1. Wiedemann-Franz Law

金属电导和导热系数(也叫热导)之间有数学关系,叫做魏德曼---弗兰兹定律(Wiedemann-Franz Law): 在不太低的温度下,金属的导热系数与电导率之比正比于温度,其中比例常数的值不依赖于具体的金属。使用条件:温度高于德拜温度(高于德拜温度时,金属热容不随时间改变)

三. Wiedemann-Franz 定律:

该定律的内容: 在不太低的温度下,金属的热导率与电导率之比正比于温度,其比例常数的数值不依赖于具体的金属。在金属理论发展史上,这个结果极其重要,因为它支持了电子气作为电荷和能量载体的观点。量子自由电子论可以很好地解释它,代入已经得到的公式,有:

$$\frac{\kappa}{\sigma} = \frac{\frac{\pi^2 n k_B^2 T}{3m} \tau_F}{\frac{n e^2 \tau_F}{m}} = \frac{\pi^2}{3} \left(\frac{k_B}{e}\right)^2 T = LT$$

这是一个令人惊讶的结果,它既不包含电子数目 n,也不包含电子质量 m

经典自由电子模型结果:
$$\frac{\kappa}{\sigma} = \frac{\frac{1}{3} \frac{3}{2} n k_{\scriptscriptstyle B} v \bar{l}}{\frac{ne^2 \bar{l}}{2m v}} = 3 \left(\frac{k_{\scriptscriptstyle B}}{e}\right)^2 T$$

其中 Lorentz numder

$$L = \frac{\pi^2}{3} \left(\frac{k_B}{e}\right)^2 = 2.45 \times 10^{-8} \text{ (watt-ohm} \cdot \text{deg}^{-2}\text{)}$$
$$= 2.72 \times 10^{-13} \text{ (erg/esu} \cdot \text{deg)}^2$$

或:
$$L = 2.45 \times 10^{-8} \left(\frac{V}{K}\right)^2$$

一些金属Lorentz数的实验值[10 ⁻⁸ (V/K) ²]									
T(°C)	Ag	Au	Cu	Cd	lr	Zn	Pb	Pt	Sn
0	2.31	2.35	2.23	2.42	2.49	2.31	2.47	2.51	2.52
100	2.37	2.40	2.33	2.43	2.49	2.33	2.56	2.60	2.49

来源: 曾长淦《自由电子论 2》

2. 用运动学方程和能量定义格林函数的等价性

Take FFF situation as an example, $\delta = 0$, equation (2) becomes

$$[(\hbar w + i\hbar \gamma_p) - (J_{p-1} + J_{p+1})]\widetilde{S}_p^{\dagger} + J_{p-1}\widetilde{S}_{p-1}^{\dagger} + J_{p+1}\widetilde{S}_{p+1}^{\dagger} = 0 \cdot \cdot \cdot \cdot \cdot \cdot (s1)$$

Because $S_p^{\dagger} = \widetilde{S}_p^{\dagger} e^{-iwt}$, we can get $\hbar w S_p^{\dagger} = i\hbar \frac{\partial S_p^{\dagger}}{\partial t}$, and equation (s1) can be rewritten as

$$i\hbar \frac{\partial S_p^{\dagger}}{\partial t} = -[i\hbar \gamma_p - (J_{p-1} + J_{p+1})]S_p^{\dagger} - J_{p-1}S_{p-1}^{\dagger} - J_{p+1}S_{p+1}^{\dagger} \cdot \cdot \cdot \cdot \cdot \cdot (s2)$$

And according to Heisenberg equation

$$i\hbar \frac{\partial S_p^{\dagger}}{\partial t} = [H, S_p^{\dagger}] \cdot \cdot \cdot \cdot \cdot \cdot (s3)$$

and commutation relation $[S_p, S_{p'}^{\dagger}] = \delta_{p,p'}$, we can get the form of Hamiltonian by comparing equation (s2) with (

$$\hat{H} = -\sum_{p} [i\hbar\gamma_{p} - (J_{p-1} + J_{p+1})] S_{p}^{\dagger} S_{p} - \sum_{p} [J_{p-1} S_{p-1}^{\dagger} S_{p} - J_{p+1} S_{p+1}^{\dagger} S_{p}] \cdot \cdots \cdot (s4)$$

and the matrix form of \hat{H} is

$$H = - \begin{pmatrix} i\hbar\gamma_1 - J_2 & J_{1,2} & \cdots & 0 & 0 \\ J_{2,1} & i\hbar\gamma_2 - (J_1 + J_3) & \cdots & 0 & 0 \\ \vdots & \vdots & \cdots & \vdots & \vdots \\ 0 & 0 & \cdots & i\hbar\gamma_{N-1} - (J_{N-2} + J_N) & J_{N-1,N} \\ 0 & 0 & \cdots & J_{N,N-1} & i\hbar\gamma_N - J_{N-1} \end{pmatrix}$$

So the Green's function has the form

Green's function has the form
$$G_0(w) = \frac{\hbar w I_{N\times N} - H}{}$$

$$= \begin{pmatrix} \hbar w + i\hbar \gamma_1 - J_2 & J_{1,2} & \cdots & 0 & 0 \\ J_{2,1} & \hbar w + i\hbar \gamma_2 - (J_1 + J_3) & \cdots & 0 & 0 \\ \vdots & \vdots & \cdots & \vdots & \vdots \\ 0 & 0 & \cdots & \hbar w + i\hbar \gamma_{N-1} - (J_{N-2} + J_N) & J_{N-1,N} \\ 0 & 0 & \cdots & J_{N,N-1} & \hbar w + i\hbar \gamma_N - J_{N-1} \end{pmatrix}$$

$$= \begin{pmatrix} f_1 & J_{1,2} & \cdots & 0 & 0 \\ J_{2,1} & f_2 & \cdots & 0 & 0 \\ \vdots & \vdots & \cdots & \vdots & \vdots \\ 0 & 0 & \cdots & f_{N-1} & J_{N-1,N} \\ 0 & 0 & \cdots & J_{N,N-1} & f_N \end{pmatrix}$$