We present an \textit{ab initio} GW calculation to study dynamical effects on an organic compound (TMTSF)$_2$PF$_6$. Calculated polarized reflectivities reproduce experimental plasma edges at around 0.2 eV for $E|b|$ and 1.0 eV for $E|a$. The low-energy plasmons come out from the low-energy narrow bands energetically isolated from other higher-energy bands, and affect the low-energy electronic structure via the GW-type self-energy. Because of the quasi-one-dimensional band structure, a large plasmon-induced electron scattering is found in the low-energy occupied states along the X-M line.

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\section{Introduction}

Physics and chemistry of organic conductors have recently attracted much attention owing to its low dimensionality, strong electron correlation, and material variety and flexibility. Despite the complicated structure of the molecules themselves, rather simple and energetically isolated band structure commonly seen in these materials provides ideal basis for studying fundamental physics of electron correlation. Among a number of organic conductors, (TMTSF)$_2$PF$_6$ has been of particular interest ever since its discovery as the first organic superconductor\textsuperscript{1} in this material, the molecules are stacked along the $a$-axis, and this is the most conductive axis because the molecular orbitals are elongated in the stack direction. A small overlap between neighboring molecular orbitals in the interstack direction gives rise to a weak two-dimensionality. The importance of electron correlation can readily be seen from the presence of the spin density wave (SDW) phase, which takes place below 12K at ambient pressure\textsuperscript{2}. The SDW transition temperature decreases upon applying hydrostatic pressure, and superconductivity sits next to the SDW phase in the temperature-pressure phase diagram. The superconducting state also shows some interesting features suggesting unconventional pairing, which may also be a manifestation of electron correlation\textsuperscript{3}.

Theoretically, the microscopic origin of the density waves and superconductivity has been intensively investigated on simplified Hubbard type models where on-site and/or short-ranged off-site repulsions are taken into account\textsuperscript{4}. On the other hand, recent \textit{ab initio} studies on organic materials show that the long-range part of the Coulomb interactions is appreciably present\textsuperscript{5},\textsuperscript{6} suggesting that dielectric properties can also be of interest. In fact, reflectance measurements of (TMTSF)$_2$PF$_6$ show presence of plasma edge\textsuperscript{7-10} indeed indicating the importance of the long range Coulomb interaction.

In general in solids, the energy scale of the plasmon excitation is of the order of 10 eV and therefore it is believed that such excitations are irrelevant to the low-energy physics of the order of 0.1-1 eV. However, in the organic materials, low-energy bands around the Fermi level tend to be isolated from other high-energy bands, resulting in a plasmon characterized by the bandwidth and occupancy of the isolated low-energy bands. Since their bandwidth is typically of the order of ~1 eV, the plasma frequency can also be in this energy scale. Then, the plasmon excitation may produce new aspects in the low-energy electronic states through self-energy effects. Since recent progress in angle-resolved photo-emission spectroscopy\textsuperscript{11-13} has made it possible to measure quasiparticle band structure and to perform detailed self-energy analyses, corresponding first-principle calculations are highly desired.

In the present study, we present an \textit{ab initio} GW calculation to study dynamical effects on the electronic structure of the organic compound (TMTSF)$_2$PF$_6$. The GW calculation takes into account the effect of plasmon excitation\textsuperscript{14-18}. The calculated reflectances well reproduce experimental results, identifying the experimentally-observed plasma edges to the plasmons within the low-energy bands. By calculating GW self energy and spectral function, we will show that this low-energy plasmon excitation affects the low-energy electronic structure. Since the isolated band character inducing the low-energy plasmon is ubiquitous in strongly-correlated electron systems such as organic compounds and transition-metal compounds, the present result will provide a general basis for analyzing various correlated materials.

\section{Method}

Here we describe our scheme. The non-interacting Green’s function is given by

\begin{equation}
G_0(r, r', \omega) = \sum_{\alpha k} \frac{\psi_{\alpha k}(r)\psi_{\alpha k}^*(r')}{\omega - \epsilon_{\alpha k} + i\delta \text{sgn}(\epsilon_{\alpha k} - \epsilon_f)},
\end{equation}

where $\psi_{\alpha k}(r)$ and $\epsilon_{\alpha k}$ are the Kohn-Sham (KS) wavefunction and its eigenvalue of band $\alpha$ and wavevector $k$, and $\epsilon_f$ is the Fermi level. $\delta$ is chosen to be a small but
finite positive value to stabilize numerical calculations. A polarization function of a type $-iG_0G_0$ is written in a form in the plane wave basis as

$$\chi_GG\!(q, \omega) = \sum_{\alpha} 2 \sum_{\kappa} \sum_{\beta} M_{\alpha\beta}(k, q) M_{\alpha\beta}^*(k, q) \times \left( \frac{1}{\omega - \epsilon_{\alpha k q} + i\delta} + \frac{1}{\omega + \epsilon_{\alpha k q} - i\delta} \right)$$

with $M_{\alpha\beta}(k, q) = \langle \psi_{\alpha k + q} | e^{i(q + G) r} | \psi_{\beta k} \rangle$.

Optical properties in a metal are related to the symmetric dielectric function in the $q \rightarrow 0$ limit

$$\epsilon_{GG'}(\omega) = \delta_{GG'} - \frac{(\omega_{pl, \mu\nu})^2}{\omega(\omega + i\delta)} \delta_{G0} \delta_{G'0} \left[ \text{Im} \left( \frac{4\pi}{\omega} \frac{\chi_{\text{inter}}(q, \omega)}{\omega^{1/2}} \right) \right]$$

with $q$ approaching zero along the Cartesian $\mu$ direction. $N$ is the total number of sampling $k$ points and $\Omega$ is the unit cell volume. The second term is the Drude term due to the intra band transitions.

The GW self-energy is given by

$$\Sigma(r, r', \omega) = \int \frac{d\omega'}{2\pi} G_0(r, r', \omega + \omega') W(r, r', \omega).$$

The screened Coulomb interaction $W(\omega) = v_{\chi}^2 \epsilon^{-1}(\omega) v_{\chi}^2$ is decomposed into the bare Coulomb interaction $v$ and the frequency-dependent part $W_C(\omega) = W(\omega) - v$. The frequency integral of $iG_0W$ gives the bare exchange term $\Sigma_X$ and that of $iG_0W_C$ gives the correlation term $\Sigma_C(\omega)$ including the retardation effect. The calculation of $\Sigma_X$ is straightforward while that of $\Sigma_C(\omega)$ is somewhat technical.

The resulting matrix elements of $\Sigma_C(\omega)$ is

$$\langle \psi_{\alpha k} | \Sigma_C(\omega) | \psi_{\alpha k} \rangle = \sum_{jnq} \langle \psi_{\alpha k} \psi_{n k - q} | a_j(r) \psi_{n k - q} \psi_{\alpha k} \rangle \delta(\omega_{n k - q} - (z_j - i\delta)) \sum_{\epsilon} \chi(\epsilon_{n k - q} - \epsilon, \omega).$$

The spectral function is calculated by

$$A(k, \omega) = \frac{1}{\pi} \sum_{\alpha} \text{Im} \left( \frac{1}{\omega - (\epsilon_{\alpha k} + \Delta \Sigma_{\alpha k}(\omega) + \Delta)} \right).$$

III. RESULTS AND DISCUSSIONS

Our density-functional calculations are based on Tokyo Ab-initio Program Package (TAPP) (Ref. 38) with plane-wave basis sets, where we employ norm-conserving pseudopotentials and generalized gradient approximation (GGA) for the exchange-correlation potential. The experimental structure of ($\text{TMTSF})_2\text{PF}_6$ obtained by a neutron measurement at 20 K is adopted. The cutoff energies in wavefunction and in charge densities are 36 Ry and 144 Ry, respectively, and an $11 \times 11 \times 3$ $k$-point sampling is employed.

The integral over the Brillouin-zone (BZ) is evaluated by the generalized tetrahedron method. The polarization up to $\omega = 86$ eV is calculated in a logarithmic mesh with 110 energy points.
The smaller energy scale of $\delta$ and $E_0$ for the theoretical data, $(TMTSF)_2PF_6$, along the high-symmetry lines in the $ab$ plane, where $\Gamma=(0, 0, 0)$, $X=(a^*/2, 0, 0)$, $M=(a^*/2, b^*/2, 0)$, $Y=(0, b^*/2, 0)$. The Fermi level is at zero energy. (b) Schematic crystal structure in the $ab$ plane, where the unit cell contains two TMTSF molecules denoted by the ellipsoids. The number in the ellipsoids represent the transfer integral (in the unit of meV) between the highest-occupied molecular orbitals at the starred site and each site. The tight-binding bands [blue dotted curves in the panel (a)] are calculated from these transfers.

FIG. 1: (Color online) (a) GGA band structure of $(TMTSF)_2PF_6$, along the high-symmetry lines in the $ab$ plane, where $\Gamma=(0, 0, 0)$, $X=(a^*/2, 0, 0)$, $M=(a^*/2, b^*/2, 0)$, $Y=(0, b^*/2, 0)$. The Fermi level is at zero energy. (b) Schematic crystal structure in the $ab$ plane, where the unit cell contains two TMTSF molecules denoted by the ellipsoids. The number in the ellipsoids represent the transfer integral (in the unit of meV) between the highest-occupied molecular orbitals at the starred site and each site. The tight-binding bands [blue dotted curves in the panel (a)] are calculated from these transfers.

those along the $b$ axis, reflecting a quasi-one-dimensional structure of the compound.

Figure 2 (a) shows the calculated energy loss function $-\text{Im}^{-1}(\omega)$. The red-solid and green-dotted curves are results for the light polarization $E$ parallel to $a$ (along $x$ axis) and $b'$ (along $y$ axis), respectively. In the low-energy region, we find two plasma peaks, at $\sim 0.2$ eV for $E \parallel b'$ and $\sim 1.0$ eV for $E \parallel a$. These peaks result from the plasmon excitations within the isolated target bands which have a low carrier density and small band widths. These plasmons are distinct from the plasmon seen at around 20 eV, which is relevant to the total charge density and the bare electron mass. We note that the difference between the plasmon peaks for $E \parallel a$ and $E \parallel b'$ reflects the difference in the transfer integrals ($\sim 260$ meV along the $a$ axis and $\sim 60$ meV along the $b$ axis).

Figure 2 (b) compares the reflectance,

$$R_{\mu}(\omega) = \frac{1 - \sqrt{\epsilon^{-1}_\mu(\omega)}}{1 + \sqrt{\epsilon^{-1}_\mu(\omega)}},$$

between our theory (circles) and the experiment (crosses) of Ref. 7. The calculated result reproduces the experimental one fairly well, in particular for $E \parallel a$ (dark red). The smaller energy scale of $E \parallel b'$ (light green) is also qualitatively reproduced.

To quantify the comparison, we fit the following function to theoretical and experimental reflectance data

$$\epsilon_\mu(\omega) = \epsilon_{\text{core}, \mu} - \frac{\omega_{pl, \mu}^2}{\omega(\omega + i\delta)}.$$  

For the theoretical data, $\omega_{pl, \mu}$ is calculated with Eq. (10) and $\delta$ is fixed at 0.02 eV, so that the effective dielectric constant $\epsilon_{\text{core}, \mu}$ is the only free parameter in the fitting. Table I summarizes the values of $\epsilon_{\text{core}, \mu}$ and $\omega_{pl, \mu}$. The calculated results well reproduce the experimental ones, although the theoretical plasma edge of $E \parallel b'$ is by $\sim 1.5$ times higher than that of experiment.

FIG. 2: (Color online) (a) Calculated energy loss function of $(TMTSF)_2PF_6$. The red-solid and green-dotted curves represent the spectra for $E \parallel a$ and $E \parallel b'$, respectively. (b) Ab initio reflectivity (circles) and experimental one (crosses) at 25 K (Ref. 7). The results for $E \parallel a$ and $E \parallel b'$ are displayed by dark red and light green, respectively. The solid and dotted curves are the fits by Eq. (11) with parameters shown in Table I.

TABLE I: Comparison of Drude-model parameters in Eq. (11) for $(TMTSF)_2PF_6$ between theory and experiment of Ref. 7. The unit of the plasma frequency is cm$^{-1}$.

|        | $E \parallel a$ | $E \parallel b'$ |
|--------|-----------------|-----------------|
| $\epsilon_{\text{core}}$ | 2.5             | 3.7             |
| $\omega_{pl}$        | 10074           | 3331            |
| Expt.   | 11400           | 2360            |

The low-energy plasmons found in Fig. 2 can affect the low-energy electronic structure. To see this effect, we show in Fig. 3 (a) the GW spectral function $A(k, \omega)$ [Eq. (9)]. While the quasiparticle band structure around $-1.0-0.1$ eV is similar to that of KS (red solid curves), we see an appreciable weight transfer to higher energy due to the self-energy effects. Along the Y-Γ line, the new states emerge around by 1 eV above the unoccupied states, and around by 1 eV below the occupied states. Along the X-M line, the spectra are more broadened and spread in the range from $-1.5$ to 0 eV. In the panel (b), the density of states calculated by KS (red-solid curve) and by GW (green-dotted one) is displayed, from which we see that a considerable amount of weight is transferred...
to higher energy due to the self-energy effect.

\[ \text{FIG. 3: (Color online) (a) Calculated spectral function } A(k, \omega) \text{ of (TMTSF)}_2\text{PF}_6, \text{ superposed by the Kohn-Sham band structure (red curves). The Fermi level is at zero energy. (b) Density of states obtained by KS (red-solid curve) and GW (green-dotted one).} \]

To get insight into the relation between the dielectric function (Fig. 2) and the spectral function (Fig. 3), we plot in Fig. 4 \( \text{Im}\Sigma(k, \omega) = \sum_\alpha |\text{Im}\Sigma_\alpha(k, \omega)| \text{ [a]} \) and \( \text{Im}\Sigma(\omega) = \int d k \text{Im}\Sigma(k, \omega) \text{ [b]} \). \( \text{Im}\Sigma(k, \omega) \) is directly related to the dielectric function through Eq. 4, and to the spectral function through Eq. 2. We see that \( \text{Im}\Sigma(k, \omega) \) has strong intensities at \( 0.5 \sim 1.0 \text{ eV} \) and \( -2.0 \sim -0.5 \text{ eV} \); about \( 0.5 \text{ eV} \) above the unoccupied states and about \( 0.5 \text{ eV} \) below the occupied states. The energy scale of \( 0.5 \text{ eV} \) roughly corresponds to the average of \( \omega_{pl,b,1} \sim 0.2 \text{ eV} \) and \( \omega_{pl,a,1} \sim 1.0 \text{ eV} \). Since the plasmons are known to make a peak in \( \text{Im}\Sigma \) at energy \( \epsilon_{\text{unocc}} + \omega_{pl} \) or \( \epsilon_{\text{occ}} - \omega_{pl} \), the bright region in Fig. 4(a) can be interpreted as an effect of the low-energy plasmons in Fig. 2 although the electron-electron scattering other than the plasmon excitation can also contribute to \( \text{Im}\Sigma(k, \omega) \). Since the strong peak of \( \text{Im}\Sigma(k, \omega) \) causes a large variation of \( \text{Re}\Sigma(k, \omega) \) through the Kramers-Kronig relation, new poles of the Green’s function can be created just outside of the peak of \( \text{Im}\Sigma(k, \omega) \). This is consistent with \( A(k, \omega) \) in Fig. 3.

\[ \text{FIG. 4: (Color online) Calculated spectrum of (a) Im}\Sigma(k, \omega) \text{ and (b) Im}\Sigma(\omega) \text{ of (TMTSF)}_2\text{PF}_6. \text{ The Fermi level is at zero energy. The Kohn-Sham band structure (red solid curves) is superposed in the panel (a).} \]

**IV. CONCLUSION**

In summary, we study low-energy dynamical properties of an organic compound \((\text{TMTSF})_2\text{PF}_6\) from first principles. Theoretical reflectance reproduces experimentally-observed plasma edges, and their anisotropy due to the quasi-one dimensional nature. The low-energy plasmons come out from the energetically-isolated bands around the Fermi level. The self-energy effect due to these plasmon excitations on the low-energy electronic structure is studied within the GW approximation. We have found that the self-energy effect is appreciable at energy by \( \sim 0.5 \text{ eV} \) above unoccupied states and below occupied states, suggesting that the plasmons can influence low-energy physics. Since organic conductors, or more generally, strongly-correlated electron materials, often have such isolated bands around the Fermi level, we expect that similar low-energy plasmon excitation can be relevant to physical properties of these materials. A detection of these effects in experiments such as photoemission spectroscopy is an interesting future issue.

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