

14 Coupled-Cluster Theory for Materials Science

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1 Introduction

Coupled cluster theories are widely-used to study many-body systems in nuclear physics, molecular quantum chemistry and solid state physics. This chapter introduces fundamental concepts of coupled cluster (CC) theory and discusses its application to the electronic structure theory problem. The present chapter serves as a primer to this topic. A more general overview of coupled cluster theory and its applications in quantum chemistry can be found in Ref. [1]. For an introduction to the theoretical formalism from the perspective of theoretical chemistry we recommend Refs. [2–5]. During the past decades a large body of well-written scientific articles and text books on coupled cluster theory has been published. Many of these can be found in the bibliographies of Refs. [1–4].

Coupled cluster theory was first proposed by Fritz Coester and Hermann Kümmel in the field of nuclear physics [6, 7]. Jiri Cizek and Josef Paldus introduced the method for electron correlation [8, 9]. Since then, coupled cluster theory has successfully been applied to study many-electron Hamiltonians for a wide range of systems, including atoms, molecules and even solids. At the same time, many of the most popular model Hamiltonians including lattice Hamiltonians and the uniform electron gas have also been explored and used to benchmark the accuracy of coupled cluster theories. It is therefore fair to say that CC theories are among the most successful approaches to treat many-body problems in quantum physics.

2 Fundamental concepts of coupled cluster theory

A fundamental approach to solve the time-independent Schrödinger equation for many-electron systems is based on finding accurate approximations to the true many-electron wavefunction $|\Psi\rangle$. An important challenge of these so-called wavefunction based methods revolves around finding a representation of the many-electron wavefunction that is at the same time compact and accurate in describing electronic correlation effects. Here, compactness not only means that the number of parameters used in the expansion of the wavefunction is within the limits of the available computational resources and scales with a favorable power law with respect to the system size. It also implies that the evaluation of the required matrix elements of quantum mechanical operators can be carried out in a computationally efficient manner. Successful wavefunction based methods typically optimize the balance between complexity in the ansatz and efficiency in evaluating matrix elements or expectation values. In this regard, for example, variational quantum Monte Carlo techniques achieve a good balance by combining stochastic integration techniques with a sophisticated many-body correlation function referred to as Jastrow factor. As will be explained in the present section, coupled cluster methods employ an Ansatz for the wavefunction that benefits significantly from an effective factorization of the many-electron wavefunction that can be systematically improved.

2.1 Hartree-Fock theory and Slater determinants

Hartree-Fock theory employs the simplest possible Ansatz to the many-electron wavefunction that is antisymmetric under exchange of two coordinates or orbitals, as required for a fermionic wave function. For an N -electron wavefunction in real space the Hartree-Fock wavefunction is given by a Slater determinant constructed from one-electron (Bloch) orbitals with an appropriate pre-factor to ensure normalization such that

$$\Phi^{\text{HF}}(\mathbf{x}_1, \dots, \mathbf{x}_n) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\mathbf{x}_1) & \cdots & \varphi_n(\mathbf{x}_1) \\ \vdots & \ddots & \vdots \\ \varphi_1(\mathbf{x}_n) & \cdots & \varphi_n(\mathbf{x}_n) \end{vmatrix}. \quad (1)$$

The HF determinant is constructed from a set of orthonormal one-electron orbitals, $\varphi_i(\mathbf{x})$, that are obtained by minimizing the Hartree-Fock energy, whereby all the coupling terms of the Hamiltonian between the Hartree-Fock determinant and the corresponding single-excited Slater determinants vanish, which is also referred to as Brillouin's theorem. Here \mathbf{x} is a compound index of spatial and spin coordinate. In periodic systems the index i is a compound index of the Bloch wave vector k_i used to sample the first Brillouin zone and the band index n_i . Hartree-Fock (HF) theory can be regarded as a low rank tensor approximation to the many-electron wavefunction, employing an antisymmetrized outer product of single electron orbitals to approximate the many-body wavefunction. Hence, by construction, HF theory neglects electronic correlation effects that cannot be captured using products of one-electron functions only. For brevity we will use the following notation for the HF wavefunction $|0\rangle = |\Phi^{\text{HF}}\rangle$.

2.2 The exponential Ansatz

The CC approximation is based on an exponential *Ansatz* for the electronic wavefunction [8, 1] acting on a single Slater determinant $|0\rangle$,

$$|\Psi_{\text{CC}}\rangle = e^{\hat{T}} |0\rangle, \quad (2)$$

where the *cluster operator* consists of second-quantized neutral excitation operators

$$\hat{T} = \sum_{\mu} t_{\mu} \hat{\tau}_{\mu}, \quad t_{\mu} \in \mathbb{C} \quad (3)$$

with μ labeling excitation configurations. For instance, when considering only singles and doubles excitations (Coupled Cluster Singles Doubles (CCSD)) the unrestricted CCSD cluster operator is given by

$$\hat{T} = \sum_{a,i} t_i^a \hat{a}_a^{\dagger} \hat{a}_i + \frac{1}{4} \sum_{a,b,i,j} t_{ij}^{ab} \hat{a}_a^{\dagger} \hat{a}_b^{\dagger} \hat{a}_j \hat{a}_i \quad (4)$$

where the indices in $\{a, b, c, \dots\}$ denote virtual or unoccupied spin orbitals and $\{i, j, k, \dots\}$ denote occupied spin orbitals. Orbitals are occupied or unoccupied with respect to the reference

Slater determinant $|0\rangle$, which may come from a HF calculation. The excitation operators are defined such that they create excited determinants when acting on $|0\rangle$ such that

$$\hat{a}_a^\dagger \hat{a}_i |0\rangle = \left| \begin{matrix} a \\ i \end{matrix} \right\rangle \quad \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i |0\rangle = \left| \begin{matrix} ab \\ ij \end{matrix} \right\rangle. \quad (5)$$

Note that the following equation is satisfied.

$$\langle 0 | \hat{a}_a^\dagger \hat{a}_i = 0. \quad (6)$$

We note in passing, that the n th-order CC ansatz including up to the n th-order excitation operator is exact for n -electron systems. One advantage of the different approximations to the cluster operator is that they constitute a hierarchy, which starting from the one-particle HF approximation, allows for a systematic treatment of the quantum many-body effects that are captured with an increasing level accuracy by employing CCSD, CCSDT and CCSDTQ theories. Calculated ground state properties typically exhibit decreasing errors using higher levels of theory.

Here, we will restrict the discussion to the case of CCSD. Applying the Coupled Cluster (CC) *ansatz* to the time-independent many-body electronic Schrödinger equation results in

$$\bar{H} |0\rangle = e^{-\hat{T}} \hat{H} e^{\hat{T}} |0\rangle = E_{CC} |0\rangle \quad (7)$$

where E_{CC} is the coupled cluster energy, and we have implicitly defined the similarity transformed Hamiltonian \bar{H} . The state $|\Psi_{CC}\rangle$ is parametrized by the coefficients t_μ , which can be obtained by projection. In the case of CCSD one projects the Schrödinger equation onto the singles and doubles sectors of the Hilbert space

$$E_{CC} = \langle 0 | \bar{H} |0\rangle \quad (8)$$

$$0 = \langle 0 | \hat{a}_i^\dagger \hat{a}_a \bar{H} |0\rangle \quad (9)$$

$$0 = \langle 0 | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_b \hat{a}_a \bar{H} |0\rangle. \quad (10)$$

Equations (8–10) are a set of coupled non-linear equations in terms of the amplitudes t_i^a and t_{ij}^{ab} that are solved by iterative methods.

2.3 Hausdorff expansion

The similarity transformed Hamiltonian $\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$ occurring in the coupled cluster equations is an effective and non-Hermitian Hamiltonian, which can be expressed using the Hausdorff expansion

$$\bar{H} = \hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2!} [[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{3!} [[[\hat{H}, \hat{T}], \hat{T}], \hat{T}] + \frac{1}{4!} [[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}], \hat{T}] + \dots \quad (11)$$

Recalling that \hat{H} in second quantization is given by

$$\hat{H} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{4} \sum_{pqrs} g_{pqrs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r \hat{a}_s \quad (12)$$

and

$$[\hat{a}_p^\dagger \hat{a}_q, \hat{a}_a^\dagger \hat{a}_i] = \hat{a}_p^\dagger \delta_{qa} \hat{a}_i - \hat{a}_a^\dagger \delta_{ip} \hat{a}_q, \quad (13)$$

it follows that Eq. (11) terminates exactly after the fourth nested commutator. We stress that the set of indices $\{p, q, r, s, \dots\}$ denotes both occupied or unoccupied orbitals.

Substituting the expression for \bar{H} in the equation for the coupled cluster energy yields

$$E_{CC} = \langle 0 | \bar{H} | 0 \rangle = \langle 0 | \hat{H} | 0 \rangle + \langle 0 | \hat{H} \hat{T} | 0 \rangle = E_{HF} + \langle 0 | \hat{H} \left(\hat{T}_2 + \frac{1}{2} \hat{T}_1^2 \right) | 0 \rangle. \quad (14)$$

Note that this equation simplifies significantly using the Brillouin theorem ($\langle 0 | \hat{H} \hat{a}_a^\dagger \hat{a}_i | 0 \rangle = 0$), the fact that \hat{H} can de-excite at most two electrons and due to $\langle 0 | \hat{a}_a^\dagger \hat{a}_i = 0$. Consequently, only singles and doubles amplitudes contribute to the CC energy. If higher-order excitations in the cluster operator are considered, their contribution to the energy is only indirect by the amplitude equations. We note that the correlation energy is implicitly defined as the difference between the exact ground state energy and the HF energy E_{HF} . Similarly to the energy, the singles and doubles amplitude equations defined in Equations (9–10) can be obtained.

2.4 Beyond the ground state

A common way to obtain excited states based on the CCSD theory is through diagonalizing the similarity transformed Hamiltonian \bar{H} in a suitable subspace of the Hilbert space [10]. We present the neutral variant of this approach, also called electronically excited equation of motion, for which the number of electrons is conserved. In consequence, restricting from now on again the analysis to singles and doubles excitations, the ansatz for an excited state $\hat{R} |\Psi_{CC}\rangle$ is

$$\hat{Q} \hat{H} \hat{R} |\Psi_{CC}\rangle = \hat{Q} \hat{H} \hat{R} e^{\hat{T}} |0\rangle = E_R \hat{Q} \hat{R} |\Psi_{CC}\rangle \quad (15)$$

where

$$\hat{R} = r_0 + \sum_{a,i} r_i^a \hat{a}_a^\dagger \hat{a}_i + \frac{1}{4} \sum_{a,b,i,j} r_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i, \quad r_\mu \in \mathbb{C} \quad (16)$$

is a linear excitation operator, E_R is its excitation energy and \hat{Q} is the projector onto the singles and doubles excitations manifold of the Hilbert space, this is,

$$\hat{Q} = \sum_{a,i} \left| \begin{array}{c} a \\ i \end{array} \right\rangle \left\langle \begin{array}{c} a \\ i \end{array} \right| + \frac{1}{4} \sum_{a,b,i,j} \left| \begin{array}{c} ab \\ ij \end{array} \right\rangle \left\langle \begin{array}{c} ab \\ ij \end{array} \right|. \quad (17)$$

Equation (15) is equivalent to a commutator equation only involving \bar{H} and the excitation energy difference ΔE_R between E_R and the correlated ground state E_{CC} ,

$$[\hat{Q} \bar{H}, \hat{R}] |0\rangle = \Delta E_R \hat{Q} \hat{R} |0\rangle. \quad (18)$$

It is worthwhile noting that the commutator on the left-hand-side means that only connected diagrams need to be considered in the expansion. Equation (18) motivates the name *equation of motion* due to its resemblance to the time-dependent *Heisenberg picture* differential equation for the time evolution of an operator.

2.5 The coupled cluster doubles equations

For computer implementations it is necessary to rewrite the above equations only in terms of one- and two-electron integrals. Here we seek to give the final result of the corresponding expressions for CCD theory only. We note that in the case of, for instance, the uniform electron gas (UEG) Hamiltonian, due to the symmetry, single excitations are absent. Therefore we consider CCD a particularly instructive case to learn more about CC theory. The cluster amplitudes t_{ij}^{ab} are obtained by solving the quadratic amplitude equations $\langle ij| e^{-\hat{T}_2} \hat{H} e^{\hat{T}_2} ||0\rangle = 0$ that in a spin-orbital basis read

$$\begin{aligned}
 t_{ij}^{ab} = \frac{1}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} & \left(\langle ij||ab\rangle + \langle cj||kb\rangle t_{ik}^{ac} + \langle ci||ka\rangle t_{jk}^{bc} + \langle cd||kl\rangle t_{ij}^{db} t_{ik}^{ac} \right. \\
 & + \frac{1}{2} \langle cd||ab\rangle t_{ij}^{cd} + \frac{1}{2} \langle ij||kl\rangle t_{kl}^{ab} + \frac{1}{4} \langle cd||kl\rangle t_{ij}^{cd} t_{kl}^{ab} \\
 & - \langle cj||ka\rangle t_{ik}^{bc} - \langle ci||kb\rangle t_{jk}^{ac} - \langle cd||kl\rangle t_{lj}^{da} t_{ik}^{bc} \\
 & \left. + \frac{1}{2} \langle cd||kl\rangle [t_{lj}^{ab} t_{ik}^{cd} - t_{li}^{ab} t_{jk}^{cd} + t_{ij}^{db} t_{kl}^{ac} - t_{ij}^{da} t_{kl}^{bc}] \right). \quad (19)
 \end{aligned}$$

In the above equation repeated indices are summed over. We recall that the indices i, j, k and l label occupied orbital indices, whereas a, b, c and d label virtual orbital indices. ε correspond to the HF one-electron energies and the anti-symmetrized two-electron integrals are defined by $\langle ij||ab\rangle = \langle ij|ab\rangle - \langle ij|ba\rangle$, where

$$\langle ij|ab\rangle = \int_{\Omega} \int_{\Omega} d\mathbf{x}_1 d\mathbf{x}_2 \frac{\varphi_i^*(\mathbf{x}_1) \varphi_j^*(\mathbf{x}_2) \varphi_a(\mathbf{x}_1) \varphi_b(\mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (20)$$

In the above expression the spin-orbitals φ depend on the space-spin coordinate $\mathbf{x} = (\mathbf{r}, \sigma)$ and the spatial coordinates are integrated over all space. Equation (19) is solved for the amplitudes in an iterative manner by updating the amplitudes in every iteration using the right-hand side of Eq. (19). Convergence can be accelerated using standard techniques such as direct inversion of the iterative subspace (DIIS) [11]. Once the amplitudes are obtained, the CCD correlation energy can be calculated by

$$E_c^{\text{CCD}} = \sum_{ijab} \frac{1}{4} \langle ij||ab\rangle t_{ij}^{ab}. \quad (21)$$

2.6 Size consistency and extensivity

We now discuss size extensivity and the convergence of computed ground state energies to the thermodynamic limit (TDL). These concepts are highly relevant for the application to solids. In contrast to molecular systems, properties of solids have to be calculated in the thermodynamic limit to enable a direct comparison to experiment. The TDL can be approached using; for example, (i) sampling of the Brillouin zone with increasingly dense k -point meshes and in periodic boundary conditions, (ii) studying increasingly large supercells in periodic boundary conditions, or employing (iii) increasingly large clusters with open boundary conditions and/or

embedding methods. Once the thermodynamic limit is approached with respect to the number of k -points or the number of atoms in the cluster, extensive properties such as the correlation energy per atom are converged to a constant value.

An important advantage of truncated coupled cluster theories compared to, for instance truncated configuration interaction methods is their size consistency. Size consistency is a concept of particular importance in quantum chemistry, which judges if the calculated quantities have the correct asymptotic size dependence or not. For extensive quantities, like the (correlation) energy, a given size-consistent method should yield the asymptotic K^1 dependence where K is the number of wave vector sampling points in the Brillouin zone [12]. Obviously, the methods with incorrect asymptotic K^α dependence of $\alpha < 1$, like the truncated configuration-interaction methods, lead, in the thermodynamic limit, to the total energy per unit cell equal to that of the HF mean-field approximation. The size consistency of coupled cluster theories can also be understood via either the diagrammatic criteria [13] or the supermolecule criterion [4]. It was argued that approximate post-HF correlation methods cannot capture the variational and size-consistent properties simultaneously [14].

The thermodynamic limit is approached as $N \rightarrow \infty$, where N is the number of particles in the simulation (super-)cell while the density is kept constant. Once the thermodynamic limit is approached, correlation energies per atom need to be converged to a constant for periodic systems, corresponding to $\alpha = 1$. Finite size errors are defined as the difference between the TDL and the finite simulation cell results. However, the convergence of calculated properties to the thermodynamic limit is very slow, often exceeding the computational resources of even modern supercomputers due to the steep scaling of the computational complexity of most post-HF methods with respect to system size. We stress that many properties such as the binding energy of molecules on surfaces converge slower than their counterparts calculated on the level of mean-field theories such as density-functional theory (DFT). This originates from the fact that correlated post-HF methods capture long-range electronic correlation effects such as van der Waals interactions explicitly. Even though the corresponding long-ranged contribution to the electronic correlation energy is small compared to short-ranged correlation energy contributions, the accumulation of weak van der Waals interactions can become a non-negligible contribution to the property of interest. Different strategies have been developed to correct for finite size errors that are defined as the difference between the thermodynamic limit and the finite simulation cell results. These strategies often involve extrapolation methods or range-separation techniques. Local theories that employ correlation energy expressions depending on localized electron pairs, can approximate correlation energy contributions of long-distant pairs using computationally more efficient yet less accurate theories. Alternatively local theories can account for electron pairs that are disregarded based on a distance criterion by using an R^{-6} -type extrapolation [15]. Canonical implementations of periodic post-HF methods employ scaling laws for extrapolations to the thermodynamic limit that are based on an analogue rationale [16–18]. Auxiliary field quantum Monte Carlo theory employs finite-size corrections that are based on parametrized density functionals obtained from finite uniform electron gas simulation cells [19].

2.7 Caveats of coupled cluster theory

2.7.1 Basis set convergence

The many-electron wavefunctions introduced above are expanded in a basis of Slater determinants constructed from (unoccupied) Hartree-Fock orbitals. The computational complexity of canonical coupled-cluster methods scales polynomially with respect to the number of unoccupied orbitals. Therefore the ability to span the relevant parts of the Hilbert space with as few orbitals as possible is crucial for the implementation of efficient periodic correlated methods. In practice all calculated quantities suffer from a basis-set incompleteness error that is caused by the truncation of the employed unoccupied orbital manifold. The optimal choice of the unoccupied orbital manifold minimizes the incompleteness error of the calculated quantity in a controllable manner.

Some of the most widely-used basis sets for the expansion of unoccupied orbitals include plane waves and Gaussian-type orbitals (GTOs). As an illustration of their respective characteristic properties we consider two limiting cases, the uniform electron gas and an atom in a box. From the perspective of the uniform electron gas, plane waves are the natural choice of basis to expand one- and many-electron wavefunction quantities. Plane waves are eigenfunctions of the kinetic energy operator, and exhibit the same periodicity as the simulation cell. In *ab initio* calculations, these plane waves also have a number of appealing features. A single cutoff parameter that limits the kinetic energy of the included plane waves is used to systematically expand the plane wave basis to completeness which is free from basis-set superposition errors (BSSE) and linear dependencies. However, there are obvious drawbacks to plane wave expansions. They lack reference to the nature of the atomic environment, having equal basis coverage throughout the cell. This can lead to a substantial waste of computational effort when studying an atom or molecule in a box [20].

For atoms or molecules, GTOs form a very compact orbital basis. Their widespread use in the field of quantum chemistry has led to standardized tabulated basis sets of increasing size and flexibility [21, 22]. Orbitals beyond the core and valence shells are included to account for appropriate polarization of the atomic wavefunctions in bonding environments, and to provide a description of correlation effects. Basis sets are commonly arranged in hierarchies so that they can be systematically expanded to allow for consistent and extrapolatable convergence. Gaussian-type orbitals are used in a range of periodic electronic structure codes. However, the introduction of such local basis sets also leads to several shortcomings such as basis set superposition errors (BSSE) and linear dependencies of diffuse atom-centered basis functions in densely packed solids. These problems can partly be accounted for by counterpoise BSSE corrections and removing linearly dependent basis functions. The local nature of these functions is often used for reduced scaling techniques in order to approach linear scaling mean-field treatments, and can also be extended to local treatment of correlation.

For the calculation of energy differences such as the adsorption energy of a molecule on a surface it is beneficial to employ basis sets that can be truncated such that a large fraction of the incompleteness error cancels in a controllable manner. GTOs exhibit this advantageous prop-

erty, allowing for obtaining accurate estimates of interaction energies between weakly interacting fragments such as binding energies of physisorbed molecules on surfaces, despite suffering from large incompleteness errors in the respective absolute energies.

Another approach to obtain compact unoccupied orbital manifolds for the expansion of many-electron wavefunctions is provided by natural orbitals [23]. Natural orbitals are obtained by diagonalizing the unoccupied-unoccupied orbital block of the reduced density matrix and truncating the obtained natural orbital manifold according to their occupation number. This procedure yields for many applications an optimal unoccupied orbital manifold. To reduce the computational cost of this procedure it is possible to approximate the reduced density matrix at a lower-level of theory such as low-order perturbation theory only. Natural orbitals “down-fold” the unoccupied orbitals calculated using plane-wave basis sets for atoms and molecules in a box to manifolds that are similarly compact as GTOs [20].

Despite all the considerations outlined above, the convergence of the many-electron wavefunction and that of calculated expectation values such as the correlation energy is frustratingly slow with respect to the number of unoccupied orbitals [5, 24]. Therefore extrapolation techniques that remove the remaining basis set incompleteness error are needed on top of these fairly large basis set calculations. In the case of plane wave basis set calculations analytic and numerical results from perturbation theory suggest a $1/M$ decay of the basis-set incompleteness error where M is the number of plane waves used in the calculation, allowing for straightforward extrapolation to the complete basis set (CBS) limit [25]. Similar scaling laws are employed for the extrapolation of correlation energies to the complete basis set limit using GTOs [5].

The slow convergence of properties calculated using wavefunction based methods with respect to the number of orbitals originates from the difficulty to describe the many-electron wavefunction in the vicinity of the electron cusp. As the electrons coalesce, a derivative discontinuity or ‘cusp’ must arise, so that a divergence in the kinetic energy operator cancels an opposite one in the potential. The shape of the wavefunction at the cusp is exactly defined to first-order in the interelectronic distance by the Kato cusp conditions [26, 27]. The *a priori* inclusion of the cusp conditions in the wavefunction ansatz is a cornerstone of explicitly correlated or so-called F12 theories [28, 24, 29, 30]. Explicitly correlated methods augment the conventional wavefunction expansions discussed in the previous section with additional terms that account for the cusp conditions explicitly. Since electronic correlation is for the most part a short-ranged phenomenon, the proper description of the wavefunction shape at short interelectronic distances allows for capturing the largest fraction of the correlation energy in solids and molecules.

2.7.2 Computational cost

The scaling of the computational cost of canonical coupled cluster theory is dominated by the contractions present in the amplitude equations. Although some terms can be contracted efficiently by finding the optimal order of contraction over the nested summations over orbital indices, a limiting scaling remains. The scaling of CCSD and CCSDT is $\mathcal{O}(N^6)$ and $\mathcal{O}(N^8)$, where N is a measure of the system size (occupied or unoccupied orbitals) and arises from the

use of spatially delocalized canonical orbitals. Canonical orbitals are conceptually and computationally convenient. They are orthogonal and diagonalize the Fock matrix, greatly simplifying the post-HF correlation schemes. However, these orbitals are spatially delocalized and their use does not allow one to exploit the fact that electronic correlation is a short-ranged phenomenon. The use of spatially localized, instead of canonical, orbitals allows to construct coupled cluster algorithms that scale more favorably with system size, down to even $\mathcal{O}(N)$, at the price of a significant increase in complexity of the underlying equations with respect to their canonical counterparts. Some of the most notable amongst them are (based on) the local correlation method of Pulay and Saebø [31, 32], the so-called “Local Ansatz” of Stollhof and Fulde [33], the method of increments of Stoll [34–36], or the use of truncated pair natural orbitals [37, 38]. The reduced scaling algorithms mentioned above require that the occupied orbitals can be localized, i.e., a unitary transformation over the manifold of occupied orbitals can be found which optimizes the expectation value of an operator measuring the degree of localization. There exist systems which do not allow for a sufficient degree of orbital localization. In these systems, the character of electronic correlation is intrinsically more delocalized. A prominent example where this is the case corresponds to the uniform electron gas.

3 Coupled cluster theory and its relation to the RPA

The random phase approximation (RPA) to the correlation energy dates back to the 1950s. It was first introduced by Macke to predict convergent correlation energies [39] in the uniform electron gas and was also developed by Bohm and Pines [40] for the collective description of electron interactions. In the case of the uniform electron gas, the RPA captures the most important terms of the correlation energy expansion around the high-density limit ($r_s \rightarrow 0$). In the field of *ab initio* computational materials science the exact-exchange plus correlation in the random-phase approximation has attracted renewed and widespread interest in the last two decades. This is due to the fact that computationally increasingly efficient implementations have become available and that this method is capable of describing all interatomic bonding situations reasonably well: ionic, covalent, metallic, and even van der Waals bonding. The computational complexity can even be lowered to $\mathcal{O}(N^3)$ in real space formulations [41]. Thus, the complexity of an RPA calculation does not exceed that of a canonical hybrid density functional theory calculation, the prefactor is however considerably larger. The RPA correlation energy can be derived from many-electron Green function theory, or using the adiabatic-connection fluctuation-dissipation theorem (ACFDT) – or from coupled-cluster theory.

As shown in [42], it is possible to transform the RPA equations, that are usually expressed in a general eigenvalue problem, to a quadratic Riccati equation that reads

$$t_{ij}^{ab} = \frac{1}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \left(\langle ij|ab \rangle + \langle cj|kb \rangle t_{ik}^{ac} + \langle ci|ka \rangle t_{jk}^{bc} + \langle cd|kl \rangle t_{lj}^{db} t_{ik}^{ac} \right). \quad (22)$$

In the above equation we sum over repeated indices. We stress that in the above equation the ε correspond to the DFT one-electron energies. Once the amplitudes are obtained, the RPA

correlation energy can be calculated by

$$E_c^{\text{RPA}} = \sum_{ijab} \frac{1}{2} \langle ij|ab \rangle t_{ij}^{ab}. \quad (23)$$

Although the above formulation does not allow for an efficient computer implementation of the RPA, it illustrates that the RPA and CCSD are closely related.

In the rings-only approximation, the second, third and fourth lines of Eq. (19) are disregarded. Furthermore the random-phase approximation includes the direct rings only. This implies that instead of using the (double bar) anti-symmetrized integrals, only $\langle ij|ab \rangle$ integrals are employed in the RPA amplitude and energy equations, making it necessary to employ a different prefactor in the correlation energy expression to stay consistent with many-body perturbation theory. Consequently, RPA can not be viewed as a wavefunction theory although it can be obtained from the coupled cluster amplitude equations as explained above. In a diagrammatic formulation the close relationship between coupled cluster theory and the RPA becomes more obvious for both ground and excited state properties as discussed in detail in Refs. [43, 42].

4 Coupled cluster theory applied to the uniform electron gas

One of the best studied systems in electronic structure theory is the uniform electron gas (UEG). Here, we seek to illustrate important concepts of CC theory for the example of the UEG. In the UEG, the one-electron orbitals are plane waves with wave vectors \vec{k}_i, \vec{k}_j and \vec{k}_a, \vec{k}_b . This allows to write the two-electron repulsion integral as $\langle ij|ab \rangle = v_{ij}^{ab} = v(\mathbf{q}) \delta_{\mathbf{k}_i - \mathbf{k}_a, \mathbf{k}_b - \mathbf{k}_j}$. The momentum transfer vector is given by $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_a$. The Coulomb kernel is defined as $v(\mathbf{q}) = \frac{4\pi}{\Omega |\mathbf{q}|^2}$, with Ω being the volume of the simulation cell. We stress again that, due to the symmetry of the UEG Hamiltonian, single excitations are absent. With this, the CCD correlation energy is defined as

$$E_c^{\text{CCD}} = \sum_{ijab} v_{ij}^{ab} (2t_{ij}^{ab} - t_{ji}^{ab}) = \sum_{\mathbf{q}} v(\mathbf{q}) S^{\text{CCD}}(\mathbf{q}). \quad (24)$$

The amplitudes t_{ij}^{ab} are obtained by solving the CCD amplitude equations. We note, however, that this section employs a notation where the orbital indices refer to spatial orbitals, i.e., the spin-coordinates have been integrated, which results in slightly different expressions. It is important to note that in the UEG t_{ij}^{ab} inherits the momentum conservation of the two-electron operator in the Hamiltonian such that $t_{ij}(\mathbf{q}) = t_{ij}^{ab} \delta_{\mathbf{q}, \mathbf{k}_b - \mathbf{k}_j} \delta_{\mathbf{q}, \mathbf{k}_i - \mathbf{k}_a}$. The quantity $t_{ij}(\mathbf{q})$ has two indices that correspond to occupied orbital indices, representing plane wave vectors inside the Fermi sphere, whereas \mathbf{q} corresponds to a momentum transfer vector that excites electronic states into regions outside the Fermi sphere. Likewise the transition structure factor $S(\mathbf{q})$, introduced in Eq. (24), depends on \mathbf{q} , which gives access to the dependence of the correlation energy on the interelectronic interaction distance. The transition structure factor is defined as

$$S^{\text{CCD}}(\mathbf{q}) = \sum_{ijab} \frac{\delta v_{ij}^{ab}}{\delta v(\mathbf{q})} (2t_{ij}^{ab} - t_{ji}^{ab}). \quad (25)$$

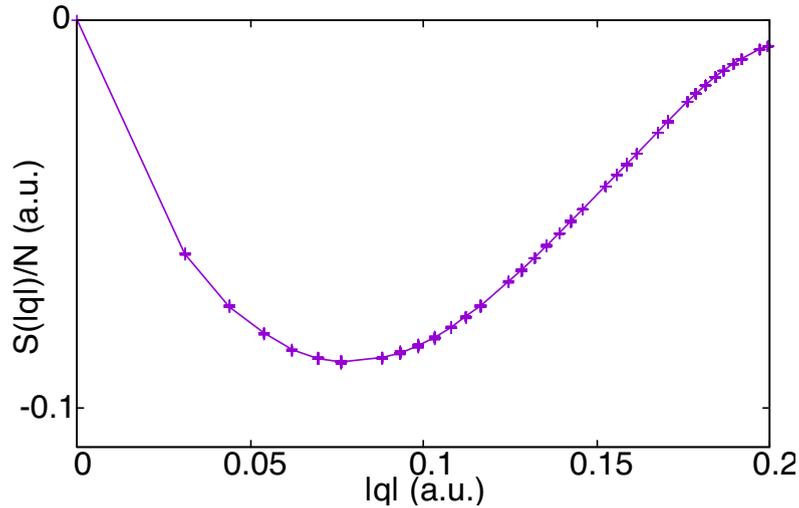


Fig. 1: Twist-averaged structure factors for CCD and 246 electrons in the uniform electron gas simulation cell at density corresponding to $r_s = 20$.

In the above equation, the functional derivative $\frac{\delta v_{ij}^{ab}}{\delta v(\mathbf{q})} = \delta_{\mathbf{q}, \mathbf{k}_b - \mathbf{k}_j} \delta_{\mathbf{q}, \mathbf{k}_i - \mathbf{k}_a}$ enables a concise notation.

We now study the behavior of the CCD correlation energy contribution for $\lim_{|\mathbf{q}| \rightarrow \infty}$ and short $\lim_{|\mathbf{q}| \rightarrow 0}$. Figure 1 depicts the computed CCD transition structure factor for 246 electrons at a density corresponding to $r_s = 20$ a.u., showing that $S(\mathbf{q})$ decays to zero in both limits. As already discussed by Bishop and Lührmann [44, 45] as well as Emrich and Zabolitzky [46], $\lim_{|\mathbf{q}| \rightarrow 0} S(\mathbf{q}) \propto |\mathbf{q}|$ and $\lim_{|\mathbf{q}| \rightarrow \infty} S(\mathbf{q}) \propto 1/|\mathbf{q}|^4$. It is important to note that the functional behavior in these limits originates from two important physical principles. The $\lim_{|\mathbf{q}| \rightarrow \infty}$ corresponds to the short-range limit in real space. It is known that as the electrons coalesce, a derivative discontinuity or ‘cusp’ must arise, so that a divergence in the kinetic energy operator cancels an opposite one in the interelectronic potential. Without proof, we stress that a linear behavior in the wavefunction as a function of the interelectronic distance results in a $1/|\mathbf{q}|^4$ behavior of $S(\mathbf{q})$. In fact the relatively slow convergence of $S(\mathbf{q})$ for large $|\mathbf{q}|$ is the cause for the slow basis set convergence of correlation energies. In other words, large numbers of unoccupied orbitals are needed in practice to capture significant contributions to the electronic correlation energy in the vicinity of the cusp. In practice one might perform several correlation energy calculations for different numbers of virtual orbitals and extrapolates the computed energies to the complete basis set (CBS) limit. The $\lim_{|\mathbf{q}| \rightarrow 0}$ corresponds to the long-range behavior of the electronic correlation energy. Unlike the short-range, the long-range behavior qualitatively differs between insulators and metals. Here, we consider the metallic uniform electron gas, which leads to a linear slope of $S(\mathbf{q})$ around $|\mathbf{q}| = 0$. This behavior can be understood by the close relationship between the RPA and CCD. Without proof, we stress that in the $\lim_{|\mathbf{q}| \rightarrow 0}$ RPA becomes identical to CCD, [46] which also explains the slow convergence of computed correlation energies to the thermodynamic limit.

5 Conclusion and summary

In this chapter we have discussed fundamental concepts of coupled cluster theory and its relation to other widely-used methods. CC theories offer a systematically improvable hierarchy of wavefunction based methods for the study of many-body problems. Due to their computational complexity, however, most coupled cluster calculations in electronic structure theory are performed at the truncation levels of CCSD and CCSD(T), where the effect of T is approximated in a perturbative manner. We have discussed for the example of the uniform electron gas, that converging the CC correlation energies to the complete basis set limit and the thermodynamic limit is difficult, which can partly be explained by the slow asymptotic convergence of the underlying electron structure factor. Another caveat of CC theories, which was not discussed in the present chapter, is that these approximate wavefunction theories are not well-suited to treat systems with strong static correlation effects, for example, bond dissociation problems. However, CCSD(T) theory is one of the most accurate *ab initio* methods currently available to compute, for example, reaction energies for a wide range of systems. Recent applications to solids have also shown that CCSD(T) can achieve a similar level of accuracy for semiconductors and insulators. More work remains to be done to expand the scope of CC theories to more complex systems and a larger number of properties which is beyond the scope of discussion of the present chapter.

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