

5.4 紧束缚模型 (tight-binding model)

- 一、定性说明
- 二、微扰计算
- 三、具体例子

参考：黄昆书**4.5节p189**
阎守胜书**3.3节p75**

和近自由电子近似认为原子实对电子的作用很弱相反，本节，我们假定原子实对电子的束缚作用很强，因此，当电子距某个原子实比较近时，电子的运动主要受该原子势场的影响，受其它原子势场的影响很弱。因此固体中电子的行为同孤立原子中电子的行为更为相似。这时可将孤立原子看成零级近似，而将其他原子势场的影响看成小的微扰，由此可以给出电子的原子能级和晶体能带之间的相互联系。这种方法称为紧束缚近似 (Tight Binding Approximation)。

一. 定性说明:

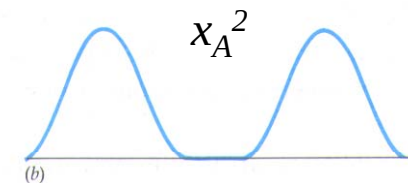
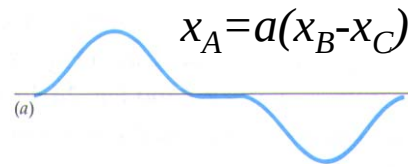
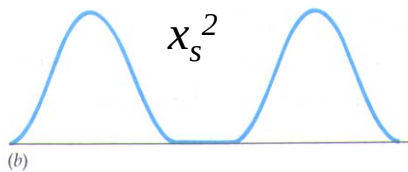
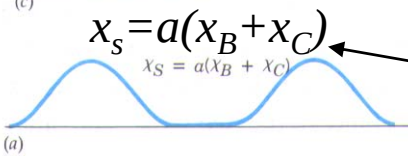
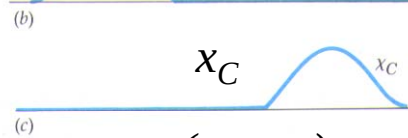
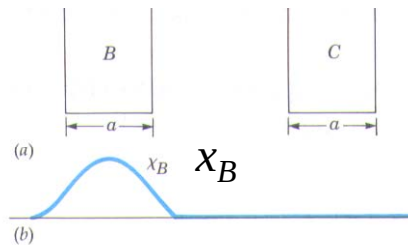


FIGURE 24-13 (a) Two finite potential wells B and C (b) Eigenfunction associated with an electron in well B with the ground state energy. (c) Eigenfunction associated with an electron in well C with the ground state energy.

FIGURE 24-14 (a) Symmetric eigenfunction representing an electron that can be found with equal probability in the two wells of Fig. 24-13 with the ground state energy. (b) Probability density associated with the symmetric eigenfunction in (a).

FIGURE 24-15 Antisymmetric eigenfunction representing an electron that can be found with equal probability in the two wells of Fig. 24-13 with the ground state energy. (b) Probability density associated with the antisymmetric eigenfunction of (a).

没有相互作用的双势阱

对称本征波函数

反对称本征波函数

势阱靠近并产生相互作用

对称本征波函数（成键态）

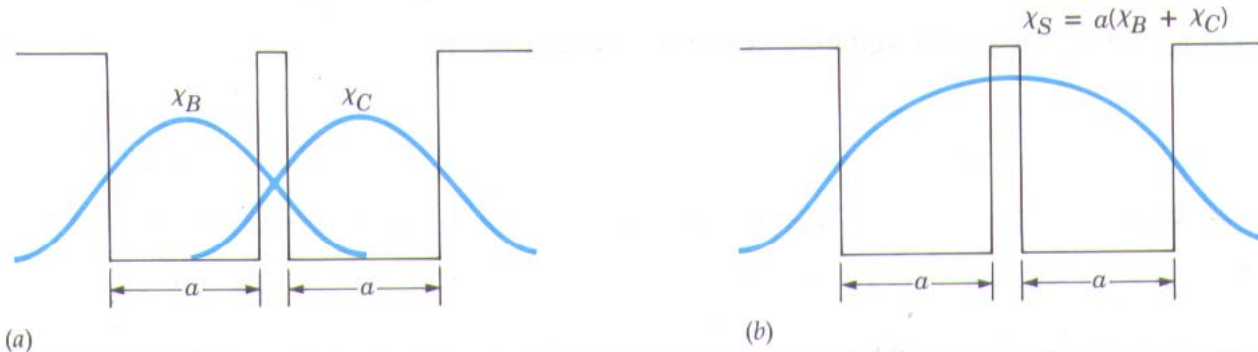


FIGURE 24-16 When the two wells are very close together, the symmetric eigenfunction of Fig. 24-14 looks like the ground state eigenfunction for a finite well of width $2a$ (see Fig. 24-12a).

反对称本征波函数（反键态）

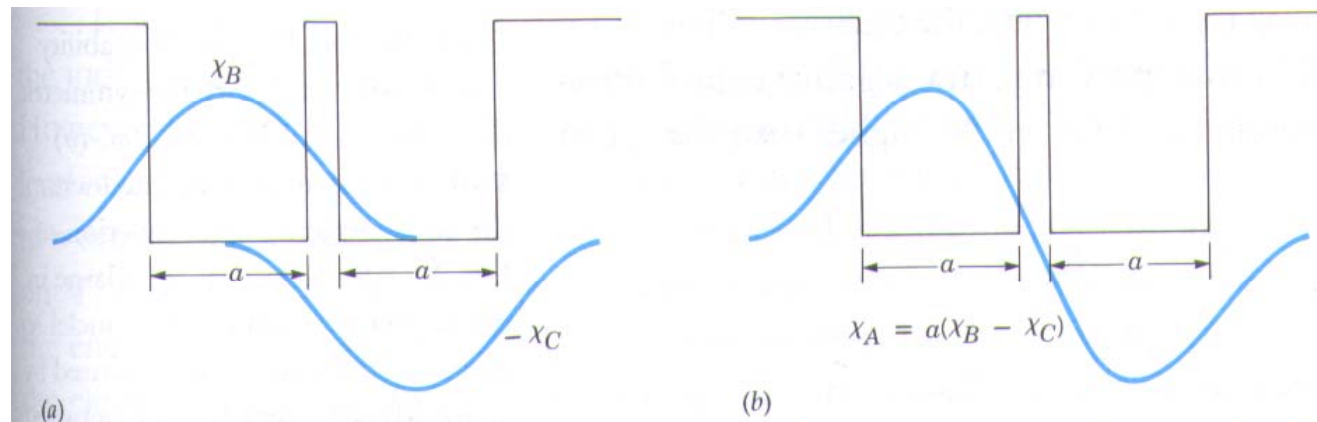


FIGURE 24-17 When the wells are very close together, the antisymmetric eigenfunction of Fig. 24-15 looks like the first excited state of a finite well of width $2a$ (see Fig. 24-12b).

紧束缚模型：体系波函数是原子波函数的线性组合
- Linear combination of atomic orbitals (LCAO)

首先忽略电子之间相互作用，其次采用单电子近似

$$H\psi_i = \left[-\frac{\hbar^2}{2m}\nabla^2 + V_{Ai} + V_{Bi}\right]\psi_i = \varepsilon_i\psi_i$$

则猜测波函数为两个原子的线性组合：

$$\psi_i = C_i[\varphi_A(r_i) + \lambda_i\varphi_B(r_i)]$$

若两个波函数相等，可以解出 $\lambda = \pm 1$

$$\psi_+ = C_+(\varphi_A + \varphi_B)$$

$$\psi_- = C_-(\varphi_A - \varphi_B)$$

$$\varepsilon^+ = \frac{\int \psi_+^* H \psi_+ dr}{\int \psi_+^* \psi_+ dr} = 2C_+^2(H_{aa} + H_{ab})$$

$$\varepsilon^- = \frac{\int \psi_-^* H \psi_- dr}{\int \psi_-^* \psi_- dr} = 2C_-^2(H_{aa} - H_{ab})$$

$$\varepsilon^+ = \frac{\int \psi_+^* H \psi_+ dr}{\int \psi_+^* \psi_+ dr} = 2C_+^2 (H_{aa} + H_{ab}) \quad \text{成键轨道, 对称波函数} \\ \text{Bonding orbital}$$

$$\varepsilon^- = \frac{\int \psi_-^* H \psi_- dr}{\int \psi_-^* \psi_- dr} = 2C_-^2 (H_{aa} - H_{ab}) \quad \text{反键轨道, 反对称波函数} \\ \text{Anti-bonding orbital}$$

$$H_{aa} = \int \varphi_A^* H \varphi_A dr = \int \varphi_B^* H \varphi_B dr \approx \varepsilon_0$$

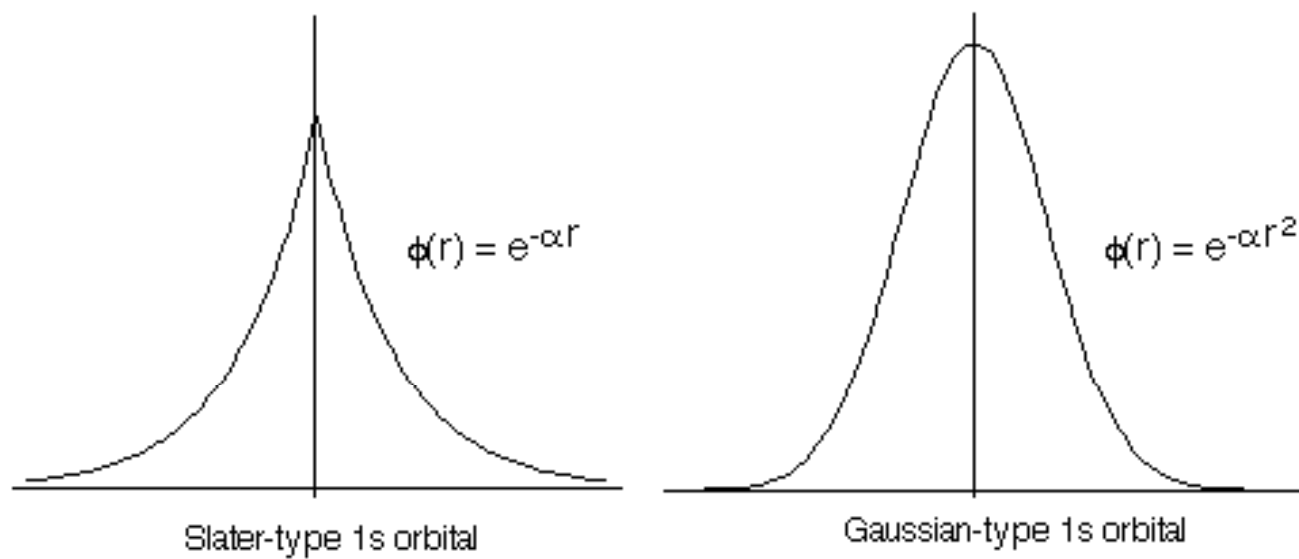
$$H_{ab} = \int \varphi_A^* H \varphi_B dr < 0$$

H_{ab} 表征了电子受到两个原子核的库仑相互作用，与两个原子波函数重叠成正比，这个波函数的重叠也被称为重叠积分，表征了共价键中相互作用的强弱。

两个电子同时占据成键轨道，因此能量得以下降

原子轨道线形组合方法（**LCAO**）是化学学科常用说法，其物理思想本质和固体物理中的紧束缚方法（**tight-binding**）方法是完全一致的。

常用原子轨道基组形式：Slater基组与Gaussian基组



Slater基组双原子成键与反键轨道

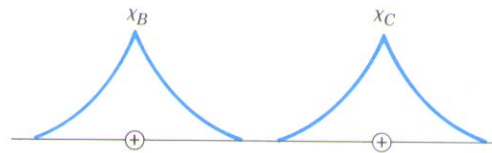


FIGURE 24-18 Radial part of the ground state eigenfunctions of two isolated hydrogen atoms as a function of the distance of the electrons from the respective nuclei.

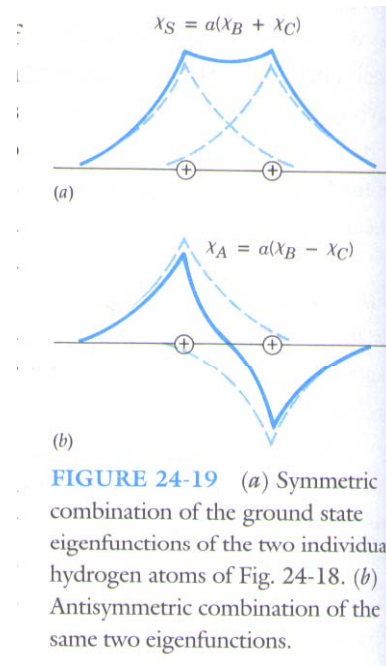


FIGURE 24-19 (a) Symmetric combination of the ground state eigenfunctions of the two individual hydrogen atoms of Fig. 24-18. (b) Antisymmetric combination of the same two eigenfunctions.

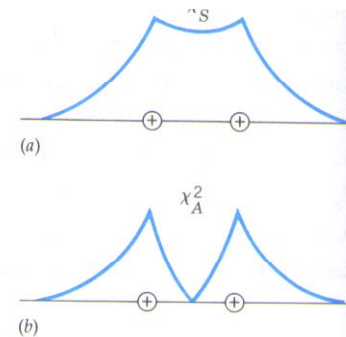


FIGURE 24-20 (a) Probability density associated with the symmetric eigenfunction of Fig. 24-19a. (b) Probability density associated with the antisymmetric eigenfunction of Fig. 24-19b. Note that χ_S^2 is large in the region between the two nuclei so therefore the electron represented by χ_S spends considerable time between both nuclei. χ_A^2 does not have this feature.

六个原子轨道的线性组合

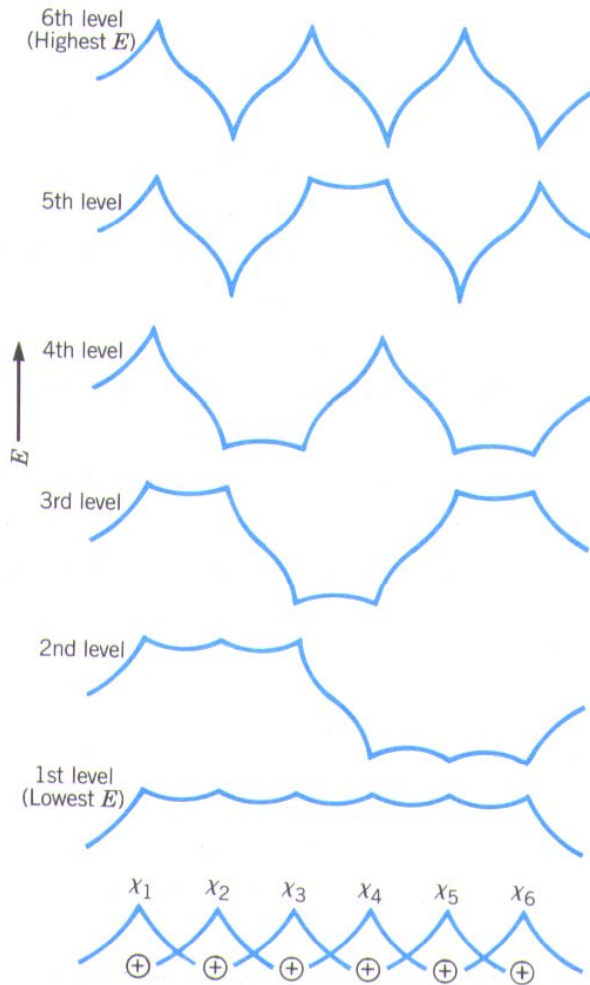


FIGURE 24-21 Six possible combinations of the ground state eigenfunctions of six hydrogen atoms, each corresponding to a different energy state. At the bottom of the figure the six individual eigenfunctions are sketched. The sketches above them represent six possible ways of adding them either symmetrically or antisymmetrically.

Splitting of 1s State of Six Atoms

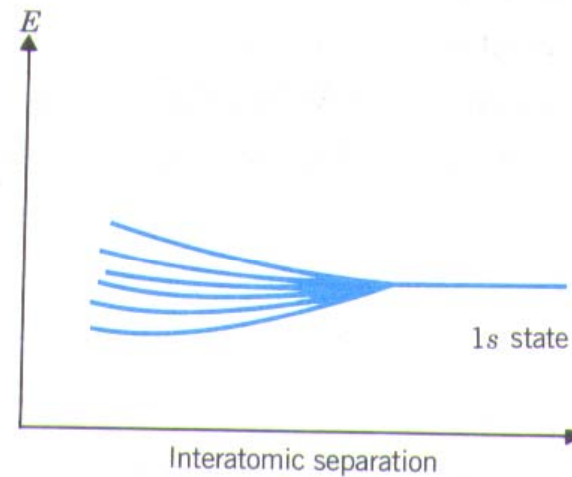


FIGURE 24-22 Splitting of the 1s state of six hydrogen atoms into a band of six energy levels as the separation between the atoms decreases. Note the increase in the bandwidth with decreasing interatomic separation.

Splitting of Atomic Levels in Sodium

Tight-binding 模型Na原子形成晶体的原理

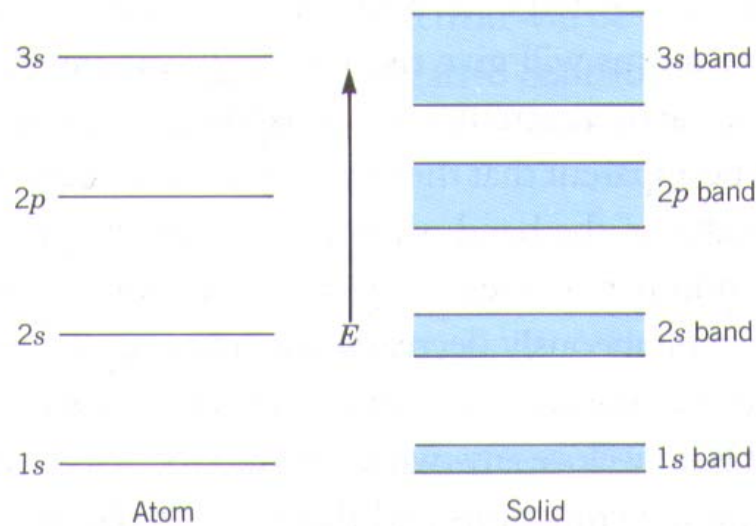


FIGURE 24-23 Expected splitting of the first four atomic levels of sodium into four energy bands in a sodium crystal.

Occupation of Bands Sodium

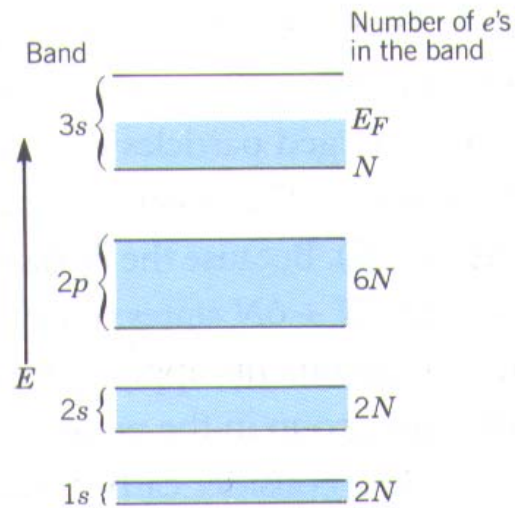
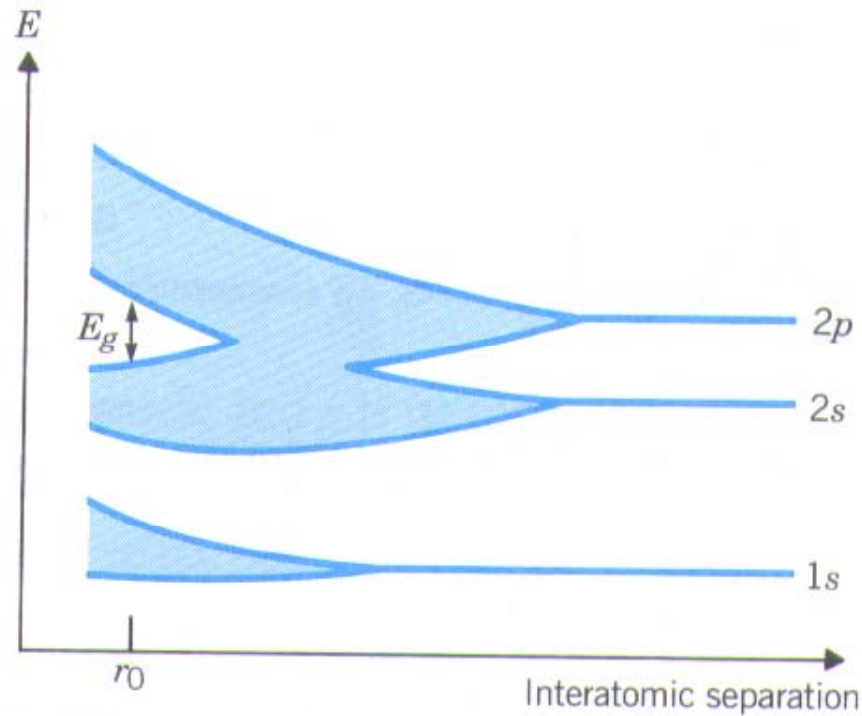


FIGURE 24-24 Schematic of the occupation of the bands by electrons in a sodium crystal of N atoms and having, therefore, $11N$ electrons. The highest energy band with electrons (3s band) is only half full with N electrons, and thus sodium is a monovalent metal. The 3s band is the conduction band of sodium.

Splitting of Atomic Levels in Carbon

Tight-binding 模型C原子形成晶体，原子轨道形成能带原理

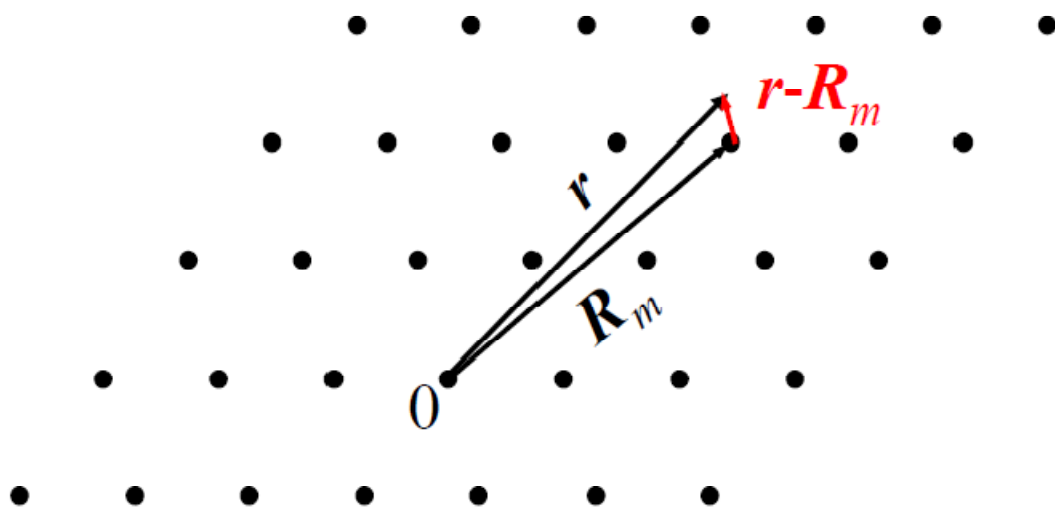


RE 24-27 The splitting of the atomic energy levels of carbon into energy bands is followed by the merging of the $2s$ and $2p$ bands and a subsequent splitting of these bands as the interatomic separation decreases. At the equilibrium inter-atomic spacing r_0 , an energy gap E_g separates two hybrid energy bands in a diamond crystal.

二、微扰计算

如果完全不考虑原子间的相互影响，在某个格点 $\mathbf{R}_m$ 附近的电子将以原子束缚态 $\varphi_j(\mathbf{r} - \mathbf{R}_m)$ 的形式环绕 $\mathbf{R}_m$ 点运动（这里设为简单晶格，每个原胞中只有一个原子） φ_j 表示孤立原子波动方程的一个本征态。

$$\vec{R}_m = m_1 \vec{a}_1 + m_2 \vec{a}_2 + m_3 \vec{a}_3$$



第 m 个孤立原子的波动方程：

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r} - \mathbf{R}_m) \right] \varphi_i(\mathbf{r} - \mathbf{R}_m) = \varepsilon_i \varphi_i(\mathbf{r} - \mathbf{R}_m)$$

$V(\mathbf{r} - \mathbf{R}_m)$ 是 $\mathbf{R}_m$ 格点的原子势场， ε_i 为某原子能级。

在晶体中，电子运动的波动方程为：

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right] \psi(\mathbf{r}) = E \psi(\mathbf{r})$$

周期场 $U(\mathbf{r})$ 是晶体中各格点原子势场之和，在**紧束缚近似**中，我们将孤立原子看成零级近似，而将其他原子势场 $[U(\mathbf{r}) - V(\mathbf{r} - \mathbf{R}_l)]$ 的影响看成微扰。由于电子可以环绕不同的格点运动，而环绕不同的格点可得到 N 个类似的原子波函数，它们具有相同的能量 ε_i ，即这 N 个态的能量是简并的，晶体中的电子构成了一个 N 度简并的系统。

所以，把原子间的相互影响当作微扰是一种简并微扰法。

$$\psi(\mathbf{r}) = \sum_m a_m \varphi_i(\mathbf{r} - \mathbf{R}_m)$$

代入晶体中电子的波动方程，并利用原子波动方程得

$$\sum_m a_m [\varepsilon_i + U(\mathbf{r}) - V(\mathbf{r} - \mathbf{R}_m)] \varphi_i(\mathbf{r} - \mathbf{R}_m) = E \sum_m a_m \varphi_i(\mathbf{r} - \mathbf{R}_m)$$

在紧束缚近似中，认为原子间距比原子轨道半径大，因此可以认为不同格点的 φ_i 重叠很少，可以近似地认为：
(这个近似只是为了数学表述上的简化，没有实质影响)

$$\int \varphi_i^*(\mathbf{r} - \mathbf{R}_n) \varphi_i(\mathbf{r} - \mathbf{R}_m) d\mathbf{r} = \delta_{nm}$$

以 $\varphi_i^*(\mathbf{r} - \mathbf{R}_n)$ 同时乘方程两边，积分得

$$\sum_m a_m \left\{ \varepsilon_i \delta_{nm} + \int \varphi_i^*(\mathbf{r} - \mathbf{R}_n) [U(\mathbf{r}) - V(\mathbf{r} - \mathbf{R}_m)] \varphi_i(\mathbf{r} - \mathbf{R}_m) d\mathbf{r} \right\} = E a_n$$

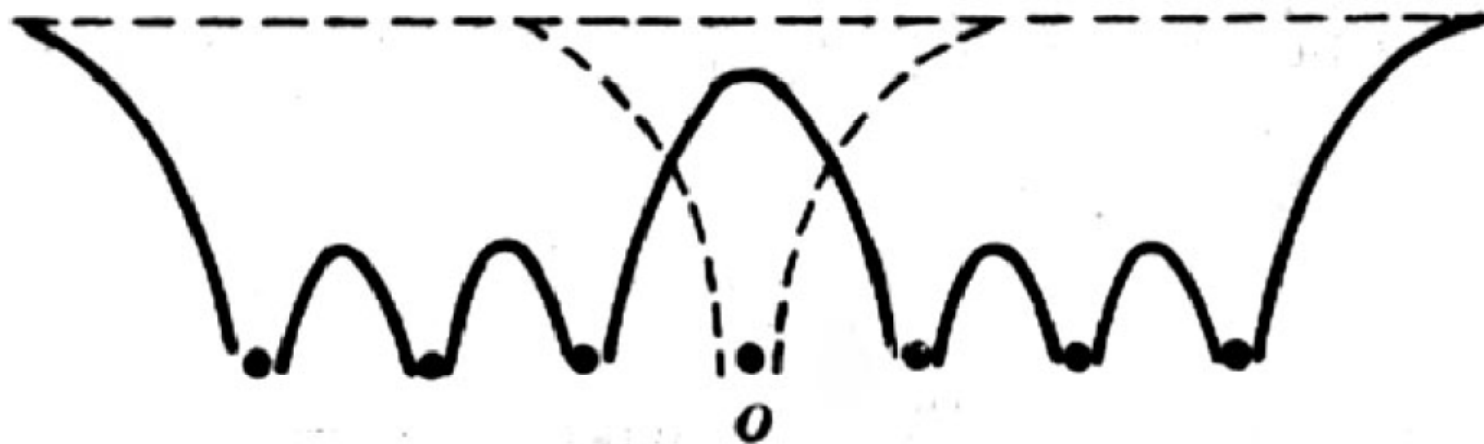
令 $\xi = \mathbf{r} - \mathbf{R}_m$ ，并根据 $U(\mathbf{r}) = U(\mathbf{r} + \mathbf{R}_m)$ ，将上式积分简化为

$$\int \varphi_i^* [\xi - (\mathbf{R}_n - \mathbf{R}_m)] [U(\xi) - V(\xi)] \varphi_i(\xi) d\xi = -J(\mathbf{R}_n - \mathbf{R}_m)$$

这表明，积分值仅与两格点的相对位置 $(\mathbf{R}_n - \mathbf{R}_m)$ 有关，

因此引入符号 $J(\mathbf{R}_n - \mathbf{R}_m)$ ，式中引入负号的原因是：

$U(\xi) - V(\xi)$ 就是周期势场减去在原点的原子势场，
如下图所示，这个场仍为负值。



晶体势场与原子势场差值示意图（黄昆书p191）

于是有
$$-\sum_m a_m J(\mathbf{R}_n - \mathbf{R}_m) = (E - \varepsilon_i) a_n$$

这是关于未知数 a_m ($m = 1, 2, \dots, N$) 的线性齐次方程组。由于方程组中的系数由 $(\mathbf{R}_m - \mathbf{R}_n)$ 决定，所以，方程组有如下简单形式的解：

$$a_m = C e^{ik \cdot \mathbf{R}_m}$$

其中 C 为归一化因子。代入方程组得

$$\begin{aligned} E - \varepsilon_i &= -\sum_m J(\mathbf{R}_n - \mathbf{R}_m) e^{-ik \cdot (\mathbf{R}_n - \mathbf{R}_m)} \\ &= -\sum_s J(\mathbf{R}_s) e^{-ik \cdot \mathbf{R}_s} \quad \mathbf{R}_s = \mathbf{R}_n - \mathbf{R}_m \end{aligned}$$

由于上式与 n 或 m 都无关，这表明，这种形式的解对所有联立方程组都化为同一条件。上式确定了这种形式解所对应的能量本征值。

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于是, 对于一个确定的 $\mathbf{k}$, 电子运动的波函数为

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_m e^{i\mathbf{k} \cdot \mathbf{R}_m} \varphi_j(\mathbf{r} - \mathbf{R}_m) \quad C = \frac{1}{\sqrt{N}}$$

容易验证 $\psi_{\mathbf{k}}(\mathbf{r})$ 为 Bloch 函数

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} \left[\frac{1}{\sqrt{N}} \sum_m e^{-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{R}_m)} \varphi_i(\mathbf{r} - \mathbf{R}_m) \right] = e^{i\mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$

相应的能量本征值为

$$E(\mathbf{k}) = \varepsilon_j - \sum_s J(\mathbf{R}_s) e^{-i\mathbf{k} \cdot \mathbf{R}_s}$$

利用Born—Karman周期性边界条件，可得 $\mathbf{k}$ 的取值为

$$\mathbf{k} = \frac{h_1}{N_1} \mathbf{b}_1 + \frac{h_2}{N_2} \mathbf{b}_2 + \frac{h_3}{N_3} \mathbf{b}_3 \quad h_1, h_2, h_3 = \text{整数}$$

由此可知，在简约区中，波矢 $\mathbf{k}$ 共有 N 个准连续的取值，即可得 N 个电子的本征态 $\psi_{\mathbf{k}}(\mathbf{r})$ 对应于 N 个准连续的 $\mathbf{k}$ 值。这样， $E(\mathbf{k})$ 将形成一个准连续的能带。

以上论述说明，形成固体时，一个原子能级将展宽为一个相应的能带，其 Bloch 函数是各格点上原子波函数 $\varphi_j(\mathbf{r}-\mathbf{R}_m)$ 的线性组合。

通常，能量本征值 $E(\mathbf{k})$ 的表达式可进一步简化。

$$-J(\mathbf{R}_s) = \int \varphi_i^*(\xi - \mathbf{R}_s) [U(\xi) - V(\xi)] \varphi_i(\xi) d\xi$$

$\varphi_i^*(\xi - \mathbf{R}_s)$ 和 $\varphi_i(\xi)$ 表示相距为 $\mathbf{R}_s$ 的格点上的原子波函数，显然积分值只有当它们有一定相互重叠时，才不为零。当 $\mathbf{R}_s = 0$ 时，两波函数完全重叠。

$$J_0 = - \int |\varphi_i(\xi)|^2 [U(\xi) - V(\xi)] d\xi$$

其次，考虑 $\mathbf{R}_s =$ 近邻格矢，一般只需保留到近邻项，而略去其他影响小的项，即可得

$$E(\mathbf{k}) = \varepsilon_i - J_0 - \sum_{\mathbf{R}_s = \text{近邻}} J(\mathbf{R}_s) \exp(-i\mathbf{k} \cdot \mathbf{R}_s)$$

这是紧束缚近似给出的最有用的结论。

例1、一维单原子链轨道

$$E(\mathbf{k}) = \varepsilon_i - J_0 - \sum_{\mathbf{R}_s = \text{近邻}} J(\mathbf{R}_s) \exp(-i\mathbf{k} \cdot \mathbf{R}_s)$$

$$\mathbf{R}_s = \pm a$$

$$E(k) = \varepsilon^s - J_0 - 2J_1 \cos ka$$

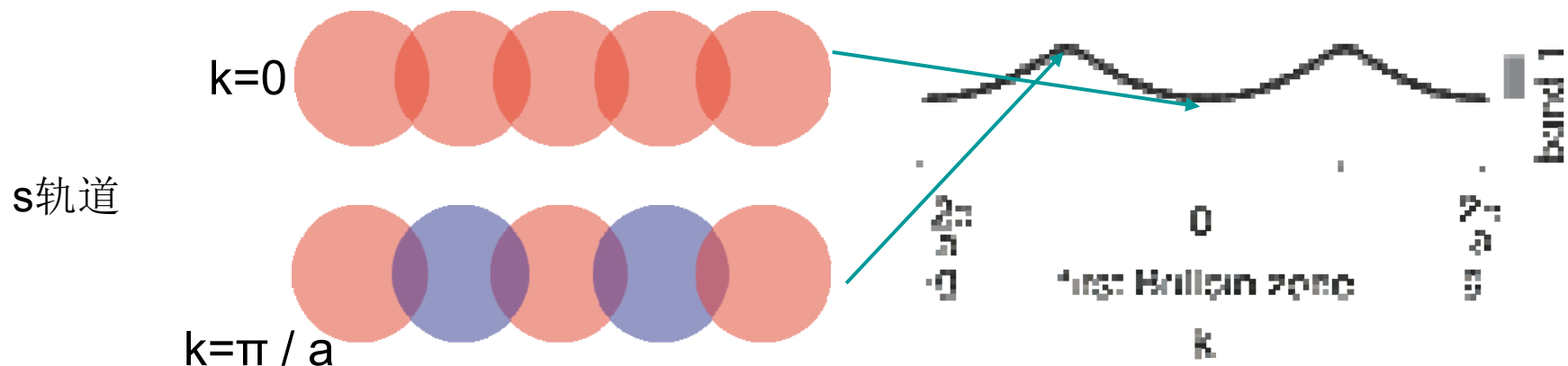
$$\psi_k(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_m e^{i\mathbf{k} \cdot \mathbf{R}_m} \varphi_j(\mathbf{r} - \mathbf{R}_m)$$

$$k = 0$$

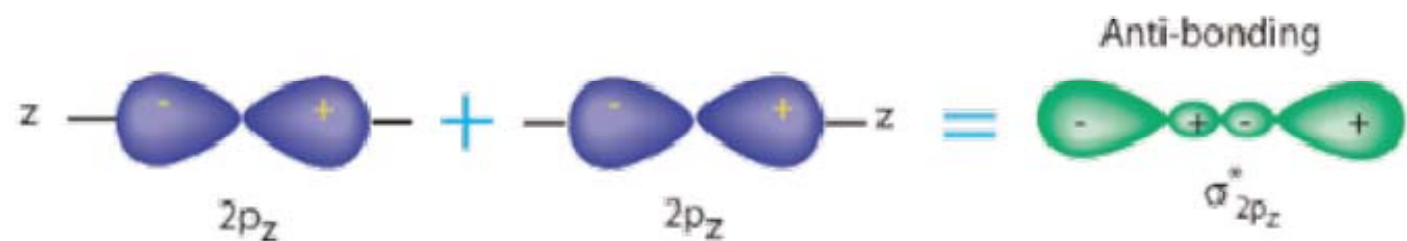
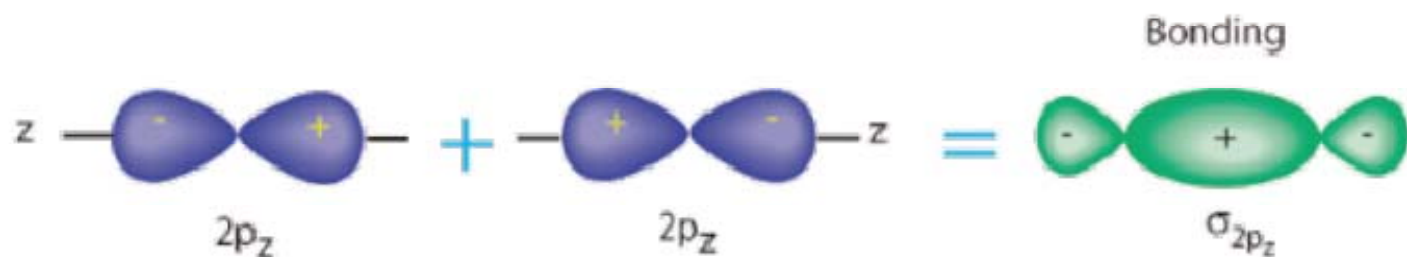
$$\psi_k(r) = \frac{1}{\sqrt{N}} \sum_m \varphi_j(r - R_m)$$

$$k = \pm \frac{\pi}{a}$$

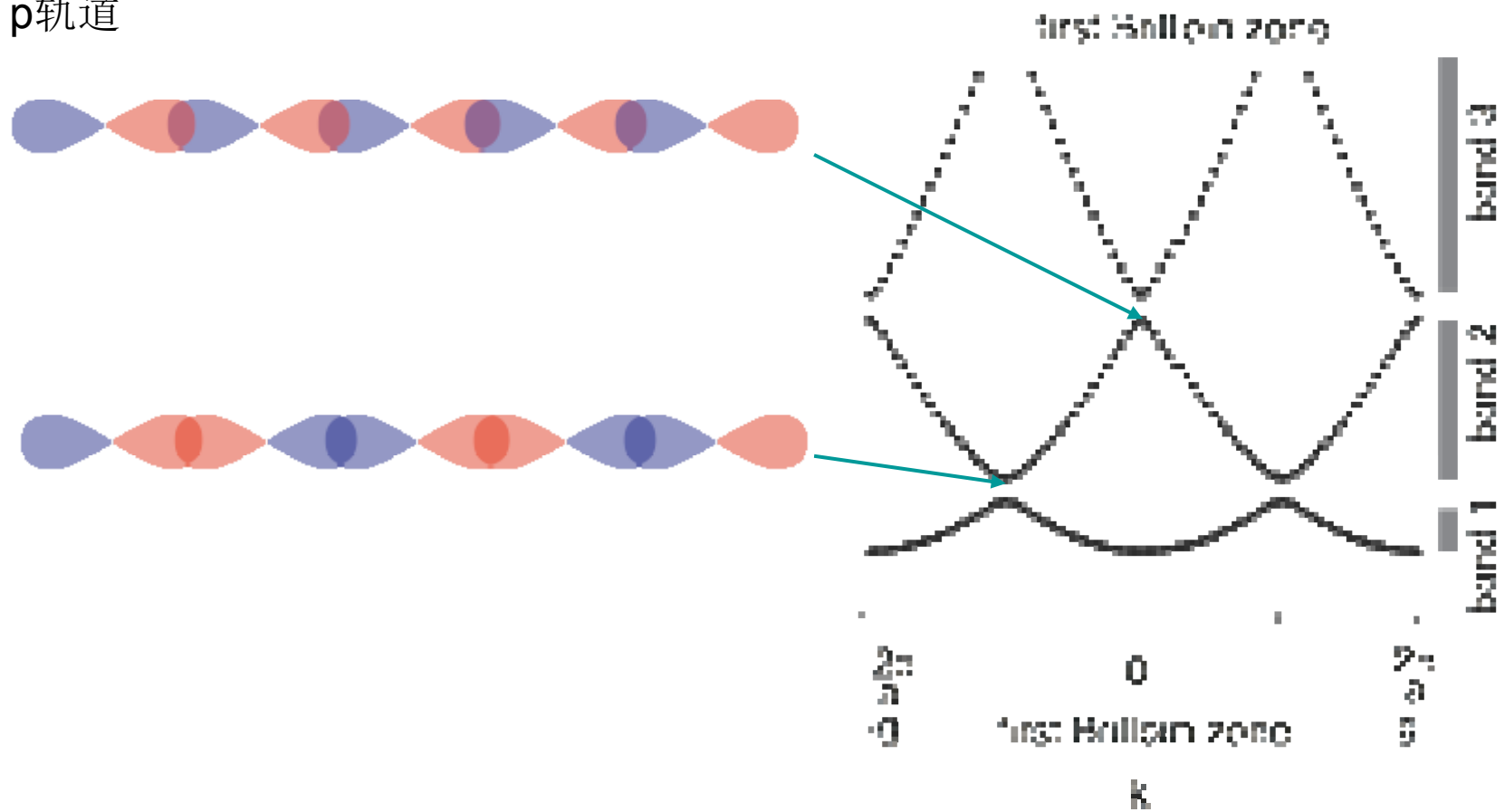
$$\psi_k(r) = \frac{1}{\sqrt{N}} \sum_m (-1)^{m+1} \varphi_j(r - R_m)$$



p-orbitals forming σ -bonds are antibonding!



p轨道

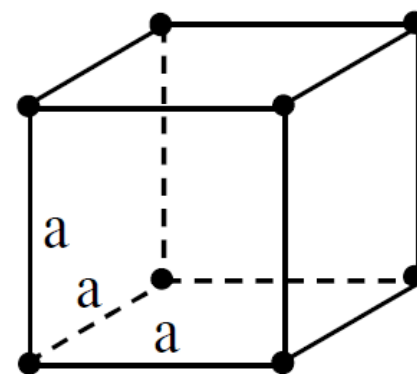


p轨道是奇宇称态，反对称轨道，因此重叠积分 $J_1 < 1$

例2 求简单立方晶体中由电子的 s 态所形成的能带

由于 s 态的原子波函数是球对称的，沿各个方向的重叠积分相同。因此，对于不同方向的近邻，有相同的值：

$$J(\mathbf{R}_s) = J_1 \quad \mathbf{R}_s = \text{近邻格矢}$$



对于简单立方：

$$\mathbf{R}_s = (\pm a, 0, 0), (0, \pm a, 0), (0, 0, \pm a)$$

$$\begin{aligned} \therefore E(\mathbf{k}) &= \varepsilon_s - J_0 - J_1 \left(\underbrace{e^{ik_x a} + e^{-ik_x a}}_{\downarrow} + \underbrace{e^{ik_y a} + e^{-ik_y a}}_{\swarrow} + \underbrace{e^{ik_z a} + e^{-ik_z a}}_{\searrow} \right) \\ &= \varepsilon_s - J_0 - 2J_1 \left(\cos k_x a + \cos k_y a + \cos k_z a \right) \end{aligned}$$

在简单立方晶格的简约区中

Γ 点: $\mathbf{k}=(0, 0, 0)$

$$E(\Gamma) = \varepsilon_s - J_0 - 6J_1$$

X点: $\mathbf{k}=(\pi/a, 0, 0)$

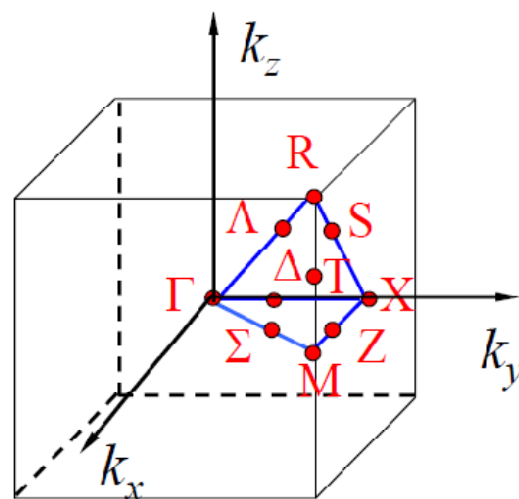
$$E(X) = \varepsilon_s - J_0 - 2J_1$$

R点: $\mathbf{k}=(\pi/a, \pi/a, \pi/a)$

$$E(R) = \varepsilon_s - J_0 + 6J_1$$

M点: $\mathbf{k}=(\pi/a, \pi/a, 0)$

$$E(M) = \varepsilon_s - J_0 + 2J_1$$

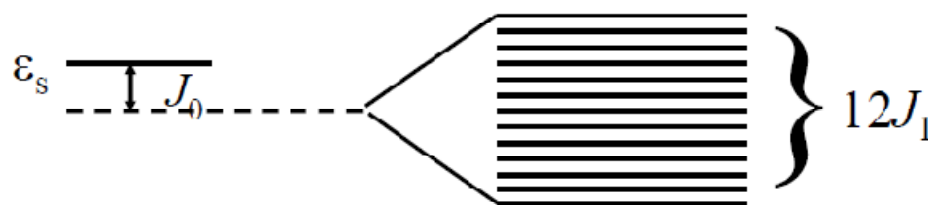


由于s态波函数是偶宇称, $\varphi_s(\mathbf{r}) = \varphi_s(-\mathbf{r})$, 所以, 在近邻重叠积分中波函数的贡献为正, 即 $J_1 > 0$ 。

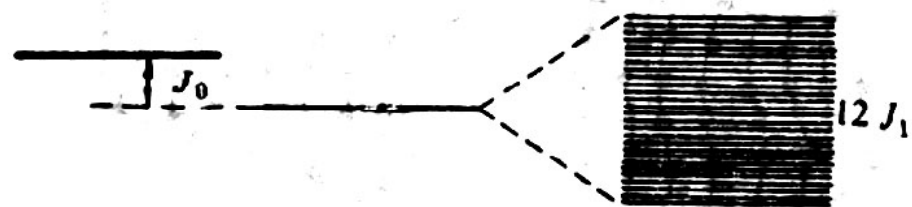
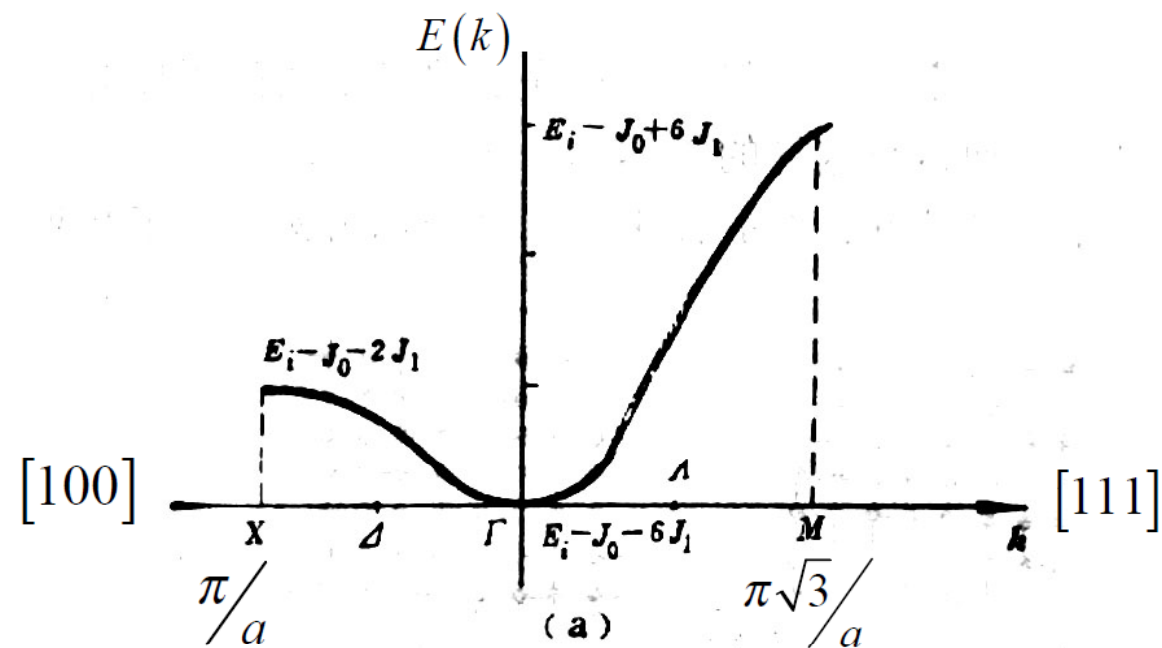
Γ 点和 R 点分别对于能带底和能带顶，所以，能带宽度

$$\Delta E = E(R) - E(\Gamma) = 12J_1$$

由此可见，能带的宽度决定于 J_1 ，而 J_1 的大小取决于近



邻原子波函数间的重叠，重叠越多，形成的能带就越宽。能量越低，能带就越窄；能量越高，能带就越宽。这是由于能量最低的带对应于最内层的电子，其电子轨道很小，不同原子间波函数的重叠很少，因而能带较窄；而能量较高的能带对应于外层电子，不同原子间波函数有较多的重叠，因此形成的能带就较宽。



(b)

简立方情形 (a) 能带和原子能级 E_i 之间的关系 (b) 原子能级分裂成能带

例3：求简单立方晶体由原子 p 态所形成的能带
原子的 p 态为三重简并，其原子轨道可表为

$$\left\{ \begin{array}{l} \varphi_{p_x} = x f(r) \\ \varphi_{p_y} = y f(r) \\ \varphi_{p_z} = z f(r) \end{array} \right.$$

在简单立方晶体中，三个 p 轨道各自形成一个能带，

其波函数是各自原子轨道的线性组合。

$$\left\{ \begin{array}{l} \psi_k^{p_x} = C \sum_{\ell} e^{i\mathbf{k} \cdot \mathbf{R}_{\ell}} \varphi_{p_x}(\mathbf{r} - \mathbf{R}_{\ell}) \\ \psi_k^{p_y} = C \sum_{\ell} e^{i\mathbf{k} \cdot \mathbf{R}_{\ell}} \varphi_{p_y}(\mathbf{r} - \mathbf{R}_{\ell}) \\ \psi_k^{p_z} = C \sum_{\ell} e^{i\mathbf{k} \cdot \mathbf{R}_{\ell}} \varphi_{p_z}(\mathbf{r} - \mathbf{R}_{\ell}) \end{array} \right.$$

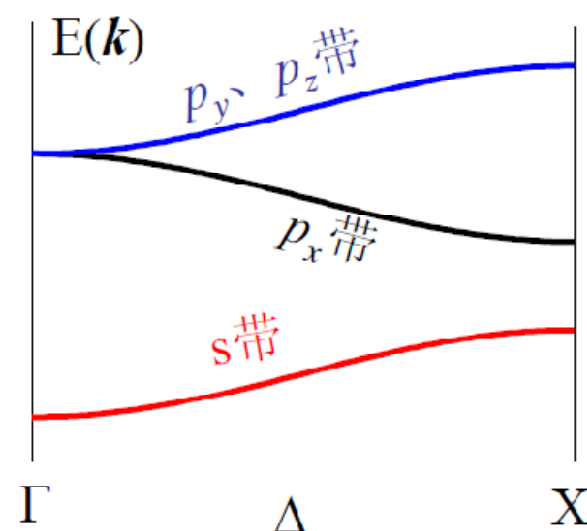
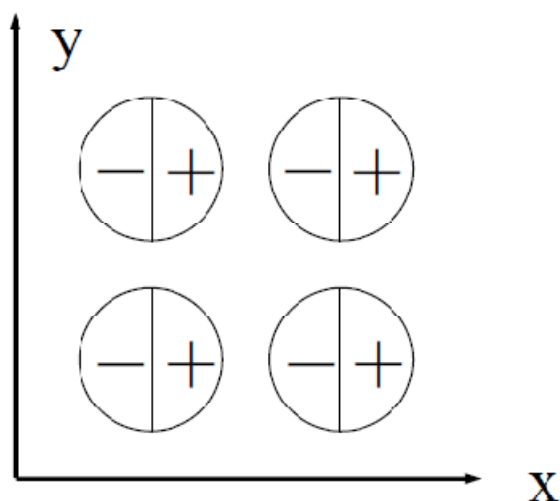
由于p轨道不是球对称的，因此，沿不同方向的近邻重叠积分 $J(\mathbf{R}_s)$ 不完全相同。如 φ_{p_x} ，电子主要集中在 x 轴方向，在六个近邻重叠积分中，沿 x 轴方向的重叠积分较大，用 J_1 表示；沿 y 方向和 z 方向的重叠积分用 J_2 表示。

$$E^{p_x}(\mathbf{k}) = \varepsilon_p - J_0 - 2J_1 \cos k_x a - 2J_2 (\cos k_y a + \cos k_z a)$$

$$E^{p_y}(\mathbf{k}) = \varepsilon_p - J_0 - 2J_1 \cos k_y a - 2J_2 (\cos k_z a + \cos k_x a)$$

$$E^{p_z}(\mathbf{k}) = \varepsilon_p - J_0 - 2J_1 \cos k_z a - 2J_2 (\cos k_x a + \cos k_y a)$$

由于原子的 p 态是奇宇称， $\varphi_{p_x}(-x) = -\varphi_{p_x}(x)$ ，所以， φ_{p_x} 沿 x 轴方向的重叠积分 $J_1 < 0$ ，而 $J_2 > 0$ 。



科研中常用的tight-binding方法简单步骤(假设 J_0 是个可以忽略的小量)



Hamiltonian

$$H = [E_0]$$

Eigenvalues:

$$E_1 = E_0$$



$$H = \begin{pmatrix} E_0 & J_1 \\ J_1 & E_0 \end{pmatrix}$$

Eigenvalues:

$$E_1 = E_0 + J_1$$

$$E_2 = E_0 - J_1$$



$$H = \begin{pmatrix} E_0 & J_1 & J_1 \\ J_1 & E_0 & J_1 \\ J_1 & J_1 & E_0 \end{pmatrix}$$

Eigenvalues:

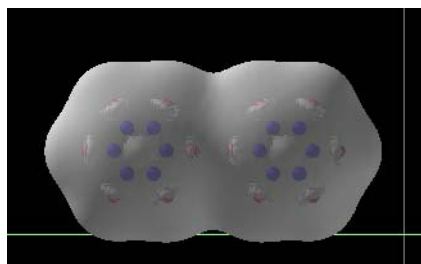
$$E_1 = E_0 - 2J_1$$

$$E_2 = E_0 + J_1$$

$$E_3 = E_0 + J_1$$

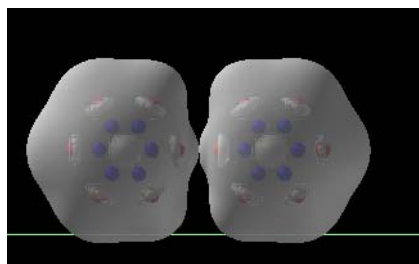
J_1 is the orbital interaction between the nearest neighbours

J_1 即波函数重叠积分



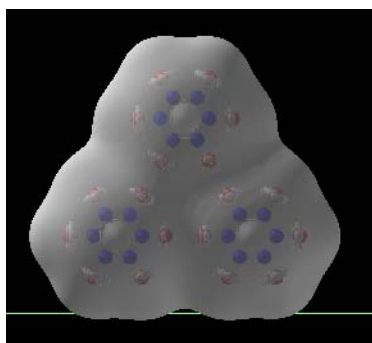
$$\varphi_1 = \frac{\sqrt{2}}{2} \varphi_0(r_1) + \frac{\sqrt{2}}{2} \varphi_0(r_2)$$

$$E_1 = E_0 - J_1$$



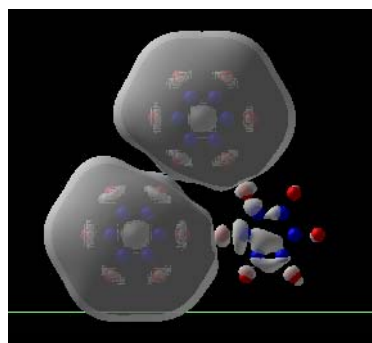
$$\varphi_2 = \frac{\sqrt{2}}{2} \varphi_0(r_1) - \frac{\sqrt{2}}{2} \varphi_0(r_2)$$

$$E_1 = E_0 + J_1$$



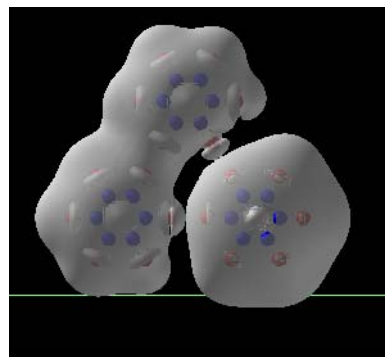
$$\varphi_1 = \frac{\sqrt{3}}{3} \varphi_0(r_1) + \frac{\sqrt{3}}{3} \varphi_0(r_2) + \frac{\sqrt{3}}{3} \varphi_0(r_3)$$

$$E_1 = E_0 - 2J_1$$



$$\varphi_2 = \frac{\sqrt{2}}{2} \varphi_0(r_1) - \frac{\sqrt{2}}{2} \varphi_0(r_2)$$

$$E_1 = E_0 + J_1$$

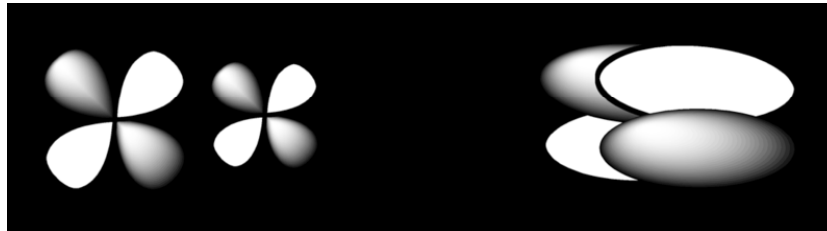


$$\varphi_3 = -\frac{1}{\sqrt{6}} \varphi_0(r_1) - \frac{1}{\sqrt{6}} \varphi_0(r_2) + \frac{2}{\sqrt{6}} \varphi_0(r_3)$$

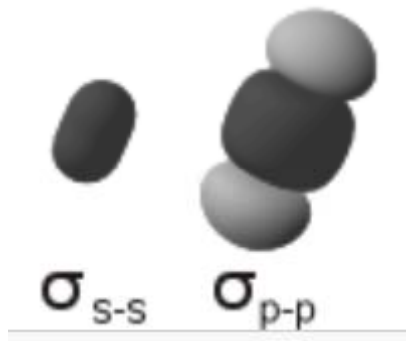
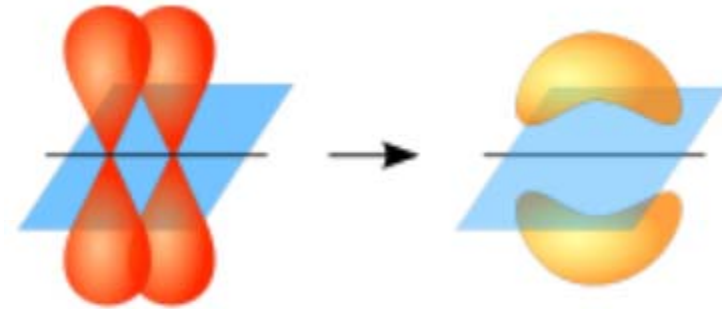
$$E_1 = E_0 + J_1$$

重叠积分 J_1 的算法：通常由实验曲线拟合得到或第一性原理计算得到

例如：如果我们知道 $V_{ss\sigma}$, $V_{pp\pi}$ and $V_{dd\delta}$ 就可以得到不同轨道的重叠积分



δ bond



$$E_{s,s} = V_{ss\sigma}$$

$$E_{s,x} = lV_{sp\sigma}$$

$$E_{x,x} = l^2V_{pp\sigma} + (1 - l^2)V_{pp\pi}$$

$$E_{x,y} = lmV_{pp\sigma} - lmV_{pp\pi}$$

$$E_{x,z} = lnV_{pp\sigma} - lnV_{pp\pi}$$

$$E_{s,xy} = \sqrt{3}lmV_{sd\sigma}$$

$$E_{s,x^2-y^2} = \frac{\sqrt{3}}{2}(l^2 - m^2)V_{sd\sigma}$$

$$E_{s,3z^2-r^2} = [n^2 - (l^2 + m^2)/2]V_{sd\sigma}$$

$$E_{x,xy} = \sqrt{3}l^2mV_{pd\sigma} + m(1 - 2l^2)V_{pd\pi}$$

$$E_{x,yz} = \sqrt{3}lmnV_{pd\sigma} - 2lmnV_{pd\pi}$$

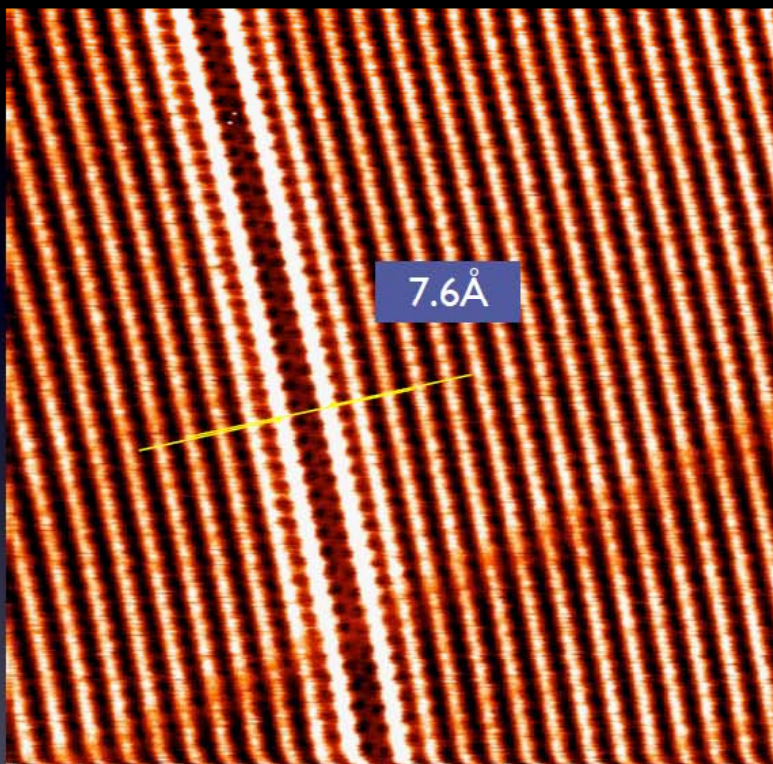
$$E_{x,zx} = \sqrt{3}l^2nV_{pd\sigma} + n(1 - 2l^2)V_{pd\pi}$$

$$E_{x,x^2-y^2} = \frac{\sqrt{3}}{2}l(l^2 - m^2)V_{pd\sigma} + l(1 - l^2 + m^2)V_{pd\pi}$$

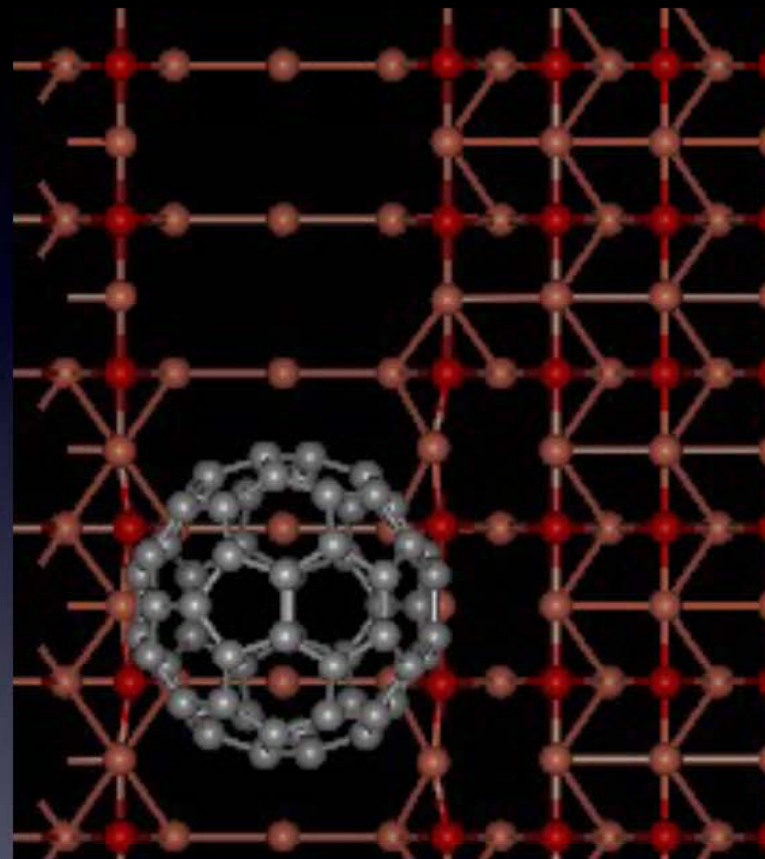
Walter Ashley Harrison (1989).

[Electronic Structure and the Properties of Solids.](#)

C_{60} molecules will be our atoms!



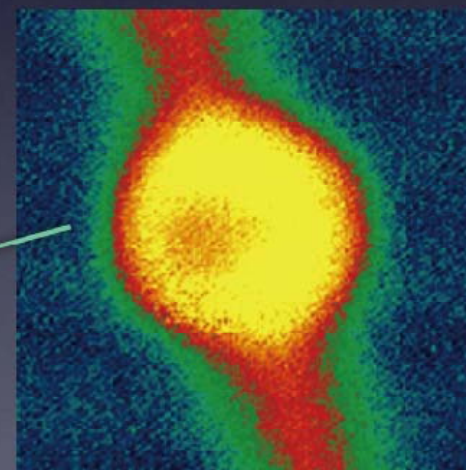
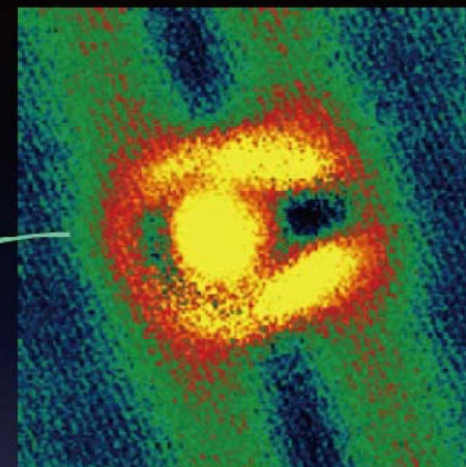
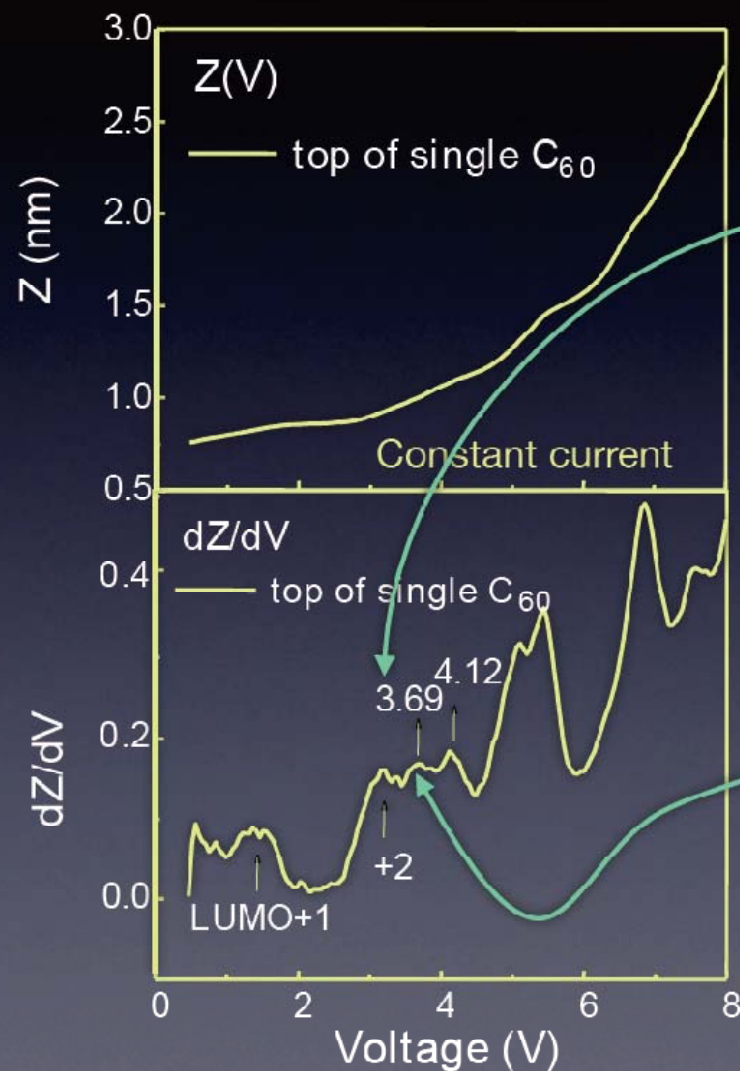
Cu(110)-(2x1)-O 10×10nm template



Measuring the local density of state of single C_{60} molecules

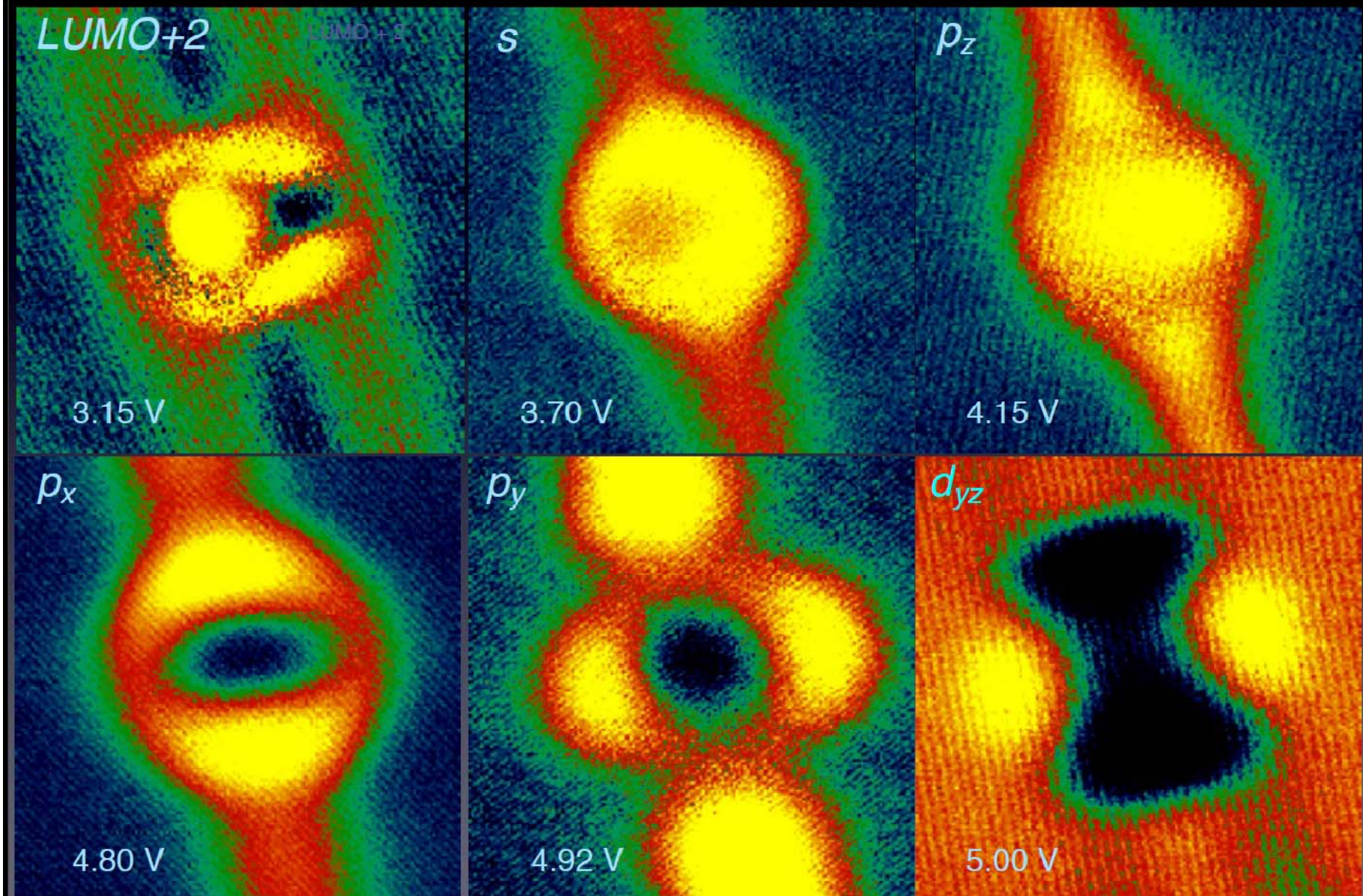


Single C_{60} Topography



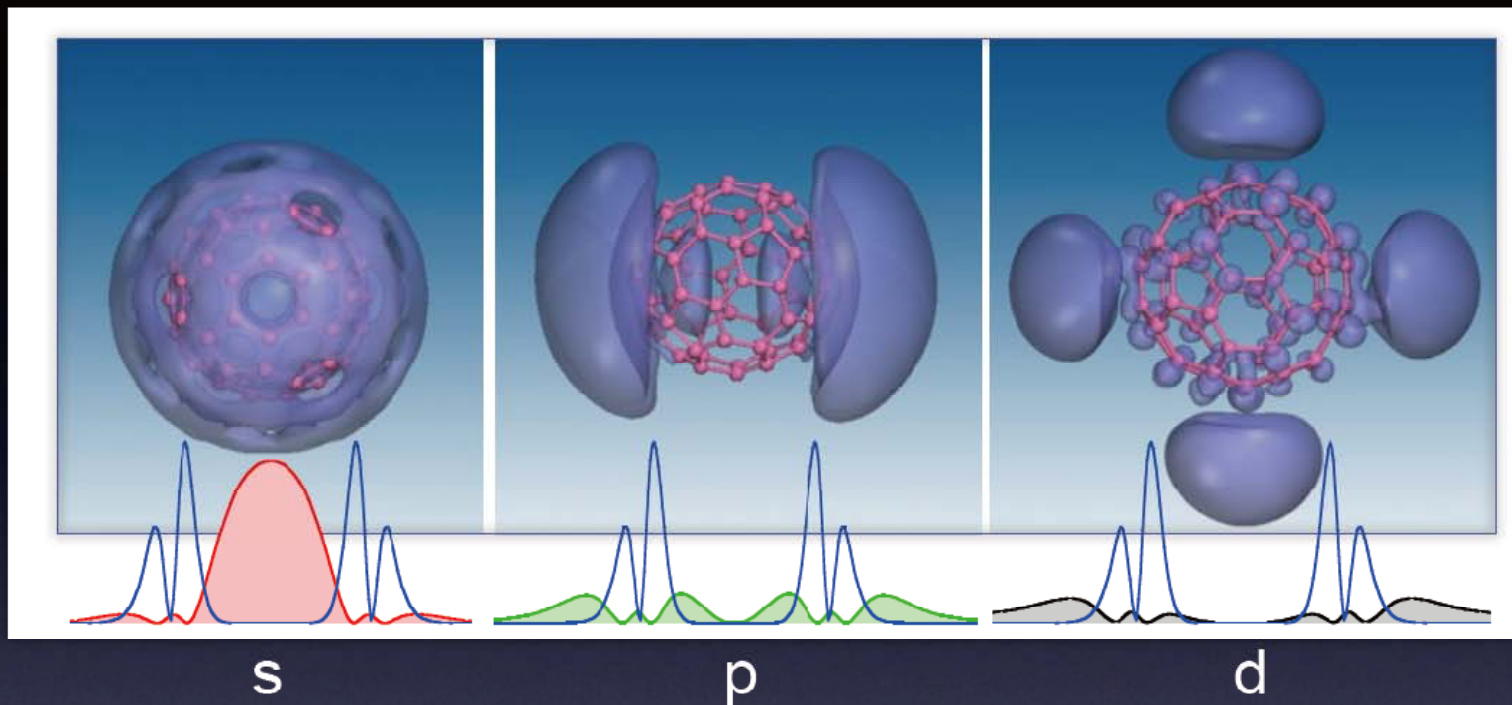
We found our atoms - superatom orbitals of C_{60}

Science 320, 359 (2008)

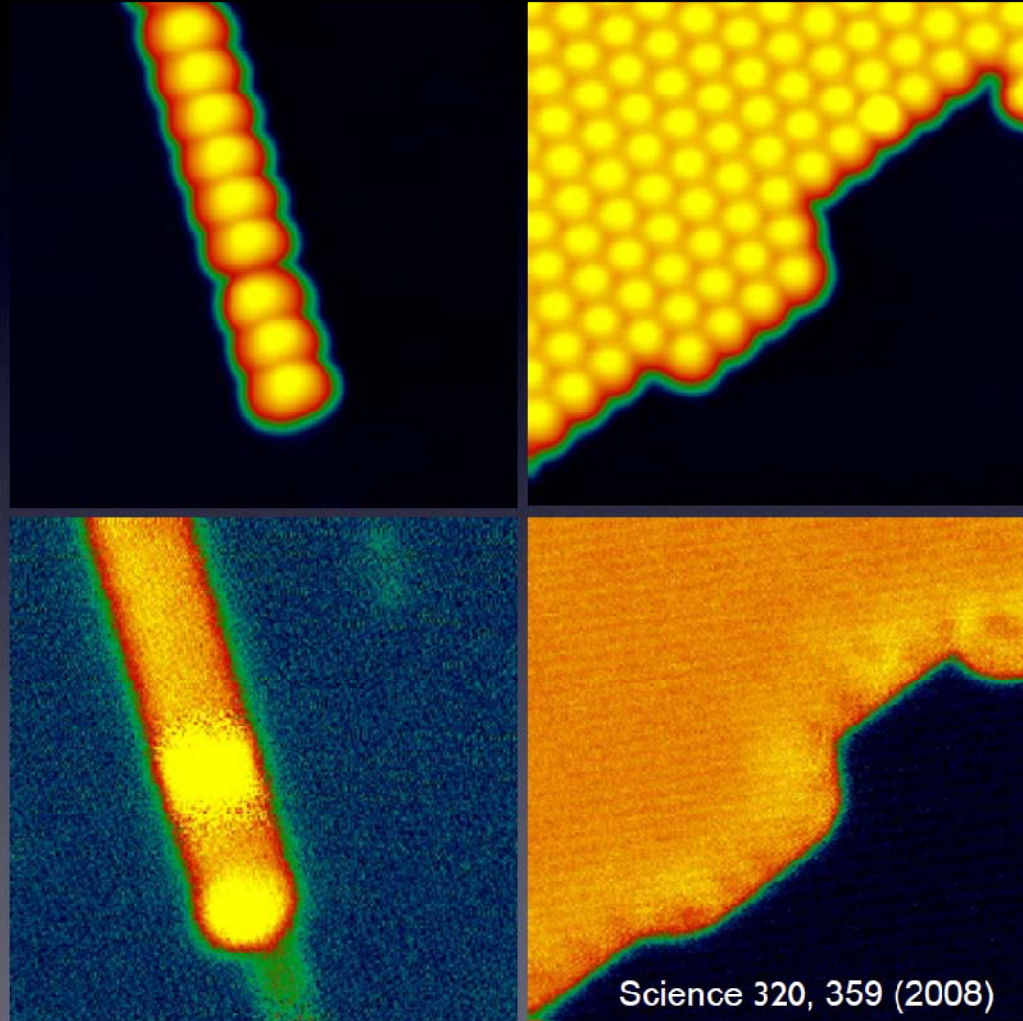


Superatom orbitals of C_{60} molecules

C_{60}
superatom
molecular
orbitals
(SAMO)

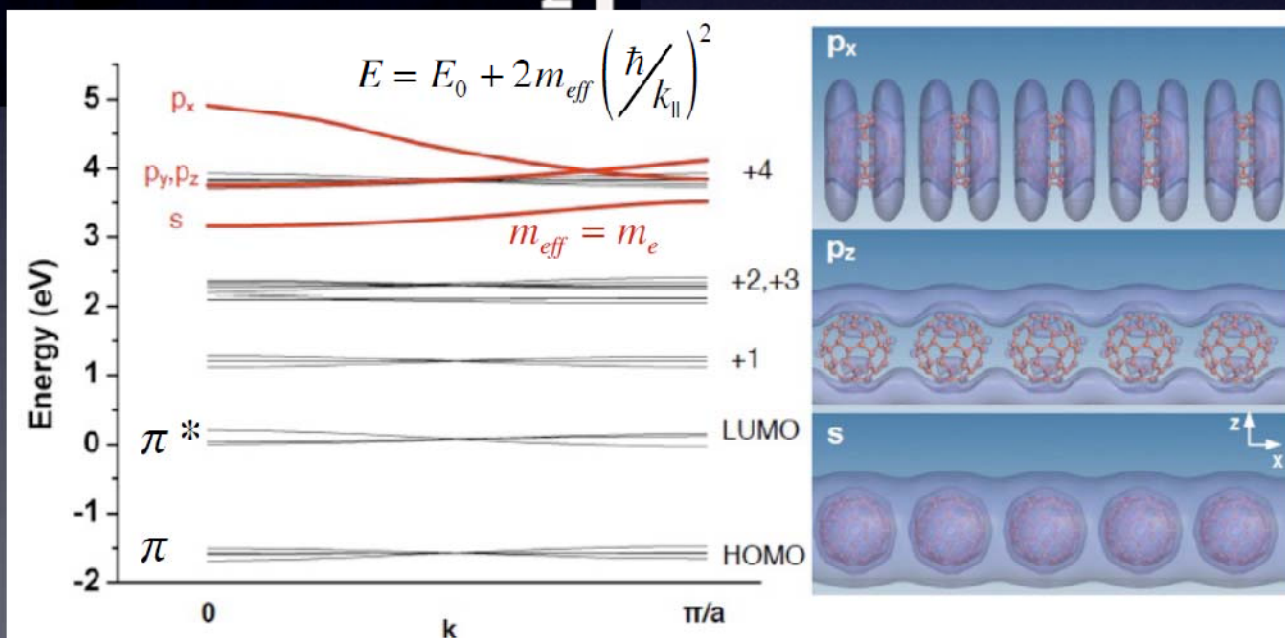
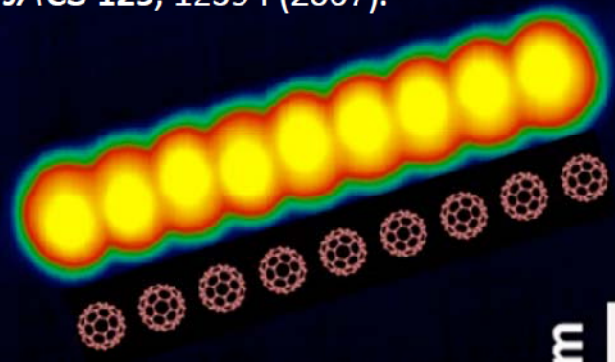


1D and 2D electron delocalization in C_{60} aggregates



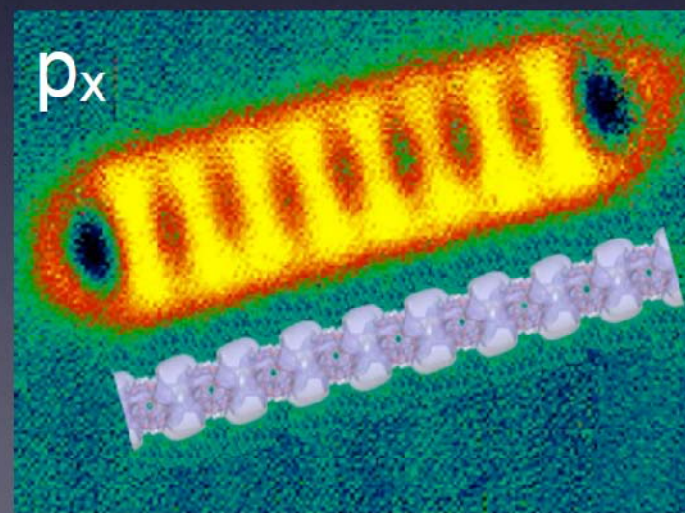
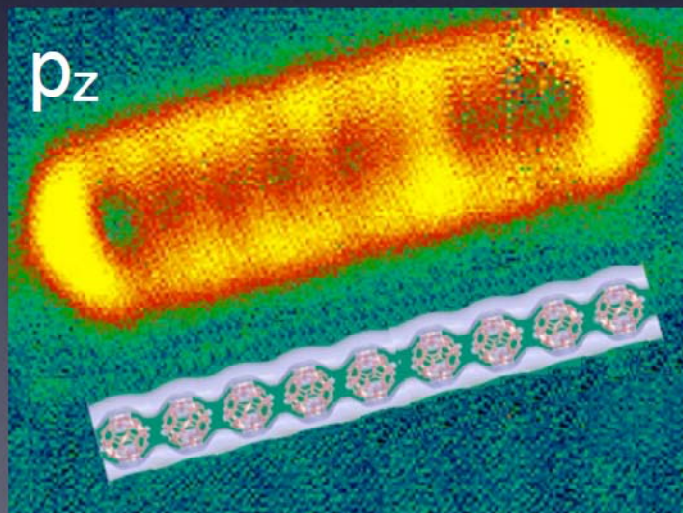
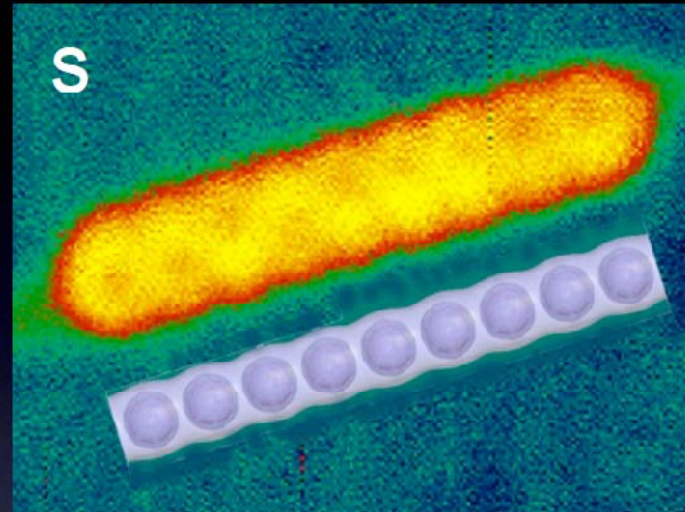
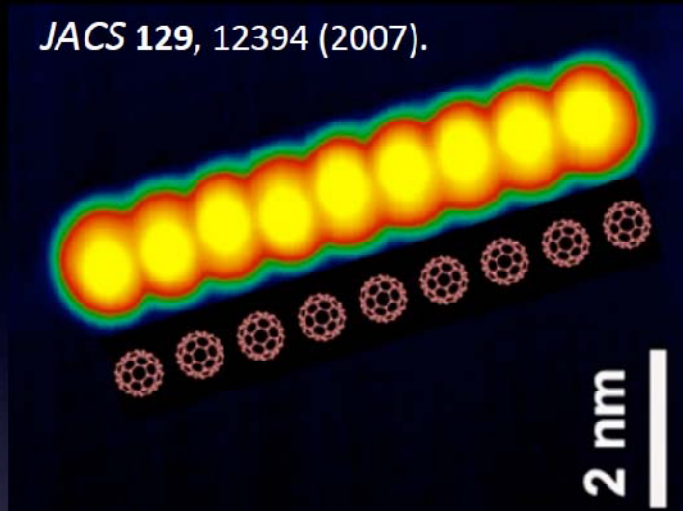
1D band formation in C₆₀ single molecule lines

JACS 129, 12394 (2007).

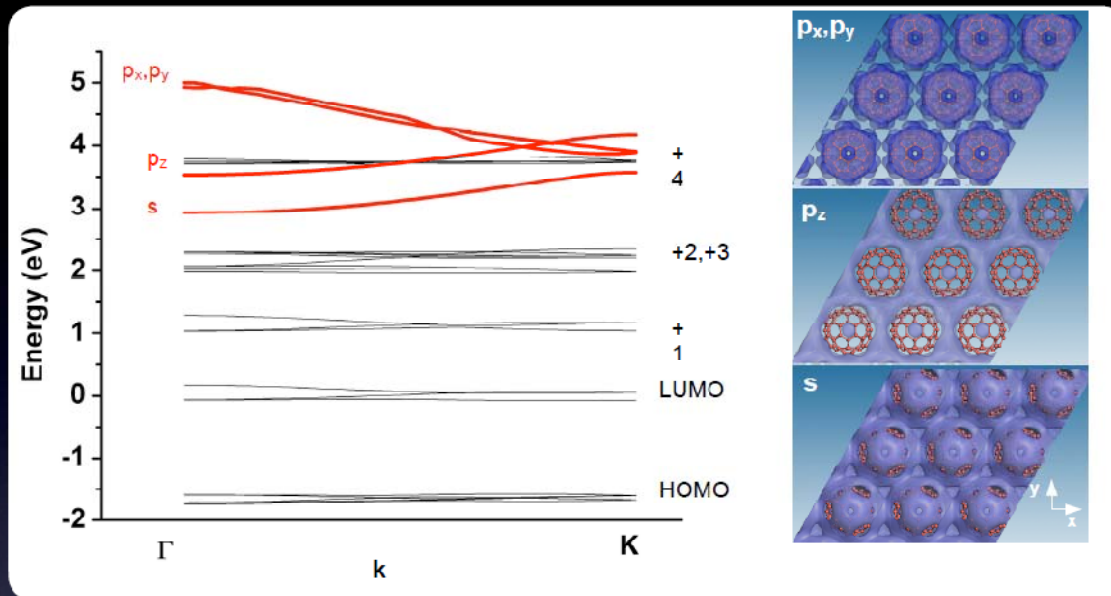


1D band formation in C_{60} single molecule lines

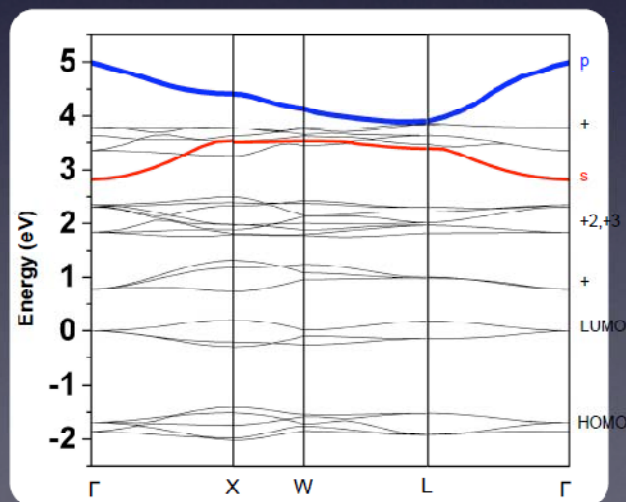
JACS 129, 12394 (2007).



2D superatom bands



3D superatom band



✿ 单胞中有两个原子，则布洛赫态可以写成

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{s=1}^2 c_s \left[\frac{1}{\sqrt{N_c}} \sum_L e^{i\mathbf{k} \cdot \mathbf{R}_L} \phi_s(\mathbf{r} - \mathbf{R}_L - \boldsymbol{\tau}_s) \right] = \sum_{s=1}^2 c_s \phi_{s,\mathbf{k}}(\mathbf{r}) \quad (31)$$

✿ 代入单电子薛定谔方程，我们得到

$$\hat{H} \left[\sum_{s=1}^2 c_s |\phi_{s,\mathbf{k}}(\mathbf{r})\rangle \right] = \epsilon_{\mathbf{k}} \left[\sum_{s=1}^2 c_s |\phi_{s,\mathbf{k}}(\mathbf{r})\rangle \right] \quad (32)$$

✿ 在上式两边乘上 $\langle \phi_{t,\mathbf{k}}(\mathbf{r}) |$

$$\begin{aligned} \langle \phi_{t,\mathbf{k}}(\mathbf{r}) | \cdot \hat{H} \left[\sum_{s=1}^2 c_s |\phi_{s,\mathbf{k}}(\mathbf{r})\rangle \right] &= \epsilon_{\mathbf{k}} \langle \phi_{t,\mathbf{k}}(\mathbf{r}) | \cdot \left[\sum_{s=1}^2 c_s |\phi_{s,\mathbf{k}}(\mathbf{r})\rangle \right] \\ \Rightarrow \sum_{s=1}^2 \langle \phi_{t,\mathbf{k}}(\mathbf{r}) | \hat{H} | \phi_{s,\mathbf{k}}(\mathbf{r}) \rangle \cdot c_s &= \epsilon_{\mathbf{k}} \sum_{s=1}^2 \langle \phi_{t,\mathbf{k}}(\mathbf{r}) | \phi_{s,\mathbf{k}}(\mathbf{r}) \rangle \cdot c_s \end{aligned} \quad (33)$$

✿ 单胞中有两个原子，则布洛赫态可以写成

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{s=1}^2 c_s \left[\frac{1}{\sqrt{N_c}} \sum_L e^{i\mathbf{k} \cdot \mathbf{R}_L} \phi_s(\mathbf{r} - \mathbf{R}_L - \boldsymbol{\tau}_s) \right] = \sum_{s=1}^2 c_s \phi_{s,\mathbf{k}}(\mathbf{r}) \quad (31)$$

✿ 代入单电子薛定谔方程，我们得到

$$\hat{\mathcal{H}} \left[\sum_{s=1}^2 c_s |\phi_{s,\mathbf{k}}(\mathbf{r})\rangle \right] = \epsilon_{\mathbf{k}} \left[\sum_{s=1}^2 c_s |\phi_{s,\mathbf{k}}(\mathbf{r})\rangle \right] \quad (32)$$

✿ 写成矩阵方程

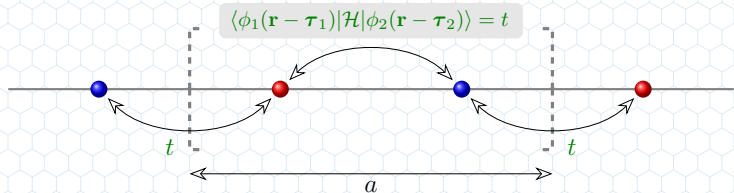
$$\begin{bmatrix} H_{11}(\mathbf{k}) & H_{12}(\mathbf{k}) \\ H_{21}(\mathbf{k}) & H_{22}(\mathbf{k}) \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \epsilon_{\mathbf{k}} \begin{bmatrix} S_{11}(\mathbf{k}) & S_{12}(\mathbf{k}) \\ S_{21}(\mathbf{k}) & S_{22}(\mathbf{k}) \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} \quad (34)$$

其中

$$H_{st}(\mathbf{k}) = \langle \phi_{s,\mathbf{k}}(\mathbf{r}) | \hat{\mathcal{H}} | \phi_{t,\mathbf{k}}(\mathbf{r}) \rangle = \sum_M \langle \phi_s(\mathbf{r} - \boldsymbol{\tau}_s) | \hat{\mathcal{H}} | \phi_t(\mathbf{r} - \boldsymbol{\tau}_t - \mathbf{R}_M) \rangle e^{i\mathbf{k} \cdot \mathbf{R}_M} \quad (35)$$

$$S_{st}(\mathbf{k}) = \langle \phi_{s,\mathbf{k}}(\mathbf{r}) | \phi_{t,\mathbf{k}}(\mathbf{r}) \rangle = \sum_M \langle \phi_s(\mathbf{r} - \boldsymbol{\tau}_s) | \phi_t(\mathbf{r} - \boldsymbol{\tau}_t - \mathbf{R}_M) \rangle e^{i\mathbf{k} \cdot \mathbf{R}_M} \approx \delta_{st} \quad (36)$$

一维单带、双原子紧束缚模型



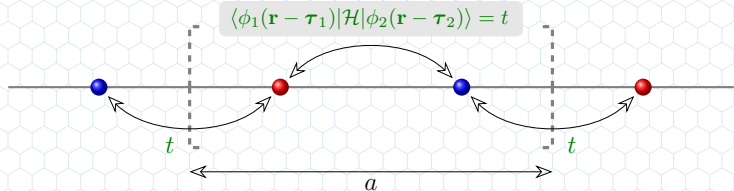
✿ 在最近邻近下，我们可以得到以下矩阵元

$$\begin{aligned} H_{11}(\mathbf{k}) &= \sum_M \langle \phi_1(\mathbf{r} - \boldsymbol{\tau}_1) | \hat{\mathcal{H}} | \phi_1(\mathbf{r} - \boldsymbol{\tau}_1 - \mathbf{R}_M) \rangle e^{i\mathbf{k} \cdot \mathbf{R}_M} \\ &= \langle \phi_1(\mathbf{r} - \boldsymbol{\tau}_1) | \hat{\mathcal{H}} | \phi_1(\mathbf{r} - \boldsymbol{\tau}_1) \rangle = \epsilon_1 \end{aligned} \quad (37)$$

$$H_{22}(\mathbf{k}) = \langle \phi_2(\mathbf{r} - \boldsymbol{\tau}_2) | \hat{\mathcal{H}} | \phi_2(\mathbf{r} - \boldsymbol{\tau}_2) \rangle = \epsilon_2 \quad (38)$$

$$\begin{aligned} H_{12}(\mathbf{k}) &= \sum_M \langle \phi_1(\mathbf{r} - \boldsymbol{\tau}_1) | \hat{\mathcal{H}} | \phi_2(\mathbf{r} - \boldsymbol{\tau}_2 - \mathbf{R}_M) \rangle e^{i\mathbf{k} \cdot \mathbf{R}_M} \\ &= \langle \phi_1(\mathbf{r} - \boldsymbol{\tau}_1) | \hat{\mathcal{H}} | \phi_2(\mathbf{r} - \boldsymbol{\tau}_2) \rangle + \langle \phi_1(\mathbf{r} - \boldsymbol{\tau}_1) | \hat{\mathcal{H}} | \phi_2(\mathbf{r} - \boldsymbol{\tau}_2 + a) \rangle e^{-ik \cdot a} \\ &= t + te^{-ika} = H_{21}(\mathbf{k})^* \end{aligned} \quad (39)$$

一维单带、双原子紧束缚模型



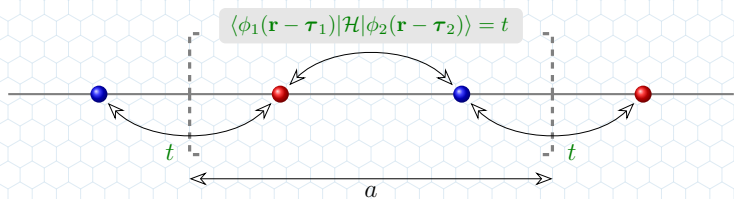
✿ 于是，矩阵本征值方程变成

$$\begin{bmatrix} \epsilon_1 - \epsilon_{\mathbf{k}} & t[1 + e^{-ika}] \\ t[1 + e^{ika}] & \epsilon_2 - \epsilon_{\mathbf{k}} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \quad (40)$$

矩阵对角化之后，得到

$$\epsilon_{\pm} = \frac{\epsilon_1 + \epsilon_2}{2} \pm \frac{1}{2} \sqrt{(\epsilon_1 - \epsilon_2)^2 + 8t^2(1 + \cos(ka))} \quad (41)$$

一维单带、双原子紧束缚模型



✿ 色散关系如下

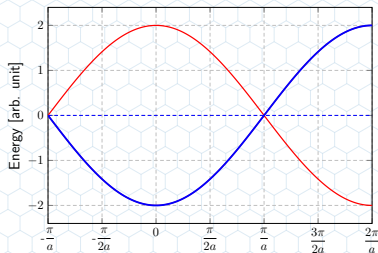
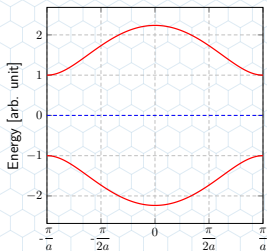
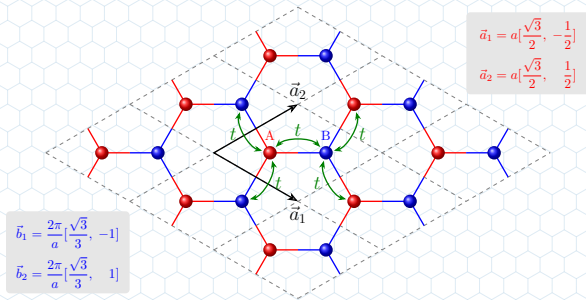


图 — 一维单带、双原子链紧束缚模型的色散关系：左图中 $\epsilon_1 \neq \epsilon_2$ ，右图中 $\epsilon_1 = \epsilon_2$ 。

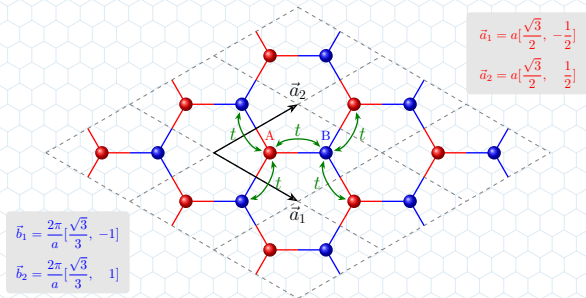
蜂巢格子紧束缚模型



✿ 在最近邻近下，我们可以得到以下矩阵元

$$\begin{aligned}
 H_{12}(\mathbf{k}) &= \sum_M \langle \phi_1(\mathbf{r} - \boldsymbol{\tau}_1) | \hat{\mathcal{H}} | \phi_2(\mathbf{r} - \boldsymbol{\tau}_2 - \mathbf{R}_M) \rangle e^{i\mathbf{k} \cdot \mathbf{R}_M} \\
 &= \langle \phi_1(\mathbf{r} - \boldsymbol{\tau}_1) | \hat{\mathcal{H}} | \phi_2(\mathbf{r} - \boldsymbol{\tau}_2) \rangle + \langle \phi_1(\mathbf{r} - \boldsymbol{\tau}_1) | \hat{\mathcal{H}} | \phi_2(\mathbf{r} - \boldsymbol{\tau}_2) \rangle e^{-i\mathbf{k} \cdot \mathbf{a}_1} \\
 &\quad + \langle \phi_1(\mathbf{r} - \boldsymbol{\tau}_1) | \hat{\mathcal{H}} | \phi_2(\mathbf{r} - \boldsymbol{\tau}_2) \rangle e^{-i\mathbf{k} \cdot \mathbf{a}_2} \\
 &= t \left[1 + e^{-i\mathbf{k} \cdot \mathbf{a}_1} + e^{-i\mathbf{k} \cdot \mathbf{a}_2} \right]
 \end{aligned} \tag{42}$$

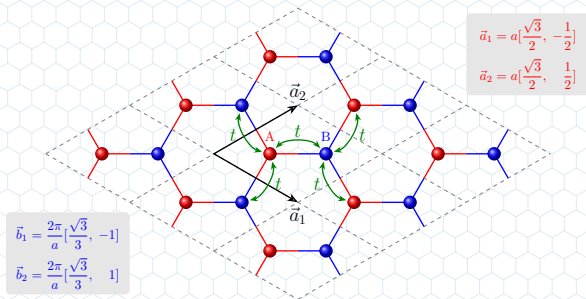
蜂巢格子紧束缚模型



✿ 在最近邻近似下，我们可以得到以下矩阵元

$$\begin{aligned}
 H_{21}(\mathbf{k}) &= \sum_M \langle \phi_2(\mathbf{r} - \boldsymbol{\tau}_2) | \hat{\mathcal{H}} | \phi_1(\mathbf{r} - \boldsymbol{\tau}_1 - \mathbf{R}_M) \rangle e^{i\mathbf{k} \cdot \mathbf{R}_M} \\
 &= \langle \phi_2(\mathbf{r} - \boldsymbol{\tau}_2) | \hat{\mathcal{H}} | \phi_1(\mathbf{r} - \boldsymbol{\tau}_1) \rangle + \langle \phi_2(\mathbf{r} - \boldsymbol{\tau}_2) | \hat{\mathcal{H}} | \phi_1(\mathbf{r} - \boldsymbol{\tau}_1) \rangle e^{i\mathbf{k} \cdot \mathbf{a}_1} \\
 &\quad + \langle \phi_2(\mathbf{r} - \boldsymbol{\tau}_2) | \hat{\mathcal{H}} | \phi_1(\mathbf{r} - \boldsymbol{\tau}_1) \rangle e^{i\mathbf{k} \cdot \mathbf{a}_2} \\
 &= t \left[1 + e^{i\mathbf{k} \cdot \mathbf{a}_1} + e^{i\mathbf{k} \cdot \mathbf{a}_2} \right]
 \end{aligned} \tag{43}$$

蜂巢格子紧束缚模型



✿ 于是，矩阵本征值方程变成

$$\begin{bmatrix} \epsilon_1 - \epsilon_k & t[1 + e^{-i\mathbf{k} \cdot \mathbf{a}_1} + e^{-i\mathbf{k} \cdot \mathbf{a}_2}] \\ t[1 + e^{i\mathbf{k} \cdot \mathbf{a}_1} + e^{i\mathbf{k} \cdot \mathbf{a}_2}] & \epsilon_2 - \epsilon_k \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \quad (44)$$

✿ 假设 $\epsilon_1 = \epsilon_2 = \epsilon_0$ ，则可以容易算出上式的本征值为：

$$\begin{aligned}\epsilon_{\pm}(\mathbf{k}) &= \epsilon_0 \pm t\sqrt{[1 + e^{i\mathbf{k}\cdot\mathbf{a}_1} + e^{i\mathbf{k}\cdot\mathbf{a}_2}] \cdot [1 + e^{-i\mathbf{k}\cdot\mathbf{a}_1} + e^{-i\mathbf{k}\cdot\mathbf{a}_2}]} \\ &= \epsilon_0 \pm t\sqrt{[1 + e^{i\mathbf{k}\cdot\mathbf{a}_1} + e^{i\mathbf{k}\cdot\mathbf{a}_2}] + [e^{-i\mathbf{k}\cdot\mathbf{a}_1} + 1 + e^{-i\mathbf{k}\cdot(\mathbf{a}_2 - \mathbf{a}_1)}] + [e^{-i\mathbf{k}\cdot\mathbf{a}_2} + e^{-i\mathbf{k}\cdot(\mathbf{a}_1 - \mathbf{a}_2)} + 1]} \\ &= \epsilon_0 \pm t\sqrt{3 + 2\cos(\mathbf{k} \cdot \mathbf{a}_1) + 2\cos(\mathbf{k} \cdot \mathbf{a}_2) + 2\cos(\mathbf{k} \cdot (\mathbf{a}_1 - \mathbf{a}_2))}\end{aligned}\quad (45)$$

而 $\mathbf{a}_1$ 和 $\mathbf{a}_2$ 定义为

$$\begin{aligned}\vec{a}_1 &= a\left[\frac{\sqrt{3}}{2}, -\frac{1}{2}\right] \\ \vec{a}_2 &= a\left[\frac{\sqrt{3}}{2}, \frac{1}{2}\right]\end{aligned}\quad (46)$$

于是我们得到

$$\epsilon_{\pm}(\mathbf{k}) = \epsilon_0 \pm t\sqrt{3 + 2\cos\left[\frac{\sqrt{3}}{2}k_x a - \frac{1}{2}k_y a\right] + 2\cos\left[\frac{\sqrt{3}}{2}k_x a + \frac{1}{2}k_y a\right] + 2\cos[k_y a]}\quad (47)$$

利用公式

$$\cos(x \pm y) = \cos(x)\cos(y) \mp \sin(x)\sin(y); \quad 1 + \cos(x) = 2\cos^2\left(\frac{x}{2}\right)\quad (48)$$

✿ 整理之后，我们得到蜂巢格子紧束缚近似下的色散关系

$$\epsilon_{\pm}(\mathbf{k}) = \epsilon_0 \pm t \sqrt{1 + 4 \cos^2 \left[\frac{k_y a}{2} \right] + 4 \cos \left[\frac{k_y a}{2} \right] \cos \left[\frac{\sqrt{3} k_x a}{2} \right]} \quad (49)$$

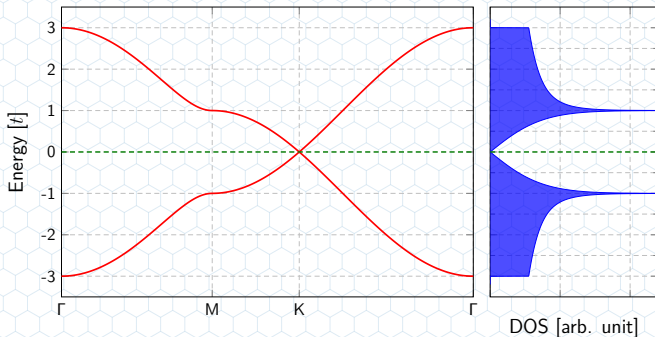


图 - 紧束缚模型下的石墨烯能带（左）以及态密度（右）。⁵

⁵ 石墨烯三维色散关系图: <http://staff.ustc.edu.cn/~zqj/posts/Plotly-TB-Graphene/>

石墨烯狄拉克点附近色散关系

✿ 在六角格子布里渊区高对称点 K/K' 附近, $\mathbf{k}$ 可以写成

$$\mathbf{k} = \mathbf{K} + \mathbf{q} \quad \begin{pmatrix} \mathbf{K} = \frac{1}{3}\mathbf{b}_1 + \frac{2}{3}\mathbf{b}_2 \\ \mathbf{K}' = \frac{2}{3}\mathbf{b}_1 + \frac{1}{3}\mathbf{b}_2 \end{pmatrix}$$

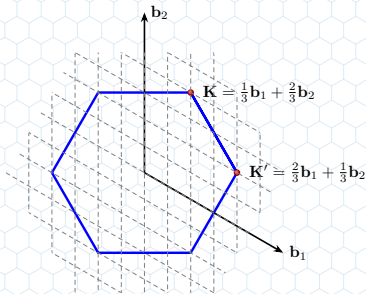
因此, 在 K 附近 ($|\mathbf{q}| \approx 0$) $H_{12}(\mathbf{k})$ 可以写成:

$$\begin{aligned} H_{12}(\mathbf{k}) &= t \left[1 + e^{-i(\mathbf{K}+\mathbf{q}) \cdot \mathbf{a}_1} + e^{-i(\mathbf{K}+\mathbf{q}) \cdot \mathbf{a}_2} \right] \\ &= t \left[1 + e^{-i\frac{2}{3}\pi} e^{-i\mathbf{q} \cdot \mathbf{a}_1} + e^{-i\frac{4}{3}\pi} e^{-i\mathbf{q} \cdot \mathbf{a}_2} \right] \\ &\approx t \left[1 + \left[-\frac{1}{2} - i\frac{\sqrt{3}}{2} \right] [1 + i\mathbf{q} \cdot \mathbf{a}_1] + \left[-\frac{1}{2} + i\frac{\sqrt{3}}{2} \right] [1 + i\mathbf{q} \cdot \mathbf{a}_2] \right] \\ &= \frac{\sqrt{3}}{2} at [-iq_x - q_y] = H_{21}(\mathbf{k})^* \end{aligned} \quad (50)$$

于是, 在 K/K' 附近, 色散关系 $\epsilon(\mathbf{q})$ 变成:

$$\epsilon(\mathbf{q}) = \pm |H_{12}(\mathbf{q})| = \pm \frac{\sqrt{3}}{2} at \cdot |\mathbf{q}| \quad (51)$$

✿ 即在 K 附近, 色散关系是**线性的**, 因此态密度 $\rho(\epsilon) \propto \epsilon$, 也是**线性的**。



✿ 在 K/K' 点附近，石墨烯的色散是线性的

$$\epsilon_{n\mathbf{k}} = \pm \frac{\sqrt{3}}{2} at |\mathbf{k} - \mathbf{K}| \quad (52)$$

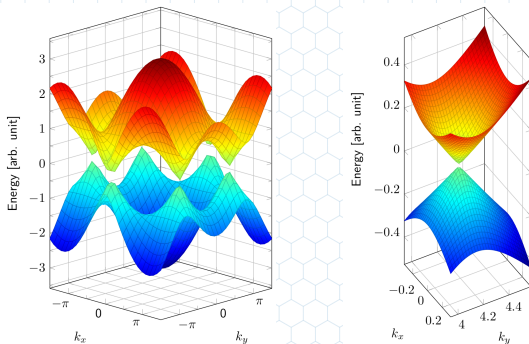


图 — 紧束缚近似下石墨烯的能带（左），以及在狄拉克点附近的局部能带（右）。

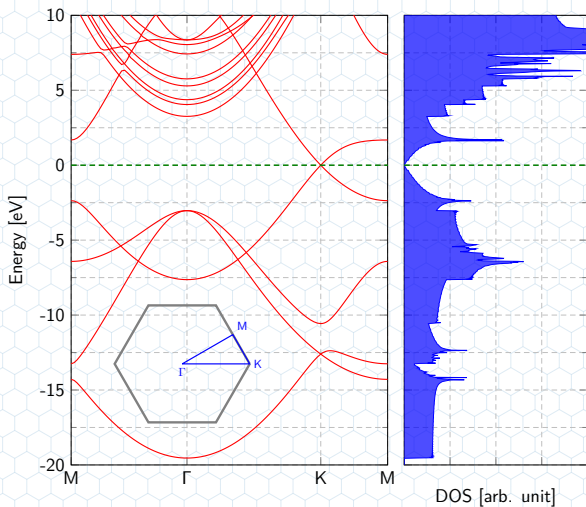
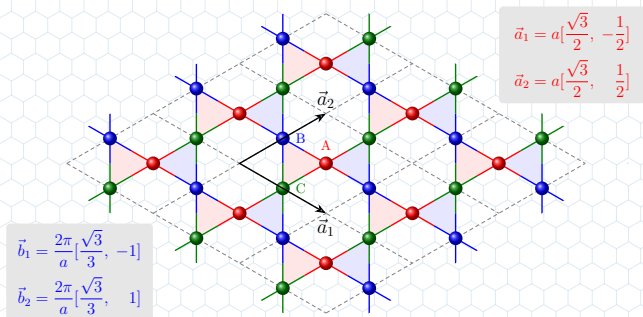


图 – DFT 计算得到的石墨烯**能带**（左）以及**态密度**（右），由 VASP 计算得到。

笼目格子 (Kagome Lattice) 紧束缚模型



✿ 笼目格子 (*Kagome Lattice*)⁶在最近邻紧束缚近似下的哈密顿量为:

$$H(\mathbf{k}) = \epsilon_0 - t \begin{bmatrix} 0 & 1 + e^{i\mathbf{k} \cdot \mathbf{a}_1} & 1 + e^{i\mathbf{k} \cdot \mathbf{a}_2} \\ 1 + e^{-i\mathbf{k} \cdot \mathbf{a}_1} & 0 & 1 + e^{i\mathbf{k} \cdot (\mathbf{a}_2 - \mathbf{a}_1)} \\ 1 + e^{-i\mathbf{k} \cdot \mathbf{a}_2} & 1 + e^{i\mathbf{k} \cdot (\mathbf{a}_1 - \mathbf{a}_2)} & 0 \end{bmatrix} \quad (53)$$

⁶Kagome 是日语“笼目”的罗马音。

✿ 易得如下关系：

$$H = \begin{bmatrix} -\lambda & a & b \\ a^\dagger & -\lambda & c \\ b^\dagger & c^\dagger & -\lambda \end{bmatrix} \quad (54)$$

$$\Rightarrow \det(H) = -\lambda^3 + [a^\dagger a + b^\dagger b + c^\dagger c] \lambda + ab^\dagger c + a^\dagger bc^\dagger \quad (55)$$

其中

$$a = 1 + e^{i\mathbf{k} \cdot \mathbf{a}_1}; \quad b = 1 + e^{i\mathbf{k} \cdot \mathbf{a}_2}; \quad c = 1 + e^{i\mathbf{k} \cdot (\mathbf{a}_2 - \mathbf{a}_1)} \quad (56)$$

✿ 把 a, b, c 的值代进去，我们可以得到

$$a^\dagger a + b^\dagger b + c^\dagger c = 2 \cos(\mathbf{k} \cdot \mathbf{a}_1) + 2 \cos(\mathbf{k} \cdot \mathbf{a}_1) + 2 \cos(\mathbf{k} \cdot (\mathbf{a}_2 - \mathbf{a}_1)) + 6 \quad (57)$$

$$ab^\dagger c + a^\dagger bc^\dagger = 4 \cos(\mathbf{k} \cdot \mathbf{a}_1) + 4 \cos(\mathbf{k} \cdot \mathbf{a}_1) + 4 \cos(\mathbf{k} \cdot (\mathbf{a}_2 - \mathbf{a}_1)) + 4 \quad (58)$$

✿ 于是 H 矩阵的本征值可以通过 Sympy、Matlab 等工具求解 $\det(H) = 0$ 得到。

✿ 哈密顿量式(53)的本征值为:

$$\epsilon_1(\mathbf{k}) = \epsilon_0 + 2t \quad (59)$$

$$\epsilon_2(\mathbf{k}) = \epsilon_0 - t \left[1 - \sqrt{2 \cos(\mathbf{k} \cdot \mathbf{a}_1) + 2 \cos(\mathbf{k} \cdot \mathbf{a}_1) + 2 \cos(\mathbf{k} \cdot (\mathbf{a}_2 - \mathbf{a}_1)) + 3} \right] \quad (60)$$

$$\epsilon_3(\mathbf{k}) = \epsilon_0 - t \left[1 + \sqrt{2 \cos(\mathbf{k} \cdot \mathbf{a}_1) + 2 \cos(\mathbf{k} \cdot \mathbf{a}_1) + 2 \cos(\mathbf{k} \cdot (\mathbf{a}_2 - \mathbf{a}_1)) + 3} \right] \quad (61)$$

其中, $\epsilon_1(\mathbf{k})$ 是一个平带 (flat band), 而 $\epsilon_2(\mathbf{k})$ 和 $\epsilon_3(\mathbf{k})$ 和石墨烯紧束缚近似能带仅差一个平移量。

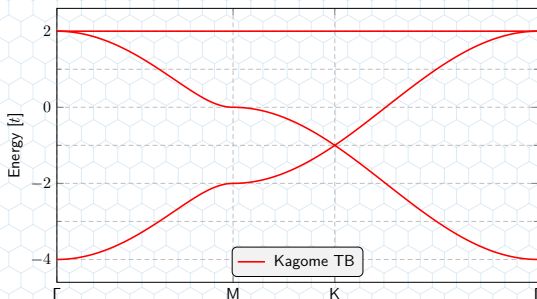


图 - 笼目格子紧束缚近似下的能带: 狄拉克锥与拓扑平带并存。

✿ 假设某一个能带 $\psi_{n\mathbf{k}}(\mathbf{r})$ 与其他能带不相交，则可以定义瓦尼尔函数 (Wannier Function) : 7

$$w(\mathbf{r} - \mathbf{R}_L) = \frac{1}{\sqrt{N_c}} \sum_{\mathbf{k} \in \text{BZ}} e^{-i\mathbf{k} \cdot \mathbf{R}_L} \psi_{n\mathbf{k}}(\mathbf{r}) \quad (62)$$

✿ 不同格点上的瓦尼尔函数是相互正交的，即

$$\int_{\text{crys}} w(\mathbf{r} - \mathbf{R}_L)^* w(\mathbf{r} - \mathbf{R}_P) d\mathbf{r} = \frac{1}{N_c} \sum_{\mathbf{k}, \mathbf{q} \in \text{BZ}} \int_{\text{crys}} e^{i\mathbf{k} \cdot \mathbf{R}_L} \psi_{n\mathbf{k}}(\mathbf{r})^* e^{-i\mathbf{q} \cdot \mathbf{R}_P} \psi_{n\mathbf{q}}(\mathbf{r}) d\mathbf{r} \quad (63)$$

$$= \frac{1}{N_c} \sum_{\mathbf{k}, \mathbf{q} \in \text{BZ}} e^{i\mathbf{k} \cdot \mathbf{R}_L} e^{-i\mathbf{q} \cdot \mathbf{R}_P} \times \left[\int_{\text{crys}} \psi_{n\mathbf{k}}(\mathbf{r})^* \psi_{n\mathbf{q}}(\mathbf{r}) d\mathbf{r} \right] \quad (64)$$

$$= \frac{1}{N_c} \sum_{\mathbf{k}, \mathbf{q} \in \text{BZ}} e^{i\mathbf{k} \cdot \mathbf{R}_L} e^{-i\mathbf{q} \cdot \mathbf{R}_P} \times \delta_{\mathbf{k}, \mathbf{q}} \quad (65)$$

$$= \frac{1}{N_c} \sum_{\mathbf{k} \in \text{BZ}} e^{i\mathbf{k} \cdot [\mathbf{R}_L - \mathbf{R}_P]} = \delta_{L, P} \quad (66)$$

7 "Maximally localized Wannier functions: Theory and applications", *Rev. Mod. Phys.*, **84**, 1419 (2012)

作业：黄昆书4.4, 4.5, 4.6