Short-Range Electron Correlations of CO₂ Molecule by First Principles *T*-Matrix Calculations

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In this paper, we obtain the double ionization energy spectra and the two-electron distribution functions from the first principles evaluating the ladder diagrams up to the infinite order (*T*-matrix) and discuss the short-range electron correlations. The *T*-matrix, which describes the multiple scattering between electrons (or holes), can accurately represent the short-range repulsive Coulomb interaction. The double ionization energy spectra calculated for the CO₂ molecule agree with the corresponding experiments very well. And the two-electron distribution function obtained from the *T*-matrix clearly shows “Coulomb hole” due to the avoidance of the antiparallel spin electrons confined in a small region. [doi:10.2320/matertrans.48.638]

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1. Introduction

Spectra of the double ionization energy (DIE), which is defined as an energy required for removing two electrons from the neutral system, are useful quantities to discuss the short-range repulsive Coulomb interactions (or electron correlations). As is well known, the major effects in the DIE are the hole-hole short-range repulsive Coulomb interactions. In particular for small-sized systems such as isolated atoms or molecules, the effect of the short-range interactions, namely the multiple scattering between two holes, is important. Theoretically, the short-range interactions are described by the electron-electron (or hole-hole) ladder diagrams up to the infinite order (the so-called ladder approximation).

Recently, it became possible to evaluate from the first principles the DIE spectra using Green's function methods, based on the many-body perturbation theory beyond the density functional theory.^{1,2)} One of the most efficient methods to calculate the DIE spectra is to expand the electron-electron (or hole-hole) two-particle Green's function G_2 using the ladder approximation as follows:

$$\int d3'd4'T(1,2|3',4')G_1(3,3')G_1(4,4') = U(1,2)G_2(1,2|3,4), \quad (1)$$

where T is a *T*-matrix (see eq. (2)), G_1 is a one-particle Green's function, and U is a bare Coulomb interaction given by $1/r$. As is seen in Fig. 1, the *T*-matrix is diagrammatically defined as the electron-electron (or hole-hole) ladder diagrams up to the infinite order and describes the accurate behavior of particles in the short distance limit.

There are large number of discussions of the electron correlations in an electron gas system. In fact, the radial pair distribution functions have already been calculated by many authors using various approximations, *e.g.*, the Hartree-Fock approximation, the random phase approximation,³⁾ or the

Fig. 1 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_1 .

ladder approximation,^{4–6)} and discussed the electron distribution when the interelectron distance is very small. Carbotte, *et al.*,^{4,5)} found that, in the radial pair distribution function for antiparallel spin electrons, the ladder approximation can evaluate the “Coulomb hole” that is an avoidance of the antiparallel spin electrons due to the short-range electron correlations.

The insight of the short-range electron correlations obtained from discussions of the DIE spectra and Coulomb hole is quite important, in particular, to study the strongly correlated systems. We calculated in Ref. 7) the on-site Coulomb interaction and the Coulomb hole for a Mott insulator of the organic radical 1,3,5-trithia-2,4,5-triazapentalenyl (TTTA) and consequently showed the significant effect of the short-range electron correlations. We believe that the present calculation method studied here is capable of being a powerful candidate to treat from first principles the strongly correlated systems, such as a single electron device in the future study.

In this paper, we applied the first principles *T*-matrix calculation to a CO₂ molecule and compared the resulting DIE spectra with the experiments. To help understanding the short-range electron correlations, we visually showed the two-electron distribution function obtained from the *T*-matrix theory. We confirmed the Coulomb hole in it as in the case of electron gas.

2. Calculation Method

We employed an all-electron mixed basis approach in which one-particle wave functions are expressed in a linear combination of the atomic orbitals (AOs) and the plane waves (PWs). First of all, we solved the local density approximation (LDA) based on the density functional theory as the starting point of our calculation. Next step is the *GW* approximation (GWA)⁸⁾ in which a one-electron self energy operator is approximated as a product of the LDA one-particle Green's function G_1^0 and the dynamically screened Coulomb interaction W^0 within the random phase approximation. The GWA accurately evaluates the first ionization energy or the electron affinity (see Refs. 9–12)). The calculation up to the GWA should be regarded as the calculation within one-particle picture. Then, going into two-particle picture and taking over the information obtained within one-particle picture, *e.g.*, the LDA one-particle wave functions and the quasiparticle energies, we constructed the Bethe-Salpeter equation for the *T*-matrix theory:¹³⁾

$$T(1, 2|3, 4) = U(1, 2)\delta(1 - 3)\delta(2 - 4) + U(1, 2) \times \int d1'd2' K(1, 2|1', 2')T(1', 2'|3, 4), \quad (2)$$

where K is a non-interacting two-particle Green's function defined as $K(1, 2|1', 2') = iG_1(1', 1)G_1(2', 2)$. To solve the Bethe-Salpeter equation, we define the two-particle Hamiltonian H together with a definition of $f_{v\mu}$ as $f_{v\mu} = -\delta_v^{occ}\delta_\mu^{occ} + \delta_v^{emp}\delta_\mu^{emp}$,

$$H_{\alpha\beta v\mu} \equiv \left(\frac{f_{v\mu}}{K_{v\mu}(\omega)} - \omega \right) \delta_{\alpha v} \delta_{\beta \mu} - U_{\alpha\beta v\mu} f_{v\mu}. \quad (3)$$

Note that the ω -dependence in $K_{v\mu}(\omega)$ is eliminated by subtracting ω in eq. (3) and thus $H_{\alpha\beta v\mu}$ is independent of ω . Then, we solve the eigenvalue problem as follows:

$$\sum_{v\mu} H_{\alpha\beta v\mu} A_{v\mu}(\Omega) = \Omega A_{\alpha\beta}(\Omega), \quad (4)$$

where the eigenvalues Ω , which are the poles of the *T*-matrix, directly provide the DIE spectra and the eigenfunctions $A_{v\mu}$ represent the coefficients (in the double expansion using the LDA one-particle wave functions) for the spatial part of the Bethe-Salpeter amplitude (two-particle wave function),

$$\Psi_\Omega(\mathbf{r}_1, \mathbf{r}_2) = \sum_{v\mu} A_{v\mu}^*(\Omega) \psi_v(\mathbf{r}_1) \psi_\mu(\mathbf{r}_2). \quad (5)$$

As is seen in eq. (5), the Bethe-Salpeter amplitude is in a double space referring to the coordinates of the position of electrons. If the $A_{v\mu}$ is replaced by the Kronecker's delta $\delta_{v\mu}$, the Bethe-Salpeter amplitude becomes a simple product of the two one-particle wave functions. This procedure means to neglect the repulsive Coulomb interaction between two electrons located at $\mathbf{r}_1$ and $\mathbf{r}_2$. To discuss the effect of the repulsive Coulomb interaction, we fix one electron at the position $\mathbf{r}_2$ and get the distribution probability amplitude of the other electron, which is affected from the fixed electron, as the function $\mathbf{r}_1$. In this paper, we compare the absolute square of the Bethe-Salpeter amplitudes (the two-electron distribution functions) with and without the interaction, fixing the position of one electron.

Table 1 The DIEs of CO₂ (in eV). “*T*-matrix” and “ $U_{v\mu v\mu}$ ” denote the results obtained by the *T*-matrix and the matrix element (of the bare Coulomb interaction) carrying the largest contribution to the DIEs, respectively. The available experimental data are given for comparison.

	$E_v + E_\mu$	<i>T</i> -matrix	$U_{v\mu v\mu}$	EXP
³ Σ	27.37	37.95	13.41	37.35 ^a , 37.65 ± 0.3 ^b
¹ Δ	27.37	38.44	13.46	38.52 ^a
¹ Σ	27.37	38.75	13.41	39.30 ^a
³ Π	31.89	41.10	12.78	41.43 ^a
¹ Π	31.89	41.52	12.78	42.30 ^a

^aReference 15)

^bReference 16)

3. Results

At first, we obtained the first ionization energies of CO₂ molecule at the LDA and the GWA level of the calculation to be about 9.2 eV and 13.7 eV, respectively. As is well-known, the LDA underestimates the experimental value, and, in fact, the LDA eigenvalue largely differs from the experiment (13.8 eV)¹⁴⁾ by about 4.6 eV. On the other hand, the GWA is in good agreement with the experiment (the difference is only about 0.1 eV).

3.1 Double ionization energy spectra

Table 1 shows the calculated DIE spectra together with the corresponding experiments. The left column denotes the characteristics of the two-hole states determined from the information of the eigenfunctions $A_{v\mu}(\Omega)$. The characteristics are consistent with the experiments. If we neglect the interaction between the created holes, the DIE is a simple summation of two single ionization energies $E_v + E_\mu$ of the v th and μ th valence levels, estimated by the GWA (see the column of “ $E_v + E_\mu$ ”). Because the highest occupied molecular orbital (HOMO) of CO₂ molecule is a two-fold degenerated, the corresponding DIEs, characterized as Σ and Δ, are same value in the column of “ $E_v + E_\mu$ ”. Moreover, the results significantly differ from the experimental values^{15,16)} by about 10 eV.

As a next step, we add to the values of “ $E_v + E_\mu$ ” the bare Coulomb interaction listed in the column of the “ $U_{v\mu v\mu}$ ” which carries the main contribution to the DIEs. Then, the DIEs (“ $E_v + E_\mu$ ” + “ $U_{v\mu v\mu}$ ”), although these values are not shown in Table 1, are about 40.8 eV for ³Σ, 40.4 eV for ¹Δ, and 40.8 eV for ¹Σ. The resulting DIEs significantly improve the “ $E_v + E_\mu$ ” values, and the remaining error is a few electron volt. However, “ $E_v + E_\mu$ ” + “ $U_{v\mu v\mu}$ ” are still indistinguishable for the different spin states, ³Σ and ¹Σ (or ³Π and ¹Π).

Finally, the DIE spectra calculated by the *T*-matrix theory, which accurately include the effect of the short-range interaction between holes, is found to be in good agreement with the experiments (see the column of “*T*-matrix”). The final results differ from the corresponding experiments by about only 0.6 eV or less for five states listed in Table 1.

3.2 Two-electron distribution function

To investigate the short-range repulsive Coulomb interaction (or electron correlations), we showed the two-electron

Fig. 2 The two-electron distribution functions of CO₂ molecule without (a) and with (b) the interaction. The center closed circle is a carbon atom and the others are oxygen atoms. In the figure (b), the one electron is fixed at the point marked by the cross.

distribution functions $|\Psi_{\Omega}(\mathbf{r}_1, \mathbf{r}_2)|^2$ with one electron fixed at $\mathbf{r}_2$ (see Fig. 2), where the Ω is corresponding to the $^1\Delta$. The three black circles are an oxygen atom, a carbon atom, and an oxygen atom from upper to lower. The fixed electron is marked by the cross in Fig. 2(b). Note that the two-electron distribution function evaluated from a simple product of two one-particle wave functions (Fig. 2(a)) is independent from the position of the fixed electron because of the lack of the interaction between two electrons. Therefore, the two-electron distribution function without the interaction is identical to the one-electron distribution function $|\psi_v(\mathbf{r}_1)|^2$ in the HOMO level of CO₂ molecule. On the other hand, the two-electron distribution evaluated from eq. (5) (Fig. 2(b)) largely changes the electron distribution. A remarkable point in Fig. 2(b) is the strong depletion of the electron distribution around the fixed electron comparing with Fig. 2(a) because the depletion clearly shows the Coulomb hole and provides an good evidence that the present calculation accurately estimates the short-range electron correlations.

4. Summary

In summary, we calculated the DIE spectra of CO₂ molecule from the first principles using the T -matrix theory to take into account the short-range repulsive Coulomb

interaction and compared it to the available experiments. The present results agree with the experiments very well. To discuss the short-range repulsive Coulomb interaction in detail, we visually showed the two-electron distribution functions with and without the interaction between two electrons assuming the fixed electron and confirmed the Coulomb hole in the two-electron distribution function. The resulting Coulomb hole clearly demonstrates that the present method accurately evaluates the short-range repulsive Coulomb interaction between two electrons.

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