NANO 705-Notes

Level Broadening

Assume we have solved the time-independent Schrödinger equation for some system.

$$\hat{H}\phi_\alpha(\mathbf{r}) = \varepsilon_\alpha \cdot \phi_\alpha(\mathbf{r})$$

where ε_α are the energy eigenvalues and $\phi_\alpha(\mathbf{r})$ are the eigenfunctions. We can express the SE in matrix form in a basis in which the hamiltonian is a diagonal matrix

$$[H'] = \begin{pmatrix} \varepsilon_1 & 0 & 0 \\ 0 & \varepsilon_2 & 0 \\ 0 & 0 & \ddots \end{pmatrix}$$

The SE in matrix form is

$$[H']\{\phi'_\alpha\} = \varepsilon_\alpha \cdot \{\phi'_\alpha\}$$

In this basis, the wavevectors $\{\phi'_\alpha\}$ are column vectors simply containing 0 in every row, except row α, which contains 1, i.e., $\{\phi'_\alpha\}_i = \delta_{i\alpha}$. The DOS is

$$D(E) = \sum_\alpha \delta(E - \varepsilon_\alpha)$$

We may want to know how much of each state resides at a particular position r. This is the local DOS

$$D(\mathbf{r};E) = \sum_\alpha |\phi_\alpha(\mathbf{r})|^2 \delta(E - \varepsilon_\alpha)$$

The local DOS can be related to the spectral function, which can be written in the eigenstate basis as

$$A(\mathbf{r},\mathbf{r}';E) = 2\pi \sum_\alpha \phi_\alpha(\mathbf{r}) \cdot \delta(E - \varepsilon_\alpha) \cdot \phi_\alpha^*(\mathbf{r}')$$

Clearly

$$D(\mathbf{r};E) = \frac{1}{2\pi} A(\mathbf{r},\mathbf{r};E)$$

Consider a matrix containing a collection of all eigenstates in their direct-space representation

$$[V] = (\{\phi_1\} \quad \{\phi_2\} \quad \cdots)$$

We can interpret each $\{\phi_\alpha\}$ as a column vector containing the components of $\phi_\alpha(\mathbf{r}) \cdot d^{3/2}r$ at every position, i.e., $\{\phi_\alpha\}_i = \phi_\alpha(\mathbf{r}_i) \cdot d^{3/2}r_i$.

This allows us to relate the two representations using

$$\{\phi_\alpha\} = [V]\{\phi'_\alpha\}$$

We know that the $\phi_\alpha(\mathbf{r})$ are orthonormal. Notice that

$$\{\phi_\alpha\}^\dagger \{\phi_\beta\} = \sum_i [\phi_\alpha(\mathbf{r}_i)]^* \cdot \phi_\beta(\mathbf{r}_i) \cdot d^3 r_i \to \int_\mathbf{r} [\phi_\alpha(\mathbf{r})]^* \cdot \phi_\beta(\mathbf{r}) \cdot d^3 r = \delta_{\alpha\beta}$$

In other words, $\left([V]^{\dagger}[V]\right)_{\alpha\beta}=\delta_{\alpha\beta}$, so $[V]^{\dagger}[V]=[I]$, where $[V]^{\dagger}=\left([V]^{T}\right)^{*}$. This indicates that $[V]$ is unitary, i.e., that $[V]^{\dagger}=[V]^{-1}$. So $[V][V]^{\dagger}=[I]$. This is $\left([V][V]^{\dagger}\right)_{ij}=\delta_{ij}$. This represents

$$\sum_{\alpha}[\phi_{\alpha}(\mathbf{r}_i)]^{*}\cdot\phi_{\alpha}(\mathbf{r}_j)\cdot d^{3/2}r_i\cdot d^{3/2}r_j=\delta_{ij}$$

In particular, notice that

$$\sum_{\alpha}|\phi_{\alpha}(\mathbf{r})|^{2}\cdot d^{3}r=1$$

In other words, each point in space is equally represented by some combination of wave functions. We cannot claim that the wave functions are equally populated, however, only that they are available. This is called the *sum rule*. Take, for example, a 1-D particle in a box, with potential energy $U(x)=0$ in the range $0<x<L$ and $U(x)\to\infty$ elsewhere. The energy eigenfunctions in this region are

$$\phi_{\alpha}(x)=\sqrt{\frac{2}{L}}\cdot\sin\left(\frac{\alpha\pi x}{L}\right)$$

At some position in the box, find the sum

$$\sum_{\alpha=1}^{\infty}|\phi_{\alpha}(x)|^{2}\cdot dx=\frac{2\cdot dx}{L}\cdot\sum_{\alpha=1}^{\infty}\sin^{2}\left(\frac{\alpha\pi x}{L}\right)$$

Divide the box into N points, with $dx=L/N$ and use $\sin^{2}(u)=[1-\cos(2u)]/2$. The discrete lattice can accommodate N orthogonal states.

$$\sum_{\alpha=1}^{\infty}|\phi_{\alpha}(x)|^{2}\cdot dx=1-\frac{1}{N}\cdot\sum_{\alpha=1}^{N}\cos\left(\frac{2\alpha\pi x}{L}\right)$$

We are assured $-1<\cos(2\alpha\pi x/L)<1$ in the range $0<x<L$, so

$$\left|\sum_{\alpha=1}^{N}\cos(2\alpha\pi x/L)\right|<N$$

Taking the limit $N\to\infty$, we have $\sum_{\alpha=1}^{\infty}|\phi_{\alpha}(x)|^{2}\cdot dx\to 1$.

Notice that

$$\int_{E}dE\cdot D(\mathbf{r};E)\cdot d^{3}r=\int_{E}dE\cdot\sum_{\alpha}|\phi_{\alpha}(\mathbf{r})|^{2}\cdot\delta\left(E-\varepsilon_{\alpha}\right)\cdot d^{3}r=\sum_{\alpha}|\phi_{\alpha}(\mathbf{r})|^{2}\cdot d^{3}r=1$$

Recall that, if $[H']\{\phi'_{\alpha}\}=\varepsilon_{\alpha}\cdot\{\phi'_{\alpha}\}$, then $[H'][V]^{\dagger}\{\phi_{\alpha}\}=\varepsilon_{\alpha}\cdot[V]^{\dagger}\{\phi_{\alpha}\}$, so $[V][H'][V]^{\dagger}\{\phi_{\alpha}\}=\varepsilon_{\alpha}\cdot\{\phi_{\alpha}\}$. Apparently, $[H]=[V][H'][V]^{\dagger}$. In fact, any matrix operator in the unprimed basis transforms to its equivalent in the primed representation in the same way. We can write

$$[A(E)]_{ij}=2\pi\sum_{\alpha}\{\phi_{\alpha}\}_i\cdot\delta\left(E-\varepsilon_{\alpha}\right)\cdot\left(\{\phi_{\alpha}\}^{\dagger}\right)_j$$

The transformed version is $[A'(E)]=[V]^{\dagger}[A(E)][V]$

$$[A'(E)]_{\alpha\beta} = 2\pi \cdot \sum_{ij} (\phi_\alpha(\mathbf{r}_i))^* \cdot \left(\sum_\gamma \phi_\gamma(\mathbf{r}_i) \cdot \delta(E-\varepsilon_\gamma) \cdot (\phi_\gamma(\mathbf{r}_j))^*\right) \cdot \phi_\beta(\mathbf{r}_j) \cdot d^{3/2} r_i \cdot d^{3/2} r_j$$
$$= 2\pi \cdot \sum_\gamma \delta_{\alpha\beta} \delta(E-\varepsilon_\gamma)$$

The corresponding matrix is

$$[A'(E)] = 2\pi \cdot \delta(E \cdot [I] - [H])$$

In this energy eigenstate basis, the matrix looks like

$$[A'(E)] = 2\pi \cdot \begin{pmatrix} \delta(E-\varepsilon_1) & 0 & 0 \\ 0 & \delta(E-\varepsilon_2) & 0 \\ 0 & 0 & \ddots \end{pmatrix}$$

We can write any of the diagonal elements as

$$[A'(E)]_{\alpha\alpha} = 2\pi \cdot \delta(E-\varepsilon_\alpha) = \lim_{\eta \to 0} \left(\frac{2\eta}{(E-\varepsilon_\alpha)^2 + \eta^2} \right)$$

For this to hold, the expression must satisfy the sampling property of the delta function. More simply stated, it must be infinite when the argument is zero, and normalizable. The first is clear by inspection, since the the ratio becomes $2/\eta$ when $E = \varepsilon_\alpha$. Now let's check the normalization. Define $x = (E-\varepsilon_\alpha)/\eta$

$$\int_{E=-\infty}^{\infty} dE \cdot \frac{2\eta}{(E-\varepsilon_\alpha)^2 + \eta^2} = 2 \cdot \int_{x=-\infty}^{x} \frac{dx}{x^2 + 1^2}$$

Now define $x = \tan\theta$, so $dx = \left(1 + \tan^2\theta\right) \cdot d\theta$. This gives

$$2 \cdot \int_{\theta=-\pi/2}^{\pi/2} d\theta = 2\pi$$

as required. Now observe that we can split the ratio into a sum of two ratios

$$\frac{2\eta}{(E-\varepsilon_\alpha)^2 + \eta^2} = \frac{i}{(E-\varepsilon_\alpha) + i\eta} - \frac{i}{(E-\varepsilon_\alpha) - i\eta}$$

So

$$2\pi \cdot \delta(E-\varepsilon_\alpha) = \lim_{\eta \to 0} \left[i\left(((E-\varepsilon_\alpha) + i\eta)^{-1} - ((E-\varepsilon_\alpha) - i\eta)^{-1} \right) \right]$$

We can now write the spectral function in matrix form as

$$[A'(E)] = \lim_{\eta \to 0} \left[i\left(((E+i\eta)[I] - [H'])^{-1} - ((E-i\eta)[I] - [H'])^{-1} \right) \right]$$

These two terms are only distinguished by the sign of η, and there are Hermitian adjoints of each other. So we pick $\eta > 0$, i.e., $\eta \to 0^+$. The same form holds in any other basis, by applying the appropriate unitary transformation of the hamiltonian matrix. The two terms are then called the retarded and advanced Green's functions.

$$[G(E)] = \lim_{\eta \to 0^+} ((E + i\eta)[I] - [H])^{-1} \qquad \text{//retarded}$$

$$[G(E)]^\dagger = \lim_{\eta \to 0^+} ((E - i\eta)[I] - [H])^{-1} \qquad \text{//advanced}$$

So

$$[A(E)] = i\left([G(E)] - [G(E)]^\dagger\right)$$

We often are primarily interested in the retarded Green's function, which is usually just called the Green's function. From $[G(E)]$, we can easily find $[G(E)]^\dagger$. We may choose to write the quantity $\lim\left(\eta \to 0^+\right)$ as just 0^+. Say we have some system with hamiltonian $[\bar{H}]$. The Green's function is

$$[\bar{G}(E)] = \left(\left(E + i0^+\right)[\bar{I}] - [\bar{H}]\right)^{-1}$$

We would like to extract the Green's function representing just part of the system (i.e., the channel). We somehow know that the isolated channel has hamiltonian $[H]$; the rest of the system, called the reservoir, has hamiltonian $[H_R]$. These two subsytems are coupled through some matrix $[\tau]$. Write

$$[\bar{H}] = \begin{pmatrix} [H] & [\tau] \\ [\tau]^\dagger & [H_R] \end{pmatrix}$$

The Green's function for the whole system is

$$[\bar{G}(E)] = \begin{pmatrix} \left(E + i0^+\right)[I] - [H] & -[\tau] \\ -[\tau]^\dagger & \left(E + i0^+\right)[I_R] - [H_R] \end{pmatrix}^{-1} = \begin{pmatrix} [G(E)] & [g(E)] \\ [g(E)]^\dagger & [G'_R(E)] \end{pmatrix}$$

The terms $[G'_R(E)]$ and $[g(E)]$ are not of immediate interest. Our focus is $[G(E)]$ for the channel. We can also say that the Green's function of the isolated reservoir is

$$[G_R(E)] = \left(\left(E + i0^+\right)[I_R] - [H_R]\right)^{-1}$$

Say we want to know some quadrant of the inverse of a matrix. We can say

$$\begin{pmatrix} [A] & [B] \\ [C] & [D] \end{pmatrix}^{-1} = \begin{pmatrix} [a] & [b] \\ [c] & [d] \end{pmatrix}$$

Then

$$\begin{pmatrix} [A] & [B] \\ [C] & [D] \end{pmatrix} \cdot \begin{pmatrix} [a] & [b] \\ [c] & [d] \end{pmatrix} = \begin{pmatrix} [I] & [0] \\ [0] & [I] \end{pmatrix}$$

A little matrix algebra shows that $[a] = \left([A] - [B][D]^{-1}[C]\right)^{-1}$. So

$$[G(E)] = \left(\left(E + i0^+\right)[I] - [H] - [\tau][G_R(E)][\tau]^\dagger\right)^{-1}$$

The Green's function describing the channel coupled to the reservoir looks like the form we would expect for the isloated channel, but with a correction, called the self-energy.

$$[\Sigma(E)] = [\tau][G_R(E)][\tau]^\dagger$$

which incorporates the effects of exchange with the reservoir. Finally

$$[G(E)] = \left(\left(E + i0^+\right)[I] - [H] - [\Sigma(E)]\right)^{-1}$$

Now let's simplify considerably by assuming our channel supports a single level, with only one energy eigenvalue ε, and that self energy is neither a matrix, nor energy dependent. Instead it is just a complex number $\Sigma = \Sigma_r + i\Sigma_i$. So the channel Green's function is

$$G(E) = \frac{1}{\left(E + i0^+\right) - \varepsilon - (\Sigma_r + i\Sigma_i)} = \frac{1}{(E - \varepsilon') + i\gamma/2}$$

where we have defined $\varepsilon' - \varepsilon - \Sigma_r$ and $\gamma = -2\Sigma_i$, and used the fact that $|\Sigma_i| \gg 0^+$. Now let's find the spectral function of the channel

$$A(E) = i\left(G(E) - G^\dagger(E)\right)$$
$$= i\left(\frac{1}{(E - \varepsilon') + i\gamma/2} - \frac{1}{(E - \varepsilon') - i\gamma/2}\right)$$
$$A(E) = \frac{\gamma}{(E - \varepsilon')^2 + (\gamma/2)^2}$$

From this, we can find the local DOS using $D(E) = A(E)/2\pi$

$$D(E) = \frac{\gamma/2\pi}{(E - \varepsilon')^2 + (\gamma/2)^2} = \frac{2}{\pi\gamma} \cdot \frac{1}{\left(\dfrac{E - \varepsilon'}{\gamma/2}\right)^2 + 1}$$

The channel level has been shifted in energy and broadened, with a FWHM of γ. Let's verify the number of states in the channel.

$$\int_{E=-\infty}^{\infty} dE \cdot D(E) = \frac{\gamma/2\pi}{(E - \varepsilon')^2 + (\gamma/2)^2} = \frac{2}{\pi\gamma} \cdot \int_{E=-\infty}^{\infty} \frac{dE}{\left(\dfrac{E - \varepsilon'}{\gamma/2}\right)^2 + 1}$$

Define $x = (E - \varepsilon')/(\gamma/2)$

$$\frac{2}{\pi\gamma} \cdot \frac{\gamma}{2} \cdot \int_{x=-\infty}^{\infty} \frac{dx}{x^2 + 1} = 1$$

as expected.