tag{11}
\]

The corresponding Fourier transform then gives rise to the CCGF in the frequency domain

\[
G_{pq}(\omega) = \langle \Psi | a_p (\omega - (H - E_0) + i \eta)^{-1} a_q^T | \Psi \rangle + \langle \Psi | a_q^T (\omega + (H - E_0) - i \eta)^{-1} a_p | \Psi \rangle. \tag{12}
\]

Here, the \(a_p (a_q^T)\) operator is the annihilation (creation) operator for electron in the \(p\)-th spin-orbital (we use \(p, q, r, s, \ldots\) for the general spin-orbital indices, \(i, j, k, l, \ldots\) for the occupied spin-orbital indices, and \(a, b, c, d, \ldots\) for the virtual spin-orbital indices), \(E_0\) is the ground-state energy, and \(\eta\) is the broadening factor introduced numerically to provide the width of the computed spectral bands. The normalized ground-state wavefunction of the system, \(|\Psi\rangle\), is formulated through CC biorthogonal parametrization on the reference state \(|\Phi\rangle\), i.e.

\[
|\Psi\rangle = e^{T} |\Phi\rangle, \quad \langle \Psi | = \langle \Phi | (1 + \Lambda) e^{-T}, \tag{13}
\]

where the cluster operator \(T\) and the de-excitation operator \(\Lambda\) are obtained from solving the conventional CC equations. Eqs. (11) and (12) can be further transformed to a compact form

\[
G_{pq}(t) = \langle \Phi | (1 + \Lambda) a_p e^{i 2 \pi \hat{H}_N t} a_q^T | \Phi \rangle + \langle \Phi | (1 + \Lambda) a_q^T e^{-i 2 \pi \hat{H}_N t} a_p | \Phi \rangle \tag{14}
\]

\[
G_{pq}(\omega) = \langle \Phi | (1 + \Lambda) a_p (\omega - \hat{H}_N + i \eta)^{-1} a_q^T | \Phi \rangle + \langle \Phi | (1 + \Lambda) a_q^T (\omega + \hat{H}_N - i \eta)^{-1} a_p | \Phi \rangle. \tag{15}
\]

with the normal product form of similarity transformed Hamiltonian \(\hat{H}_N\) being defined as \(\hat{H} - E_0\). Here, the
similarity transformed operators \( \tilde{A} \) (\( A = H, a_\mu, a_\mu^\dagger \)) are defined as \( \tilde{A} = e^{-T}A e^T \). The self-energy can be obtained directly through Dyson’s equation,

\[
\Sigma = G_0^{-1} - G^{-1}.
\] (16)

Here \( G_0 \) is the reference Green’s function chosen to be free-particle Helmholtz equation.

### B. Numerical approaches for computing CCGF

The development of the numerical approaches following Eqs. (11) and (14) for computing time-dependent CCGF is still at its early stage, and has only been studied for model systems\(^5\) and small molecular systems\(^6\).\(^7\)\(^8\)\(^9\)\(^10\) For the latter, the reported studies are focused on propagating the state in the \( (N - 1) \)-electron space within the cumulant approximation at the CC level to resolve the real-time evolution of the core ionized state, in particular for the simulation of the x-ray absorption spectra (XAS) from a deep core level. In the following, we will mainly focus on the review of the intensively developed numerical approaches for the CCGF calculations in the frequency space in recent years.

In the frequency space, to compute the \( \omega \)-dependent CCGF matrix, in a straightforward manner, one can diagonalize the non-Hermitian similarity transformed Hamiltonian \( \tilde{H} \) in the \( (N \pm 1) \)-particle space to construct the sum-over-states representation

\[
G_{pq}(\omega) = \sum_{\mu=1}^{M(N+1)} \frac{\langle \tilde{p} | R_\mu^{(N+1)} | \tilde{q} \rangle \langle L_\mu^{(N+1)} | \tilde{q} \rangle}{\omega - (E^{(N+1)}_\mu - E_0) + i\eta}
+ \sum_{\mu=1}^{M(N-1)} \frac{\langle \tilde{q} | R_\mu^{(N-1)} | \tilde{q} \rangle \langle L_\mu^{(N-1)} | \tilde{p} \rangle}{\omega - (E_0 - E^{(N-1)}_\mu) - i\eta}.
\] (17)

Here \( R_\mu^{(N\pm1)} \)'s and \( L_\mu^{(N\pm1)} \)'s are right and left eigenvectors of \( \tilde{H} \) in the \( (N \pm 1) \)-electron space with \( E^{(N\pm1)}_\mu \)'s the corresponding eigenvalues and \( M(N\pm1) \) the total number of eigenpairs. Therefore, if based on Eq. (17), direct computing of the CCGF matrix would require the diagonalization of the similarity transformed Hamiltonian matrix to obtain the non-negligible excited state eigenvalues and eigenvectors. Unfortunately, as the dimension of the Hamiltonian matrix grows polynomially with the number of orbitals used to describe the system, solving such an eigen-problem, if the Hamiltonian is a large dense matrix (e.g. dimension \( 10^{10} \)), would become challenging. In this scenario, direct diagonalization via, for example, LAPACK and ScaLAPACK quickly become infeasible, and one may need to switch to utilize standard matrix-free iterative Krylov subspace methods such as Arnoldi’s methods and variants\(^11\) to obtain the eigenpairs in the extreme ends of the spectrum of the Hamiltonian. Obviously, there are two clear disadvantages in this sum-over-states approach, (1) the choice of states to be included in Eq. (17) may be strongly \( \omega \)-dependent, and there are no clear criteria for how many states would need to be included in Eq. (17), which jeopardizes its practical applications. (2) Due to the polynomial scaling of the CC calculations and the large dimension of the Hamiltonian matrix, only a limited number of states can be obtained with the help of iterative methods, and if the target states are embedded deep in the spectral interior of the Hamiltonian, the convergence performance of the standard Arnoldi’s method would significantly deteriorate. For the latter, to reduce scaling and improve performance, one might need to employ spectral transformation\(^12\)\(^13\) or introduce other physics-inspired approximations. For example, early attempts perturbatively treated the sub-blocks of the similarity transformed Hamiltonian, and achieved \( O(n^3) \) scaling by treating the double-double block as diagonal (or the zeroth order) and truncating other blocks at the second order\(^10\).

Another typical approximation is core-valence separation (CVS)\(^14\) which has been routinely applied in the CC methods and algebraic-diagrammatic construction (ADC) method.\(^15\) In the approximation, the coupling between core- and valence-excited states is neglected to reduce the dimension of the effective Hamiltonian and accelerate the convergence. It has been reported that the typical error brought by the CVS approximation in the calculations of the K-shell ionization spectra of small and medium-size molecules\(^16\)\(^17\) would be between 0.4 to 1.0 eV. Nevertheless, for smaller errors and higher resolution of the spectra, the CVS may not be sufficient and other robust methods would be required. In the context of the relevant equation-of-motion (EOM) and linear response (LR) CC calculations, recent years have witnessed the development of some variants of the Krylov subspace methods along this line—asymmetric Lanczos-chain-driven subspace algorithm\(^18\)\(^19\)\(^20\), energy-specific Davidson algorithm\(^21\)\(^22\) and Generalized Preconditioned Locally Harmonic Residual (GPLHR) method\(^23\) to name a few. Remarkably, to serve the reduced scaling purpose in the coupled cluster calculations, local descriptions of the correlation wavefunction, for example, the pair natural orbitals (PNOs)\(^24\)\(^25\) or its modern version domain-based local pair natural orbitals (DLPNO)\(^26\)\(^27\)\(^28\) can be further used. There have been reports using these techniques to reduce the size of the space for the diagonalization of the similarity transformed Hamiltonian\(^29\)\(^30\)\(^31\).

Beside computing the CCGF matrix through an eigensolving process, the analytical CCGF form in Eq. (15) also allows computing CCGF matrix in the frequency domain through linear solvers\(^32\)\(^33\)\(^34\). In this approach, one need to first obtain the auxiliary many-body solutions \( \chi(p)(\omega) \) and \( \psi(q)(\omega) \) through solving the following linear systems in the \( (N \pm 1) \)-particle space

\[
(\omega - \tilde{H}_N + i\eta)\psi(q)(\omega) = \tilde{a}_q\chi(p)(\omega),
(\omega + \tilde{H}_N - i\eta)\chi(p)(\omega) = \tilde{a}_p\psi(q)(\omega).
\] (18)

Then the CCGF matrix can be computed through con-
\[ G_{pq}(\omega) = \langle \Phi|(1 + \Lambda)\Pi_{\alpha,\beta}Y_{p,q}(\omega)|\Phi\rangle + \langle \Phi|(1 + \Lambda)\pi_{\alpha,\beta}X_{p,q}(\omega)|\Phi\rangle. \] (19)

Here, the structures of \(\omega\)-dependent many-body operators \(X_{p}(\omega)\) and \(Y_{q}(\omega)\) can be expressed as
\[
Y_{q}(\omega) = Y_{q,1}(\omega) + Y_{q,2}(\omega) + \ldots
= \sum a_{a}y_{a,\omega}a_{a}^{\dagger} + \sum_{i,a < b}g_{ab}(\omega)a_{a}^{\dagger}a_{b}^{\dagger}a_{i} + \ldots (20)
\]
\[
X_{p}(\omega) = X_{p,1}(\omega) + X_{p,2}(\omega) + \ldots
= \sum_{i}x_{i}(\omega)p_{i}a_{i} + \sum_{i < j, a}x_{ij}(\omega)p_{i}^{\dagger}a_{j}a_{i} + \ldots (21)
\]
which similar to the cluster amplitudes \(T\) and \(\Lambda\) can be truncated at different many-body levels. At the two-body level, the obtained approximate formulation of Eq. (19) can be written as
\[
G_{pq} = \langle \Phi|(1 + \Lambda_{1} + \Lambda_{2})\Pi_{\alpha,\beta}(Y_{q,1} + Y_{q,2})|\Phi\rangle + \langle \Phi|(1 + \Lambda_{1} + \Lambda_{2})\pi_{\alpha,\beta}(X_{p,1} + X_{p,2})|\Phi\rangle, \quad (22)
\]
which is the so-called CCSDG approximation (CCG with singles and doubles). Fig. 1 exhibits all the connected diagrams contributing to the CCGDF matrix.

Comparing the eigen-solving and linear-solving approaches towards computing CCGF matrix, we can see that (1) the eigen-solving process needs to resolve all the necessary states or the necessary bases (e.g. Lanczos bases) for reproducing all the states to suppress the error due to the missing states, and (2) the linear-solving approach bypasses the ambiguity of choosing the \(\omega\)-dependent states to be included in Eq. (17) while requires to sweep a range of frequency to resolve the pole positions. Therefore, during the linear-solving process the number of frequencies (or the number of the sampled \(k\) points when dealing with a periodic system) will impose a larger overhead on the cost of computing CCGF matrix if a much higher resolution is required. To solve this problem, recent computation for the CCGF of periodic systems showed that the self-energy-mediated interpolation utilizing Wannier orbitals to compute Green's function via Dyson equation can be used to accommodate a large number of sampled \(k\) points\cite{28,41}. More recently, a more general interpolation technique has been reported in the CCGF calculations of small and medium-size molecular systems utilizing the so-called model-order-reduction (MOR) technique\cite{29}. Essentially, MOR helps projects the target linear problem to Krylov subspace such that the solution of the original linear system over a broad frequency regime can be approximated through a more easily solvable model linear system over the same frequency regime. For the CCGF-associated linear problem, the MOR projection can be expressed as
\[
\begin{align*}
\langle \omega - i\eta + \hat{H}_{N}\rangle X &= b_{1}, \\
\langle \omega + i\eta - \hat{H}_{N}\rangle Y &= b_{2}, \\
\end{align*}
\]
and
\[
\tilde{G} = c_{1}^{T}X + c_{2}^{T}Y, \quad (24)
\]
where an orthonormal subspace \(S = \{v_{1}, v_{2}, \ldots, v_{m}\}\) (the rank \(m\) is much smaller than the dimension of the Hamiltonian) is construct to project \(\hat{H}_{N} = S^{T}\hat{H}_{N}S, \quad X = S^{T}X, \quad Y = S^{T}Y, \quad b_{i} = S^{T}b_{i}, \) and \(c_{i}^{T} = c_{i}^{T}S (i = 1, 2)\) with the columns of \(b_{1}\) and \(b_{2}\) corresponding to \(\langle \phi|(1 + \Lambda)\pi_{\alpha,\beta}|\Phi\rangle\) or \(\langle \Phi|(1 + \Lambda)\pi_{\alpha,\beta}|\phi\rangle\), respectively.

The overall cost of performing CCGF simulations comes from several parts. First of all, the conventional Hartree-Fock (HF) and CC calculations (this could also include \(\lambda\)-CC calculations) need to be performed to prepare \(|\Phi\rangle\). The conventional HF calculation scales as \(O(n^{3})\). The conventional \((\lambda\)-)CC calculation scales as \(O(n^{6})\). Secondly, the linear-solving process in the \(\omega\)-dependent CCGF calculation needs to be performed for all the spin-orbitals and frequencies. For a given frequency, one CCSDG calculation scales as \(O(n^{6})\). In addition, there is a prefactor, the number of frequencies, applying on the top of the cost. If applying MOR, the prefactor can be significantly reduced, with the trade-off being the orthonormalization of the subspace, subspace projection, and solving Eq. \(23\). Typically, a Gram-Schmidt (GS) orthogonalization would scale as \(O(mn^{3})\), the projection scales as \(O(mn^{5})\), and solving the projected linear system scales as \(O(N_{\omega}m^{5})\) with \(N_{\omega}\) the total number of frequencies.

From the above analysis, it is obvious that the practical CCGF calculation is mainly subject to (a) intensive compute/contraction and communication of multi-dimension tensors and (b) performance of the iterative solver. Remarkably, both (a) and (b) are shared between CC and CCGF calculations, and can be utilized to ease the implementation. For example, the direct inverse of iterative subspace (DIIS) solver\cite{66,67} is usually employed in the non-linear ground-state CC calculations. For the CCGF calculations, it has been reported that DIIS solver that is also employed to solve CCGF linear systems exhibited faster convergence than the Lanczos iterative method for computing the valence ionization potentials of CO and \(N_{2}\) molecules\cite{28,40}. Other solvers such as biconjugate gradient (BiCG)\cite{28} and generalized minimal residual (GMRes)
method\textsuperscript{24} have also been reported in the CCGF calculations. In particular, GMRes is the only Krylov-based solver for treating general matrices (note that the similarity transformed hamiltonian in GFCC is non-symmetric) and, in principle, able to converge to the exact solution after at most $O(2^2V)$ steps. However, in comparison with the DIIS whose cost is constant about $O(2^2V)$, the cost of GMRes grows as $O(k^22^2V)$ with $k$ being the iteration number.

C. The state-of-the-art implementation and software development towards scalable simulations

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{infrastructure.png}
\caption{Infrastructure of GFCClib\textsuperscript{33}, a library package for performing scalable CCGF calculations.}
\end{figure}

In the frequency space, the algebraic structure of the $\omega$-dependent CCGF equations intuitively enables scalable implementation—parallel execution through frequencies and/or spin-orbitals. However, a rudimentary implementation based on the intuitive parallelism would quickly encounter bottlenecks, in particular, the ones associated with expensive high dimensional tensor contractions, expensive inter-processor communication, and severe load imbalance, which prohibit the development of highly scalable CCGF library and its routine application in large scale simulations. Based on our previous experience on designing and developing computational chemistry packages to work efficiently on massively parallel processing supercomputers (e.g NWChem\textsuperscript{25} and more recently NWChemEx\textsuperscript{26}), properly addressing these bottlenecks requires developments of new computational strategy and solvers, and the systematic software engineering of an up-to-date inclusive computing infrastructure that efficiently utilizes the highly scalable computing resource. Especially, the efficient implementations of CCGF utilizing presently available supercomputers need to focus on the specialized form of tensor libraries to provide tools for distributing multidimensional tensors across the network, performing tensor contractions in parallel, and utilizing computational resources offered by existing GPU architectures. Take the high dimensional tensor contractions for an example, the most expensive tensor contraction in the CCSDGF approach can be expressed as

\begin{equation}
R(i, j, a, b)+ = \sum_{c,d} T(i, j, c, d) \times V(a, b, c, d) \quad (25)
\end{equation}

where $V$ and $T$ are four-index two-electron integral tensor and CC double amplitude tensor, respectively, and $R$ is an four-index intermediate tensor. The multidimensional tensor contraction shown in Eq. (25) is both computation and communication intensive. In the early developments of parallel tensor algebra systems for dealing with this type of tensor contraction\textsuperscript{79–81}, progress has been made towards automated code generators, memory reduction, and the real-space many-body calculations.

Early this year, we released a new library, named GFCCLib\textsuperscript{33} for routinely performing CCGF calculations in scalable computing resources. Fig. 2 exhibits the infrastructure of GFCCLib. Basically, there are two layers inside the GFCCLib: (1) At the application layer, there are essentially three major modules to perform Hartree-Fock (HF), ground-state CC, and CCGF calculations, respectively; (2) The application layer routinely calls the functions provided by the kernel layer for performing tensor related operations. The tensor data distribution, memory management, and parallel runtime scheduling are dealt with inside the kernel through invoking external vendor libraries. Specifically, the kernel, which can also be viewed as an independent tensor algebra library for many-body methods\textsuperscript{26}, is implemented using Global Arrays (GA)\textsuperscript{79,81} and message passing interface (MPI) targeting high-performance parallelization on distributed memory platforms. Here, the kernel API directly takes the distributed block-sparse tensors and decomposes the contractions into a set of dependent operations that are then passed to a backend for scheduling and execution. High performance is obtained in the backend by focusing upon a small number of operations that are extensively optimized by the vendor libraries or by code generation plus auto-tuning. Also, inside the kernel, the execution of tensor operations involves multi-granular dependence analysis and task-based execution. The dependence analysis splits the tensor operations into independent execution levels, and operations at the same level can be executed concurrently with synchronizations between levels. Note that this allows multiple operations to be executed at the same time, exposing more parallelism and improving processor utilization. Furthermore, each operation is partitioned into tasks that can be scheduled to compute a portion of the operation on any compute unit. To further speed up the tensor operation, a GPU execution and launch scheme (with TALSH\textsuperscript{22} as the underlying GPU tensor algebra engine) is also developed inside the kernel to make use of the GPU acceleration for localized summation loops and enable data transfer and compute overlap between successive summation loop iterations.
III. RECENT APPLICATIONS

![Coupled cluster Green's function simulations](image)

FIG. 3. The CCGF approach facilitated by scalable implementation on the modern supercomputing facility is now developing towards large-scale simulations.

So far, the CCGF approach is mainly utilized for the accurate electronic structure studies of molecular systems and condensed-matter materials. Early implementation of CCGF formalism relying on the eigen-solvers was essentially carrying out ionization potential and electron attachment EOM-CC calculations to resolve the pole positions in the valence region. The CCSDGF results for predicting the ionization energies in the valence band of small benchmark systems such as Ne, HF, H₂O, N₂, and nucleobases employing triple-ζ basis sets agree well with the experimental photoelectron spectra data[17]. Further development of the CCGF approach involving linear-solvers enabled the computation of spectral functions for single atoms and small molecules over a broad frequency range. Employing the simple Gaussian basis set, the CCSDGF quasiparticle energy spectra of isolated atoms from H to Ne exhibited excellent agreement with the full-configuration interaction results reproducing not only correct quasiparticle peaks but also satellite peaks[20]. Similar calculations have also been carried out for 3d transition metal atoms from V to Cu and simple periodic systems such as 1D LiH chain, 1D C chain, and 1D Be chain, and comparison has been made between CCSDGF and GFs from single-particle theories such as Hartree-Fock and density functional theory (DFT) to exhibit the capability of the CCSDGF approach for computing the satellites of the spectral functions. The CCSDGF calculation of the ionization of H₂O, N₂, CO, s-trans-1,3-butadiene, benzene, and adenine molecules were found to be able to provide a qualitative or semi-quantitative level of description for the ionization processes in both the core and valence regimes[23]. Large-scale CCSDGF simulations were rarely reported until recently alongside the release of the scalable GFCCLib. In one of the reports[24], the spectral functions of several guanine–cytosine (G–C) base pair structures have been reliably computed at the CCSD level employing the CCSDGF approach with 400~1200 basis functions for the first time in a relatively broad near-valence regime, where the many-body description of the near-valence ionization of the large DNA fragments features the important transition from the intra-base-pair cytosine π → π⁺ excitation to the inter-base-pair electron excitation as the fragment size increases. In another report[25], CCSDGF calculations employing >800 basis functions were performed for the first time for computing the many-body electronic structure of the fullerene C60 molecule covering up to ~25 eV near-valence spectral region. It is worth mentioning that it has been observed from these reported large-scale CCSDGF simulations that good weak scaling behavior supports multiple GFCCSD calculations to be efficiently performed in parallel, while improved strong scaling can enable the use of fewer parallel tasks and thus reduce load imbalance.

For condensed-phase materials, an early test of the CCSDGF approach was performed for computing the spectral function of the uniform electron gas[26], which was found to provide an improvement over GW and GW-cumulant results. More recently, the CCSDGF as an impurity solver has been applied in the embedding theoretical framework to compute the electronic structure of 1D and 2D Hubbard model[27,28] and limited solid[29] exhibiting the reliability of CCSDGF solver in treating weakly and even moderately strongly correlated materials. For more realistic solids such as antiferromagnetic MnO₂ and paramagnetic SrMnO₃ whose insulating character the GW level of theory has difficulty predicting, recent examination of the corresponding impurity self-energies and local density-of-states has illustrated that the CCSDGF solver is able to provide a satisfactory description in particular for impurities containing Mn t₂g and e_g orbitals, while exhibit larger discrepancies for impurities containing O 2p orbitals concluding that higher-order excitations need to be included in the CCGF solver for describing stronger correlation[30].

Regarding including higher-order excitations in CCGF calculations, take triples for example, due to the prohibitive O(N⁸) scaling in the formal CCSDT/CCSDTGF approach, pragmatic choice could be focused on reduced cost iterative and non-iterative triples corrections. Remarkably, the triples corrections such as EOMIP-CCSD[31], CCSDT-nc (n=1,2,3)[32,33], CCSDT[34], stochastic EOM-CC(Π)[35,36], EOM-CC(m,n)[37], EOM-CCSD(T)(a)[38,39], and method-of-moments based non-iterative triple correction[40,41] have been extensively developed, and could be migrated to the CCGF framework. Recently, based on the analysis of the connectedness of the CCGF[38,39], as well as the lack of the size-intensivity in the EOM-CC(m,n) class of methods[42], Peng and Kowalski proposed to extend the excitation level of the inner auxiliary operators X_ρ(ω) and Y_q(ω) in the linear-solving CCSDGF approach to triples to implicitly include triples corrections to the CCSDGF results[43]. Preliminary results for computing the spectral functions of N₂ and CO molecules in the inner and outer valence regimes exhibited better agreement with the experimental results than the CCSDGF. So far, the benchmark studies of these triples corrections are
still focused on small and simple molecular systems, the evaluation of their impact on the description of larger and/or strongly correlated systems, as well as what we can learn from the evaluation to come up with a general guideline for the applications, are still scientific and computational challenging, and might need to introduce further approximations. From this perspective, approximations such as active space [119–121] and local-correlation/multi-level approach [122–124] that have been studied in the EOM-CC framework can be directly tested and applied in the CCGF approach.

IV. POTENTIAL FUTURE APPLICATIONS

During decades of development in theory, numerical approach, and software, we envision the applications of CCGF approach is reaching its prime. In the following, we highlight three areas in which one might witness CCGF applications in the near future.

A. Quantum transport

Recent years have witnessed the considerate progress in the experimental and theoretical studies of quantum transport in molecular nanostructures, in particular molecular junctions. To understand interesting phenomena observed in the experiments such as Coulomb blockade [125–128] Franck-Condon blockade [111,112] spin blockade [113] Kondo effect [115] quantum interference and decoherence [119,120] etc. the theoretical description is required to be formulated within the non-equilibrium many-body framework. This requirement becomes especially important when the qualitative physics incorporated in the Hamiltonian of the overall system cannot be properly described by an effective single-particle picture due to strong electron-electron and/or electron-vibronic interactions. On the other hand, the estimates of IPs and EAs for small molecules based on single-particle theory typically deviate from higher-level methods by 1 eV or more [118]. For larger molecules or metallic wires, the absolute error in IPs and EAs sometimes does not necessarily increase with the system size, particularly when the work function is dominated by a subsystem (e.g. a large metallic segment) and the DFT results are satisfactory. However, it is worth pointing out for higher computed IPs and EAs, as well as the alignments of these levels, the errors in these large molecular junctions remain large. Therefore, higher-level methods, such as the CCGF theory, should provide better and the next generation standard tools of ab initio transport calculations. Here, developed scalable CCGF libraries (for example, GFCCCLib) open prospects for treating strong electron-electron interaction and large extended molecular complex (including both molecule and parts of leads described by thousands of atoms and large enough basis sets) so that scalable simulations can be performed with size-convolved computational parameters.

B. Double ionization and double electron attachment

Development of computationally robust and efficient wavefunction approaches which can handle open-shell and multi-reference situation remains one of the central topics in electronic-structure theory. Both double ionization potential (DIP) and double electron attachment (DEA) methods are economical for describing multi-reference systems. Nooijen and Bartlett introduced [120] both approaches for similarity transformed EOM in 1997. Later on, numerous DIP/DEA-EOMCC economical development in high-order excitation manifold (e.g. with the design of active spaces), and their benchmark and applications have been reported [121–123]. In DIP, the two electrons get removed from the N-electron reference state to obtain N − 2 electron-deficient target state. On the other hand, in DEA, two electrons are attached to an N-electron reference to obtain N + 2 electron target state.

When two electrons distribute on top of a closed shell, forming open-shell species (also known as diradicals). The DEA method can describe the ground-state and excited-state of diradicals very efficiently. Spin-flip (SF) is another method that provides highly accurate singlet-triplet gaps of diradicals. However, for computing excitation energy of higher excited states in diradicals, DEA performs better compared to SF due to its extensive accessibility to fock-space [110].

The DIP method helps interpret Auger spectra. Although the intensities depend on the particular site of core ionization in Auger spectra, one can restrict the removal of one electron from the core and still get a good approximation of Auger peaks. Another application of DIP is the ionization spectra of doublet radical. First, ionization targets neutral radical and its excited states, while second, ionization targets the ionized radical and its excited states. One can also try targeting the multi-reference neutral by performing the DIP method on the dianionic reference. However, complications due to instability of the dianionic reference limit this path of studying the neutral [124].

Extending the capabilities of DEA and DIP within the CCGF approach will provide a new pathway of studying the electronic structure of multi-reference states spanning from low-energy to high energy regimes at one go. Furthermore, borrowing the ideas from EOMCCSD formalism and truncating the DEA and DIP operators at doubles excitation as follows:

\[ \hat{R}_{DIP} = \frac{1}{2} \sum_{ij} r_{ij} a^\dagger_{ij} a_{ij} + \frac{1}{6} \sum_{ij} r^a_{ij} a^\dagger_{ij} a_{ij} a^\dagger_{ij} a_{ij} \]  \hspace{1cm} (26)

\[ \hat{R}_{DEA} = \frac{1}{2} \sum_{ab} r^{ab} a^\dagger_{a} a^\dagger_{b} + \frac{1}{6} \sum_{abc} r^{abc} a^\dagger_{a} a^\dagger_{b} a^\dagger_{c} a_{c} \]  \hspace{1cm} (27)
where \( r \) represents amplitude tensors, will provide tractable and easy-to-implement equations.

C. Fingerprint spectroscopy

The calculation of the vertical excitation spectrum, defined as the initial and final states having the same geometry (usually the equilibrium geometry of the ground state), is a natural starting point for investigating excited states of any polyatomic system. However, spectral features such as peak width, position, and intensity require more than interpretation at a single geometry. This is justifiable when we consider that electron ionization, attachment, and excitation process can result in potential energy landscapes that are very different from their parent surface, as abstractly illustrated in Fig. 5. Techniques such as extended x-ray absorption fine structure, x-ray photoelectron diffraction, and core-level photoelectron spectroscopy are just some experimental means of analyzing structural and dynamical traits unique to molecules and characterizing regions of spectra known as fingerprint regions. To accurately describe these distinct molecular spectroscopy motifs and their finer details, accurate computational methods need to be coupled with ways of analyzing the potential energy surface.

Analytical gradients based on CCGF approach have yet to be developed, but this does not preclude such methods from being combined with existing analytical gradient techniques of other approaches. For example, analytical gradients for various flavors of EOMCC approaches have been developed that can be leveraged. Most recently, a great deal of effort is being put forth to bring these analytical gradient techniques to utilize massively parallel architectures in the recent redesign of NWChem and NWChemEx. This implementation relies heavily on the many-body tensor library for the tensor contractions and the Libint library for the evaluation of molecular integrals over Gaussian Functions and their derivatives. Ideally, these standard methods of analyzing the potential energy surface, when combined with the CCGF methodology, ought to enhance the analysis and generation of spectra.

V. CONCLUSION

In this work, following brief historical notes on the history of the development of Green’s function method, in particular how it convoluted with wavefunction, we reviewed early and recent development of CCGF theory and elaborated its theoretical foundation and some state-of-the-art numerical approaches, as well as its more recently scalable software development. At the end, we highlighted some of recent applications of CCGF approach and proposed some potential applications that would emerge in this field in the near future.

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