Single-Particle Green Function Approach and Correlated Atomic or Molecular Orbitals

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Abstract

In this paper, we propose a generic and systematic approach for study of the electronic structure for atoms or molecules. In particular, we address the issue of single particle states, or orbitals, which should be one of the most important aspects of a quantum many-body theory. We argue that the single-particle Green function provides a most general scheme for generating these single particle states or orbitals. We call them the correlated atomic or molecular orbitals to make a distinction from those determined from Hartree−Fock equation. We present the calculation of the single particle properties (i.e., the electron affinities (EA’s) and ionization potentials (IP’s)) for the H₂O molecule using the correlated molecular orbitals in the context of quantum chemistry with a second-order self energy. We also calculate the total ground state energy with a single Slater wavefunction determined only from the hole states. Comparisons are made with available experimental data as well as with those from the Hartree−Fock or density functional theory (DFT) calculations. We conclude that the correlated atomic or molecular orbital approach provides a strictest and most powerful method for studying the single-particle properties of atoms or molecules. It also gives a better total energy than do the Hartree−Fock and DFT even at the single Slater determinant level.
It promises that a correlation theory based on the correlated atomic or molecular orbitals will become an approach which possesses the advantages and also overcomes their shortcomings of current quantum chemistry methods based on either the conventional quantum many-body theory or the DFT.

1 Introduction

The single particle approximation, or the concept of atomic or molecular orbitals in the context of quantum chemistry, is a natural and almost a necessary scenario for solving an interacting many-electron system for atoms, molecules, or solids [1]. This is a reflection of not only a physical existence but also possibly a mathematical reality. The usual equation which is being used to determine the orbitals is the Hartree–Fock equation [2, 3]. The rest of endeavor to remedy the approximation resulting from a replacement of the whole many-body wavefunction by a single determinant used in the HF scheme is called the correlation issue. This is a most difficult problem and constitutes the major activity of researches for the quantum chemistry community in the last 50 years [4]. According to the energy scale principle we described in paper [5], the Hartree–Fock scheme should be a good approximation when the single determinant wavefunction dominates and there is no any significant mixing with the nearby configurations. This is typically the case when we compute the energetics for molecules with a stable geometric structure. The subsequent perturbation correction for the correlation such as MPPT is also proved to be powerful [6]. However, there are the situations when the configuration mixing is a prominent or dominant phenomenon, and
the description with more than one single configuration seems necessary. This includes the calculation of transition states or excited states, and for open-shell molecules, etc. The computation based on the Hartree – Fock equation has shown to be insufficient, and the corresponding perturbation correction has proved not to be convergent [7, 8, 9]. The MCSCF approaches have been introduced to investigate this type of nondynamic or static correlation issue, and they have become one of the most popular approaches for the study of molecular electron correlation [5, 10, 11, 12]. However, the size of molecular systems that this type of approaches can address are still limited because of the difficulties in selecting the appropriate configuration states and in achieving the convergence to the correct state of the interest [12].

Another important and significant advance in the fields of electron correlation is the development of density function theory (DFT) [13, 14]. Instead of working with a multi-configurational framework, it intents to incorporate the exchange-correlation effect into a single-particle potential formalism. It has already shown its very usefulness in the study of the electronic structure for large systems with utilization of relatively smaller computational efforts. Nevertheless, there exist some serious drawbacks for the method when seen either from theoretical consideration or from the practical performance in calculation. One shortcoming is that the theory can only study the ground state problem, and cannot treat the same eigenstate problem for excited states within one theoretical framework. Another serious problem is that the actual form for the exchange-correlation is unknown, or the theory itself gives no clue for how to approach it. Moreover, the approach fails to or can not do the accurate computation for the points or situations when the configuration
mixing is important \[15, 16, 17\]. Indeed, it should be a very difficult thing, intending to replace the intrinsic *many*-body effects such as static correlation or configuration mixing with a *single*-particle formalism.

Recently, we have demonstrated that a general quantum many-body perturbation theory can not only be used for understanding the various electronic phenomena including the nature of chemical bonds but also serve as a unified theme for constructing general electronic structure theories and calculation schemes. This also includes the study of important issues of electron correlation \[5\]. This pinpoints the direction and paves the way for the future investigation. In this paper, we add another important ingredient to the field of electron correlation or electronic structure theory in general. We emphasize our investigation on the issue of single particle approximation, or the atomic or molecular orbitals for the quantum chemistry calculation. From the perturbation point of view, this corresponds to defining a reference Hamiltonian \[5, 18\]. We will show that there exists a strict theoretical formalism, called the single-particle *Green* function, which provides a most general scheme for generating or determining these single-particle states up to present time. The theory of single-particle *Green* function has been developed for a long time and used in many different ways but its full physical meaning or context is not totally understood or appreciated. This paper aims at a beginning for a systematic investigation of electron correlation based on the single-particle *Green* function formalism and within the quantum many-body perturbation theory \[5\]. In the next Section, we present its definitions and equations in both time and energy domains. In particular, we give an energy eigenequation that solves the single-particle states. We analyze its
intrinsic structure and compare it with other methods. In Section 3, we calculate both the single-particle properties and the total energies for the \( H_2O \) molecule using the Hartree – Fock, DFT, and correlated molecular orbital approaches. In the final Section, we analyze and discuss our results for the calculations and also do the comparison with each other including the corresponding experimental data. We also propose a generic electronic structure theory and outline the future research.

### 2 Theory

Two time \((t, t')\) and single-particle (or hole) Green function is defined as \(^{[19, 20]}\)

\[
G(\vec{x}t, \vec{x}'t') = -i \langle \Psi_0 | T \{ \hat{\psi}(\vec{x}, t) \hat{\psi}^+(\vec{x}', t') \} | \Psi_0 \rangle,
\]

(1)

where \( T \) is Wick time-ordering operator, and \( \hat{\psi}(\vec{x}, t) \) and \( \hat{\psi}^+(\vec{x}', t') \) are the field operators in the Heisenberg picture associated with the coordinates \( \vec{x} \), which includes both spatial \( \vec{r} \) and spin \( \chi \) degrees of freedom. The \( |\Psi_0\rangle \) is the exact ground state of an \( N \)-electron system being studied. Its Hamiltonian in the field operator representation can be written as

\[
H = \int \hat{\psi}^+(\vec{x})h(\vec{x})\hat{\psi}(\vec{x})d\vec{x} + \frac{1}{2} \int \hat{\psi}^+(\vec{x})\hat{\psi}^+(\vec{x}')v(\vec{r}, \vec{r}')\hat{\psi}(\vec{x}')\hat{\psi}(\vec{x})d\vec{x}d\vec{x}',
\]

(2)

where the one-body operator \( h(\vec{x}) \) is the sum of the electronic kinetic energy operator and its interaction with the nucleus

\[
h(\vec{x}) = -\frac{\hbar^2}{2m} \nabla^2 - \sum_p Z_p v(\vec{x}, \vec{R}_p),
\]

(3)
and the two-body operator $v(\vec{r}, \vec{r}')$ is the Coulomb potential

$$v(\vec{r}, \vec{r}') = \frac{1}{|\vec{r} - \vec{r}'|}. \quad (4)$$

In the energy domain, the Green function takes the form

$$G(\vec{x}, \vec{x}'; \omega) = \sum_n \frac{\phi_n(\vec{x})\phi_n^*(\vec{x}')}{\omega - \epsilon_n}, \quad (5)$$

where

$$\phi_n(\vec{x}) = \langle \Psi_0|\hat{\psi}(\vec{x})|\Psi_n(N + 1) \rangle, \quad \epsilon_n = E_n(N + 1) - E_0 \quad \text{for} \quad \epsilon_n \geq \mu, \quad (6)$$

or

$$\phi_n(\vec{x}) = \langle \Psi_n(N-1)|\hat{\psi}(\vec{x})|\Psi_0 \rangle, \quad \epsilon_n = E_0 - E_n(N-1) \quad \text{for} \quad \epsilon_n < \mu. \quad (7)$$

The wavefunctions $|\Psi_n(N \pm 1)\rangle$ and energy levels $E_n(N \pm 1)$ are for the $N \pm 1$ electronic systems. The functions \{\phi_n(\vec{x})\} are the ones of single-particle coordinates, and are called the particle states for those defined by Eq. (6) ($\epsilon_n \geq \mu$), and the hole states for those defined by Eq. (7) ($\epsilon_n < \mu$), where $\mu$ is the chemical potential. The corresponding energy $\epsilon_n$ are the electron affinity or the electron ionization potential, respectively. A very important feature of these single-particle states \{\phi_n(\vec{x})\} is that they form a complete set as shown below,

$$\sum_n \phi_n(\vec{x})\phi_n^*(\vec{x}') = \delta(\vec{x} - \vec{x}'), \quad (8)$$

where $n$ is for all the hole or particle states. The Eq. (5) is called the Lehmann representation.

Define the average classical Coulomb potential by

$$V(\vec{x}) = \int v(\vec{x}, \vec{x}')\rho(\vec{x}')d\vec{x}', \quad (9)$$
where
\[ \rho(\vec{x}) = \langle \Psi_0 | \hat{\psi}^+(\vec{x}) \hat{\psi}(\vec{x}) | \Psi_0 \rangle, \] (10)
is the one-electron probability density, then the Green function in the energy domain satisfies the following equation,
\[ \{ \epsilon - h(\vec{x}) - V(\vec{x}) \} G(\vec{x}, \vec{x}'; \epsilon) - \int \Sigma(\vec{x}, \vec{x}'; \epsilon) G(\vec{x}', \vec{x}; \epsilon) d\vec{x}' = \delta(\vec{x} - \vec{x}'), \] (11)
where the operator \( \Sigma(\vec{x}, \vec{x}'; \epsilon) \) is called the self-energy operator which is non-local and energy dependent. From this equation for the single-particle Green function and its Lehmann representation (5), we can get an equation that the single-particle states \( \{ \phi_n(\vec{x}) \} \) satisfy
\[ \{ h(\vec{x}) + V(\vec{x}) \} \phi_n(\vec{x}) + \int \Sigma(\vec{x}, \vec{x}'; \epsilon_n) \phi_n(\vec{x}') d\vec{x}' = \epsilon_n \phi_n(\vec{x}), \] (12)
or
\[ \{ h + V + \Sigma(\epsilon_n) \} |\phi_n\rangle = \epsilon_n |\phi_n\rangle \] (13)
in a more general Dirac notation. It is called the Dyson equation or the energy eigenequation for the quasi-particles in the current literature \[20, 21, 22, 23\]. When we do the comparison with the Hartree–Fock equation or the Kohn–Sham equation \[2, 3, 13\], it seems that the self-energy operator \( \Sigma \) is related to the exchange and correlation effects of an interacting many-electron system beyond that of the classical Coulomb interaction. Unlike the Kohn–Sham equation, however, where the explicit analytical potential for the exchange-correlation potential is unknown, the self-energy operator has intrinsic structure, and, for example, can be expanded as a perturbation series as follows,
\[ \Sigma = \Sigma^{(0)} + \Sigma^{(1)} + ... + \Sigma^{(n)} + .... \] (14)
They have explicit physical interpretations and therefore can be approached in a systematic way \[20, 21, 22, 23, 24, 25, 26, 27, 28, 29\]. Another important feature of Eq. (12) is that the single-particle states are defined for both hole state (Eq. (6)) and particle states (Eq. (7)), and therefore there exists the concept of a fundamental excitation in the present formalism. In other words, we can form the configurations based on these single particle states. Furthermore, since they constitute a complete set of single-particle states, as shown in Eq.(8), any \(N\)-electron wavefunctions can be expanded as a linear combination of these configurations. For these reasons, we can regard the equation (12) as a most general eigenequation for creating the single-particle states or the atomic or molecular orbitals at present time. It is the corresponding one-particle description of an \(N\) interacting many-body system \[30\]. For clearness and easiness to be understood, we call the single-particle states determined by Eq. (12) as the correlated atomic or molecular orbitals in order to make a distinction from those determined from the Hartree – Fock equation. Obviously, they will catch the full Hamiltonian (2) more than do the Hartree – Fock orbitals.

The successfulness for obtaining the most appropriate correlated atomic or molecular orbitals \(\{\phi_n(\vec{x})\}\) will depend on how well we can obtain the correct self-energy operator \(\Sigma\). This will in turn depend on what kind of wavefunctions or what level of theories we select as the reference or the initial wavefunction for our construction of \(\Sigma\) since the Eq. (12) is an iterative equation for determination of \(\{\epsilon_n\}\) and \(\{\phi_n(\vec{x})\}\). Obviously, there will be different choices for different species or for different molecular geometries being studied as have already been demonstrated in many existing quantum chem-
istry calculations. Several types of perturbation schemes for the self-energy operator have already been developed either from solid state physics community or by quantum chemists \[20, 21, 22, 23, 24, 25, 26, 27, 28, 29\]. These include the functional derivative method \[20, 21, 22, 23\], the superoperator formalism \[24, 25, 26, 27\], the diagrammatic expansion method \[28\], and the equation of motion approach \[29\].

3 Calculation and Results

In this section, we present the computation of the single-particle properties and total energies for \(H_2O\) molecule. We employ the Hartree—Fock method, \(DFT\), and correlated molecular orbital approach we describe above for the calculation and do the corresponding comparison.

The geometric parameters for the water molecule are taken from experimental observation which are \(R(O–H) = 0.957\,\text{Å}\) and \(\angle\text{HOH} = 104.5(\text{deg})\) \[31\]. For the Hartree—Fock calculation, we use the \(cc-pVTZ\) basis set \[32\]. The calculated energies for the first ten molecular orbitals are listed in the second column of Table 1. The computed total energy is shown in the Table 2. For the \(DFT\) calculation, we use the same set of basis functions. The exchange-correlation functional is approximated with the \(B3LYP\) scheme \[33, 34\]. The result for the first ten \(Kohn—Sham\) orbital energies is listed in the third column of the Table 1. The total energy is shown in the Table 2. For the computation based on the correlated molecular orbitals, we take the second-
order approximation for the self-energy operator,

\[ \Sigma_{ij}(E) = \Sigma_{ij}^{(1)}(E) + \Sigma_{ij}^{(2)}(E). \]  

(15)

The detailed forms for the self-energy operator with different orders are dependent upon the reference states chosen [21, 35]. For the closed-shell molecules, if we pick the Hartree–Fock orbitals as the reference states, the first-order self-energy vanishes, and the second-order self-energy is given by

\[ \Sigma_{ij}^{(2)}(E) = \sum_{ars}^{N/2} \frac{\langle rs|ia \rangle (2\langle ja|rs \rangle - \langle aj|rs \rangle)}{E + \epsilon_a - \epsilon_r - \epsilon_s} + \sum_{abr}^{N/2} \frac{\langle ab|ir \rangle (2\langle jr|ab \rangle - \langle rj|ab \rangle)}{E + \epsilon_r - \epsilon_a - \epsilon_b}, \]  

(16)

where \( a, b, \ldots \) are the spatial hole states, and \( r, s, \ldots \) are the spatial particle states. If we choose the Kohn–Sham orbitals as the reference states, however, the first-order self-energy takes the form

\[ \Sigma_{ij}^{(1)}(E) = -\langle i|V_{xc}|j \rangle - \sum_{a} \langle ia|a j \rangle, \]  

(17)

and the second-order self-energy remains the same as that for the case of the Hartree–Fock orbitals. We solve the eigenequation (12) for the quasi-particles with the \( cc - pVTZ \) basis set. When the Hartree–Fock orbitals are used as the reference state, the calculated quasienegies for the first ten correlated molecular orbitals are shown in the third column of the Table 1. The resulting total energy with the single determinant using the first five doubly-occupied hole states is also listed in the table 2. When the DFT determinant is employed as the reference state, the corresponding results are listed in the forth column of table 1 or table 2. All the computations are done with the Hondo – v99.6 suite [36].
4 Discussion and Conclusions

In this paper, we present a novel approach for the study of electronic structure of atoms and molecules related to the single-particle Green function theory. We argue that the single-particle Green function provides a most general theoretical framework for generating the atomic or molecular orbitals for the atoms and molecules. Based on this statement, we have calculated both the energies of these single-particle states and total energies for the $H_2O$ molecule [37, 38, 39]. For the total energy, a single-determinant wavefunction composed of hole states only is used for the computation. At the same time, the calculations are also performed with the Hartree – Fock and DFT methods.

When compared with the experimental ionization energy or electron affinity for $H_2O$ molecule [40], we see that the correlated molecular orbitals with the Hartree – Fock orbitals as the reference state gives the better results than the ones from the Hartree – Fock or DFT methods. The total energies obtained with three different methods are also compared to the one obtained from the experimental observation [31, 37, 38, 39]. The correlated molecular orbital approach results in the best value. Of course, the calculation can be further improved by choosing the DFT as a reference wavefunction. We have the similar conclusion.

Since the work of Heitler and London in the calculation of the electronic structure for $H_2$ molecule, which is the indication of the beginning of the field of quantum chemistry, it has the history of development for more than eighty years. However, there is a fundamental issue, i.e., the quality of atomic or molecular orbitals, which has been neglected for a long time. This paper
addresses this "quality" issue for single-particle states or orbitals in many-body theory. From the perturbation theory point of view, this corresponds to a definition of the reference Hamiltonian, which is crucial in the minimization of dynamic correlation energy or convergence of perturbation series. It is also critical in providing the best single particle properties. Both of the calculated single-particle properties and total energies have explicit physical interpretation and are subject to the test from experimental observations [41].

From above analysis, it is obvious that when the concept of correlated atom or molecular orbital is incorporated into the quantum many-body perturbation or coupled cluster theory, it will provide a most powerful quantum many-body approach for the study of electronic structure of atoms or molecules. On one hand, its single-particle properties have obvious physical meanings which is in contrast to the case for the DFT. Furthermore, it can go beyond the single-determinant level and form configurations. Therefore, it can study the issues when configuration mixing is important. On the other hand, when doing the comparison to the traditional quantum many-body theory based on the Hartree – Fock or MCSCF orbitals, the correlated orbital method not only has provided a better description of single-particle properties, but also gives us the better convergence at the configuration level and therefore provides a more powerful computational scheme. For these reasons, we could claim that the correlated atomic or molecular approach will be a most general ab initio correlation method for electron structure calculations. It possesses the advantages and also overcomes their shortcomings of current DFT and conventional correlation approaches based on the atomic or molecular orbitals determined from the Hartree – Fock or MCSCF.
Of course, it has been a very difficult task for a long time to get the approximate self-energy operator to the higher orders. However, the intrinsic structure such as its perturbation series expansion has offered us a possibility instead of an outside model for the approximation. Furthermore, the further study of this underlying intrinsic structure will tell us more universal things which might be true even for a many-body theory or system in general. Henceforth, the continuing investigation of the higher order self-energy operators and their relations will be a rewarding research [42].

An interesting point needed to be mentioned is that the self-energy operator in Eq. (12) does not have to be Hermitian which corresponds to the situation when $\psi_n(\vec{x})$ is a real orbital. Here the imaginary case for the operator is related to the electron dynamics which is left as a future investigation [20].

Finally, if we fully explore the usefulness of the pseudopotential theory, combined $QM/MM$ approach, or linear scaling algorithms and so forth, the correlation theory based on the correlated atomic or molecular orbitals will provide to us a most robust approach for the study of electronic structure even for large systems [5].

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Table Caption

Table 1. The single-particle properties or orbital energies (in a.u.) of $H_2O$ molecule from the calculations based on the Hartree – Fock, DFT and correlated molecular orbital approaches as well as from the experimental measurement.

Table 2. The total energies (in a.u.) of $H_2O$ molecule from the calculations based on the Hartree – Fock, DFT and correlated molecular orbital approaches as well as from the experimental measurement or CI calculation.