



CHAPTER 2

Tight binding method and the calculation of energy bands

In this chapter we will discuss briefly the tight-binding method⁽¹¹⁾. The method will then be used to calculate the energy bands of La_2CuO_4 in the tetragonal phase.

The application of the tight-binding or the so-called the linear combination of atomic orbitals (LCAO) method to the energy bands of solid was introduced in the year 1954 by Slater and Koster⁽¹¹⁾. In the method, the Bloch states are linear combinations of the atomic orbitals relevant to the solid under consideration. Electronic wave functions are considered as linear combinations of the Bloch states. Using the Bloch states as a basis, the matrix representation of the crystal Hamiltonian can be obtained. Let $\phi(\vec{r} - \vec{r}_1)$ be an atomic orbital corresponding to an atom at site \vec{r}_1 . The corresponding Bloch state is

$$\Psi_{\vec{k}}(\vec{r}) = (1/\sqrt{N}) \sum_1 e^{i\vec{k} \cdot \vec{r}_1} \phi(\vec{r} - \vec{r}_1) \quad (2.1)$$

N is the number of unit cells in the crystal under consideration.

The summation is over all unit cells.

If H is the crystal Hamiltonian, the interaction matrix element is

$$\langle \vec{k} | H | \vec{k} \rangle = \langle \Psi_{\vec{k}}(\vec{r}) | H(\vec{r}) | \Psi_{\vec{k}}(\vec{r}) \rangle$$

$$\langle \vec{k} | H | \vec{k} \rangle = (1/N) \sum_m \sum_1 e^{-i\vec{k} \cdot (\vec{r}_m - \vec{r}_1)} \int \phi^*(\vec{r} - \vec{r}_m) H(\vec{r}) \phi(\vec{r} - \vec{r}_1) dV \quad (2.2)$$

The integration is over the whole crystal

Setting $\vec{r}_m - \vec{r}_1 = \vec{\rho}_m$, we get

$$\langle \vec{k} | H | \vec{k} \rangle = (1/N) \sum_1 \left[\sum_m e^{-i\vec{k} \cdot \vec{\rho}_m} \int \phi^*(\vec{r} - \vec{\rho}_m - \vec{r}_1) H(\vec{r}) \phi(\vec{r} - \vec{r}_1) dV \right]$$

The summation of all transfer integrals over m are identical at every r_1 , therefore, we get

$$\langle \vec{k} | H | \vec{k} \rangle = (N/N) \sum_m e^{-i\vec{k} \cdot \vec{\rho}_m} \int \phi^*(\vec{r} - \vec{\rho}_m) H(\vec{r}) \phi(\vec{r}) dV$$

$$\langle \vec{k} | H | \vec{k} \rangle = \sum_m e^{-i\vec{k} \cdot \vec{\rho}_m} \int \phi^*(\vec{r} - \vec{\rho}_m) H(\vec{r}) \phi(\vec{r}) dV \quad (2.3)$$

Similarly, we can get matrix elements between different Bloch states. They are found to be

$$\langle \xi_{\vec{k}} | H | \xi_{\vec{k}} \rangle = \sum_m e^{-i\vec{k} \cdot \vec{\rho}_m} \int \phi^*(\vec{r} - \vec{\rho}_m) H(\vec{r}) \psi(\vec{r}) dV \quad (2.4)$$

where $\xi_{\vec{k}}$ and $\psi_{\vec{k}}$ are Bloch states with wave vector \vec{k}
 $\phi(\vec{r} - \vec{\rho}_m)$ and $\psi(\vec{r})$ are atomic orbitals centered
 at $\vec{\rho}_m$ and the origin respectively

H is the crystal Hamiltonian

The integration is over the whole crystal.

In the K_2NiF_4 structure, each copper atom of La_2CuO_4 occupies a site $R_{nn} = n_1a_1 + n_2a_2$ of a square Bravais lattice (CuO_2 plane), and is surrounded by an octahedra of six neighbouring oxygen atoms, two of them lying above or below the plane, and the four others occupying the sites $R_{nn} + a_i/2$, $i = 1$ or 2 , inside the plane, chosen as the (x,y) - plane (Fig.1). The oxygen octahedra and the neighbouring copper atoms give rise to a strong crystal field, the leading term of which is cubic and thus splits the five d-orbitals of copper into a t_{2g} -triplet (d_{xy} , d_{yz} and d_{zx}) which lies far below the Fermi energy, and is thus completely occupied, and an e_g -doublet ($d_{x^2-y^2}$ and $d_{3z^2-r^2}$), which is only partially occupied (Fig.2a). We shall neglect the splitting of the e_g -doublet by the next term in the crystal field. The oxygen atoms experience an axial field produced by the non-cubic distribution of the La-and Cu-atoms. Therefore, the three degenerate oxygen p-states are split by the axial crystal field into a twofold level ($p_{||}$) and a singlet (p_{\perp})(Fig.2b). Since it is possible that the states responsible for the superconductivity in the CuO_2 planes^(8,9), we, therefore, consider 2D electronic band structure corresponding to a Cu - O plane. A Cu - O plane can be viewed as that in Fig .3 Five Bloch sums corresponding to the five atomic orbitals of atoms in the plane are chosen as our bases (Fig .4). They are



free atoms in the crystal field

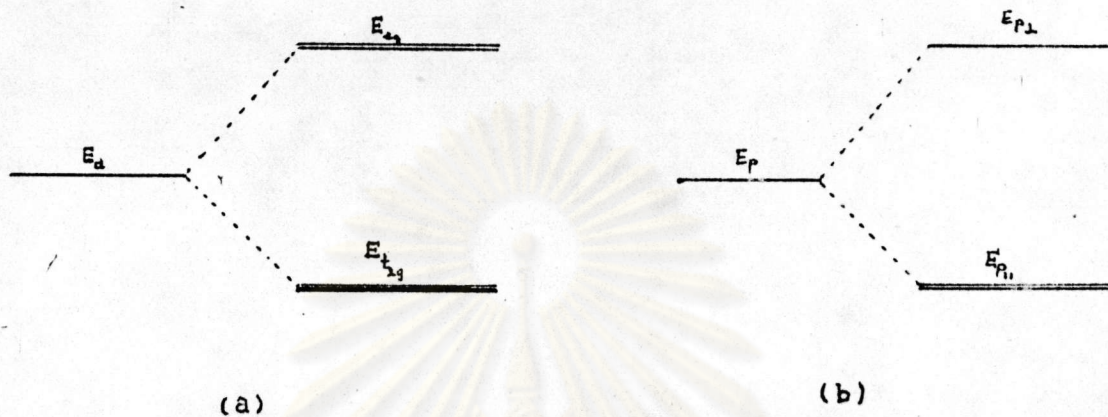


Fig 2. a) Crystal field splitting of d-orbitals of copper
 b) Crystal field splitting of p-orbitals of oxygen

$$\phi_1 = (1/\sqrt{N}) \sum_1 e^{i\vec{k} \cdot \vec{r}_1} s(\vec{r}-\vec{r}_1) \tag{2.5}$$

$$\phi_2 = (1/\sqrt{N}) \sum_1 e^{i\vec{k} \cdot \vec{r}_1} d_{3z^2-r^2}(\vec{r}-\vec{r}_1) \tag{2.6}$$

$$\phi_3 = (1/\sqrt{N}) \sum_1 e^{i\vec{k} \cdot \vec{r}_1} d_{x^2-y^2}(\vec{r}-\vec{r}_1) \tag{2.7}$$

$$\phi_4 = (1/\sqrt{N}) \sum_1 e^{i\vec{k} \cdot \vec{r}_1} p_x(\vec{r}-2\vec{a}_1-\vec{r}_1) \tag{2.8}$$

$$\phi_5 = (1/\sqrt{N}) \sum_1 e^{i\vec{k} \cdot \vec{r}_1} p_y(\vec{r}-2\vec{a}_2-\vec{r}_1) \tag{2.9}$$

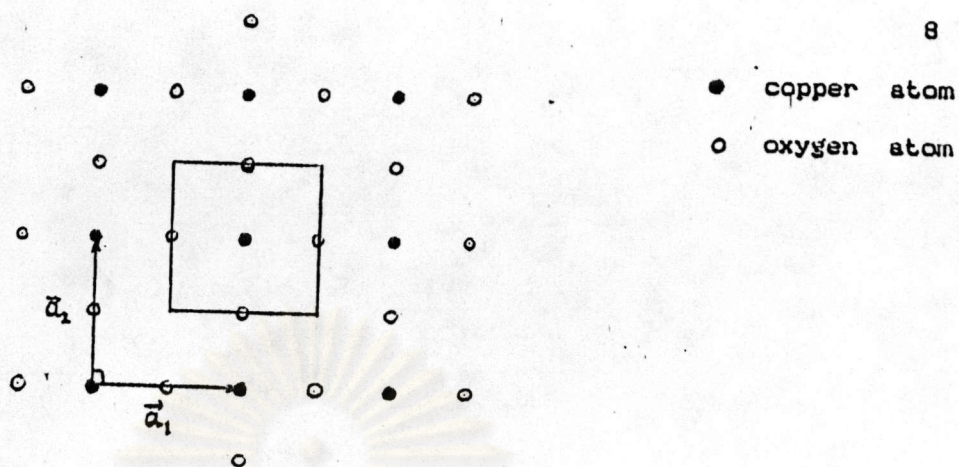


Fig.3 a) 2D crystal structure of Cu-O plane
b) The square is a unit cell

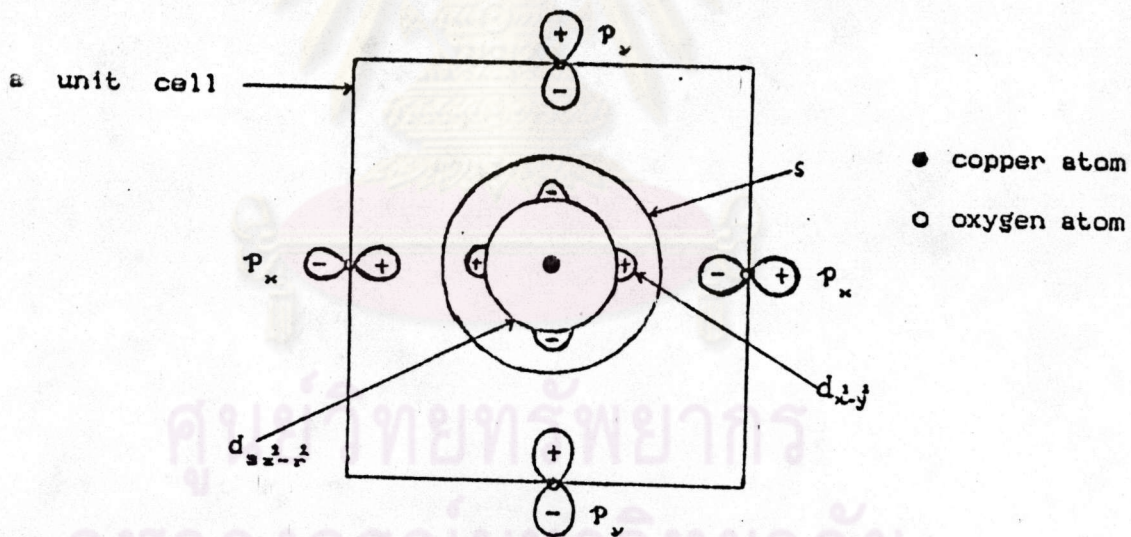


Fig.4 s-, p-, and d- orbitals involved in our model

$s(\vec{r}-\vec{r}_1)$, $d_{x^2-y^2}(\vec{r}-\vec{r}_1)$ and $d_{xz}(\vec{r}-\vec{r}_1)$ are atomic orbitals corresponding to Cu-atom at site \vec{r}_1 . $p_x(\vec{r}-\frac{1}{2}\vec{a}_1-\vec{r}_1)$ and $p_y(\vec{r}-\frac{1}{2}\vec{a}_2-\vec{r}_1)$ are atomic orbitals of oxygen at site $\vec{r}_1+\frac{1}{2}\vec{a}_1$ and $\vec{r}_1+\frac{1}{2}\vec{a}_2$ respectively. N

is the total number of unit cells contained in the plane. If we consider only the integral with integrand consisting of atomic orbitals within one unit cell and neglect the overlapping between atomic orbitals, we can easily get the matrix elements, $\langle \phi_i | H | \phi_j \rangle$, with no need in detail about the Hamiltonian. The ways to get some matrix elements are now shown as follows

The first matrix element to be considered is $\langle \phi_i | H | \phi_i \rangle$. From eq. (2.4) and eq. (2.5), we get

$$\langle \phi_i | H | \phi_i \rangle = \sum_m e^{-i\vec{k} \cdot \vec{\rho}_m} \int s^*(\vec{r} - \vec{\rho}_m) H(\vec{r}) s(\vec{r}) dV \quad (2.10)$$

Considering only the integral with integrand consisting of atomic orbitals within one unit cell makes us consider only the term with $\vec{\rho}_m = 0$. We can also write the Hamiltonian, $H(\vec{r})$, as $H(\vec{r}) = H_0(\vec{r}) + H(\vec{r})$, $H_0(\vec{r})$ is atomic Hamiltonian. Now eq. (2.10) becomes

$$\langle \phi_i | H | \phi_i \rangle = \int s^*(\vec{r}) H_0(\vec{r}) s(\vec{r}) dV + \int s^*(\vec{r}) H(\vec{r}) s(\vec{r}) dV.$$

$$\langle \phi_i | H | \phi_i \rangle = E_m + \int s^*(\vec{r}) H(\vec{r}) s(\vec{r}) dV.$$

Because $H(\vec{r})$ is small in the atomic region, we can neglect the second term on the right-hand side and get

$$\langle \phi_i | H | \phi_i \rangle = E_m \quad (2.11)$$

The matrix element $\langle \phi_2 | H(\vec{r}) | \phi_1 \rangle$ is the second example. Similarly to the preceding, we have

$$\langle \phi_2 | H | \phi_1 \rangle = \sum_m e^{-i\vec{k} \cdot \vec{\rho}_m} \int d^3 r_{\frac{1}{2}-\vec{\rho}_m} (\vec{r}-\vec{\rho}_m) H(\vec{r}) s(\vec{r}) dV.$$

As before we consider only the term with $\vec{\rho}_m = 0$ and we also write $H(\vec{r}) = H_0(\vec{r}) + H(\vec{r})$. We get

$$\langle \phi_2 | H | \phi_1 \rangle = E \int d^3 r_{\frac{1}{2}-\vec{\rho}_m} (\vec{r}) s(\vec{r}) dV + \int d^3 r_{\frac{1}{2}-\vec{\rho}_m} (\vec{r}) H(\vec{r}) s(\vec{r}) dV.$$

The first term on the right-hand side is the overlapping between atomic orbitals and is, therefore, neglected. The second term on the right-hand side, as in the case of $\langle \phi_1 | H | \phi_1 \rangle$, can be neglected. These give

$$\langle \phi_2 | H | \phi_1 \rangle = 0 \quad (2.12)$$

The last matrix element to be considered is

$$\langle \phi_4 | H | \phi_1 \rangle = \sum_m e^{-i\vec{k} \cdot \vec{\rho}_m} \int P_x^* (\vec{r}-\frac{1}{2}\vec{a}_1 - \vec{\rho}_m) H(\vec{r}) s(\vec{r}) dV.$$

From fig.4, we see that in a unit cell there are only cases where $\vec{\rho}_m = 0$ and $\vec{\rho}_m = -\vec{a}_1$ to be considered. This gives

$$\begin{aligned} \langle \phi_4 | H | \phi_1 \rangle &= \int P_x^* (\vec{r}-\frac{1}{2}\vec{a}_1) H_0(\vec{r}) s(\vec{r}) dV \\ &\quad + \int P_x^* (\vec{r}-\frac{1}{2}\vec{a}_1) H(\vec{r}) s(\vec{r}) dV \\ &\quad + e^{i\vec{k} \cdot \vec{a}_1} \int P_x^* (\vec{r}+\frac{1}{2}\vec{a}_1) H_0(\vec{r}) s(\vec{r}) dV \\ &\quad + e^{i\vec{k} \cdot \vec{a}_1} \int P_x^* (\vec{r}+\frac{1}{2}\vec{a}_1) H(\vec{r}) s(\vec{r}) dV. \end{aligned}$$

At the right-hand side, the first and the third terms are overlapping between atomic orbitals, we thus neglect these terms. The atomic orbitals involved in the second and the fourth terms do not correspond to the same atoms, therefore $H(\vec{r})$ is not in the atomic region and it needs not be small, we thus cannot neglect these terms. These two terms are equivalent and it is convenient to define an integral as a parameter α . In term of the parameter, we get

$$\langle \Phi_4 | H | \Phi_1 \rangle = \alpha - \alpha e^{ik_x a} \quad (2.13)$$

where

$$\alpha = \int \Phi_x^* (\vec{r} - \frac{1}{2} \vec{a}_1) H(\vec{r}) s(\vec{r}) dV \quad (2.14)$$

$$- \alpha = \int \Phi_x^* (\vec{r} + \frac{1}{2} \vec{a}_1) H(\vec{r}) s(\vec{r}) dV \quad (2.15)$$

In the same way, the remaining matrix elements are obtain.

The interaction matrix is as shown below

$$\begin{bmatrix} E_a & 0 & 0 & \alpha(1-e^{-ik_x a}) & \alpha(1-e^{-ik_y a}) \\ 0 & E_d & 0 & \beta(1-e^{-ik_x a}) & \beta(1-e^{-ik_y a}) \\ 0 & 0 & E_d & \gamma(1-e^{-ik_x a}) & -\gamma(1-e^{-ik_y a}) \\ \alpha(1-e^{ik_x a}) & \beta(1-e^{ik_x a}) & \gamma(1-e^{ik_x a}) & E_p & 0 \\ \alpha(1-e^{ik_y a}) & \beta(1-e^{ik_y a}) & -\gamma(1-e^{ik_y a}) & 0 & E_p \end{bmatrix} \quad (2.16)$$

where

E_s is the energy of the s-orbital of copper

E_d is the energy of the e_g -doublet of copper in the crystal field

E_p is the energy of the p_1 - orbital of oxygen

α is the transfer integral between the orbitals $s(\vec{R}_{n_1, n_2})$ and $p_x(\vec{R}_{n_1, n_2} + \frac{1}{2}\vec{a}_1)$, or $p_y(\vec{R}_{n_1, n_2} + \frac{1}{2}\vec{a}_2)$

β is the transfer integral between the orbitals $d_{z^2-y^2}(\vec{R}_{n_1, n_2})$ and $p_x(\vec{R}_{n_1, n_2} + \frac{1}{2}\vec{a}_1)$, or $p_y(\vec{R}_{n_1, n_2} + \frac{1}{2}\vec{a}_2)$

γ is the transfer integral between the orbitals $d_{x^2-y^2}(\vec{R}_{n_1, n_2})$ and $p_x(\vec{R}_{n_1, n_2} + \frac{1}{2}\vec{a}_1)$, or $p_y(\vec{R}_{n_1, n_2} + \frac{1}{2}\vec{a}_2)$

$$\beta = \int p_x^*(\vec{r} - \frac{1}{2}\vec{a}_1) H'(\vec{r}) d_{z^2-y^2}(\vec{r}) d\tau \quad (2.17)$$

$$-\beta = \int p_x^*(\vec{r} + \frac{1}{2}\vec{a}_1) H'(\vec{r}) d_{z^2-y^2}(\vec{r}) d\tau \quad (2.18)$$

$$\gamma = \int p_x^*(\vec{r} - \frac{1}{2}\vec{a}_1) H'(\vec{r}) d_{x^2-y^2}(\vec{r}) d\tau \quad (2.19)$$

$$-\gamma = \int p_x^*(\vec{r} + \frac{1}{2}\vec{a}_1) H'(\vec{r}) d_{x^2-y^2}(\vec{r}) d\tau \quad (2.20)$$

The determinant of the corresponding secular equation is made easier, from 5 x 5 matrix to 4 x 4 matrix, by using the transformation by Heine⁽¹²⁾. The transformed secular equation is

$$\begin{array}{cccc}
 E_d - E & 0 & \beta(1 - e^{-ikx^a}) & \beta(1 - e^{-iky^a}) \\
 0 & E_d - E & \gamma(1 - e^{-ikx^a}) & -\gamma(1 - e^{-iky^a}) \\
 \beta(1 - e^{ikx^a}) & \gamma(1 - e^{ikx^a}) & E_p - E - \frac{\alpha^2(1 - e^{ikx^a})(1 - e^{-ikx^a})}{E_s - E} & -\frac{\alpha^2(1 - e^{ikx^a})(1 - e^{-iky^a})}{E_s - E} \\
 \beta(1 - e^{iky^a}) & -\gamma(1 - e^{iky^a}) & -\frac{\alpha^2(1 - e^{iky^a})(1 - e^{-ikx^a})}{E_s - E} & E_p - E - \frac{\alpha^2(1 - e^{iky^a})(1 - e^{-iky^a})}{E_s - E}
 \end{array} = 0 \quad (2.21)$$

Using the conventional method in calculating the determinant, we get

$$\begin{aligned}
 & (E_d - E)^2 (E_p - E)^2 - (\gamma + \beta)^2 (E_d - E) (E_p - E) \{ (1 - e^{ikx^a})(1 - e^{-ikx^a}) + (1 - e^{iky^a})(1 - e^{-iky^a}) \} \\
 & + 4\beta\gamma (1 - e^{ikx^a})(1 - e^{-ikx^a})(1 - e^{iky^a})(1 - e^{-iky^a}) - (E_d - E)^2 (E_p - E) \cdot \\
 & \cdot \frac{\alpha^2(1 - e^{ikx^a})(1 - e^{-ikx^a})}{E_s - E} - (E_d - E)^2 (E_p - E) \frac{\alpha^2(1 - e^{iky^a})(1 - e^{-iky^a})}{E_s - E} + 4\alpha^2\gamma(E_d - E) \cdot \\
 & \cdot \frac{(1 - e^{ikx^a})(1 - e^{-ikx^a})(1 - e^{iky^a})(1 - e^{-iky^a})}{E_s - E} = 0 \quad (2.22)
 \end{aligned}$$

Eq.(2.22) can be easily solved by the quadratic formula if we define a parameter $R = \frac{E_d - E}{E_s - E}$ and solve the equation in terms of R. Substituting R into the equation gives

$$\begin{aligned}
& (E-E_d)^2(E-E_p)^2 - (\gamma+\beta)^2(E-E_d)(E-E_p)\{(1-e^{ikx^a})(1-e^{-ikx^a})+(1-e^{iky^a})\cdot \\
& \cdot (1-e^{-iky^a})\} + 4\gamma^2(1-e^{ikx^a})(1-e^{-ikx^a})(1-e^{iky^a})(1-e^{-iky^a}) - (E-E_d)(E-E_p)\alpha R \cdot \\
& \cdot (1-e^{ikx^a})(1-e^{-ikx^a}) - (E-E_d)(E-E_p)\alpha R(1-e^{iky^a})(1-e^{-iky^a}) + 4\alpha^2\gamma R \\
& (1-e^{ikx^a})(1-e^{-ikx^a})(1-e^{iky^a})(1-e^{-iky^a}) = 0 \\
& (E-E_d)^2(E-E_p)^2 - (\gamma+\beta+\alpha R)^2(E-E_d)(E-E_p)\{(1-e^{ikx^a})(1-e^{-ikx^a})+(1-e^{iky^a})\cdot \\
& \cdot (1-e^{-iky^a})\} + 4\gamma(\beta+\alpha R)(1-e^{ikx^a})(1-e^{-ikx^a})(1-e^{iky^a})(1-e^{-iky^a}) = 0
\end{aligned}$$

Applying the quadratic formula , we get

$$(E-E_d)(E-E_p) = \chi_{\pm} \quad (2.23)$$

where

$$\begin{aligned}
\chi_{\pm} &= \frac{(\gamma+\beta+\alpha R)\{(1-e^{ikx^a})(1-e^{-ikx^a})+(1-e^{iky^a})(1-e^{-iky^a})\}}{2} \\
&\pm \frac{1}{2} [(\gamma+\beta+\alpha R)^2\{(1-e^{ikx^a})(1-e^{-ikx^a})+(1-e^{iky^a})(1-e^{-iky^a})\}^2 - 16\gamma(\beta+\alpha R) \cdot \\
&\cdot (1-e^{ikx^a})(1-e^{-ikx^a})(1-e^{iky^a})(1-e^{-iky^a})]^{1/2} \quad (2.24)
\end{aligned}$$

Equation (2.23) can be rewritten as

$$E^2 - (E_d+E_p)E + (E_dE_p - \chi_{\pm}) = 0 \quad (2.25)$$

Applying the quadratic formula again gives the solutions

$$E = \frac{(E_d + E_p) \pm [(E_d + E_p)^2 - 4(E_d E_p - \chi_{\pm})]^{1/2}}{2}$$

$$E = \frac{(E_d + E_p) \pm [(E_d - E_p)^2 + 4\chi_{\pm}]^{1/2}}{2}$$

We define

$$E_{\pm\pm} = \frac{(E_d + E_p)}{2} \pm \left[\left(\frac{E_d - E_p}{2} \right)^2 + \chi_{\pm} \right]^{1/2} \quad (2.26)$$

The complete solutions of eq.(2.26) are obtained after we have evaluated R. Substituting one of the solutions of eq. (2.26) into the definition

$$R = \frac{(E - E_d)}{(E - E_p)} \quad (2.27)$$

will give us the corresponding R. In general R may be a positive or a negative value, it is equal to zero at $E = E_d$ and undefined at $E = E_p$. In our case study E may be expected closer to E_d than E_p so |R| is less than one. From eq. (2.24), we see that $\chi_+ > \chi_-$, therefore, $\Delta_+ > \Delta_-$, where $\Delta_{\pm} = \left\{ \left(\frac{E_d - E_p}{2} \right)^2 + \chi_{\pm} \right\}^{1/2}$. The order of the four energy levels is, then, $E_{++} > E_{+-} > E_{--} > E_{-+}$.

The four energy bands obtained in eq. (2.26) are very complicated so using it directly will make further calculation more difficult. We, therefore, make some approximations on it. Because the orbitals d_{z^2} are directed perpendicularly to the (x,y) - plane, the absolute value of ρ is much smaller than that of γ . The transfer integral α is also smaller than γ because of more separation in

energy levels. Therefore γ is the dominating term. We thus approximate the energy bands by considering the γ term only. the approximated energy bands are

$$E_{\pm\pm}^{np} = \{(E_d + E_p)/2\} + \left[\{(E_d - E_p)/2\}^2 + \gamma_{\pm} \right]^{1/2} \quad (2.28)$$

$$\gamma_{\pm}^{np} = \begin{cases} 4\gamma^2 \left[\sin^2\left(\frac{k_x a}{2}\right) + \sin^2\left(\frac{k_y a}{2}\right) \right] \\ 0 \end{cases} \quad (2.29)$$

Eq. (2.28) and eq. (2.29) give the following conclusion : The approximated energy bands $E_{\pm\pm}^{np}$ exhibit no dispersion with constant energies E_d and E_p respectively. The dispersion ranges of the energy bands $E_{\pm\pm}^{np}$ are symmetrical and equal. Showing no dispersion indicates that the energy bands $E_{\pm\pm}^{np}$ should have the infinite density of states, therefore, the two delta functions should be seen in the density of states at the energies E_d and E_p .

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