A Comment on *p*-Orbital Bands and Crystal Structure

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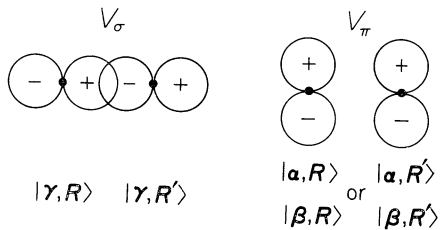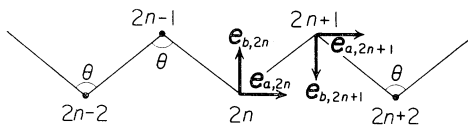
Why is a certain crystalline structure preferred to others in each element substance? This question seems to be a still difficult problem within the framework of the present solid state physics, in spite of the success of the band theory. One should, however, find out the origin which stabilizes the structure of the aggregate of atoms in the properties of individual constituent atoms. The aim of this paper is to report on an idea of our attempt to construct a primitive understanding of this problem on the basis of an idealized model

Let us consider a system consisting of one kind of atoms each of which has only a set of *p*-levels with three-fold degeneracy. It is allowed to regard the *p*-state as a three dimensional vector, because the angular relations of any two *p*-states both in the configuration space and in the Hilbert space coincide each other: If the *p*-state with the angular wave function $\sqrt{3/4\pi}(r \cdot e)/|r|$ is denoted by the ket $|e\rangle$, then

$$\langle e | e' \rangle = (e \cdot e'), \qquad (1)$$

where e and e' are arbitrarily chosen unit vectors. For simplicity orthogonality of the *p*-states of different atoms is assumed, though it is not necessary,

$$\langle e, \boldsymbol{R} | e', \boldsymbol{R}' \rangle = (e \cdot e') \delta_{\boldsymbol{R}, \boldsymbol{R}'}, \qquad (2)$$

where $|e, \boldsymbol{R}\rangle$ is the *p*-state corresponding to the unit vector e of the atom at $\boldsymbol{R}$.

The transfer integral between two atoms at $\boldsymbol{R}$ and $\boldsymbol{R}'$ has the following properties. It is convenient to introduce a set of three orthogonal unit vectors $(\boldsymbol{\alpha}, \boldsymbol{\beta}, \boldsymbol{\gamma})$, where we

Fig. 1.

Fig. 2.

choose $\boldsymbol{\gamma} = (\boldsymbol{R} - \boldsymbol{R}')/|\boldsymbol{R} - \boldsymbol{R}'|$. Then it follows from the axial symmetry of the potential v

$$\langle e, \boldsymbol{R} | v | e', \boldsymbol{R}' \rangle$$

$$= \begin{cases} 0 & \text{for } e \neq e', \\ V_\pi(|\boldsymbol{R} - \boldsymbol{R}'|) & \text{for } e = e' = \alpha, \beta, \quad (3) \\ V_\sigma(|\boldsymbol{R} - \boldsymbol{R}'|) & \text{for } e = e' = \gamma. \end{cases}$$

V_π and V_σ are defined as in Fig. 1 and are expected to be a negative and positive quantity respectively when v is negative. The general expression of the transfer integral becomes

$$\langle e, \boldsymbol{R} | v | e', \boldsymbol{R}' \rangle = V_\sigma(|\boldsymbol{R} - \boldsymbol{R}'|) P_{ee'\boldsymbol{R}\boldsymbol{R}'}$$

$$+ V_\pi(|\boldsymbol{R} - \boldsymbol{R}'|) \{(e \cdot e') - P_{ee'\boldsymbol{R}\boldsymbol{R}'}\}$$

$$P_{ee'\boldsymbol{R}\boldsymbol{R}'} \equiv \frac{\{e \cdot (\boldsymbol{R} - \boldsymbol{R}')\} \{e' \cdot (\boldsymbol{R} - \boldsymbol{R}')\}}{|\boldsymbol{R} - \boldsymbol{R}'|^2}. \quad (4)$$

Hereafter, the π-like transfer V_π is neglected because it is smaller than the σ-like transfer V_σ, as is easily seen from the spreading directions of the wave functions.

Now, let us study the electronic states of an atomic array of regular zigzag chain on a plane in which the angles between the two directions of the nearest neighbours are given by θ with $\pi/2 < \theta < \pi$ (see

Fig. 2). When V_π is neglected, the p-states perpendicular to the plane including the chain are lone and remain as degenerated levels. The mixing of the other two p-states yields two bands. Choosing the basis vectors at each atom as shown in Fig. 2 and using the formula (4) for neighbouring pairs only, one can easily obtain a 2×2 matrix for given wave number k

$$2V_\sigma \begin{pmatrix} \sin^2(\theta/2) \cdot \cos k & i \sin(\theta/2) \cdot \cos(\theta/2) \cdot \sin k \\ -i \sin(\theta/2) \cdot \cos(\theta/2) \cdot \sin k & -\cos^2(\theta/2) \cdot \cos k \end{pmatrix},$$

eigenvalues of which are given by

$$\varepsilon_k = V_\sigma [-\cos\theta \cdot \cos k \pm \sqrt{1 - \cos^2\theta \cdot \sin^2 k}].$$
$$(5)$$

The case of straight line, $\theta = \pi$, is one exception where only one band $\varepsilon_k = 2V_\sigma \cos k$ appears. If the number of electrons is two or four per atom so that a band is filled, the appearance of the band gap lowers the total electronic energy. This can be regarded as a kind of so-called the Peierls instability in p-bands.[1] Thus the properties of the p-state, being vector-like and degenerated, appear as a geometrical instability without the change of the nearest neighbour separations. From Eq. (5) we see that the smaller the angle θ becomes, the larger the gap is and the narrower the width of two bands becomes.

Finally the band width becomes zero when $\theta = \pi/2$ where two sets of degenerated levels, bonding and antibonding, arise. Such states do not extend over the system but localize between two atoms, because the matrix element is absent connecting two orthogonal p-states of the same atom. It should be noticed that so long as the π-like transfer is ignored as in the above discussions, the assumption of the atomic alignment on a plane is not essential and spectrum is common for all the chain-like arrays with the same angles.

After all the energy gain becomes the largest in the case of $\theta = \pi/2$, if the atom has two or four p-electrons. In the same way the aggregate of the atoms with three p-electrons prefers the structure with three neighbouring directions perpendicular with each other.

Though the model used here might be too simplified, the tendency thus derived will give some insight for fundamental understanding why the assembly of atoms of group VI such as selenium and tellurium prefers the chain structure and that of group V trigonal lamella structure as arsenic, antimony and bismuth.

More complete calculations are now in progress in which the effects of π-like transfer and other levels are taken into account.

1) R. E. Peierls, *Quantum Theory of Solid* (Oxford, Clarendon, 1955), Chap. 5.