# OVERVIEW ON PILLARS OF ELECTRON-CORRELATION THEORY

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**Abstract**
*There are four pillars of electron-correlation theory, i.e., configuration interaction (CI), coupled cluster (CC), many-body perturbation theory (MBPT), and many-body Green's function (MBGF). Starting from the Hartree-Fock (HF) approx-imation to provide the more accurate approximations, which include the effects of electron-correlation, this article summarizes the pillars.*

**Index Terms:** *configuration interaction; coupled cluster; many-body perturbation theories; many-body Green's function*

## 1. CONFIGURATION INTERACTION

The Hartree-Fock (HF) approximation is very success in many cases, however it has limitations. It predicts wrong results in the ordering of the ionization potentials of $N_2$. To cope with this, the form of the spin orbitals is introduced in the restricted closed-shell HF method. The method is constrained to have the same spatial function for spin up and spin down. However, the method cannot describe the molecule dissociation into open-shell fragments, for instance, $H_2 \rightarrow$ 2H. To tackle this, different spatial functions for spin up and spin down are used in the unrestricted open-shell HF method. However, the last method is not accurate for resulting potential energy curves of such dissociations, because the HF energy $E_0$ is an upper bound to the exact nonrelativistic energy $E_0$ of the system [1].

Conceptually, the simplest way for obtaining the correla-tion energy between $E_0$ and $E_0$ is using the configuration interaction (CI) method [2]. The idea is to diagonalize the *N*-electron Hamiltonian in a basis of Slater determinants. In other words, the exact wave function as a linear combination of *N*-electron trial functions. If the basis are complete, then the exact energies are obtained not only for the ground state, but it is also for all excited states of the system [1].

Configuration interaction provides an exact solution of the many-body problem using the linear variational method. However, CI is not computationally practical, because CI can only handle a finite set of *N*-electron trial functions. In other words, CI only provides the upper bounds to the exact energies. To obtain a suitable set of N-electron trial functions, one can construct $\left[\frac{2K}{N}\right]$ different *N*-electron Slater determinants for some arbitrary set of *2K* one-electron spin orbitals. Unfortunately, the number of *N*-electron determinants is huge, although he only use small molecules and one-electron basis sets. If he uses a finite one-electron basis sets, then

he has to cut the trial function, and only use a fraction of possible $N$-electron functions [1].

## 2. COUPLED CLUSTER

The energy of a system is part of a thermodynamic entity, so the amout of energy should be proportional to the number of particles. The configuration interaction makes prediction that, in this case of $H_2$ molecules, if $N$ becomes large then the correlation energy is proportional to $\sqrt{N}$. However, CI is not a satisfactory method because the correlation energy per atom in a crystal is zero. So, there needs to be another method that explains the correlation energy in proportion to the number of particles. In other words, the method yields comparable results for different molecular sizes. For instance, the method gives the same results for reactants and products in the molecular dissociation reaction. Another example, supermolecular energy is the number of N monomers times the energy of each monomer. In general, the method must be size consistent because the energy calculation is directly proportional to the number of particles [1].

Fortunately, there are some theories that accommodate size consistency, i.e., pair and coupled-pair theories, and the per-turbation theory too. The pair theory describes electron pair interactions that occupy orbitals of spin $X_a$ and $X_b$ in the HF method. A scheme is necessary for approximating the pair energy from each of electron pair in order to reduce an $N$-electron problem to $N(N-1)/2$ two-electron problems. The scheme called the independent electron pair approximation (IEPA) is derived by O. Sinanoglŭ [24]. However, the pair and perturbation theories are not variational, and the pair energy is smaller than the exact energy. In addition, the pair theory gives 120% energy bigger than the correlation energy [1].

Coupled pair theory describes coupling between electron pairs. Here J. C´ızek˘ used perturbation theory on the IEPA, and then he used the correlation function in the approximation to get the total energy [3]. However, the coupled pair theory is difficult because of its complexity. To solve the many-electron problem, one can use a fundamental approach. The approach is to express the quadruple coefficients as functions of the double coefficients. It means the excitation of the quadruple coefficient is simply the product of the excitation of two double coefficients. For instance, when two $H_2$ molecules are separated by infinity, or independent in short, the dimer wave function can be written as a product of the monomer wave functions. In general, two electron pairs are independent, and the quadruple coefficient of excited configuration is equal to the product of the double coefficients of excitation [1].

## 3. MANY-BODY PERTURBATION THEORY

Perturbation theory (PT) is a size consistent approach to calculate the correlation energy at each level. Unlike CI that is variational approach, Hamiltonian of a system in the PT is divided into two parts: a zeroth-order part $H_0$, and a perturbation part V. To calculate the exact energy, one must sum an infinite series of increasing complexity contributions.

The contributions are the $H_0$ eigenvalues, and the perturbation matrix elements of the H0 eigenfunctions. The $n^{th}$-order perturbation energy is a products of n matrix elements after grouping the same terms. The sum of the $n^{th}$-order energies converges quickly if V is small, and $H_0$ is wisely chosen [1].

In time-independent framework, Rayleigh-Schrodinger¨ per-turbation theory (RSPT) is widely used [25]. Using the Hartree-Fock Hamiltonian as zeroth-order Hamiltonian in RSPT, C. Møller and M. S. Plesset implemented this $H_0$ to the *N*-electron systems. This method is called Møller-Plesset perturbation theory [4]. But in general, the method is called many-body perturbation theory (MBPT), because it is treated in infinite systems. Therefore, a novel theory is needed for treating large systems in the scheme of size consistent [1].

K. A. Brueckner stated MBPT in each order is size con-sistent [5]. He found that MBPT energies are proportional to $N^2$ particles in large systems. For the first order, he showed that the infinite sum of contributions of increasing complexity can be cancelled, so it is true that MBPT in each order is size consistent. Unfortunately, he was not able to prove this for all the orders [1].

In quantum electrodynamics, R. P. Feynman worked out in a perturbation series at any order in order to get co-variant formulations [6]. Based on his work, J. Goldstone showed a clever way for representing algebraic expressions using diagrams [7]. The expressions usually occur in the Rayleigh-Schrodinger¨ perturbation expansion of the many-particle system energy. Unlike Brueckner, the infinite sum of contributions of increasing complexity are represented by diagrams formed of disconnected parts called unlinked. The unlinked contributions are actually can be cancelled in every order. This linked-cluster theorem states that linked diagrams represent the perturbation expansion of a many-body system energy. So, the Møller-Plesset perturbation theory is truly size consistent too [1].

Soon after Goldstone showed the pictorial techniques, H. P. Kelly implemented it to atoms [8]. He summed the certain diagram values to infinite order by incorporate certain contri-butions of increasing complexity in perturbation theory, rather than summing the perturbation energies up to second-order, and ignoring the higher order energies [1].

## 4. MANY-BODY GREEN'S FUNCTION

In many-body theory, method of Green's function is power-ful for treating large systems. At the beginning, the function is used for solving inhomogeneous differential equations. How-ever, the function can be used to calculate electron affinities (EA) and ionization potentials (IP) for one-particle of an N-electron system. So, the method is called the many-body Green's function (MBGF). Using Koopmans' theorem within the Hartree-Fock approximation, the method improves EA and IP in a systematic way [9]. In order to describe electron capture and ionization, information about the ground state energy and one-particle density matrix can be found in the method. However, the method is very different with other methods, because it can be presented using second quantization, without using diagrams like in the perturbation theory [1].

The time-dependent aspects of Green's function theory were developed by N. N. Bogolyubov and S. V. Tyablikov[10]. They resolved problems in statistical physics using two-dimensional retarded and advanced Green's functions. The ap-proximation was implemented in the Kall¨en´-Lehmann spectral representation [11] [12], so one can comprehend the physically appealing interpretation of these functions as propagators [1].

To describe the excitation spectrum of an N-electron system, V. M. Galitskii and A. B. Migdal developed two-particle MBGF [13]. They relate the two-particle Green's function with the kinetic equation, so one can calculate the total ground-

state energy. In addition, they showed the poles of a single particle propagation function determine the energy of quasiparticles.

The equation of motion of the Green function was developed by F. J. Dyson [14]. He developed a simple procedure for the Schwinger theory in radiation [15]. Further, this brought Dyson to derive scattering matrix element relations in quantum electrodynamics in a perturbative approach [16], while Schwinger used variational principle in a non-perturbative approach [17].

It is known that the potential felt by an electron due to the surrounding medium's interactions with it is called self-energy. To derive the self-energy, L. Hedin developed a set of equations which are self-consistent [18]. The equations are the self-energy , the screened coulomb interaction W, the polarizability P, and the vertex function . The equations are impossible to solve exactly for real systems, so he made a method called GW approximation. Here, is a screened exchange and correlation potential, while W is non-local in space and time.

An interesting physical quantity in Hedin's equation is the polarizability, or density response function. If a system of electrons is perturbed by an external field, then its density will change and can be calculated by the response function of the system. R. Kubo developed a mathematical formula to express the linear response of the physical quantity due to the perturbation [19]. Eventually, before the creation of the formula, D. Bohm and D. Pines has developed a method called random phase approximation to the linear response function using the equation of motion [20] [21] [22], while M. Gell-Mann and K. A. Brueckner used the many-body diagrammatic technique [23].

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