Ab initio pseudopotential calculation for $(TMTSF)_2ClO_4$

Ab initio pseudopotential calculation for (TMTSF)$_2$ClO$_4$

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Abstract. We have investigated the electronic structure of the quasi-one-dimensional organic conductor (TMTSF)$_2$ClO$_4$ by *ab initio* band calculation for the first time. Very anisotropic band dispersions and sheet-like Fermi surfaces are obtained. The present results are compared with previous tight-binding calculations. The overall agreement is good but some quantitative differences are observed. This work provides more accurate wave functions, which will be useful for estimating various physical properties and comparing with experimental results.

1. Introduction

Bis-tetramethyl-tetraselenofulvalene perchlorate (TMTSF)$_2$ClO$_4$ (TMTSF $=$ (CH$_3$)$_4$C$_6$Se$_4$) is one of the isomorphous series of Bechgaard salts described as (TMTSF)$_2$X, where X$^-$ is a monovalent anion such as PF$_6^-$, AsF$_6^-$ and SbF$_6^-$ [1]. There is a charge transfer of one electron from two TMTSF molecules to one X. Due to the stacks of planar TMTSF molecules in columns, quasi-one-dimensional conductivity appears. At low temperature, this quasi-one-dimensionality results in an exotic ground state such as spin-density-wave state or superconducting state, depending on X [2]. (TMTSF)$_2$ClO$_4$ is the first ambient-pressure organic superconductor with a transition temperature of 1.2–1.5 K [3, 4].

The lattice parameters of (TMTSF)$_2$ClO$_4$ were reported as $a = 7.266$ Å, $b = 7.678$ Å, $c = 13.275$ Å, $\alpha = 84.58°$, $\beta = 86.73°$ and $\gamma = 70.43°$ [5]. The a-axis is the axis with the highest electrical conductivity and the TMTSF molecules are stacked along this axis. TMTSF columns are arranged along the b-axis. The TMTSF networks in the ab-plane are separated by the insulating ClO$_4$ layers. As a result, good conductivity appears in the ab-plane and the conductivity is very low along the direction perpendicular to this plane [2].

Several groups reported theoretical studies of the electronic structure of (TMTSF)$_2$X [6–9]. They used the tight-binding approximation based on the extended Hückel method. Although their results are in a qualitative agreement with each other, there are some discrepancies depending on the approximations and parameters that they chose. In particular, for Se 4d, the atomic orbital parameters such as the ionization potential and exponent were not well established and determined empirically. There was some uncertainty.

In this paper, we report an *ab initio* pseudopotential band calculation for (TMTSF)$_2$ClO$_4$. There is no adjusting parameter. The shape of the Fermi surface was deduced from the band structure obtained. Tight-binding parameters were estimated and compared with the previously reported values.

2. Calculational method

Our band calculation is based on the norm-conserving pseudopotential method [10–12] within the LDA (local density approximation) framework. We used pseudopotentials proposed by Troullier and Martins [13] with the separable approximation [14] and the partial-core correction [15]. To obtain the final converged wave function, the preconditioned conjugate gradient method [16] modified by Bylander *et al* [17] with the charge-mixing scheme devised by Kerker [18], which has been shown to be suitable for large metallic systems [19], was used together with the Gaussian smearing technique [20]. The energy cut-off of the plane waves was chosen to be 67.5 Ryd following reference [13], where total-energy-convergence data are given for oxides. Oxygen requires the highest energy cut-off among the elements in $(TMTSF)_2ClO_4$. 16 k-points in the half Brillouin zone were used. We confirmed that this number is sufficient for a similar class of material, TTF-TCNQ. After the self-consistent charge density was obtained, we calculated energy eigenvalues at additional k-points in order to obtain band dispersions and the Fermi-surface morphology.

Room-temperature structural data reported by Rindorf *et al* [5] were used in the calculation except for the H-atom positions. For the H atoms, we used low-temperature data (their positions relative to other atoms) [21]. There are two equivalent choices for the orientation of ClO_4 anions. At room temperature, they are randomly distributed between the two orientations [5]. We fixed the ClO_4 orientation as one of them. In this case, the crystal loses its inversion symmetry, but the band structure retains it.

3. Results and discussion

Figure 1 represents calculated band dispersions of the topmost two bands at $k_c = 0$ (circles) and $k_c = 0.5c^*$ (crosses), where c^* is one of the reciprocal-lattice vectors and k_c is the k-vector component along this direction, which is perpendicular to the conducting ab-plane. These two sets of band dispersions are almost indistinguishable. This means that there is a very small dispersion along the c^*-direction. Figure 2 represents the partial electron charge density contributed from these topmost two bands. The charge is localized in the central part of the TMTSF molecules, showing π-character. There is no state in the ClO_4 anion clusters.
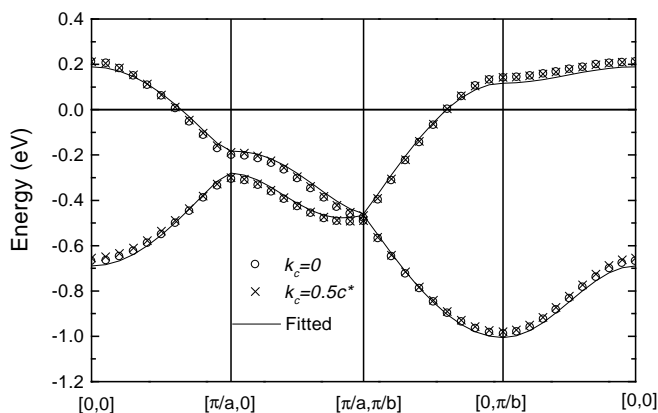

Figure 1. Calculated band dispersions of $(TMTSF)_2ClO_4$ at $k_c = 0$ (circles) and $k_c = 0.5c^*$ (crosses). The tight-binding fit is also shown (solid curves).
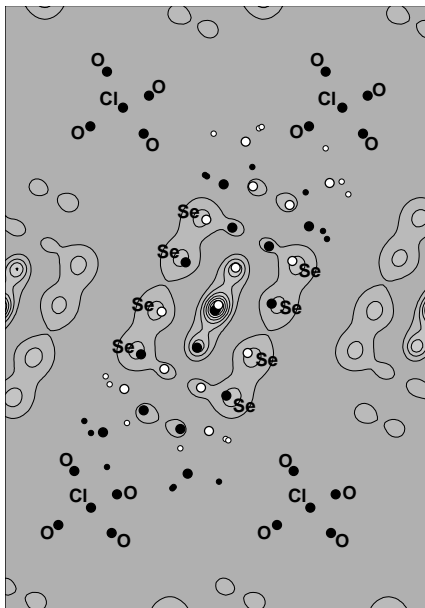
Figure 2. The electron charge density from the topmost two bands of $(TMTSF)_2ClO_4$. Large circles represent C atoms if not labelled with an elemental name and small circles represent H atoms. One TMTSF molecule is shown with closed circles and the other with open circles. They are inversions of each other.
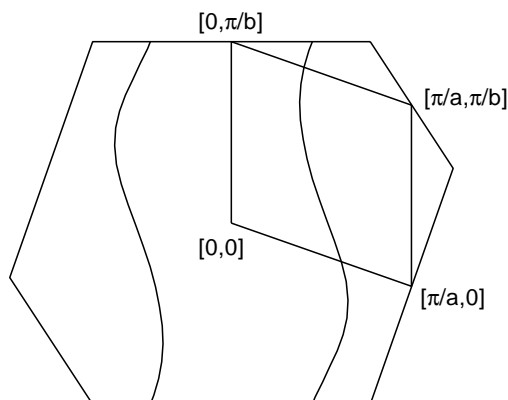

Figure 3. The calculated Fermi-surface structure of $(TMTSF)_2ClO_4$ at $k_c = 0$. The labelling represents values of $[k_a, k_b]$. The rhombus connecting four points corresponds to the path followed in figure 1.

The topmost electronic states in the TMTSF columns are well separated along the c-direction. Considering the quasi-one-dimensional conductivity in the present material, the result obtained is quite reasonable. A cut through the Fermi-surface sheets at $k_c = 0$ is shown in figure 3. The Fermi-surface shape at $k_c = 0.5c^*$ is very similar to this. The Fermi surface is described as sheets perpendicular to the a-axis corrugating along the b-axis. This Fermi-surface structure corresponds to the pseudo-one-dimensionality of the electronic properties.

Comparing the present *ab initio* results with the previous tight-binding band calculations

[6–9], there is very good agreement as regards the band dispersion curve and the Fermi-surface morphology. To make comparison easier, we estimated transfer integrals by fitting the following equations proposed by Grant [8] to the present result for $k_c = 0$ shown in figure 1:

$$E(\mathbf{k}) = 2[t_{I3} \cos \mathbf{k} \cdot \mathbf{b} + t_{I4} \cos \mathbf{k} \cdot (\mathbf{a} - \mathbf{b})] \pm |T(\mathbf{k})| \tag{1}$$

$$T(\mathbf{k}) = t_{s2} + t_{s1} \exp(-i\mathbf{k} \cdot \mathbf{a}) + t_{I2} \exp(-i\mathbf{k} \cdot \mathbf{b}) + t_{I1} \exp(-i\mathbf{k} \cdot (\mathbf{a} - \mathbf{b})). \tag{2}$$

We followed reference [8] as regards the notation for the transfer integrals. The values obtained are $t_{S1} = 263.0$ meV, $t_{S2} = 237.0$ meV, $t_{I1} = -19.1$ meV, $t_{I2} = -41.8$ meV, $t_{I3} = 53.2$ meV and $t_{I4} = -4.70$ meV. The fitted curves are shown in figure 1 (the thin solid curves). For t_{S1} and t_{S2}, which are along the conducting a-axis, the values obtained are ∼50% smaller in magnitude than those reported by Grant [8] while they agree well with those reported by Ducasse *et al* [9]. Judging from the bandwidth, the values in reference [6] seem slightly larger than the present values. For the other integrals, the present result is in a similar range to the previous values [8, 9] though there are small quantitative differences.

There are several factors that may account for the variation of the tight-binding results, as already discussed in several papers [6–9]. Among them, the choice of parameters for the Se 4d orbital seems the most crucial one [6, 7]. The present *ab initio* calculation is free from this problem. This might be advantageous when performing detailed comparison of the electronic structures among conductors of the $(TMTSF)_2X$ series and examining temperature effects, since a subtle change in the Fermi-surface shape plays an important role [22]. Furthermore, full valence-electron wave functions have been obtained by the present calculation. They might be quite useful for deducing various physical properties.

4. Summary

We have performed an *ab initio* band calculation for the quasi-one-dimensional conductor $(TMTSF)_2ClO_4$ for the first time. The result is compared with previous tight-binding calculations. The overall agreement is good but there are some quantitative differences. The present calculation is free from adjustable parameters, which sometimes cause a wide variation in the result. We expect the reliability of calculations to be enhanced by this *ab initio* method. The resulting full wave-function data might be useful for deducing various physical properties.

Acknowledgments

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