PY4T01 Condensed Matter Theory: Lecture 8

Density of States (DOS)

DOS is the *number of states S per unit energy E*

$$D(E) = \frac{\mathrm{d}S}{\mathrm{d}E} = \frac{\mathrm{d}S}{\mathrm{d}k} \cdot \left| \frac{\mathrm{d}k}{\mathrm{d}E} \right|$$

Example: H chain

Remember that for the N atom ring

$$E_k = \epsilon_0 + 2\gamma \cos ka, \quad k = \frac{2m\pi}{Na}$$

then the number of states per unit k is

$$\frac{\mathrm{d}S}{\mathrm{d}k} = 2 \cdot \frac{Na}{2\pi} = \frac{Na}{\pi}$$

and

$$\frac{\mathrm{d}E_k}{\mathrm{d}k} = 2a\gamma \sin ka$$

Hence

$$D(E) = \frac{Na}{\pi} \frac{1}{2a\gamma \sin ka} = \frac{N}{\pi} \frac{1}{[4\gamma^2 - (E - \epsilon_0)^2]^{1/2}}$$
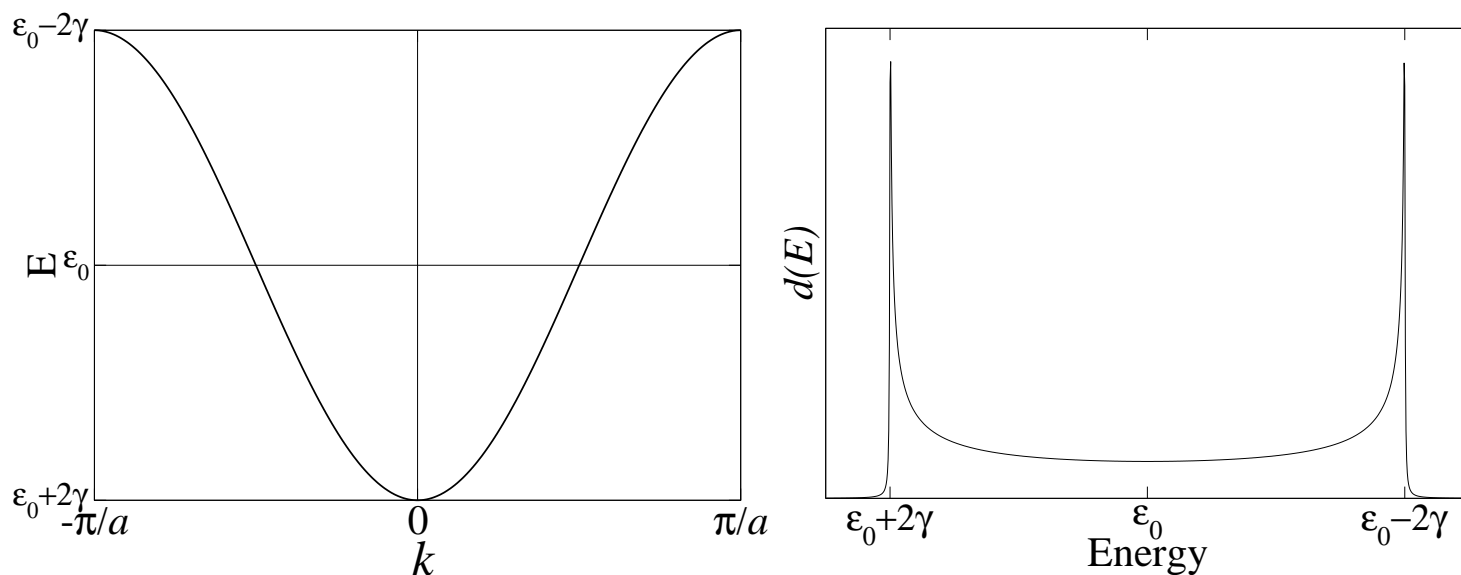
Note that:

$$\int_{-\infty}^{+\infty} D(E)\mathrm{d}E = N$$

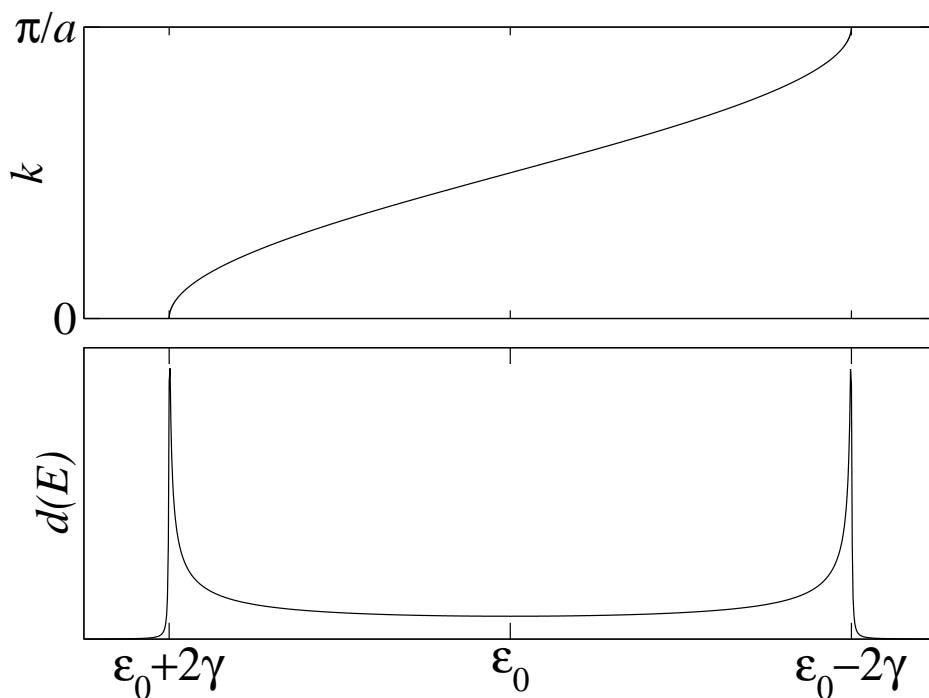Since usually we take the limit $N \to \infty$ we define the DOS per atom $d(E) = D(E)/N$

$$d(E) = \frac{1}{\pi} \frac{1}{[4\gamma^2 - (E - \epsilon_0)^2]^{1/2}}$$

where now

$$\int_{-\infty}^{+\infty} d(E)\mathrm{d}E = 1 \ .$$
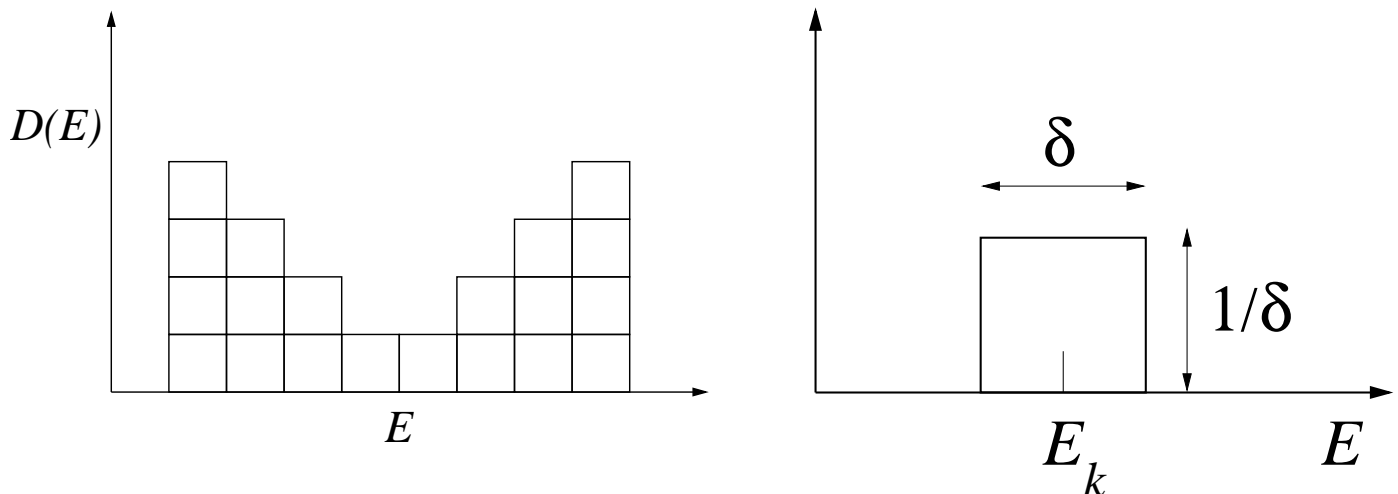
usually a better representation

The spikes in the DOS (singularities) are called **Van Hove singularities**. They are a signature of 1D system.

Alternative definition of DOS

At the end of the day $D(E)$ is a way of counting the electronic states. The total number of states below the energy E_α is

$$n_\alpha = \int_{-\infty}^{E_\alpha} D(E)\mathrm{d}E$$

For each energy E_k I draw a square centered in E_k, with width δ and unit area

Alternatively one can replace the square with a Lorentzian centered in E_k

$$f(E - E_k) = \frac{1}{\pi}\frac{\delta}{\delta^2 + (E - E_k)^2}$$
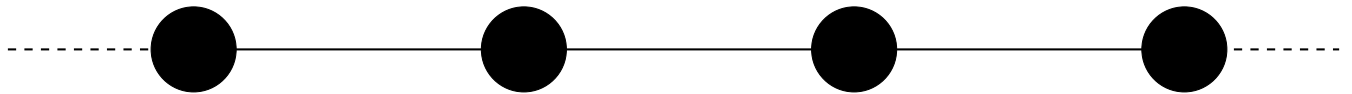
So the total DOS $D(E)$ is simply

$$D(E) = \sum_{\text{all } E_k} f(E - E_k)$$

Then we can take the limit $\lim_{\delta \to 0}$

$$D(E) \to \sum_{\text{all } E_k} \delta(E - E_k)$$

Local Density of States (LDOS)

Consider again the infinite Carbon chain

Our basis set is as usual $|j\alpha\rangle$ (j labels the atomic position, α the orbitals).

Consider a generic eigenstates $|\psi_k\rangle$. This is written as:

$$|\psi_k\rangle = \sum_j \sum_\alpha |j\alpha\rangle\langle j\alpha|\psi_k\rangle = \sum_j \sum_\alpha \langle j\alpha|\psi_k\rangle \, |j\alpha\rangle$$

As usual $|\langle j\alpha|\psi_k\rangle|^2$ is the probability to find an electron in the state $|\psi_k\rangle$ at the particular basis state $|j\alpha\rangle$

The idea is then to "weight" the total DOS $D(E)$ with the $|\langle j\alpha|\psi_k\rangle|^2$. We then define *Local Density of States* $d_{j\alpha}(E)$ as

$$d_{j\alpha}(E) = \sum_{\text{all } E_k} |\langle j\alpha|\psi_k\rangle|^2 \, f(E - E_k)$$

Note that from the orthonormality of $|j\alpha\rangle$ we have the

important *sum rule*

$$\sum_{j\alpha} d_{j\alpha}(E) = D(E)$$

This tells us the DOS of a particular orbital sitting on a particular atom (it is not the total DOS per atom !!!).

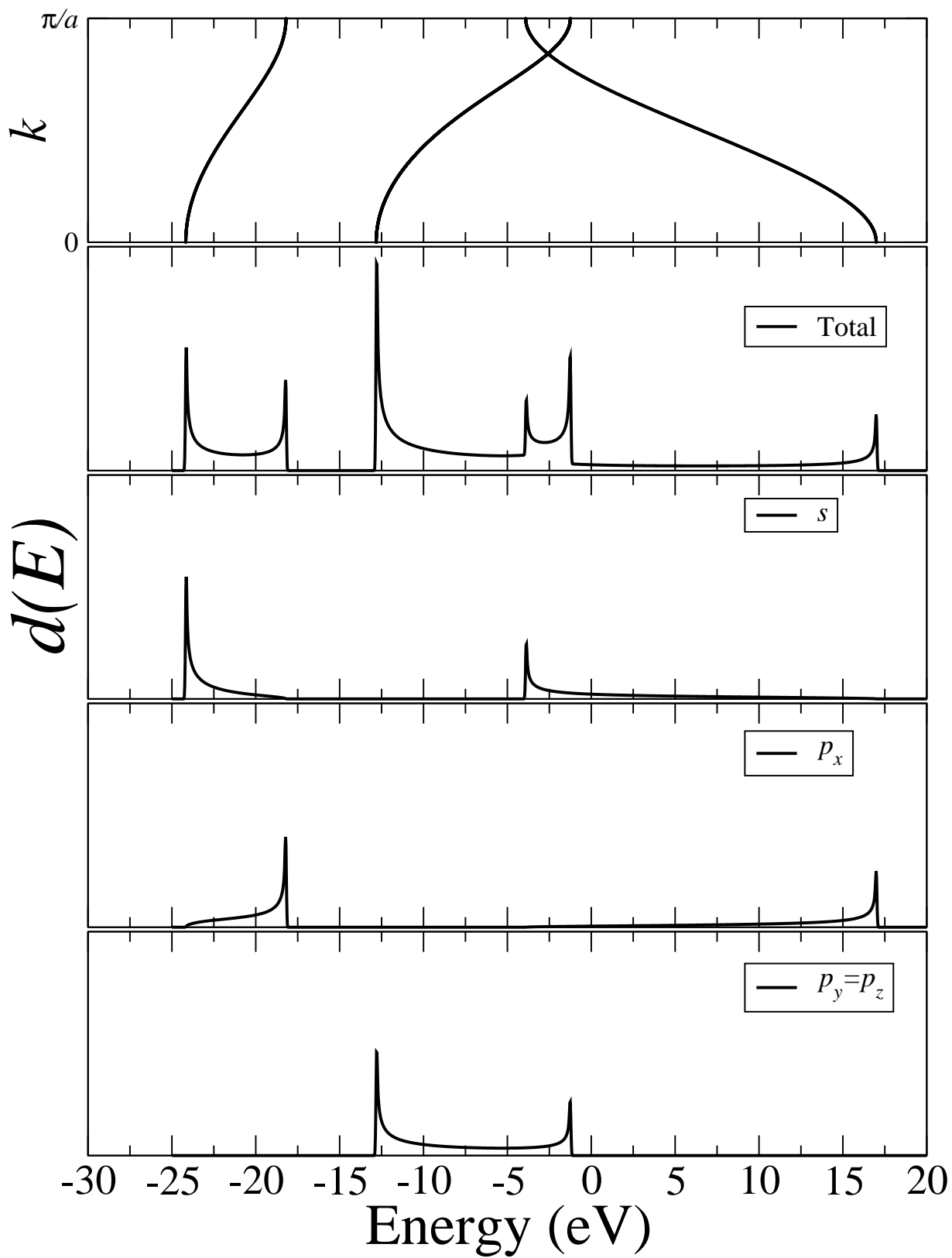In particular two quantities are usually interesting:

1. Atomic Density of States

$$d_j(E) = \sum_{\alpha} d_{j\alpha}(E) = \sum_{\alpha} \sum_{\text{all } E_k} |\langle j\alpha|\psi_k\rangle|^2 \, f(E - E_k)$$

this is important for finite system (surfaces, dots ...)

2. Orbital resolved density of states

$$d_\alpha(E) = \sum_{j} d_{j\alpha}(E) = \sum_{j} \sum_{\text{all } E_k} |\langle j\alpha|\psi_k\rangle|^2 \, f(E - E_k)$$

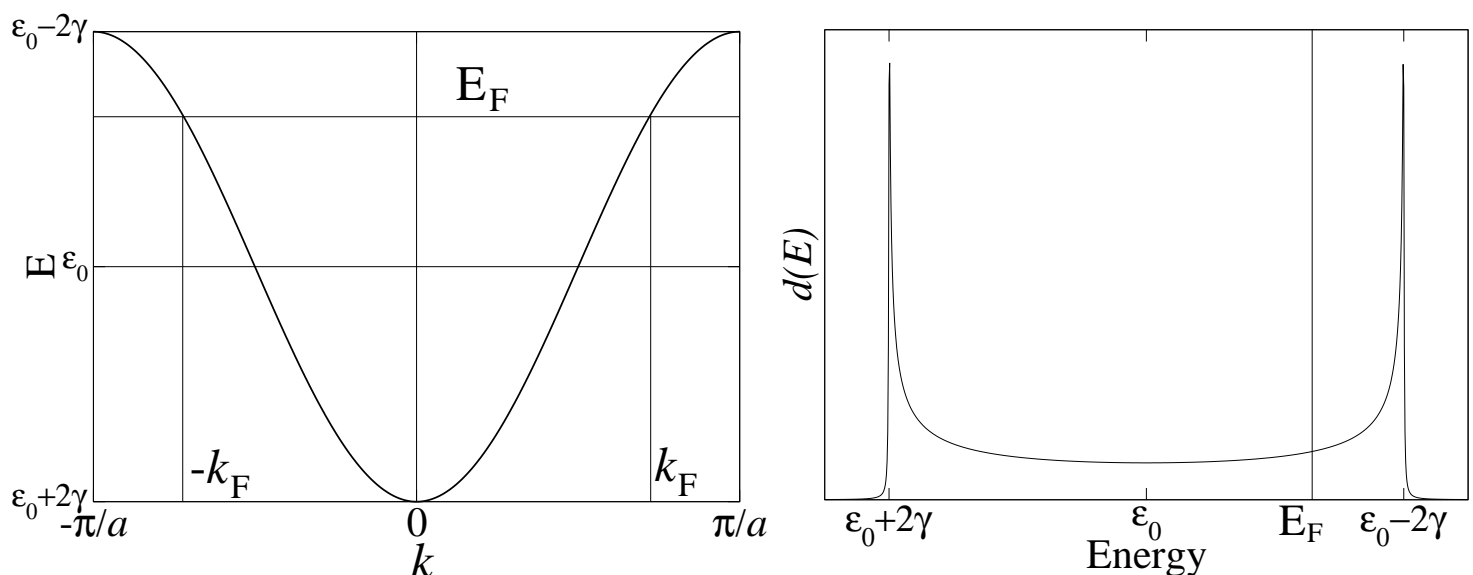this is important for understanding how the electrons distribute over the basis orbitals

Fermi Energy

Suppose we have N available electronic states and M electrons. The Fermi Energy E_F is the highest occupied energy level, and it is obtained as:

$$M = 2 \int_{-\infty}^{E_F} D(E)\mathrm{d}E = 2N \int_{-\infty}^{E_F} d(E)\mathrm{d}E$$

To get ride of the number N and M (they can go to ∞)

$$\nu = M/2N = \int_{-\infty}^{E_F} d(E)\mathrm{d}E$$

The k vector for which $E_k = E_F$ is called Fermi wave-vector.

The corresponding wave-length is called Fermi wave length

$$\lambda_F = \frac{2\pi}{k_F}$$

Example: Infinite H chain

In this case I have 1 electronic state per atom and 1 electron per atom ($N=M$). Then:

$$\nu = \frac{1}{2} \quad \text{half} - \text{filling}$$

$$1/2 = \int_{-\infty}^{E_F} d(E)\mathrm{d}E \quad \longrightarrow \quad E_F = \epsilon_0$$

So the Fermi wave vector is

$$\epsilon_0 = \epsilon_0 + 2\gamma\cos(ka) \ \rightarrow \ k_F = \frac{\pi}{2a}$$

and the Fermi wave-length

$$\lambda_F = 4a$$

Density Matrix

Let us start from the definition

$$\hat{\rho} = 2 \sum_{\text{all } E_k}^{E_F} |\psi_k\rangle\langle\psi_k|$$

The charge density is

$$\rho(x) = \langle x|\hat{\rho}|x\rangle = \sum_{\text{all } E_k}^{E_F} \langle x|\psi_k\rangle\langle\psi_k|x\rangle$$

However the states $|\psi_k\rangle$ are

$$|\psi_k\rangle = \frac{1}{N^{1/2}} \sum_{\alpha}^{N_\alpha} \sum_{j}^{N} A_\alpha^k e^{ikaj} |j\alpha\rangle$$

therefore

$$\rho(x) = \frac{2}{N} \sum_{\text{all } E_k}^{E_F} \sum_{\alpha\beta}^{N_\alpha} \sum_{jl}^{N} A_\alpha^k A_\beta^k e^{ik(j-l)a} \langle x|j\alpha\rangle\langle l\beta|x\rangle$$

Now take the continuous limit for $\sum_{\text{all } E_k}^{E_F}$

$$\sum_{\text{all } E_k}^{E_F} \longrightarrow \frac{Na}{2\pi} \int \mathrm{d}k$$

then

$$\rho(x) = \frac{a}{\pi} \sum_{\alpha\beta}^{N_\alpha} \sum_{jl}^{N} \int_{-k_F}^{k_F} \mathrm{d}k \, A_\alpha^k A_\beta^k \mathrm{e}^{ik(j-l)a} \langle x|j\alpha\rangle \langle l\beta|x\rangle =$$

$$= \sum_{\alpha\beta}^{N_\alpha} \sum_{jl}^{N} \rho_{j\alpha l\beta} \langle x|j\alpha\rangle \langle l\beta|x\rangle$$

where

$$\boxed{\rho_{j\alpha l\beta} = \frac{a}{\pi} \int_{-k_F}^{k_F} \mathrm{d}k \, A_\alpha^k A_\beta^k \mathrm{e}^{ik(j-l)a}}$$

This is again the **density matrix** !!!

Example: The infinite H chain

In this case $N_\alpha = 1 \longrightarrow A_\alpha^k = 1$. Then

$$\rho_{jl} = \frac{a}{\pi} \int_{-k_F}^{k_F} \mathrm{d}k \, \mathrm{e}^{ik(j-l)a}$$

Consider $j = l$

$$\rho_{ll} = \frac{a}{\pi} \int_{-k_F}^{k_F} \mathrm{d}k = \frac{2k_F a}{\pi}$$

Note that:

- This is the occupation of atom l

- ρ_{ll} is independent from l

- $\rho_{ll} = 0$ at the band bottom $k_F = 0$

- $\rho_{ll} = 2$ at the band top $k_F = \pi/a$

Consider $j \neq l$

$$\rho_{jl} = \frac{a}{\pi} \int_{-k_F}^{k_F} \mathrm{d}k \, \mathrm{e}^{ik(j-l)a]} = \frac{2}{\pi} \frac{\sin[k_F(j-l)a}{j-l}$$

Note that:

- This is the bond order jl

- ρ_{jl} depends on $|j - l|$

- $\rho_{jl} = 0$ for both the band top and band bottom ($k_F = 0$, and $k_F = \pi/a$)

- $\rho_{jl} = \max$ at the band center $k_F = \pi/2a$