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ON THE BAND STRUCTURE CALCULATION FOR MOLECULAR CRYSTALS OF THE SPACE GROUP $P2_1/a$

Yosihiro AIKAWA, Haruhisa SHIMODA, Mitsunori SUKIGARA, and Kenichi HONDA
Institute of Industrial Science, The University of Tokyo, Tokyo 106

The energy band structure of molecular crystals belonging to the space group $P2_1/a$, originally derived by Katz et al., is not valid. The correct band structure is derived by taking explicitly the non-spherical property of molecule in molecular crystals into consideration and using symmetry operator.

Consideration of the symmetry of crystals is one of the most important procedures of the calculation of energy band structure of crystals. This procedure is often rather simple for inorganic crystals; many of them are composed of atoms or single ions which can be treated as spheres. For organic crystals, the band calculations are usually based upon their molecular orbitals which are no longer spheres, and positions of atoms in a molecule must explicitly be taken into consideration.

The band structure calculation of organic molecular crystals was first reported by LeBlanc[1] for anthracene crystal. Anthracene crystal belongs to the space group $P2_1/a$ to which also do many other molecular crystals, such as naphthalene, phthalocyanine, etc. Each of those molecules has the center of symmetry. The unit cell of $P2_1/a$ contains two molecules; the centers of symmetry of the molecules are placed at the lattice point, ℓ, and at the center of the ab plane, $m=\ell+\frac{a+b}{2}$. The relative geometry of the molecule at m is such that the molecule at ℓ is reflected by the ac plane then translated by $\frac{a+b}{2}$.

LeBlanc[1] considered band structures for excess electrons and holes taking only translational symmetry of a hypothetical crystal with one molecule per unit cell, i.e. with lattice vectors $(\frac{a+b}{2}, \frac{a-b}{2}, c)$, into consideration. Katz et al.[2] concluded that the two branches constructed by the symmetrical and anti-symmetrical combinations of basis functions,

$$|k^{\pm}\rangle = \sum_{\ell} \exp(ik\ell)\hat{T}_{\ell}|0\rangle \pm \sum_{m} \exp(ikm)\hat{T}_{m}|0^{\sigma}\rangle \qquad (1)$$

were yielded according to the presence of two molecules in a unit cell. Here, $|0\rangle$ denotes the molecular orbital of a molecule at the lattice point 0, $|0^\sigma\rangle$ denotes the molecular orbital generated by the reflection of $|0\rangle$ by ac plane, i.e. $|0^\sigma\rangle \equiv \hat{\sigma}|0\rangle$, and $\hat{T}_\ell(\hat{T}_m)$ denotes a translation operator by vector $\ell(m)$. Energy band structure according to the above states had two branches and were expressed as[2]

$$\varepsilon_\pm(k) = \varepsilon^0 + \sum_\ell \langle 0|\hat{H}\hat{T}_\ell|0\rangle \cos(k\ell) \pm \sum_m \langle 0|\hat{H}\hat{T}_m|0^\sigma\rangle \cos(km). \tag{2}$$

The band structure calculations of molecular crystals thereafter were based upon (1) and (2).[3-5] Unfortunately, Katz et al. made an error in their process of deriving the two eigenstates because of the failure to consider the crystal symmetry. The correct eigenstates are derived as follows.

The basis states of this crystal at wave vector k can be written as[2]

$$\begin{aligned} |k^0\rangle &= \frac{1}{\sqrt{N}} \sum_\ell \exp(ik\ell)\, \hat{T}_\ell|0\rangle \\ |k^\alpha\rangle &= \frac{1}{\sqrt{N}} \sum_m \exp(ikm)\, \hat{T}_m|0^\sigma\rangle \end{aligned} \tag{3}$$

The representation of one electron Hamiltonian $\hat{H}$ by these basis states is

$$\hat{H} \sim \begin{pmatrix} \langle k^0|\hat{H}|k^0\rangle & \langle k^0|\hat{H}|k^\alpha\rangle \\ \langle k^\alpha|\hat{H}|k^0\rangle & \langle k^\alpha|\hat{H}|k^\alpha\rangle \end{pmatrix} \tag{4}$$

and the elements of this matrix are

$$\begin{aligned} \langle k^0|\hat{H}|k^0\rangle &= \sum_\ell \langle 0|\hat{H}\hat{T}_\ell|0\rangle \cos(k\ell) \\ \langle k^\alpha|\hat{H}|k^\alpha\rangle &= \sum_\ell \langle 0|\hat{H}\hat{T}_{\ell^\sigma}|0\rangle \cos(k\ell) \\ \langle k^\alpha|\hat{H}|k^0\rangle &= \langle k^0|\hat{H}|k^\alpha\rangle \\ &= \sum_m \langle 0|\hat{H}\hat{T}_m|0^\sigma\rangle \cos(km) \end{aligned} \tag{5}$$

Here, ℓ^σ is a vector generated by the reflection of vector ℓ by the ac plane. The following relations were used in the derivation of eq. (5).

$$\langle 0|\hat{H}\hat{T}_\ell|0\rangle = \langle 0|\hat{i}\hat{H}\hat{T}_\ell\hat{i}|0\rangle = \langle 0|\hat{H}\hat{T}_{-\ell}|0\rangle$$

$$\langle 0|\hat{H}\hat{T}_m|0^\sigma\rangle = \langle 0|\hat{i}\hat{H}\hat{T}_m\hat{i}|0^\sigma\rangle = \langle 0|\hat{H}\hat{T}_{-m}|0^\sigma\rangle,$$

where $\hat{i}$ is an invertion operator by the origin. One electron Hamiltonian $\hat{H}$ is expressed as

$$\hat{H} = \frac{\hat{p}^2}{2m} + \sum_{\ell} \hat{T}_{\ell}\hat{V}\hat{T}_{\ell}^{-1} + \sum_{m} \hat{T}_{m}\hat{\sigma}\hat{V}\hat{\sigma}\hat{T}_{m}^{-1} , \qquad (6)$$

where $\hat{V}$ is the potential by the molecule at the lattice point 0. Using eq. (6), the integrals in eq. (5) can be rewritten as

$$\begin{aligned} \langle 0|\hat{H}\hat{T}_{\ell}|0\rangle &= \varepsilon\delta_{\ell 0} + \langle 0|\hat{V}\hat{T}_{\ell}|0\rangle\ (1 - \delta_{\ell 0}) \\ \langle 0|\hat{H}\hat{T}_{\ell^{\sigma}}|0\rangle &= \varepsilon\delta_{\ell 0} + \langle 0|\hat{V}\hat{T}_{\ell^{\sigma}}|0\rangle\ (1 - \delta_{\ell 0}) \\ \langle 0|\hat{H}\hat{T}_{m}|0^{\sigma}\rangle &= \langle 0|\hat{V}\hat{T}_{m}|0^{\sigma}\rangle \end{aligned} \qquad (7)$$

neglecting integrals involving three molecules. Here, ε is the energy of $|0\rangle$ in the crystal;

$$\varepsilon = \varepsilon^{0} + \sum_{\ell} \langle 0|\hat{T}_{\ell}\hat{V}\hat{T}_{\ell}^{-1}|0\rangle + \sum_{m} \langle 0|\hat{T}_{m}\hat{\sigma}\hat{V}\hat{\sigma}\hat{T}_{m}^{-1}|0\rangle \qquad (8)$$

where ε^{0} denotes the energy of orbital $|0\rangle$ of an isolated molecule.

Each element of the Hamiltonian matrix in eq. (4) can be expressed as follows using eq. (7):

$$\begin{aligned} \langle k^{0}|\hat{H}|k^{0}\rangle &= \varepsilon + \sum_{\ell\neq 0} \langle 0|\hat{V}\hat{T}_{\ell}|0\rangle \cos(k\ell) \\ \langle k^{\alpha}|\hat{H}|k^{\alpha}\rangle &= \varepsilon + \sum_{\neq 0} \langle 0|\hat{V}\hat{T}_{\ell^{\sigma}}|0\rangle \cos(k\ell) \\ \langle k^{0}|\hat{H}|k^{\alpha}\rangle &= \langle k^{\alpha}|\hat{H}|k^{0}\rangle \\ &= \sum_{m}\langle 0|\hat{V}\hat{T}_{m}|0^{\sigma}\rangle \cos(km) . \end{aligned} \qquad (9)$$

The error of Katz et al. arose from their assumption

$$\langle k^{0}|\hat{H}|k^{0}\rangle = \langle k^{\alpha}|\hat{H}|k^{\alpha}\rangle .$$

As can be seen from eq. (9), this means

$$\langle 0|\hat{V}\hat{T}_{\ell}|0\rangle = \langle 0|\hat{V}\hat{T}_{\ell^{\sigma}}|0\rangle .$$

For example, this situation is shown in Fig. 1 where ℓ = a+b, then ℓ^{σ} = a-b. In this figure, the integrals $\langle 0|\hat{V}\hat{T}_{\ell}|0\rangle$ and $\langle 0|\hat{V}\hat{T}_{\ell^{\sigma}}|0\rangle$ correspond to the interaction between $|0\rangle$ and $|a+b\rangle$ and that between $|0\rangle$ and $|a-b\rangle$, respectively. This assumption is no longer correct for the actual crystals of $P2_1/a$, such as anthracene, naphthalene, phthalocyanine, etc., when the difference in the magnitude of a pair of interactions, say those between $|0\rangle$ and $|a+b\rangle$, and $|0\rangle$ and $|a-b\rangle$ in Fig. 1, can not be ignored. The correct band structure is given by eigenvalues of matrix (4) as

$$\begin{aligned}\varepsilon_{\pm}(k) = \varepsilon &+ \sum_{\ell\neq 0} \frac{1}{2}\{ \langle 0|\hat{V}\hat{T}_{\ell}|0\rangle + \langle 0|\hat{V}\hat{T}_{\ell^{\sigma}}|0\rangle \} \cos(k\ell) \\ &\pm \left([\sum_{\ell\neq 0} \frac{1}{2}\{ \langle 0|\hat{V}\hat{T}_{\ell}|0\rangle - \langle 0|\hat{V}\hat{T}_{\ell^{\sigma}}|0\rangle \} \cos(k\ell)]^{2} \right. \\ &\left. + [\sum_{m} \langle 0|\hat{V}\hat{T}_{m}|0^{\sigma}\rangle \cos(km)]^{2} \right)^{\frac{1}{2}} . \qquad (10)\end{aligned}$$

Eq. (10) coincides with eq. (8) of ref. 2 if the equality $\langle 0|\hat{V}\hat{T}_{\ell}|0\rangle=\langle 0|\hat{V}\hat{T}_{\ell^{\sigma}}|0\rangle$ is valid.

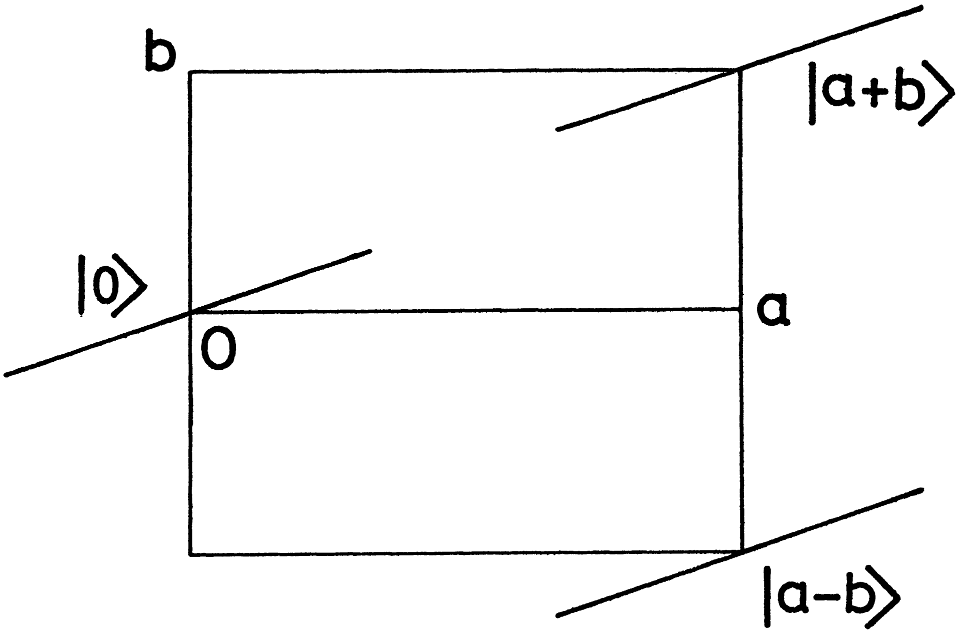

Fig. 1. Two cases of intermolecular interactions in space group $P2_1/a$.

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