Solid State Many Body Physics course

Newns-Anderson model

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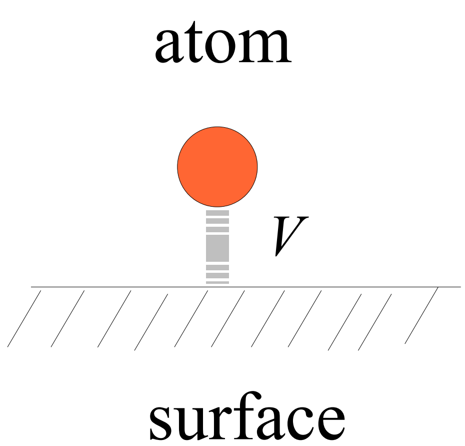
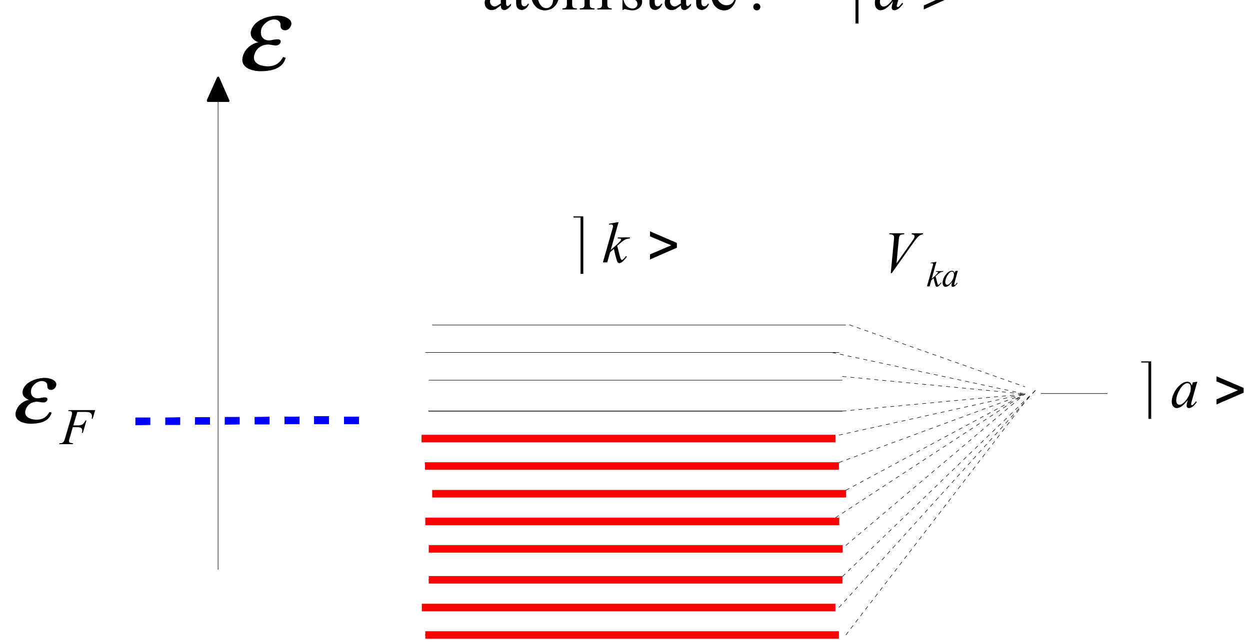
Newns-Anderson model for chemisorption



metal states : $\{ |k> \}$

atom state : $|a>$



ε_F = Fermi energy = highest occupied energy level

V_{ka} = hopping *matrix element*

Model Hamiltonian

$$H = \sum_{k\sigma} \varepsilon_k c^{+}_{k\sigma} c_{k\sigma} + \sum_{\sigma} \varepsilon_a c^{+}_{a\sigma} c_{a\sigma} +$$

$$\sum_{k\sigma} (V_{ak} c^{+}_{a\sigma} c_{k\sigma} + V_{ka} c^{+}_{k\sigma} c_{a\sigma}) + U c^{+}_{a\sigma} c_{a\sigma} c^{+}_{a-\sigma} c_{a-\sigma}$$

where U is the coulomb interaction between spin σ and -σ in orbital $|a>$

with number operators

$$H = \sum_{k\sigma} \varepsilon_k n_{k\sigma} + \sum_{\sigma} \varepsilon_a n_a + \sum_{k\sigma} (V_{ak} c^{+}_{a\sigma} c_{k\sigma} + H.C.) + U n_{a\sigma} n_{a-\sigma}$$

We now apply the Hartree-Fock approximation, neglecting correlations. The matrix elements of the retarded Greens' function G_R ,
assuming that *(|a>, { |k> })* form a complete basis set:

$$G^{\sigma}_{aa}(t) = -i\theta(t) < \{c_{a\sigma}(t), c^{+}_{a\sigma}(0)\} > \qquad (1)$$

$$G^{\sigma}_{ka}(t) = -i\theta(t) < \{c_{k\sigma}(t), c^{+}_{a\sigma}(0)\} > \qquad (2)$$

where $< \ldots\ldots > = < 0 | \ldots\ldots. | 0 >$ is the ground state average

$\{\mathrm{A}, \mathrm{B}\} = \mathrm{AB} + \mathrm{BA}$ (anti - commutator)

Determining G_R will give us the adsorbate projected density of states

$$\rho_{a\sigma}(\varepsilon) = \lim_{\delta\to 0}[-\frac{1}{\pi}\,\mathrm{Im}\,G^{\sigma}_{aa}(\varepsilon + i\delta)\,] \tag{3}$$

Time derivative of Eq. (1)

$$\frac{\partial G^{\sigma}_{aa}(t)}{\partial t} = -i\delta(t) < \{c_{a\sigma}(t), c^{+}_{a\sigma}\} > -i\theta(t) < \{\frac{\partial c_{a\sigma}(t)}{\partial t}, c^{+}_{a\sigma}\} > \tag{4}$$

where $\quad c^{+}_{a\sigma} = c^{+}_{a\sigma}(0)$

The derivative of the destruction operator in Eq. (3) is evaluated with the Heisenberg relation for the time derivative of an operator

$$\frac{\partial c_{a\sigma}(t)}{\partial t} = -i[\, c_{a\sigma}(t), H\,] \qquad (5)$$

Eq. (4) then takes the form

$$i\frac{\partial G^{\sigma}_{aa}(t)}{\partial t} = \delta(t) - i\theta(t) < \{e^{iHt}[c_{a\sigma}, H]\, e^{-iHt}, c^{+}_{a\sigma}\} > \qquad (6)$$

Home problem 1

Show in details that the Newns-Anderson model hamiltonian gives

$$[c_{a\sigma}, H] = \varepsilon_a c_{a\sigma} + \sum_k V_{ak} c_{k\sigma} + U c_{a\sigma} n_{a-\sigma}$$

We then have

$$i\frac{\partial G_{aa}^{\sigma}(t)}{\partial t} = \delta(t) - i\theta(t) < \{c_{a\sigma}(t), c_{a\sigma}^{+}\} >$$

$$- i\theta(t)\sum_{k} V_{ak} < \{c_{k\sigma}(t), c_{a\sigma}^{+}\} >$$

$$- i\theta(t)U < \{c_{a\sigma}(t)c_{a-\sigma}^{+}(t)c_{a-\sigma}(t), c_{a\sigma}^{+}\} > \qquad (7)$$

Comparing Eq. (7) with Eq. (1) and (2), we realize that the fourth term in Eq. (7) is a higher order Greens' function, thus we have an infinite hierarchy of equations. One way to break this is to apply the Hartree-Fock approximation. This means that we neglect the correlation between the “up” and “down” electron in the adsorbate orbital

$$c^{+}_{a-\sigma}(t)c_{a-\sigma}(t) = n_{a-\sigma}(t) \approx < n_{a-\sigma} >$$

where $< n_{a-\sigma} >$ is a simple number

The approximation is ok if :

1) we consider the "up" spin and the fluctuations of the "down" spin is small

$$n_{a-\sigma}(t) = \ (n_{a-\sigma}(t) - < n_{a-\sigma} >) \ + < n_{a-\sigma} > \ \approx \ < n_{a-\sigma} >$$

2) if U is small compared to the band width W
(the energy range of the $| k >$ states)

We then have

$$i\frac{\partial G^{\sigma}_{aa}(t)}{\partial t} = \delta(t) + \tilde{\varepsilon}_{a\sigma}\, G^{\sigma}_{aa}(t) + \sum_k V_{ak}(t)\, G^{\sigma}_{ka}(t) \qquad (8)$$

where

$$\tilde{\varepsilon}_{a\sigma} = \varepsilon_a + U < n_{a-\sigma} > \qquad (9)$$

Now proceed in the same way, taking the time derivative of Eq. (2). We obtain

$$i\frac{\partial G^{\sigma}_{ka}(t)}{\partial t} = \varepsilon_k\, G^{\sigma}_{ka}(t) + V_{ak}(t)\, G^{\sigma}_{aa}(t) \qquad (10)$$

Home problem 2

Evaluate the energy dependent Green's functon and show that you obtain the result

$$G_{aa}^{\sigma} = \frac{1}{\varepsilon - \tilde{\varepsilon}_{a\sigma} - \Sigma(\varepsilon)}$$

whith the self-energy of state ”a”

$$\Sigma(\varepsilon) = \sum_k \frac{|V_{ak}|^2}{\varepsilon - \varepsilon_k + i\delta}$$

The self-energy

$$\Sigma(\varepsilon) \;= \Lambda(\varepsilon) - i\Delta(\varepsilon) \qquad (11)$$

where

$$\Delta(\varepsilon) \;= \text{chemisorption function} = \pi \sum_k |\,\mathrm{V_{ak}}\,|^2 \;\delta(\varepsilon - \varepsilon_k)$$

$$\Lambda\;(\varepsilon) \;=\; \text{shift function} = P \;\sum_{\mathrm{k}} \frac{|\,\mathrm{V_{ak}}\,|^2}{\varepsilon - \varepsilon_k}$$

Ackording to Eq. (3) the adsorbate projected density of states is

$$\rho_{a\sigma}(\varepsilon) = -\frac{1}{\pi}\,\mathrm{Im}\, G^{\sigma}_{aa}(\varepsilon)\,] \;= -\frac{1}{\pi}\,\mathrm{Im}\frac{1}{\varepsilon - \tilde{\varepsilon}_{a\sigma} - \Lambda(\varepsilon) + i\Delta(\varepsilon)}$$

$$= \frac{1}{\pi}\,\frac{\Delta(\varepsilon)}{[\varepsilon - \tilde{\varepsilon}_{a\sigma} - \Lambda(\varepsilon)]^2 + \Delta^2(\varepsilon)} \qquad (12)$$

Simple 1 D model for calculation of the self-energy

Linear chain of $N+1$ metal atoms with an adsorbate at the end.

Atom site index "i". Only nearest neighbour electron hopping

$$< i \,|\, H \,|\, i \pm 1 > \; = \; -\beta \quad , \quad < i \,|\, H \,|\, i > \; = \; 0 \quad , \quad < i | j > = \delta_{ij}$$

Eigenstate $|k>$ with eigen energy ε_{k}. Set lattice constant $a = 1$

$$| k > \; = \sum_{\mathrm{i}=0}^{N} | i >< i \,|\, k > \qquad \text{with "site amplitudes"}$$

$$< i \,|\, k > \; = \sqrt{\frac{2}{N+1}} \sin(k\pi \frac{i+1}{N+1}) \qquad (13)$$

Home problem 3

Show that the energy spectrum is given by

$$\varepsilon_k = -2\beta\cos\left(\frac{k\pi}{N+1}\right) \quad , \quad \text{where} \quad k = 1,2,3,\ldots,N \qquad (14)$$

The band width

$$W = 4\beta$$

For delocalized states (metallic), hopping large, β large and thus large band width W.

We now chemisorb our adsorbate atom to the end atom denoted $''0''$. The hopping matrix element between the adsorbate and the "surface atom", denoted "0" is given by

$$V_{ak} = \langle a | V | k \rangle = \sum_{i=0}^{N} \langle a | V | i \rangle \langle i | k \rangle \approx \langle a | V | 0 \rangle \langle 0 | k \rangle$$

From Eq.(13) we have

$$V_{ak} = V_0 \sqrt{\frac{2}{N+1}} \sin(\frac{k\pi}{N+1}) \quad , \text{ with } \ V_0 =< a|V|0 >$$

The chemisorption function is then given by

$$\Delta(\varepsilon) = \pi \sum_{\mathrm{k}} |V_{ak}|^2 \ \delta(\varepsilon - \varepsilon_k) = |V_0|^2 \ \frac{2\pi}{N+1} \sum_k \sin^2(\frac{k\pi}{N+1})\, \delta(\varepsilon - \varepsilon_a)$$

Now

$$\varepsilon_k = -2\beta \cos(\frac{k\pi}{N+1})$$

change the sum over k to an integral

$$\sum_k \{.......\} \quad \rightarrow \quad \frac{N+1}{\pi}\int \{........\}\, d\varphi \qquad , \qquad \varphi = \frac{k\pi}{N+1}$$

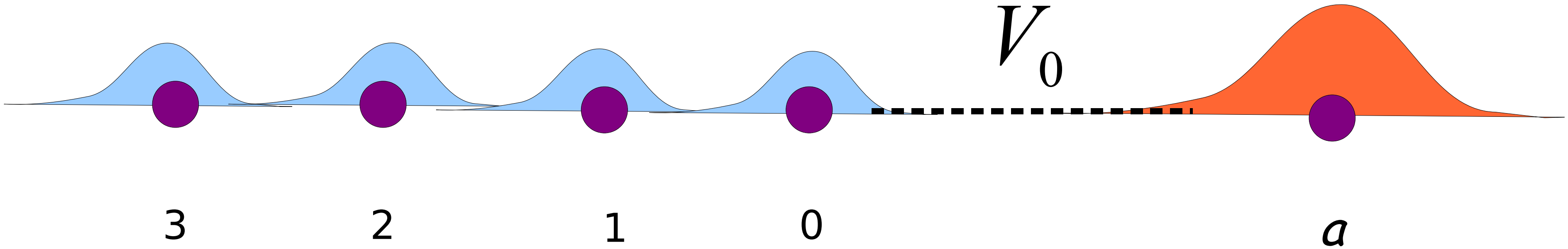
$$\Delta(\varepsilon) = 2\,|\,\beta'\,|\int_0^{\pi} \sin^2\varphi\,\delta(\varepsilon + 2\beta\cos\varphi)\,d\varphi$$

with $x = \cos\varphi \qquad ; \quad dx = -\sin\varphi\, d\varphi$

$$\Delta(\varepsilon) = 2\,|V_0\,|^2 \int_{-1}^{1} \sqrt{1\text{ - x}^2}\;\; \delta(\varepsilon + 2\beta x)\, dx \; = \frac{|V_0\,|^2}{\beta}\sqrt{1-(\frac{\varepsilon}{2\beta})^2}$$

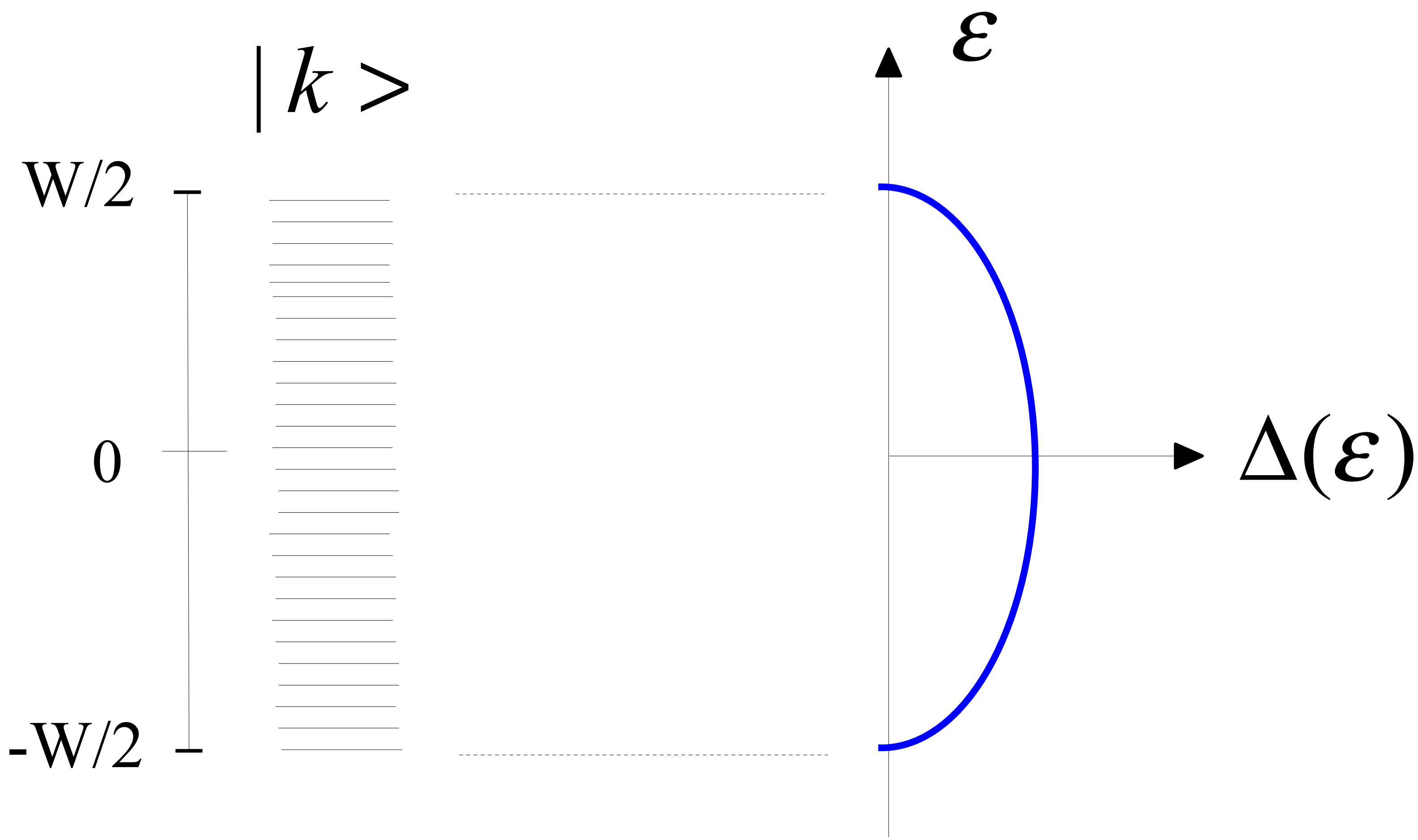
$$\Delta(\varepsilon) = \frac{4\,|V_0\,|^2}{W}\sqrt{1-(\frac{2\varepsilon}{W})^2}$$

1D Linear chain model



In this model we have obtained a semi-eliptical chemisorption function

$$\Delta(\varepsilon) = \frac{4|V_0|^2}{W}\sqrt{1-\left(\frac{2\varepsilon}{W}\right)^2}$$

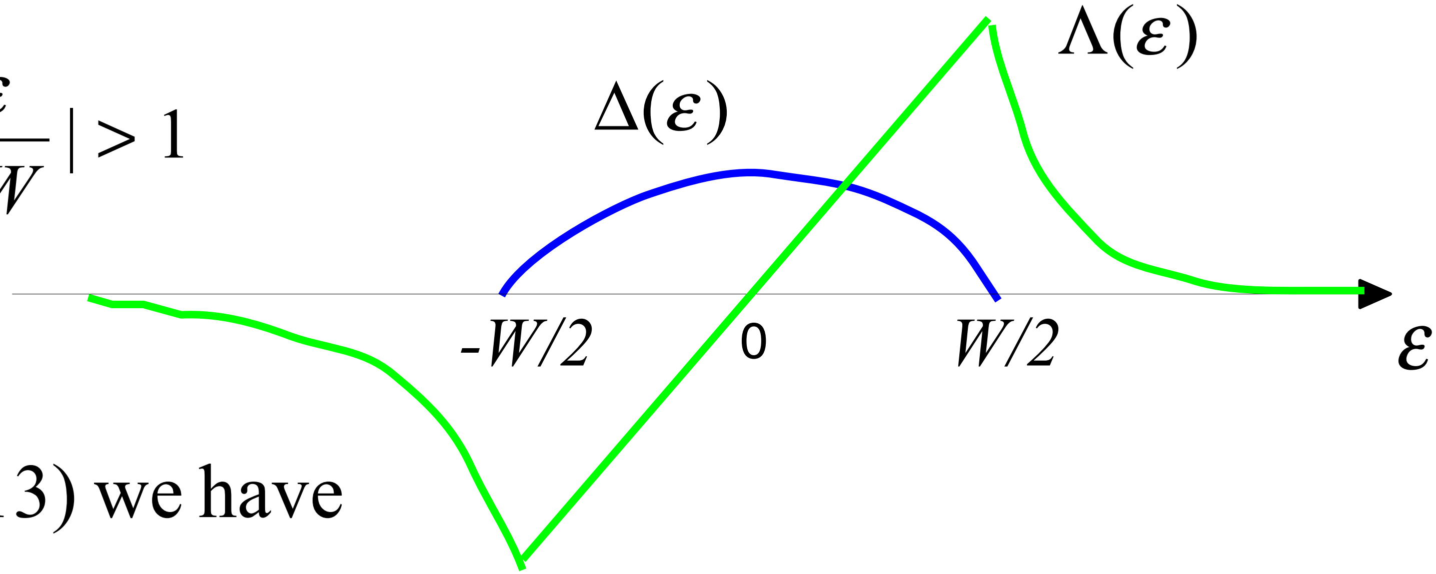


And the shift function is linear in energy within the band

$$\Lambda(\varepsilon) = 8\pi \frac{|V_0|^2}{W^2} \varepsilon \quad , \quad \text{when} \quad \left| \frac{\varepsilon}{2W} \right| < 1$$

and

$$\Lambda \to 0 \quad \text{when} \quad \left| \frac{\varepsilon}{2W} \right| > 1$$

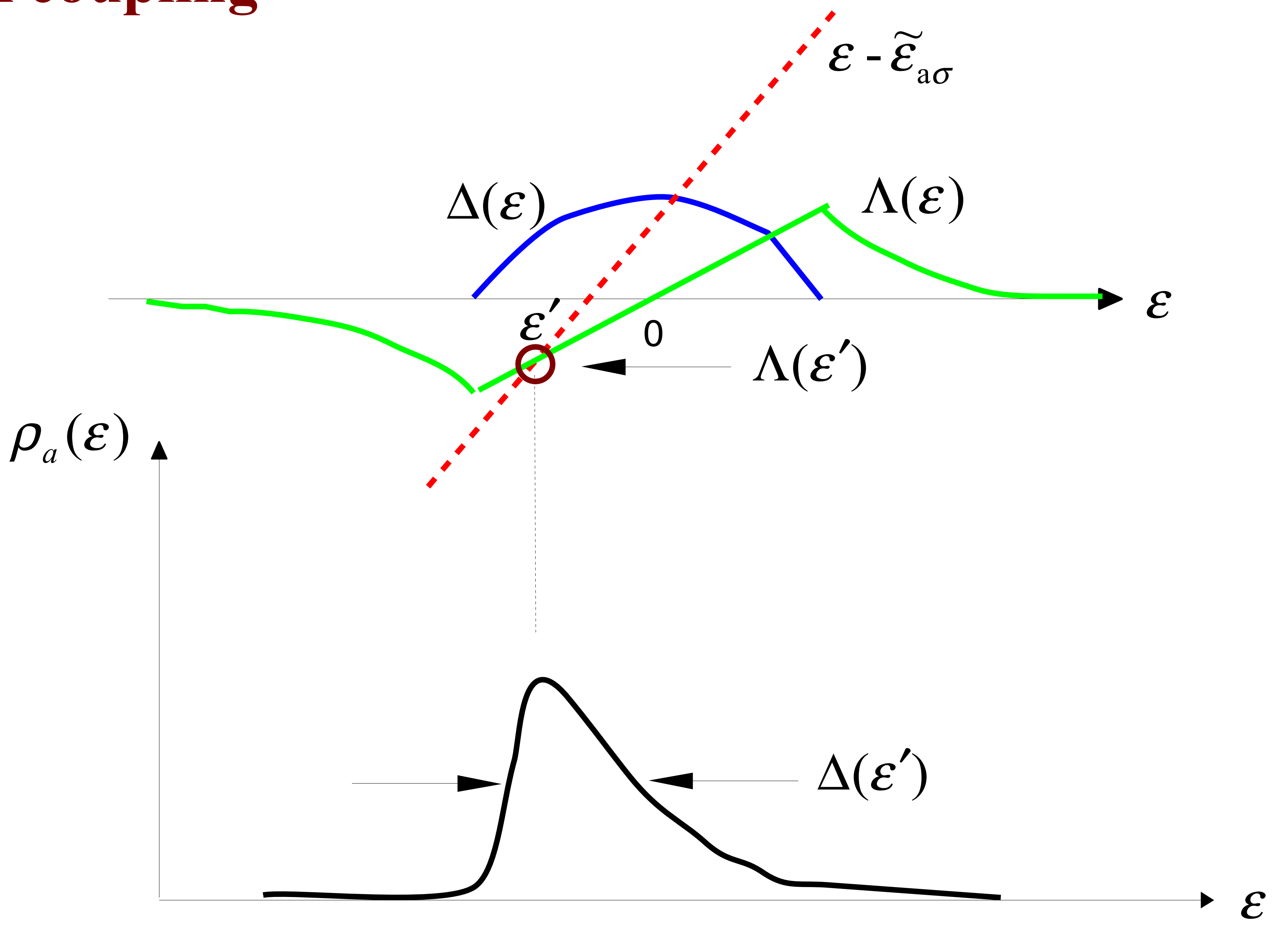


Ackording to Eq. (13) we have

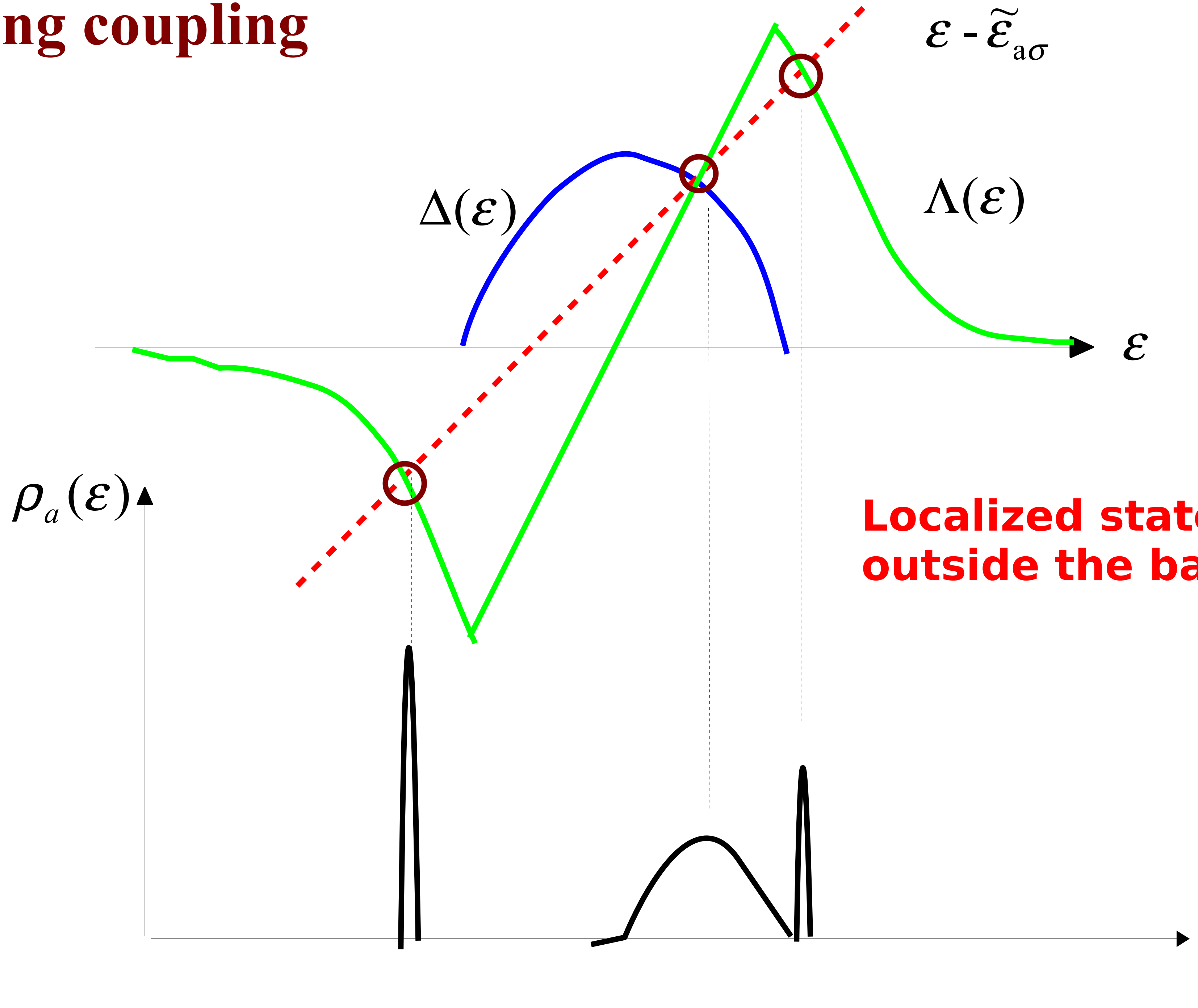
$$\rho_{a\sigma}(\varepsilon) = \frac{1}{\pi} \frac{\Delta(\varepsilon)}{[\varepsilon - \tilde{\varepsilon}_{a\sigma} - \Lambda(\varepsilon)]^2 + \Delta^2(\varepsilon)}$$

which is enhanced when $\varepsilon - \tilde{\varepsilon}_{a\sigma} - \Lambda(\varepsilon) = 0$

Weak coupling

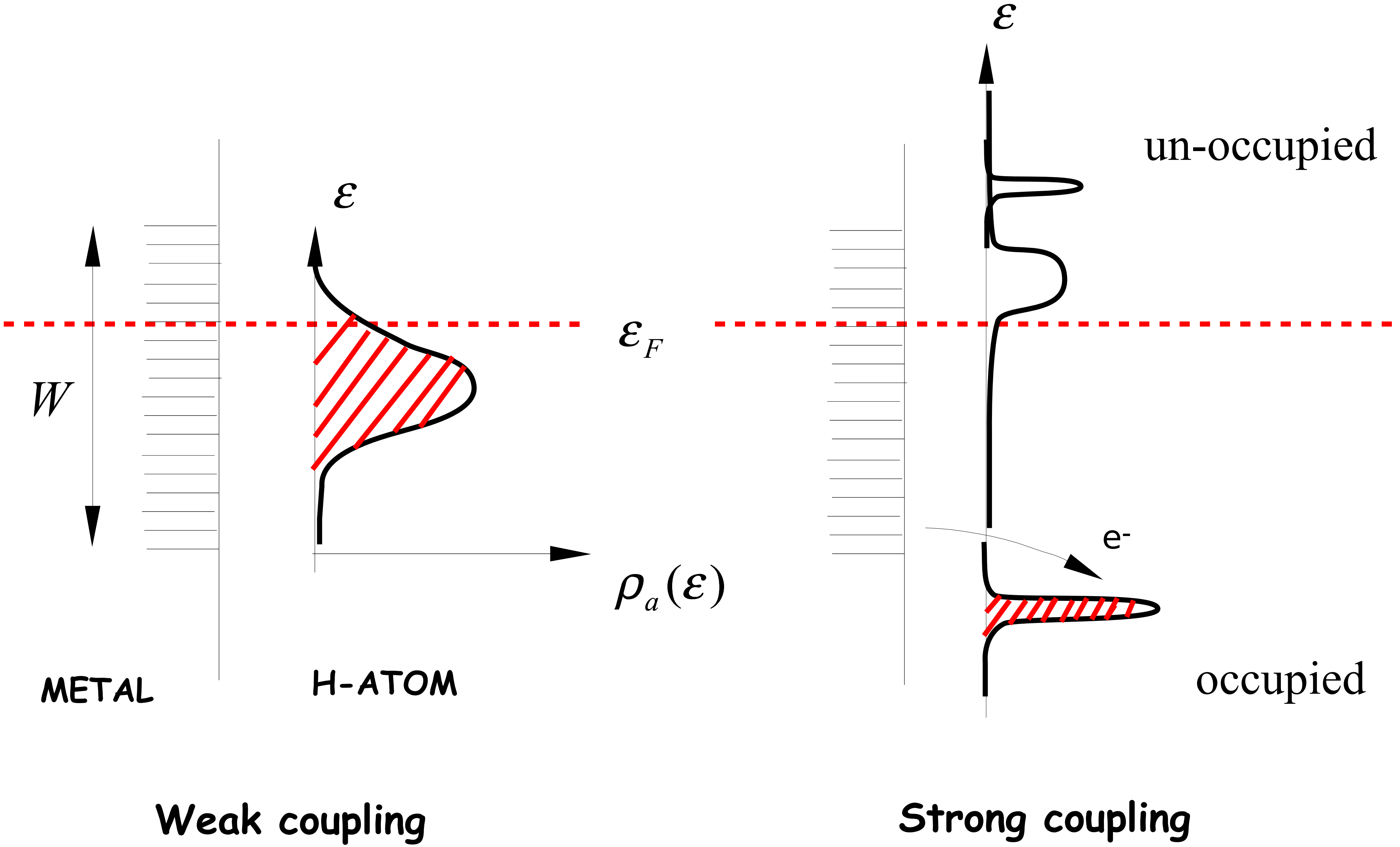


Strong coupling



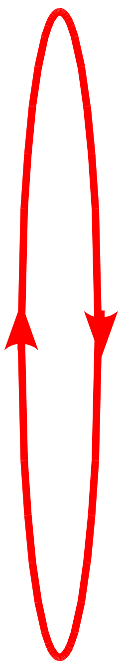
Localized states outside the band !

Hydrogen atom chemisorption



Spin polarization

$$\zeta = \frac{<n_{a\uparrow}> - <n_{a\downarrow}>}{<n_{a\uparrow}> + <n_{a\downarrow}>}$$



self - consistent loop

$<n_{a\downarrow}>$

$$\rho_{a\uparrow}(\varepsilon) = \frac{1}{\pi}\frac{\Delta(\varepsilon)}{[\varepsilon - \tilde{\varepsilon}_{a\uparrow} - \Lambda(\varepsilon)]^2 + \Delta^2(\varepsilon)} \quad \text{where } \tilde{\varepsilon}_{a\uparrow} = \varepsilon_a + U <n_{a\downarrow}>$$

$$<n_{a\uparrow}> = \int_{-\infty}^{\varepsilon_F} \rho_{a\uparrow}(\varepsilon) d\varepsilon$$

$$\rho_{a\downarrow}(\varepsilon) = \frac{1}{\pi}\frac{\Delta(\varepsilon)}{[\varepsilon - \tilde{\varepsilon}_{a\downarrow} - \Lambda(\varepsilon)]^2 + \Delta^2(\varepsilon)} \quad \text{with } \tilde{\varepsilon}_{a\downarrow} = \varepsilon_a + U <n_{a\uparrow}>$$

$$<n_{a\downarrow}> = \int_{-\infty}^{\varepsilon_F} \rho_{a\downarrow}(\varepsilon) d\varepsilon$$

simplifications

(a)

$$\Delta(\varepsilon) \equiv \Delta_0$$

$$\Lambda(\varepsilon) \equiv \Lambda_0 \qquad \Rightarrow \qquad \rho_{a\uparrow}(\varepsilon) = \frac{1}{\pi} \frac{\Delta_0}{[\varepsilon - \tilde{\varepsilon}_{a\uparrow} - \Lambda_0]^2 + \Delta_0{}^2} \qquad \text{(Lorentzian!)}$$

$$< n_{a\uparrow} >= \int_{-\infty}^{\varepsilon_F} \rho_{a\uparrow}(\varepsilon) d\varepsilon = \frac{1}{\pi} \{\arctan(\frac{\varepsilon - \tilde{\varepsilon}_{a\uparrow} - \Lambda_0}{\Delta_0}) - \frac{\pi}{2}\}$$

(b)

$$\Delta(\varepsilon) = \pi \sum_k |V_{ak}|^2 \delta(\varepsilon - \varepsilon_k) \approx \pi |V_o|^2 \sum_k \delta(\varepsilon - \varepsilon_k)$$

$$= \pi |V_o|^2 \rho_s(\varepsilon) \quad , \quad \rho_s(\varepsilon) = \text{substrate denstity of states}$$

(c) modeling in atom – surface scattering :

$$\Delta_\uparrow(z) = \Delta_0 e^{-2\gamma_{\uparrow\sigma} z} \quad , \quad \text{where } \Delta_0 \approx \pi |V_o|^2 \rho_s(\varepsilon_F)$$

$$\gamma_\uparrow = \sqrt{\frac{2m}{\hbar^2} |\varepsilon_a + U < n_{a\downarrow} >|}$$

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