First-principles Green’s Function Study on Electronic Excited States of Molecules

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Abstract. A systematic theoretical study of the spectra of the electronic excited states of molecules is carried out by means of the first-principles Green’s function methods based on the many-body perturbation theory. A merit of these methods is that all excitation spectra can be obtained accurately all at once together with the information on the corresponding quasiparticle wave functions. One-particle excitation spectra are obtained by the \( GW \) approximation, while the two-particle excitation spectra are obtained by starting from the \( GW \) approximation and solving the Bethe-Salpeter equation for the \( T \)-matrix. Here we present some of our recent results of CO and \( C_2H_2 \) molecules by using this state-of-the-art calculation. The results are in excellent agreement with experiments.

1. Introduction
The electronic excited states play a very important role in wide variety of electronic, optical and chemical functions of clusters and crystals. If we consider clusters, the energy gap is strongly dependent on the species and size of the cluster. A designed control of the energy gap using clusters would become a useful technique, for example, in solar energy transformations.

A systematic theoretical study of the spectra of the electronic excited states is possible by means of the first-principles Green’s function methods based on the many-body perturbation theory among various first-principles methods beyond the density functional theory \[1\]. A merit of these methods is that all excitation spectra can be obtained all at once together with the corresponding quasiparticle wave functions.

The one-particle excitation spectra that express the energies of adding or subtracting one electron to a neutral system can be accurately calculated by means of the \( GW \) approximation (GWA) \[2\]. So far, we have developed an all-electron \( GW \) code by using the all-electron mixed basis approach, and applied it to several clusters \[3, 4\] and crystals \[5\]. Our all-electron mixed-basis approach is a natural extension of the pseudopotential mixed-basis approach \[6\]. In this approach, a wave function is expanded by both plane waves and atomic orbitals in order to deal with the core electrons accurately. To generate atomic orbitals, we use the Herman–Skillman code \[7\] modified with a radial logarithmic mesh. This approach has been successfully applied to crystals, molecules, and clusters\[8, 9, 10\]. On the other hand, the spectra of optical absorptions \[11, 12, 13\] or two-particle excitations can be obtained by starting from the GWA and solving the Bethe–Salpeter equation (BSE) for the two-particle Green’s function or the \( T \)-matrix. Using also the all-electron mixed basis approach in this method, we have calculated the optical absorption
spectra of atoms and alkali-metal clusters [14] and Cu doped LiCl and NaCl crystals [15], and the two-particle excitation spectra of alkali-metal clusters [16, 17].

In what follows, we describe in detail the first-principles T-matrix theory for the calculation of the two-particle excitation spectra as well as the all-electron GWA for the calculation of the one-particle excitation spectra. Then we systematically apply these methods to the state-of-the-art calculation of the ionization potential (IP) and the double ionization energies (DIEs) of CO and C$_2$H$_2$ molecules. We show our results in detail and compare them with available experimental data.

**Figure 1.** Schematic representation of the self-energy in the GWA. The wavy line represents the dynamically screened Coulomb interaction, $W$, within the RPA. The solid line with an arrow represents the one-particle Green’s function, $G$.

### 2. Methodology

#### 2.1. GWA

Our formulation of the all-electron GWA is similar to that of the pseudopotential GWA developed first by Hybertsen and Louie [2]. For simplicity, we describe here the formulation for cluster calculations only, although its generalization to crystal calculations is straightforward. We start from the calculation at the LDA level, and determine the all-electron states $|\nu\rangle$ and the energy eigenvalues $\varepsilon^{\text{LDA}}_{\nu}$. Then in the GWA, the quasiparticle energies $E^{\text{GWA}}_{\nu}$ can be obtained by solving the Dyson equation,

$$
(T + V_{\text{nuc}} + V_{\text{H}})|\nu\rangle + \int dr' \Sigma(r, r'; E^{\text{GWA}}_{\nu})|\nu\rangle = E^{\text{GWA}}_{\nu}|\nu\rangle,
$$

perturbatively to the first order. Here, $T$, $V_{\text{nuc}}$, $V_{\text{H}}$, and $\Sigma$ are the kinetic energy operator, the nucleus Coulomb potential, Hartree potential and the self-energy operator. In the GWA, the self-energy operator is approximated in a form

$$
\Sigma(r, r'; \omega) = \frac{i}{2\pi} \int_{-\infty}^{\infty} d\omega' G(r, r'; \omega + \omega') W(r, r'; \omega') e^{i\eta\omega'},
$$

where $G$ is the one-particle Green’s function in the LDA and $W$ is the dynamically screened Coulomb interaction within the random phase approximation (RPA) [18, 19], and $\eta$ is a positive infinitesimal number. This self-energy is represented by a Feynman diagram as in Fig. 1. The term $GW$ comes from $G$ for the one-particle Green’s function and $W$ for the dynamically screened Coulomb interaction.

The one-particle Green’s function $G$ is given by

$$
G(r, r'; \omega) = \sum_{\nu} \frac{\psi_{\nu}(r)\psi_{\nu}^{\ast}(r')}{\omega - \varepsilon^{\text{LDA}}_{\nu} - i\delta_{\nu}},
$$

where $\delta_{\nu} = 0^+$ for occupied $|\nu\rangle$ and $\delta_{\nu} = 0^-$ for empty $|\nu\rangle$. The dynamically screened interaction in Fourier space is related to the dielectric matrix by

$$
W_{GG'}(\omega) = [\varepsilon^{-1}]_{GG'}(\omega)v(G'),
$$
where $v(G) = 4\pi/V G^2$ is the Coulomb potential in Fourier space ($V$ is the volume of the unit cell), $\varepsilon_{GG'}(\omega)$ is the dielectric matrix defined by

$$\varepsilon_{GG'}(\omega) = \delta_{GG'} - v(G)P_{GG'}(\omega),$$  \hspace{1cm} (5)$$

($P_{GG'}(\omega)$ is the polarizability function in the RPA), and $G$ and $G'$ are the reciprocal lattice vectors.

The self-energy operator $\Sigma$ can be divided into two parts: one is the Fock exchange part $\Sigma_x(r, r')$ and the other is the correlation part $\Sigma_c(r, r'; E)$. The expectation values of the Fock exchange part are given by

$$\Sigma_{x, \nu} = \langle \nu | \Sigma_x | \nu \rangle = \sum_\mu \sum_G \langle \nu | e^{iG \cdot r} | \mu \rangle \langle \mu | e^{-iG \cdot r'} | \nu \rangle v(G),$$  \hspace{1cm} (6)$$

while the correlation part of the self-energy is evaluated by means of the generalized plasmon-pole (GPP) model [2].

Finally the quasiparticle energies such as the ionization potential (IP) and the electron affinity (EA) are obtained within the first-order perturbation theory as

$$E_{\nu}^{\text{GWA}} \approx \varepsilon_{\nu}^{\text{LDA}} + \frac{1}{1 - (\partial \Sigma(\omega) / \partial \omega)_{\varepsilon_{\nu}^{\text{LDA}}}} \langle \nu | \Sigma(\varepsilon_{\nu}^{\text{LDA}} - \mu_{xc}^{\text{LDA}}) | \nu \rangle,$$  \hspace{1cm} (7)$$

where $\mu_{xc}^{\text{LDA}}$ is the exchange-correlation potential given in the LDA. The denominator in the second term is necessary to use the LDA eigenvalues instead of the GWA quasiparticle energies as the argument of the self-energy operator in the numerator.

![Figure 2](image.png)

**Figure 2.** Schematic representation of the BSE for $T$-matrix (square). The dotted line represents the bare Coulomb interaction $U$. The solid lines with arrows represent the one-particle Green’s function $G$.

### 2.2. T-matrix

In order to evaluate the DIEs, we introduce the two-particle Green’s function and $T$-matrix, which describes the multiple scattering between two particles [20] and the Coulomb hole [21].

The $T$-matrix satisfies the following BSE [22]:

$$T(1, 2|3, 4) = U(1, 2)\delta(t_1 - t_3)\delta(t_2 - t_4) + iU(1, 2) \int d1'd2' K(1, 2|1', 2')T(1', 2'|3, 4),$$  \hspace{1cm} (8)$$

where $U(r_1, r_2)\delta(t_1 - t_2)$ denotes the bare Coulomb interaction (we use the static approximation and replace the true irreducible interaction with the bare Coulomb interaction), and $K$ represents the disconnected part of the two-particle Green’s function defined by $K(1, 2|1', 2') = iG(1', 1)G(2', 2)$. The Fourier transformation of this function is given by

$$K(r_1 r_2 | r_1' r_2'; \omega) = -\sum_{\nu\mu}^{\text{occ}} \frac{\psi_\nu^*(r_1) \psi_\nu^*(r_1') \psi_\mu^*(r_2) \psi_\mu^*(r_2')}{\omega - E_{\nu}^{\text{GWA}} - E_{\mu}^{\text{GWA}} - i\eta} + \sum_{\nu\mu}^{\text{emp}} \frac{\psi_\nu^*(r_1) \psi_\nu^*(r_1') \psi_\mu^*(r_2) \psi_\mu^*(r_2')}{\omega - E_{\nu}^{\text{GWA}} - E_{\mu}^{\text{GWA}} + i\eta},$$  \hspace{1cm} (9)$$
where $E_{\nu}^{\text{GWA}}$ is the GWA quasiparticle energy and $\eta$ is a positive infinitesimal number. The diagrammatic representation of the BSE (8) is given in Fig. 2. It represents the summation of the ladder diagrams up to the infinite order.

We use the LDA wave functions for $\psi_{\nu}(r)$. The BSE (8) can be rewritten by introducing matrix elements sandwiched by the LDA wave functions as follows:

$$
\sum_{\nu\mu} \left( \frac{\delta_{\alpha\nu}\delta_{\beta\mu}}{f_{\nu\mu}K_{\nu\mu}} - U_{\alpha\beta\nu\mu} f_{\nu\mu} \right) K_{\nu\mu} T_{\nu\mu\gamma\delta} = U_{\alpha\beta\gamma\delta},
$$

(10)

$$
f_{\nu\mu} = -\delta_{\nu}^{\text{occ}} \delta_{\mu}^{\text{occ}} + \delta_{\nu}^{\text{emp}} \delta_{\mu}^{\text{emp}},
$$

(11)

where $\delta_{\nu}^{\text{occ}}$ ($\delta_{\nu}^{\text{emp}}$) is equal to unity if $\nu$ is occupied (empty) and zero otherwise. We solve the eigenvalue problem as follows:

$$
\sum_{\nu\mu} H_{\alpha\beta\nu\mu} A_{\nu\mu}(\Omega) = \Omega A_{\alpha\beta}(\Omega),
$$

(12)

where $H_{\alpha\beta\nu\mu}$ are the two-particle Hamiltonian matrix elements that are independent of $\omega$:

$$
H_{\alpha\beta\nu\mu} = \left( \frac{1}{f_{\nu\mu}K_{\nu\mu}} - \omega \right) \delta_{\alpha\nu}\delta_{\beta\mu} - U_{\alpha\beta\nu\mu} f_{\nu\mu}.
$$

(13)

It is possible to determine the two-particle wave functions of the two-particle excited states from the knowledge of the eigenstates $A_{\nu\mu}(\Omega)$ via the equation

$$
\psi_{\Omega}(r, r') = \sum_{\nu\mu} A_{\nu\mu} \psi_{\nu}(r) \psi_{\mu}(r').
$$

(14)

From the eigenvalues $\Omega$ and eigenfunctions $A_{\nu\mu}(\Omega)$, one can construct the $T$-matrix associated with both the hole-hole and electron-electron Green’s functions. The eigenvalues $\Omega$ are equal to the poles of the $T$-matrix, and therefore directly give the DIE spectra. The present $T$-matrix theory enables us to treat accurately the short-range part of the Coulomb interaction [20, 21]. This part is essentially important in determining the DIE spectra. If we neglect the interaction between the two particles, the DIE spectra simply become the sum of two one-particle energies, $E_{\nu} + E_{\mu}$, obtained from the GWA. As we will see below, however, the resulting DIEs are quite different from the simple sum of two one-particle energies.

**Table 1.** The calculated DIE spectra of the CO molecule (in eV). “GWA×2” denotes the sum of two GWA one-particle energies, and “$T$-matrix” denotes the results obtained by solving the BSE (8) for the $T$-matrix. For comparison, experimental data are listed in the last column.

|        | GWA×2 | $T$-matrix | experiment [24] |
|--------|-------|------------|----------------|
| $1^3\Pi_u$ | 30.37 | 40.66 | 41.29 |
| $1^3\Sigma_g^+$ | 27.82 | 40.79 | 41.70 |
| $1^1\Pi_g$ | 30.37 | 41.61 | 41.81 |
| $1^3\Sigma_g^+$ | 34.05 | 42.56 | 43.57 |
| $2^1\Sigma_g^+$ | 34.05 | 46.83 | 45.48 |
3. Results
For CO molecule, the result for the IP within the GWA is 13.9 eV and the corresponding value within the LDA is 9.1 eV. This GWA result is in good agreement with the experiment [23]. The DIE spectra up to 47 eV of the CO molecule are presented in Table 1 together with the corresponding experiments. In this table, the column of “T-matrix” denotes the values obtained by the T-matrix calculation. The DIEs are characterized from lower to higher energies as $1^3\Pi_u$, $1^3\Sigma_g^+$, $1^3\Pi_u$, $1^3\Sigma_g^+$, and $2^3\Sigma_e^+$, where $1\Pi$, $1\Sigma$, and $2\Sigma$ are the two-hole states composed mainly of $(1\pi)(5\sigma)$, $(5\sigma)^2$, and $(4\sigma)(5\sigma)$, respectively. All their characteristics are consistent with the experiment. Because “GWA×2” does not include the effect of the Coulomb interaction between two holes, the values of “GWA×2” are much smaller than the corresponding experimental values (by about 10 eV). The ladder diagrams up to the infinite order significantly improve the results, and the present results are in good agreement with the experiment [24].

Next, for $C_2H_2$ molecule, the result for the IP within the GWA is 11.2 eV and the corresponding value within the LDA is 7.3 eV. As in the previous case, the GWA considerably improves the result of the LDA. The five lower DIEs of $C_2H_2$ are listed in Table 2 together with the experiments [25, 26, 27] of the double charge transfer (DCT) between projectile $M^+$ ($M = H$ or OH) and the target molecule.

The characters of the double ionized states determined by the present calculation are consistent with the experiments, although $1^\Delta$ and $1^\Sigma$ are indistinguishable in the experimental $H^+/\text{DCT}$. The DIEs in the GWA×2 cannot be distinguished in the three states ($3^\Sigma_\gamma$, $1^\Delta$ and $1^\Sigma$) because of the twofold degeneracy of the one-particle ($1\pi$) level of the $C_2H_2$ molecule. In reality, however, the effect of the Coulomb interaction makes the $3^\Sigma_\gamma$ level smallest. The Coulomb interaction affects more strongly when two electrons are removed from the same orbital (HOMO or HOMO−1) rather than when they are removed individually from two different orbitals (HOMO and HOMO−1); see Table 2. If the two electrons are removed from the same orbital, the DIEs split into $3^\Sigma$ and $1^\Sigma$ or $3^\Pi$ and $1^\Pi$ according to the symmetry of spin of the created holes. From Table 2 we conclude that it is easier to remove two electrons in a triplet state $3^\Sigma$, $3^\Pi$ than in a singlet state $1^\Sigma$, $1^\Pi$.

Table 2. The DIEs of $C_2H_2$ (in eV). “GWA×2” denotes the sum of two GWA one-particle energies, and “T-matrix” denotes the results obtained by solving the BSE (8) for the T-matrix. The two kinds of experimental DCT results, $H^+/\text{DCT}$ and $OH^+/\text{DCT}$ corresponding to singlet and triplet states, respectively, are given for comparison.

| calculation | GWA×2 | T-matrix | OH$^+/\text{DCT}$ [25] | H$^+/\text{DCT}$ |
|-------------|-------|----------|-----------------|----------------|
| $3^\Sigma_\gamma$ | 22.31 | 33.69 | 32.7 ± 0.3 | — |
| $1^\Delta_g$ | 22.31 | 34.71 | — | 33.6 ± 0.5 [26], 33.7 [27] |
| $1^\Sigma_g$ | 22.31 | 35.36 | — | 33.6 ± 0.5 [26], 33.7 [27] |
| $3^\Pi_u$ | 27.81 | 38.21 | 37.9 ± 0.4 | — |
| $1^\Pi_u$ | 27.81 | 38.96 | — | 38.5 ± 0.7 [26], 38.4 [27] |

4. Concluding Remarks
In this paper we have formulated the first-principles T-matrix theory on the basis of the many-body perturbation theory and successfully applied it to the calculation of the DIE spectra of CO and $C_2H_2$ molecules. The method has an advantage to calculate all the spectra at once together with the information on the corresponding quasiparticle wave functions. A calculation
of the two-particle wave functions by this method is now in progress for some strongly correlated systems in which the so-called Coulomb hole plays an essential role. Further details of the present results as well as the results for other systems will be reported elsewhere.

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