晶格(1)三斜(1;$a_1\neq a_2\neq a_3;\alpha\neq\beta\neq\gamma$);单斜(2;$a_1\neq a_2\neq a_3;\alpha,\gamma=\pi/2\neq\beta$);正交(4;$a_1\neq a_2\neq a_3;\alpha=\beta=\gamma=\pi/2$);四角(2,$a_1=a_2\neq a_3;\alpha,\beta,\gamma=\pi/2$);立方(3;$a_1,a_2=a_3;\alpha,\beta,\gamma=\pi/2$);三角(1,$a_1,a_2=a_3;\alpha=\beta=\gamma\neq\pi/2$);六角(1;$a_1=a_2\neq a_3;\alpha=\beta=\pi/2,\gamma=2\pi/3$) **(2)**sc(简单立方,$2r=a$);bcc(体心立方,,$4r=\sqrt{3}a,\rho=2m_0/a^3,a=\sqrt[3]{2m_0/\rho}$);fcc(面心立方,$4r=\sqrt{2}a$);hcp(六角密堆积) **(3)常见结构**:NaCl(Cl面心&角+Na边中&体心);CsCl(Cs体心+Cl角);金刚石结构(fcc+000&$\frac14\frac14\frac14$);ZnS结构(金刚石结构基础上的部分替换)(Zn000, $0\frac12\frac12,\frac12 0\frac12,\frac12\frac12 0$;S$\frac14\frac14\frac14,\frac14\frac34\frac34,\frac34\frac14\frac34,\frac34\frac34\frac14$)eg1.$r_{Cs}=1.7,r_{Cl}=1.81.a=2(r_{Cs}+r_{Cl})/\sqrt{3},PF=\frac{4\pi(r_{Cs}^3+r_{Cl}^3)}{3a^3}\approx0.682,\rho=\frac{m_{Cs}+m_{Cl}}{a^3}=4.2$;eg2.NaCl下的CsCl:$a=2(r_{Cs}+r_{Cl}),PF=\frac{4\pi(r_{Cs}^3+r_{Cl}^3)\cdot4}{3a^3}\approx0.525$;**两种指标**设晶面截距为$a_1,a_2,a_3(1)(a_1^{-1}a_2^{-1}a_2^{-1})$;(2)$[a_1,a_2,a_3]$.上划线表示负号$[u\bar{v}w]$.**布拉格条件**$2d\sin\theta=n\lambda;\Delta\vec{k}=\vec{G};2\vec{k}\cdot\vec{G}=\vec{G}^2$;**劳厄条件**$\vec{a_1}\cdot\Delta\vec{k}=2\pi v_1;\vec{a_2}\cdot\Delta\vec{k}=2\pi v_2;\vec{a_3}\cdot\Delta\vec{k}=2\pi v_3$;**倒格子初基平移矢量** $\vec{b_1}=2\pi\frac{\vec{a_2}\times\vec{a_3}}{\vec{a_1}\cdot\vec{a_2}\times\vec{a_3}}$, $\vec{b_2}=2\pi\frac{\vec{a_3}\times\vec{a_1}}{\vec{a_1}\cdot\vec{a_2}\times\vec{a_3}}$, $\vec{b_3}=2\pi\frac{\vec{a_1}\times\vec{a_2}}{\vec{a_1}\cdot\vec{a_2}\times\vec{a_3}}$. $\vec{b_i}\cdot\vec{a_j}=2\pi\delta_{ij}$;**倒格矢** $\vec{G}=v_1\vec{b_1}+v_2\vec{b_2}+v_3\vec{b_3},v_i\in\mathcal{Z}$. 倒格矢$\vec{G}_{h_1h_2h_3}$垂直于实空间晶面$(h_1h_2h_3)$. 面间距$d=\frac{2\pi}{|\vec{G}_{\vec{h}}|}$**几何结构因子**前提:方向为$\vec{k'}=\vec{k}+\Delta\vec{k}=\vec{k}+\vec{G}$, $S_G=\sum_j f_je^{-i\vec{r_j}\cdot\vec{G}}=\sum_j f(j)e^{-i2\pi(x_jv_1+y_jv_2+z_jv_3)}$, 其中$f_j=\int dVn_j(\vec{r})e^{-i\vec{G}\cdot\vec{r}}$.eg1.bcc&(0,0,0) + $(\frac12,\frac12,\frac12)$, $S(v_1,v_2,v_3)=f(1+e^{-i\pi(v_1+v_2+v_3)})$;eg2.fcc&(0,0,0) + $(0,\frac12,\frac12)+(\frac12,0,\frac12)+(\frac12,\frac12,0)$, $S(v_1,v_2,v_3)=f\{1+e^{-i\pi(v_2+v_3)}+e^{-i\pi(v_1+v_3)}+e^{-i\pi(v_1+v_2)}\}$;**原子形状因子**$f_j=\int dVn_j(\vec{r})e^{-i\vec{G}\cdot\vec{r}}$,球对称极限$f_j=4\pi\int drn_j(r)r^2\frac{\sin Gr}{Gr}$;**第一布里渊区**倒格子的维格纳-塞茨原胞.晶格常数a (1)sc→sc($2\pi/a$); bcc→棱形十二面体(长对角线为$2\cdot\frac{\sqrt{2}\pi}{a}$,短对角线为$2\cdot\frac{\pi}{a}$); fcc→截角八面体(八面体每个角被切,使得相邻三个面的正方形边能围成正六边形. 小正方形和六边形的边长$l=\frac{\sqrt{2}\pi}{2a}$)

声子-振动 (1)无阻尼单原子链:$u_{s\pm1}=ue^{isKa}exp^{\pm iKa}$, 色散关系$w^2=(2C/M)(1-\cos Ka)=\omega_m^2\sin^2\frac12Ka$; $w^2=(4C/M)\sin^2\frac12Ka$; 态密度:$D(\omega)=\frac{Na}{\pi}/|\partial_K\omega|,\partial_K\omega=\frac{a}{2}\omega_m\cos\frac12Ka=\frac{a}{2}(\omega_m^2-\omega^2)^{\frac12}$ 群速:$v_g=\partial_K\omega=\sqrt{Ca^2/M}\cos\frac{Ka}{2}$; [长波极限($Ka\ll1$):$w^2=(C/M)K^2a^2,v=w/K$ 离散化为连续:$M\partial_t^2u_s=\sum_pC_p(u_{s+p}-u_s)=\sum_{p>0}C_p[(u_{s+p}-u_s)+(u_{s-p}-u_s)]=\sum_{p>0}C_p\{[u(x+pa,t)-u(x,t)]+[u(x-pa,t)-u(x,t)]\}=\sum_{p>0}C_pp^2a^2\partial_x^2u(x,t)$,试探解$u_{s+p}=ue^{-i[\omega t-(s+p)Ka]}$, $\omega^2=\frac{2}{M}\sum_{p>0}C_p(1-cospKa)\approx K^2(a^2/M)\sum_{p>0}p^2C_p=v^2K^2\to\partial_t^2u=v^2\partial_x^2u$]**(2)无阻尼双原子链**:原胞p个原子,3个声学支,3p-3个光学支.$M_1\frac{d^2u_s}{dt^2}=C(v_s+v_{s-1}-2u_s);M_2\frac{d^2v_s}{dt^2}=C(u_{s+1}+u_s-2v_s)$. 试探解$u_s=ue^{isKa}e^{-iwt},v_s=ve^{isKa}e^{-iwt}$,行列式系数为0:$M_1M_2w^4-2C(M_1+M_2)w^2+2C^2(1-\cos Ka)=0$;长波极限($Ka\ll1$):光学支$w^2=2C(\frac{1}{M_1}+\frac{1}{M_2})$,声学支$w^2=\frac{C}{2(M_1+M_2)}K^2a^2$;光学支下原子反向震动即质心固定,由光的电场来激发.**(3)波矢选择定则**:波矢$\vec{k}$非弹性散射到$\vec{k'}$,同时产生/吸收波矢为$\vec{K}$的声子:$\vec{k}=\vec{k'}\pm\vec{K}+\vec{G},\vec{G}$是倒格矢;**(4)声子能量**:$\epsilon=(n+\frac12)\hbar\omega$.若$u=u_0\cos Kx\cos\omega tE_k=\int\frac12\rho(\frac{\partial u}{\partial t})^2=\frac14\rho V\omega^2u_0^2\langle\sin^2\omega t\rangle=\frac18\rho V\omega^2u_0^2=\frac12(n+\frac12)\hbar\omega$;动能守恒:$\frac{\hbar^2k^2}{2M_n}=\frac{\hbar^2k'^2}{2M_n}\pm\hbar\omega$**(5)有阻尼单原子链**:$m\partial_t^2u_j=C(u_{j+1}+u_{j-1}-2u_j)-\Gamma\partial_tu_j$.色散关系:$\omega(k)=\sqrt{\omega_{k_0}^2-(\frac{\Gamma}{2m})^2}-\frac{i\Gamma}{2m}(\omega_{k_0}=\sqrt{\frac{4C}{m}}|\sin\frac{ka}{2}|)$弛豫时间 (a)$\omega_{k_0}\geq\Gamma/2m:\tau_k=2m/\Gamma$; (b)$\omega_{k_D}<\Gamma/2m:\tau_k=\frac{\Gamma}{2m\omega_{k_0}^2}(1+\sqrt{1-(\frac{2m\omega_{k_0}}{\Gamma})^2})$**(6)2D正方晶格**:$M\partial_t^2u_{l,m}=C[(u_{l+1,m}+u_{l-1,m}-2u_{l,m})+(u_{l,m+1}+u_{l,m-1}-2u_{l,m})]$.设$u_{l,m}=u_0e^{i(lK_xa+mK_ya-\omega t)}$,色散关系$\omega^2M=2C(2-\cos K_xa-\cos K_ya)(a)K=K(1,0),\omega^2=\frac{2C}{M}(1-\cos Ka)$;(b)$K=K(1,1)/\sqrt{2},\omega^2=\frac{4C}{M}(1-\cos\frac{1}{\sqrt{2}}Ka)$,长波极限($Ka\ll1$)$\omega^2\approx\frac{Ca^2}{M}(K_x^2+K_y^2)$,群速度$v=\partial_K\omega=(\frac{Ca^2}{M})^{\frac12}$.**(7)变C等M双原子链**.$M\partial_t^2u_s=C(v_{s-1}-u_s)+10C(v_s-u_s),M\partial_t^2v_s=10C(u_s-v_s)+C(u_{s+1}-v_s)$.试$u_s=ue^{isKa}e^{-i\omega t},v_s=ve^{isKa}e^{-i\omega t}$.行列式$\begin{vmatrix}M\omega^2-11C, & C(10+e^{-iKa})\\ C(e^{iKa}+10), & M\omega^2-11C\end{vmatrix}=0,\omega_\pm^2=\frac{C}{M}[11\pm\sqrt{121-20(1-\cos Ka)}]$**(8)**已知$\omega=\omega(K)$,则$K=\omega^{-1}(\omega)$,轨道总数$N(\omega)=(\frac{L}{2\pi})^3\frac{4\pi}{3}K^3$,态密度$D(\omega)=|\partial_\omega N|$

热学基础 (0)$\frac{\Delta a}{a}=\frac13\frac{\Delta V}{V}$,定容热容$C_V=(\frac{\partial U}{\partial T})_V$,声子温度$\tau=k_BT$,晶格内能$U_{lat}\sum_K\sum_p\langle n_{K,p}\rangle\hbar\omega_{K,p}$**(1)普朗克分布**$\langle n\rangle=(e^{\hbar\omega/\tau}-1)^{-1}$ **(2)**$U=\sum_K\sum_p\hbar\omega_{K,p}(e^{\hbar\omega_{K,p}/\tau}-1)^{-1}=\sum_p\int d\omega D_p(\omega)\hbar\omega(e^{\hbar\omega/\tau}-1)^{-1}$, $C_{lat}=k_B\sum_p\int d\omega D_p(\omega)\frac{x^2e^x}{(e^x-1)^2}(x=\hbar\omega/\tau=\hbar\omega/k_BT)$,$D(\omega)$即为态密度**(3)**一维$D(\omega)$:$L=Na$,每个间隔$\Delta K=\frac{\pi}{L}$内一个模式,每个$K$三个偏振态(两横一纵)$D(\omega)d\omega=\frac{L}{\pi}\frac{dK}{d\omega}d\omega=\frac{L}{\pi}\frac{d\omega}{d\omega/dK}$(色散关系$\omega(K)$) **(4)**三维$D(\omega)$:$\forall i,K_i=\pm\frac{2n\pi}{L}$,$\vec{K}$单位体积内模式数$(\frac{L}{2\pi})^3=\frac{V}{8\pi^3}$, 每种偏振模式总数$N=(\frac{L}{2\pi})^3(\frac{4\pi K^3}{3})$,态密度$D(\omega)=\frac{dN}{d\omega}=(\frac{VK^2}{2\pi^2})(\frac{dK}{d\omega})$

德拜模型 (0)石墨烯模型(2D).C-C距离d,声速v,晶格常数$a=\sqrt{3}d$,原胞面积$A=\frac{\sqrt{3}a^2}{2}$,德拜波矢$\pi k_D^2=\frac{(2\pi)^2}{A}$,德拜频率$\omega_D=vk_D$,德拜温度$\theta_D=\frac{\hbar\omega_D}{k_B}=\frac{\hbar vk_D}{k_B}$.$(\theta_D|_{d=1.42\mathring{A}}=2.13\times10^3K)$(1)3D下,假设(每种偏振声速恒定,$\omega=vK$)态密度$D(\omega)=\frac{V\omega^2}{2\pi^2v^3}$,德拜/截止频率$\omega_D^3=6\pi^2v^3N/V$,截止波矢$K_D=\omega_D/v=(6\pi^2\frac{N}{V})^{\frac13}$,单偏振态内能$U_i=\int d\omega D(\omega)\langle n(\omega)\rangle\hbar\omega=\int_0^{\omega_D}d\omega(\frac{V\omega^2}{2\pi^2v^3})(\frac{\hbar\omega}{e^{\frac{\hbar\omega}{\tau}}-1})$,总内能$U=3U_i=\frac{3V\hbar}{2\pi^2v^3}\int_0^{\omega_D}d\omega\frac{\omega^3}{e^{\frac{\hbar\omega}{\tau}}-1}=\frac{3Vk_B^4T^4}{2\pi^2v^3\hbar^3}\int_0^{x_D}dx\frac{x^3}{e^x-1}$(其中$x=\hbar\omega/\tau,x_D=\hbar\omega_D/\tau=\theta/T$),德拜温度$\theta=\frac{\hbar v}{k_B}(\frac{6\pi^2N}{V})^{\frac13},U=9Nk_BT(\frac{T}{\theta})^3\int_0^{x_D}dx\frac{x^3}{e^x-1}$e.g.金刚石模型(3D)C-C距离$d$,声速$v$,晶格常数$a=4d/\sqrt{3}$,原胞体积$\Omega=\frac{a^3}{4}$,德拜波矢$\frac43\pi k_D^3=\frac{(2\pi)^3}{\Omega}$,德拜温度$\theta_D=\frac{\hbar\omega_D}{k_B}=\frac{\hbar vk_D}{k_B}$.$(\theta_D|_{d=1.54\mathring{A}}=2.39\times10^3K)$(2)德拜模型低温极限($T^3$律)($\int_0^\infty dx\frac{x^3}{e^x-1}=\frac{\pi^4}{15}$):$U\approx3\pi^2Nk_BT^4/5\theta^3$,热容$C_V\approx\frac{12\pi^4}{5}Nk_B(\frac{T}{\theta})^3\approx234Nk_B(\frac{T}{\theta})^3$;**爱因斯坦模型**$N\omega_0$振子系统($D(\omega)=N\delta(\omega-\omega_0)$):一维内能$U=N\langle n\rangle\hbar\omega=N\hbar\omega/(e^{\hbar\omega/\tau}-1)$,一维比热$C_V=(\frac{\partial U}{\partial T})_V=Nk_B(\frac{\hbar\omega}{\tau})^2\frac{e^{\hbar\omega/\tau}}{(e^{\hbar\omega/\tau}-1)^2}$.3D再乘系数3.

声子热学 (1)态密度$D(\omega)$一般形式:$D(\omega)=\frac{V}{(2\pi)^3}\int_{K中\delta\omega=0}\frac{dS_\omega}{v_g}$**(2)非谐作用**($U(x)=cx^2-gx^3-fx^4$):平均位移$\langle x\rangle=\frac{\int_{-\infty}^{+\infty}dxxe^{-\beta U(x)}}{\int_{-\infty}^{+\infty}dxe^{-\beta U(x)}}(\beta=\frac{1}{k_BT}),\int dxxe^{-\beta U}\approx(\frac{3\pi^{\frac12}}{4})(\frac{g}{c^{\frac52}})\beta^{-\frac32},\int dxe^{-\beta U}\approx(\frac{\pi}{\beta c})^{\frac12},\langle x\rangle=\frac{3g}{4c^2}k_BT$**(3)热导**.一维下热流量$j_U=-K\frac{dT}{dx}$,热导率$K=\frac13Cvl$($C$:单位体积比热;$v$:粒子平均速度;$l$:平均自由程).**(4)过程**.$\vec{K}_1+\vec{K}_2=\vec{K}_3+\vec{G}$.正常(N):$\vec{G}=0$;倒逆(U):$\vec{G}\neq0$ **自由电子 (0)一维无限深井**:$\mathcal{H}\psi_n=-\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2}=\epsilon_n\psi_n;\epsilon_n=\frac{\hbar^2}{2m}(\frac{n\pi}{L})^2$ **(1)费米能**ϵ_F:N电子系统基态下的最高能级;e.g.一维无限深井+泡利原理:$2n_F=N,n=n_F,\epsilon_F=\frac{\hbar^2}{2m}(\frac{N\pi}{2L})^2$; **(2)温度变量**.$f(\epsilon,T,\mu)=(e^{[\epsilon-\mu(T)]/k_BT}+1)^{-1}(T=0时\mu=\epsilon_F)$.取高温极限时成为玻尔兹曼分布/麦氏分布. **(3)(a)3D:** $-\frac{\hbar^2}{2m}\nabla^2\psi_k(\vec{r})=\epsilon_{\vec{k}}\psi_k(\vec{r}),\psi_{\vec{k}}(\vec{r})=e^{i\vec{k}\cdot\vec{r}},(\forall i,k_i=\frac{2n\pi}{L}),\epsilon_{\vec{k}}=\frac{\hbar^2}{2m}(k_x^2+k_y^2+k_z^2)$. $\hat{p}\psi_{\vec{k}}(\vec{r})=\hbar\vec{k}\psi_{\vec{k}}(\vec{r}),\vec{v}=\frac{\hbar\vec{k}}{m}$. F波矢$k_F$, F能$\epsilon_F=\frac{\hbar^2}{2m}k_F^2$.$K$空间的每个体积元$(\frac{2\pi}{L})^3$存在一个波矢$(k_x,k_y,k_z)$. F球+泡利定理:$2\cdot\frac{4\pi k_F^3/3}{(2\pi/L)^3}=N$. F波矢$k_F=(\frac{3\pi^2N}{V})^{\frac13}=(3\pi^2n)^{\frac13}$, F能$\epsilon_F=\frac{\hbar^2}{2m}(\frac{3\pi^2N}{V})^{\frac23}=\frac{\hbar^2}{2m}(3\pi^2n)^{\frac23}$, F速度$v_F = (\frac{\hbar k_F}{m}) = \frac{\hbar}{m}(\frac{3\pi^2 N}{V})^{\frac{1}{3}}$. F温度$T_F = \epsilon_F/k_B$. 态密度$N(U \le \epsilon) = \frac{V}{3\pi^2}(\frac{2m\epsilon}{\hbar^2})^{\frac{3}{2}}, D(\epsilon) = \frac{dN}{d\epsilon} = \frac{V}{2\pi^2}(\frac{2m}{\hbar^2})^{\frac{3}{2}}\epsilon^{\frac{1}{2}} = \frac{3N}{2\epsilon}$,**0K**:$U_0 = 2\sum_{k<k_F}\frac{\hbar^2k^2}{2m}$,**K**中状态数体密度为$\frac{V}{8\pi^3}, \frac{U_0}{V} = \frac{2}{8\pi^3}\int_{k<k_F} d^3k\frac{\hbar^2k^2}{2m} = \frac{1}{\pi^2}\frac{\hbar^2k_F^5}{10m}, N = 2\cdot\frac{4\pi k_F^3}{3}\frac{V}{8\pi^3}, U_0 = \frac{3}{5}N\epsilon_F$,压强$P = -(\partial_V U_0)_N = -\frac{3}{5}(\partial_V\epsilon_F)_N = \frac{2}{3}\frac{U_0}{V}$,体模量$B = -V(\partial_V P) = -V\partial_V[\frac{N\hbar^2}{5m}(\frac{3\pi^2N}{V})^{\frac{2}{3}}\cdot\frac{1}{V}] = \frac{10}{9}\frac{U_0}{V}$ **(b)2D**: $\pi k_F^2\cdot\frac{A}{(2\pi)^2}\cdot 2 = N, k_F = \sqrt{2\pi N/A} = \sqrt{2\pi n}$. 色散关系:$\epsilon = \hbar^2k^2/2m, d\epsilon = \hbar^2kdk/m$. 态密度$D(\epsilon)d\epsilon = \frac{1}{A}\cdot 2\pi kdk\cdot\frac{A}{(2\pi)^2}\cdot 2 = \frac{kdk}{\pi d\epsilon}d\epsilon = \frac{m}{\pi\hbar^2}d\epsilon n = \int_{-\infty}^{+\infty}D(\epsilon)n_F(\epsilon)d\epsilon = \frac{m}{\pi\hbar^2}\int_0^{+\infty}\frac{d\epsilon}{e^{(\epsilon-\mu)/k_BT}+1} = \frac{mk_BT}{\pi\hbar^2}\ln(e^{\mu/k_BT}+1)$. 化学势$\mu(T) = k_BT\ln(e^{\frac{\pi n\hbar^2}{mk_BT}}-1)$ **(4)比热容**. 总电子内能$U_e \approx \frac{NT}{T_F}k_BT$, 电子比热$C_e = \frac{\partial U}{\partial T} \approx Nk_B\frac{T}{T_F}$. 低温极限($k_BT \ll \epsilon_F$):$\Delta U = \int_0^\infty d\epsilon\epsilon D(\epsilon)f(\epsilon) - \int_0^{\epsilon_F}d\epsilon\epsilon D(\epsilon) = \int_{\epsilon_F}^\infty d\epsilon(\epsilon-\epsilon_F)f(\epsilon)D\epsilon + \int_0^{\epsilon_F}d\epsilon(\epsilon_F-\epsilon)[1-f(\epsilon)]D(\epsilon)$. 电子热容$C_e = \frac{dU}{dT} = \int_0^\infty d\epsilon(\epsilon-\epsilon_F)\frac{df}{dT}D(\epsilon) \approx D(\epsilon_F)\int_0^\infty d\epsilon(\epsilon-\epsilon_F)\frac{df}{dT}$低温极限($\tau = k_BT, x = \frac{\epsilon-\epsilon_F}{\tau}$)$\int_{-\infty}^{+\infty}dxx^2\frac{e^x}{(e^x+1)^2} = \frac{\pi^2}{3}, C_e = \frac{1}{3}\pi^2D(\epsilon_F)k_B^2T(D(\epsilon_F) = \frac{3N}{2\epsilon_F}), C_e = \frac{1}{2}\pi^2Nk_BT/T_F$.**(5)金属比热**.$\frac{C}{T} = \gamma + AT^2$($\gamma$索末菲常量). **(6)电导率**.$\vec F = -e(\vec E + \frac{1}{c}\vec v\times\vec B)$. 若$\vec F = -e\vec E, \delta\vec k = -e\vec Et/\hbar, \vec v = \delta\vec k/m = -e\vec E\tau/m$. 电流密度$\vec j = nq\vec v = ne^2\tau\vec E/m, (\vec j = \sigma\vec E)\sigma = \frac{ne^2\tau}{m}, \rho = \sigma^{-1}$. [电子漂移速度v:$m(\partial_t v + v/\tau) = -eE$,试$E = E_0e^{-i\omega t}, v = v_0e^{-i\omega t}, v = \frac{-(1+i\omega\tau)}{1+(\omega\tau)^2}\frac{e\tau}{m}E, \sigma(\omega) = j/E = -env/E = \frac{e^2\tau n}{m}(\frac{1+i\omega\tau}{1+(\omega\tau)^2})$] **(7)磁场下运动**.(CGS制)$\hbar(\frac{d}{dt}+\frac{1}{\tau})\delta\vec k = \vec F = -e(\vec E + \vec v\times\vec E)$.若$\vec B = B\hat z, \{v_x = -\frac{e\tau}{m}E_x - \omega_c\tau v_y, v_y = -\frac{e\tau}{m}E_y + \omega_c\tau v_x, v_z = -\frac{e\tau}{m}E_z\}$,回旋频率$\omega_c = \frac{eB}{mc}$ [漂移速度理论:$m(\partial_t + \tau^{-1})v_x = -e(E_x + \frac{B}{c}v_y), m(\partial_t+\tau^{-1})v_y = -e(E_y - \frac{B}{c}v_x), m(\partial_t+\tau^{-1})v_z = -eE_z, j = -nev, v_x = \frac{1}{1+(\omega_c\tau)^2}(-\frac{e\tau}{m}E_x + \frac{\omega_c\tau^2e}{m}E_y), v_y = \frac{1}{1+(\omega_c\tau)^2}(-\frac{\omega_c\tau^2e}{m}E_x - \frac{e\tau}{m}E_y), v_z = -\frac{e\tau}{m}E_z, [j_x,j_y,j_z]^T = \frac{\sigma_0}{1+(\omega_c\tau)^2}[1,-\omega_c\tau,0;\omega_c\tau,1,0;0,0,1 + (\omega_c\tau)^2][E_x,E_y,E_z]^T$,其中$\sigma_0 = ne^2\tau/m, \omega_c = Be/mc$.若$j_y = 0, E_y = -\omega_c\tau E_x, j_x = \sigma_0E_x$ →自由电子理论太简单] **(8)霍尔效应.霍尔系数**$R_H = \frac{E_y}{j_xB} = -\frac{1}{nec}$(CGS). **(9)金属热导率**.$K_e = \frac{1}{3}Cvl = \frac{\pi^2}{3}\frac{nk_B^2T}{mv_F^2}v_Fl = \frac{\pi^2nk_B^2T\tau}{3m}$(10)洛伦兹常量$L = \frac{K}{\sigma T} = \frac{\pi^2}{3}(\frac{k_B}{e})^2 = 2.45\times10^{-8}(W\cdot\Omega/deg^2)$. **(10)金属受力**自由电子.($n_{Cu}\approx 10^6$) $k_F = (3\pi^2n)^{\frac{1}{3}} \propto n^{\frac{1}{3}}; \epsilon_F = \hbar^2k_F^2/2m = \hbar^2(3\pi^2n)^{\frac{2}{3}} \propto n^{\frac{2}{3}}$ $D(\epsilon)\propto\epsilon^{\frac{1}{2}}.\langle\epsilon\rangle = \frac{\int_0^{\epsilon_F}\epsilon D(\epsilon)d\epsilon}{\int_0^{\epsilon_F}D(\epsilon)d\epsilon} = \frac{3}{5}\epsilon_F$ $E = N\langle\epsilon\rangle \propto V^{-\frac{2}{3}}, P = -\frac{dE}{dV} = \frac{2}{5}n\epsilon_F \propto \epsilon_F^{\frac{5}{2}}$. $\frac{dP}{d\epsilon_F} = n \to \Delta P \approx n\Delta\epsilon_F$. **(11)求第一布里渊区能带**3D$\epsilon(\vec K) = \frac{\hbar^2}{2m}[(K_x + g_1\frac{2\pi}{a})^2 + (K_y+g_2\frac{2\pi}{a})^2 + (K_z+g_3\frac{2\pi}{a})^2]$,

近自由电子模型 **(0)一维晶体布拉格衍射条件**$(\vec k + \vec G)^2 = \vec k^2 \to k = \pm\frac{1}{2}G = \pm\frac{n\pi}{a}$(倒格矢$G = \frac{2\pi n}{a}$) **(1)驻波**.与时间无关.$\psi(+) = e^{i\pi x/a} + e^{-i\pi x/a} = 2\cos\pi x/a, \psi(-) = e^{i\pi x/a} - e^{-i\pi x/a} = 2i\sin\pi x/a$. $\rho(+) = |\psi(+)|^2 \propto \cos^2\pi x/a, \rho(-) = |\psi(-)|^2 \propto \sin^2\pi x/a$.大小关系:$\langle\psi(-)|U|\psi(-)\rangle \le \langle e^{\mp i\pi x/a}|U|e^{\pm i\pi x/a}\rangle \le \langle\psi(+)|U|\psi(+)\rangle$. 若一维$\psi(x) = \sqrt2\cos\pi x/a, \sqrt2\sin\pi x/a$,电子势能$U(x) = U\cos2\pi x/a$,则一级近似能隙$E_g = U(+) - U(-) = \int_0^1 dxU(x)[|\psi(+)|^2 - |\psi(-)|^2] = U$. **(2)布洛赫函数**.若势周期,则$\psi_{\vec k}(\vec r) = u_{\vec k}(\vec r)e^{i\vec k\cdot\vec r}$(其中$u_{\vec k}(\vec r) = u_{\vec k}(\vec r + \vec T)$). 若非简并,$\psi(x+a) = C\psi(x), C = e^{i2\pi s/N} \to \psi(x) = u_{\vec k}(x)e^{i2\pi sx/N}$. **(3)KP模型Kölnig-Penney**(周期δ势阱).$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U(x)\psi = \epsilon\psi$. $x\in(0,a):\psi = Ae^{iKx} + B^{-iKx}, \epsilon = \frac{\hbar^2K^2}{2m}; x\in(-b,0):\psi = Ce^{Qx} + De^{-Qx}, U_0 - \epsilon = \frac{\hbar^2Q^2}{2m}$. 函数连续+导数连续,有四阶系数行列式为0:$[(Q^2-K^2)/2QK]\sinh Qb\sin Ka + \cosh Qb\cos Ka = \cos k(a+b)$.取极限$b = 0, U_0 = \infty(Q \gg K, Qb \ll 1)$,即为周期性δ函数,$P = \frac{Q^2ba}{2}$结论化为$(P/Ka)\sin Ka + \cos Ka = \cos ka$. **(4)周期势下的电子波函数**.$U(x) = \sum_G U_Ge^{iGx}$,若为实则$U(x) = \sum_{G>0}2U_G\cos Gx.\psi = \sum_k C(k)e^{ikx}$. 波动方程$\sum_k\frac{\hbar^2}{2m}k^2C(k)e^{ikx} + \sum_G\sum_kU_GC(k)e^{i(k+G)x} = \epsilon\sum_k e^{ikx}$. 中心方程$(\lambda_k-\epsilon)C(k) + \sum_GU_GC(k-G) = 0$(其中$\lambda_k = \frac{\hbar^2k^2}{2m}$) **(5)求解行列式**$\det\{\{\lambda_{k-g}-\epsilon, U, 0\}, \{U, \lambda_k-\epsilon, U\}, \{0, U, \lambda_{k+g}-\epsilon\}\}$ 每一个k每个ϵ将在不同能带上. **(6)中心方程求解K-P方程**(周期δ势函数).$U(x) = Aa\sum_s\delta(x-sa), U_G = \int_0^1 dxU(x)cos(Gx) = A$.中心方程变为$(\lambda_k-\epsilon)C(k) + Af(k) = 0$,其中$f(k) = \sum_nC(k-2\pi n/a) = f(k\pm2\pi n/a)$.从而有$\frac{mAa^2}{2\hbar^2}(Ka)^{-1}\sin Ka + \cos Ka = \cos ka$.极限$P \ll 1$, **(7)布里渊区边界附近近似解**. $k^2 = (\frac{1}{2}G)^2, (k-G)^2 = (\frac{1}{2}G - G)^2 \to k = \pm\frac{1}{2}G$. ($k = \frac{1}{2}G, \lambda = \hbar^2(\frac{1}{2}G)^2/2m$)$(\lambda-\epsilon)C(\pm\frac{1}{2}G) + UC(\mp\frac{1}{2}G) = 0$. 行列式$|{}^{\lambda-\epsilon,U}_{U,\lambda-\epsilon}| = 0$,解得$\epsilon = \lambda\pm U, E_g = 2U$. 若在$\frac{1}{2}G$附近,则$(\lambda_k-\epsilon)C(k) + UC(k-G) = 0, (\lambda_{k-G})C(k-G) + UC(k) = 0(\lambda_k = \hbar^2k^2/2m)$, 系数行列式$|{}^{\lambda_k-\epsilon,U}_{U,\lambda_{k-G}-\epsilon}| = 0 \to \epsilon = \frac{1}{2}(\lambda_{k-G}+\lambda_k)\pm[\frac{1}{4}(\lambda_{k-G}-\lambda_k)^2+U^2]^{\frac{1}{2}}$ 用小量$\widetilde K = k - \frac{1}{2}G$展开,有$\epsilon_{\widetilde K} \approx \frac{\hbar^2}{2m}(\frac{1}{4}G^2 + \widetilde K^2) \pm U[1 + 2(\frac{\lambda}{U^2})(\frac{\hbar^2\widetilde K^2}{2m})]$. **(8)轨道数.N原胞一维**:$k = \pm\frac{2n\pi}{L}$.每原胞对应一个k+泡利定理→每能带2N轨道. **(9)正方晶格**$U(x) = -4U\cos\frac{2\pi x}{a}\cos\frac{2\pi y}{a}, \vec r = x\hat i + y\hat j, \vec G = G_1\hat{b_1} + G_2\hat{b_2} = \frac{2\pi}{a}(g_1\hat{b_1} + g_2\hat{b_2})$.;$U(\vec r) = -U(e^{i\frac{2\pi}{a}x} + e^{-i\frac{2\pi}{a}x})(e^{i\frac{2\pi}{a}y} + e^{-i\frac{2\pi}{a}y}) = -U[e^{i\frac{2\pi}{a}(x+y)} + e^{i\frac{2\pi}{a}(x-y)} + e^{-i\frac{2\pi}{a}(x-y)} + e^{-i\frac{2\pi}{a}(x+y)}] = U_{G(11)}e^{iG(11)\cdot\vec r} + U_{G(\bar11)}e^{iG(\bar11)\cdot\vec r} + U_{G(1\bar1)}e^{iG(1\bar1)\cdot\vec r} + U_{G(\overline{11})}e^{iG(\overline{11})\cdot\vec r} = \sum_{G(11)}e^{iG(11)\cdot\vec r}$.中心方程$(\lambda_k-\epsilon)C(\vec K) + U_G(11)C(\vec K - \vec G(11)) + U_{\vec G}(\overline{11})C(\vec K - \vec G(\bar11)) + U_G(1\bar1)C(\vec K - \vec G(1\bar1)) + U_G(\bar11)C(\vec K - \vec G(\bar11))$.若$\vec K = \vec G(\frac12\frac12) = \frac12\vec G(11), |{}^{\lambda_{\frac12G(11)}-\epsilon,-U}_{-U,\lambda_{-\frac12G(11)}-\epsilon}| = 0, \epsilon = \frac{\hbar^2\pi^2}{ma^2}\pm U$

紧束缚模型**(1)**$E(\vec k) = \epsilon_i - \sum_sJ(\vec R_s)e^{-i\vec k\cdot\vec R_s}(\vec R_s = \vec R_n - \vec R_m)$,**(2)1D,s:**$E(\vec k) = \epsilon_s - J_0 - J_1e^{-ika} - J_1e^{ika} = \epsilon_s - J_0 - 2J\cos(ka)$;**(3)2D,sc:**$E = \epsilon - 2t(\cos(k_xa)+\cos(k_ya))$;Honeycomb:$\phi(\vec r) = c_A\phi_A(\vec r) + c_B\phi_B(\vec r) = \frac{1}{\sqrt N}\sum_{\vec R_m}e^{i\vec k\cdot\vec R_m}\left[c_A\varphi(\vec r - \vec R_m^A) + c_B\varphi(\vec r - \vec R_m^B)\right], E(\vec k) = \epsilon_1 \pm J\sqrt{3 + 2\cos(\sqrt3k_ya) + 4\cos\left(\frac{\sqrt3k_ya}{2}\right)\cos\left(\frac{3k_xa}{2}\right)}$(4)3D,(sc):$\epsilon(\vec k) = \epsilon_s - J_0 - 2J_1(\cos k_xa + \cos k_ya + \cos k_za)$;(bcc):$\epsilon(\vec k) = -\alpha - 8\gamma\cos\left(\frac{k_xa}{2}\right)\cos\left(\frac{k_ya}{2}\right)\cos\left(\frac{k_za}{2}\right)$;(fcc)$\epsilon(\vec k) = -\alpha - 4\gamma\left[\cos\left(\frac{k_ya}{2}\right)\cos\left(\frac{k_za}{2}\right) + \cos\left(\frac{k_za}{2}\right)\cos\left(\frac{k_xa}{2}\right) + \cos\left(\frac{k_xa}{2}\right)\cos\left(\frac{k_ya}{2}\right)\right]$ **(5)简并:**$\phi(\vec r) = \frac{1}{\sqrt N}\sum_{\vec R_m}\sum_je^{i\vec k\cdot\vec R_m}c_j\varphi_j(\vec r - \vec R_m)$**(6)周期δ势**.

(补充)近自由电子近似(s,p)(1)非简并微扰:$\varphi_k(x) = \varphi_k^0(x) + \sum_{k'(k'\neq k)}\frac{\langle k'|V(x)|k\rangle}{E_k^0-E_{k'}^0}\varphi_{k'}(x)(\langle k'|V(x)|k\rangle = \frac1L\int e^{-i(k'-k)x}V(x)\mathrm{d}x = V_G(G = k'-k))$,即$\varphi_k = \varphi_k^0(x) + \sum_{k'(k'\neq k)}\frac{\langle k'|V(x)|k\rangle}{E_k^0-E_{k'}^0}\varphi_{k'}^0(x) = \varphi_k^0(x) + \sum_{k'(k'\neq k)}\frac{V_G}{E_k^0-E_{k'}^0}\varphi_{k'}^0(x)$,1级:$\langle k|V(x)|k\rangle = \frac1L\int_0^LV(x)\mathrm{d}x = \langle V\rangle = 0$;2级:$E_k^2 = \sum_{k'}\frac{|\langle k'|V(x)|k\rangle|^2}{E_k^0-E_{k'}^0} = \sum_G\frac{|V_G|^2}{\frac{\hbar^2}{2m}[k^2-(k+G)^2]}(I)(k+G)^2 \gg k^2$,自由电子;(II)$(k+G)^2 = k^2$,**(2)简并微扰**:$\{{}^{(E_k^0-E)a+V_G^*b=0}_{V_Ga+(E_{k'}^0-E)b=0}, |{}^{(E_k^0-E),V_G^*}_{V_G,(E_{k'}^0-E)}| = 0, E_{k\pm} = \frac12\left\{(E_k^0+E_{k'}^0)\pm\sqrt{(E_k^0+E_{k'}^0)^2+4|V_G|^2}\right\}$.(I)$E_k^0 = E_{k'}^0$(BZ边界):$E_{k\pm} = E_k^0\pm|V_G|$;(II)$|E_k^0 - E_{k'}^0| \gg |V_G|$(远离BZ):$E_{k\pm} = \{{}^{E_{k'}^0 + \frac{|V_G|^2}{E_{k'}^0-E_k^0}}_{E_k^0+\frac{|V_G|^2}{E_{k'}^0-E_k^0}}$ (III)靠近BZ边界($|E_k^0-E_{k'}^0| \ll |V_G|$):$E_{k\pm} = \frac12\left\{E_k^0+E_{k'}^0\pm\left[2|V_G| + \frac{(E_{k'}^0-E_k^0)^2}{4|V_G|}\right]\right\}$,其中$E_k^0 + E_{k'}^0 = 2E_0 + \frac{\hbar^2}{m}\left(k+\frac G2\right)^2, (E_{k'}^0-E_k^0)^2 = 4\left(\frac{\hbar^2}{2m}\right)^2G^2\left(k+\frac G2\right)^2$,即$E_{k\pm} \approx (E_0\pm|V_G|) + \frac{\hbar^2}{2m}\left(k+\frac G2\right)^2 \pm \left(\frac{\hbar^2}{2m}\right)^2\frac{G^2}{2|V_G|}\left(k+\frac G2\right)^2$

半导体价带顶($\bigcap$),导带底($\bigcup$)**(1)电子群速度**:$\vec{v}_g=\nabla_{\vec{k}}\omega(\vec{k})=\frac{1}{\hbar}\nabla_{\vec{k}}E(\vec{k})$**(2)有效质量**$\frac{1}{m^*}=\frac{1}{\hbar^2}\frac{\mathrm{d}^2E}{\mathrm{d}k^2}$,特定方向:$\left(\frac{1}{m*}\right)_{\mu\nu}=\frac{1}{\hbar^2}\frac{\mathrm{d}^2E}{\mathrm{d}k_\mu\mathrm{d}k_\nu}$;另一种定义:$m^*=\hbar^2k\left(\frac{\partial E}{\partial k}\right)^{-1}$用于线性色散$E=a(|\vec{k}-\vec{k}_0|)$:$m^*=\frac{\hbar|\vec{k}|}{v_g}=\frac{\hbar}{v_g}|\vec{k}-\vec{k}_0|$.能隙$\Delta$的关系:$\Delta=2m_0v_g^2$.**(3)空穴**:$\vec{k}_h=-\vec{k}_e$;$E_h(\vec{k}_h)=-E_e(\vec{k}_e)$;$\vec{v}_h=-\frac{1}{\hbar}\nabla_{\vec{k}_h}E_h(\vec{k}_h)=\frac{1}{\hbar}\nabla_{\vec{k}_e}E_e(\vec{k}_e)=\vec{v}_e$.**(4)激子**$\frac{1}{\mu^*}=\frac{1}{m_C^*}+\frac{1}{m_{hh}^*}$,($m_C^*=0.067m_e,m_{hh}^*=0.45m_e$),长度$a_0^*=\frac{\epsilon_rm_e}{\mu^*}\cdot a_0(a_0=\frac{\epsilon_0h^2}{\pi m_ee^2}\approx0.53\text{Å})$**(5)粒子浓度**:$\mathrm{d}n=f(E,T)g(E)\mathrm{d}E(f(E,T)=\frac{1}{1+e^{(E-\mu)/k_BT}})$.$E-\mu\gg k_BT$极限F-D 分布退化为 B 分布:$f(E,T)\approx e^{-(E-\mu)/k_BT}$.导带找到e:$f_C\approx e^{-(E-\mu)/k_BT}$;价带找到h:$f_h=1-f_V=e^{-(\mu-E)/k_BT}$.g(E)因近似抛物线色散($E-E_C=\frac{(k-k_C)^2}{2m_C^*}$,$E-E_V=-\frac{(k-k_V)^2}{2m_h^*}$),即态密度:$g_C(E)=a(m_C^*)^{\frac{3}{2}}(E-E_C)^{\frac{1}{2}}$;$g_V(E)=a(m_h^*)^{\frac{3}{2}}(E_V-E)^{\frac{1}{2}}$,$\therefore$ $n=\int_{E_C}^\infty f_Cg_C\mathrm{d}E\approx a(m_C^*)^{\frac{3}{2}}\int_{E_C}^\infty(E-E_C)^{\frac{1}{2}}e^{-\frac{E-\mu}{k_BT}}\mathrm{d}E=N_ce^{-\frac{E_C-\mu}{k_BT}}(N_C=2(\frac{k_B}{2\pi\hbar^2})^{\frac{3}{2}}(m_C^*T)^{\frac{3}{2}})$,同理 $p\approx N_Ve^{-\frac{\mu-E_V}{k_BT}}(N_V=2(\frac{k_B}{2\pi\hbar^2})^{\frac{3}{2}}(m_h^*T)^{\frac{3}{2}})$.**Law of Mass Action:**$np\approx WT^3e^{-\frac{E_g}{k_BT}}$(前提:$|\mu-E|\gg k_BT$)**(6)化学势**本征半导体$n$=$p$,$\frac{N_V}{N_C}=e^{\frac{2\mu-E_C-E_V}{k_BT}}$;$\mu=\frac{1}{2}(E_C+E_V)+\frac{3}{4}k_BT\ln\frac{m_h^*}{m_C^*}$(7)电导率(I)载流子迁移率($\mu_e,\mu_h$)$\mu=\frac{|v|}{E}$(电荷 q 的漂移速度 $v=\frac{q\tau E}{m}$,τ为碰撞时间)$\mu_{e/h}=\frac{e\tau_{e/h}}{m_{e/h}}$.半导体:$\sigma=ne\mu_e+pe\mu_h$**(7)掺杂**半导体原子价态为$\nu$,则$n$型掺杂(杂质价态为$\nu+1$);p型掺杂(杂质价态为 $\nu-1$)(I)浅掺杂能级:类H.(i)掺杂e:$E_d=-\frac{m_c^*}{m_e}\frac{1}{\epsilon_r^2\times\frac{13.6\mathrm{eV}}{n^2}}$;(2)掺杂h:$E_a=-\frac{m_V^*}{m_e}\frac{1}{\epsilon_r^2}\times\frac{13.6\mathrm{eV}}{n^2}$.参与导电.**(8)非本征载流子浓度**掺杂较少,μ还在能隙中:$np=WT^3e^{-\frac{E_g}{k_BT}}$.全电离时电荷守恒:$N-p=N_D-N_A$.半导体pn结.p型:$\mu(E_F)$比$E_i$更靠近价带顶;n型:$\mu(E_F)$比$E_i$ 更靠近导带底.e,h扩散,通过$\mu(E_F)$ 拉平.(I)金属-半导体接触:(i)肖特基:半导体$\mu(E_F)\uparrow$,e从半导体到金属;内建电场,导带能量$\uparrow$,导带底和费米能级距离$\uparrow$(ii)欧姆:半导体$\mu(E_F)$低于金属,对e无势垒.(II)金属-氧化绝缘体-半导体(MOS)费米能级独立,类电容.(i)正电压:e从半导体远端到绝缘端.$\mu(E_F)$更靠近导带底, n型强化;(ii)反电压:e向半导体远端移动.超限后,发生反型($\mu(E_F)$更靠近价带顶) **(9)布洛赫振荡**运动方程$\hbar\frac{\mathrm{d}k}{\mathrm{d}t}=-eE$,解$k(t)=k(0)-\frac{eE}{\hbar}t$.能带色散$\epsilon(k)=\epsilon_0[1-\cos{(ak)}]$,电子群速度$v(k)=\frac{1}{\hbar}\frac{\mathrm{d}\epsilon}{\mathrm{d}k}=\frac{\epsilon_0a}{\sin{(ak)}}$.$k(0)=x(0)=0$,$x(t)=\int_0^tv[k(t')]\mathrm{d}t'=\frac{\epsilon_0}{eE}\left[\cos{(\frac{eEa}{\hbar}t)}-1\right]$.振荡频率$\omega_{\mathrm{BO}}=eEa/\hbar$.观测条件$\tau\gg2\pi/\omega_{\mathrm{BO}}=h/eEa$.

布洛赫电子动力学(1)运动特征$\hbar\frac{\mathrm{d}\vec{k}}{\mathrm{d}t}=-e\vec{v}\times\vec{B}$.e群速度$\vec{v}=\frac{1}{\hbar}\nabla_kE(\vec{k})$;$\frac{\mathrm{d}E}{\mathrm{d}t}=\nabla_k(\vec{k})\frac{\mathrm{d}\vec{k}}{\mathrm{d}t}=0$. 实空间和倒空间运动方向垂直.**(2)回旋频率**$k_z=0$.周期$T=\frac{2\pi K}{\frac{evB}{\hbar}}=\frac{2\pi}{eB}\frac{\hbar K}{v}=\frac{2\pi m}{eB}$;回旋频率$\omega_c=\frac{2\pi}{T}=\frac{eB}{m_c^*}(m_c^*\ncong m^*)$**(3)磁场中的分立能**(1.抛物线色散2.忽略自旋)朗道能级$E(k)=\frac{\hbar^2}{2m}k_z^2+\left(n+\frac{1}{2}\right)\hbar\omega_c$.(I)简并度(i)无磁场:$E(\vec{k})=\frac{\hbar^2}{2m}(k_x^2+k_y^2)$(ii)有磁场:相邻的两个朗道环$L_n,L_{n+1}$所围的全部态简并到同一能级.态数目$n_k=\Delta A\times\frac{S}{4\pi^2}=\pi\left[\Delta(k_x^2+k_y^2)\right]\times\frac{S}{4\pi^2}=\frac{2\pi m\Delta E}{\hbar^2}\times\frac{S}{4\pi^2}=\frac{2\pi m\hbar\omega_c}{\hbar^2}\times\frac{S}{4\pi^2}=\frac{4\pi^2eB}{h}\times\frac{S}{4\pi^2}=\frac{eBS}{h}$,朗道能级简并度$p=2n_k=\frac{2e}{h}BS=\frac{BS}{\Phi_0}(\Phi_0=\frac{h}{2e}\approx2.067\times10^{-15}(\mathrm{Wb}))$.适用高量子态条件:$\oint\vec{p}\cdot\mathrm{d}\vec{r}=(n+\gamma)\cdot2\pi\hbar\to A_r=\frac{2\pi\hbar}{eB}(n+\gamma)$. $\because\hat{B}\times\frac{\mathrm{d}\vec{k}}{\mathrm{d}t}=-\frac{eB}{\hbar}\frac{\mathrm{d}\vec{r}_\perp}{\mathrm{d}t}$,$\therefore$ $\frac{A_k}{A_r}=\left(\frac{eB}{\hbar}\right)^2$,$\mathbf{A_k}=\frac{\mathbf{2\pi eB}}{\hbar}(\mathbf{n}+\gamma)$.变换:$\frac{1}{B}=\frac{2\pi e}{\hbar A_k}(n+\gamma)\to\Delta\left(\frac{1}{B}\right)=\left(\frac{1}{B_{n+1}}-\frac{1}{B_n}\right)=\frac{2\pi e}{\hbar}\frac{1}{A_k}$**(II)de Hass-Van Alphen效应**(i)二维情形:|▷|横轴为磁矩,横轴为磁场.$\Delta\left(\frac{1}{B}\right)=\frac{2\pi e}{\hbar}\cdot\frac{1}{A_{k_F}}$,$A_F$对应极值轨道.(ii)fcc(Au,Ag,Cu)$n=\frac{4}{a^3}$,$k_F=(3\pi^2n)^{\frac{1}{3}}=\left(\frac{12\pi^2}{a^3}\right)^{\frac{1}{3}}\approx4.90a^{-1}$,跨越BZ最短距离:$\sqrt{3}b=\left(\frac{2\pi}{a}\right)\approx10.88a^{-1}$,$\frac{4\pi}{a}\approx12.57a^{-1}$,Au:$\Delta\left(\frac{1}{B}\right)=2\times10^{-9}\mathrm{G}^{-1}$,极值轨道:$S=\frac{2\pi e}{\hbar}\cdot\left[\Delta\left(\frac{1}{B}\right)\right]^{-1}\approx4.8\times10^{16}\mathrm{cm}^{-2}$**(4)磁场下2D电子**$E=\left(n+\frac{1}{2}\right)\hbar\omega_c$(I)展宽(i)本征:$\delta E\approx\frac{\hbar}{\tau}$,分辨条件$\omega_c\cdot\tau\gg1$;(ii)温度:分辨条件$\hbar\omega_c>k_BT$(低温极限)(II)简并度:单位面积内每个朗道能级的电子数.单位面积内朗道能级简并度:$n_L=\frac{2eB}{h}$(i)电导极小(态密度谷):$N_L=n\frac{2eB}{h}$,(ii)电导极大(态密度峰):$N_L=\left(n+\frac{1}{2}\right)\frac{2eB}{h}$,电导周期:$\Delta\left(\frac{1}{B}\right)=\frac{2e}{hN_L}$(III)霍尔效应.$\overleftrightarrow{\sigma}=\frac{\sigma_0}{1+(\omega_c\tau)^2}\begin{bmatrix}1,-\omega_c\tau\\\omega_c\tau,1\end{bmatrix}$,霍尔系数$R_H=\frac{E_y}{j_xB}=\frac{\sigma_{xy}}{\sigma_{xx}^2+\sigma_{xy}^2}\cdot\frac{1}{B}=\frac{-1}{B}\cdot\frac{\omega_c\tau}{\sigma_0}=-\frac{1}{ne}$.二维各向同性:$\begin{bmatrix}J_x\\J_y\end{bmatrix}=\begin{bmatrix}\sigma_{xx},\sigma_{xy}\\-\sigma_{xy},\sigma_{yy}\end{bmatrix}\begin{bmatrix}E_x\\E_y\end{bmatrix}$,霍尔效应:$\begin{Bmatrix}\rho_{xx}=\frac{E_x}{J_x}=\frac{\sigma_{xx}}{\sigma_{xx}^2+\sigma_{xy}^2}\\\rho_{xy}=\frac{E_y}{J_x}=\frac{\sigma_{xy}}{\sigma_{xx}^2+\sigma_{xy}^2}\end{Bmatrix}$.极限$\omega_c\tau\gg1\to\sigma_{xy}\gg\sigma_{xx}$: $\begin{Bmatrix}\rho_{xx}=\frac{\sigma_{xx}}{\sigma_{xy}^2}\\\rho_{xy}=\frac{1}{\sigma_{xy}}=R_HB\end{Bmatrix}$;$R_H=\frac{E_y}{J_xB}$.**(5)电阻**(I)电子-声子散射(准弹性散射)$E_{k'}=E_k\pm\hbar\omega,\vec{k}'=\vec{k}\pm\vec{q}+\vec{G}$.弛豫时间和散射概率:$\frac{1}{\tau}=\left(\frac{1}{2\pi}\right)^3\int\omega_{\vec{k},\vec{k}'}(1-\cos\theta)\mathrm{d}\vec{k}'$(i)高T($T>\Theta_D$) : $\rho\propto\frac{1}{\tau}\propto T$(高温) (ii)低T($q\ll k_F$) : $N_{\text{声子}}\propto T^3$(低温) : $1-\cos\theta=2\sin^2\left(\frac{\theta}{2}\right)=\frac{1}{2}\left(\frac{q}{k_F}\right)^2$($\theta$很小).低温条件:$q\approx E\approx k_BT,1-\cos\theta\approx T^2,\omega_{\vec{k},\vec{k}'}\propto T^3$: $\rho\propto\frac{1}{\tau}\propto T^5$(II)剩余电阻率(杂质贡献).$\left(\frac{\partial\rho}{\partial T}\right)_{T\to0}=0\Rightarrow\rho_{T\to0}=const.$ **(6)磁阻**(电阻随磁场的变化)(O)理想:一种载流子,完美球形费米面,洛伦兹力平衡于电场力,电子的运动将对是否有磁场不敏感,磁阻为0.(I)真实:(i)E_F并不是严格球形,v_F,m^*,τ各向异性;(ii)多条能带经过E_F,各能带v_F,m^*,τ不同.[例]两能带:$\frac{\Delta\sigma}{\sigma_0}=-\frac{\sigma_{10}\sigma_{20}}{(\sigma_{10}+\sigma_{20})^2}(\omega_{c1}\tau_1-\omega_{c2}\tau_2)^2\Rightarrow\frac{\Delta\rho}{\rho_0}=\frac{\rho(B)-\rho(0)}{\rho(0)}\propto B^2>0$**(7)相位效应**(O)与杂质弹性散射,e相干:$\vec{k}\to\vec{k}'(|\vec{k}|=|\vec{k}'|),\phi\to\phi'$;与声子非弹性散射,e非相干:$\phi=e^{-iEt/h}$.相位相干长度$l_\phi=v_F\tau_2$.(I)从$x'$ 到 x'' 的总概率:$P=|\sum_iA_i|^2=|\sum_iA_i^2|+\sum_{i\neq j}A_iA_j$.(II)弱局域化.环路:$P=|A_+|^2+|A_-|^2+A_+A_-^*+A_+^*A_-=4A^2$,大于经典概率$P'=2\cdot A^2=2A^2$,电导变小, 电阻增大.对2D:$\Delta\sigma=-\sigma_{00}\ln\frac{\tau_2}{\tau_1}=\sigma_{00}p\ln T$.(III)负磁阻:$\vec{B}=\nabla\times\vec{A},\varphi(\vec{r})=\varphi_0(\vec{r})=e^{-\frac{ie}{\hbar}\int\vec{A}(\vec{r}')\cdot\mathrm{d}\vec{r}'}$,$A_+\to A_+e^{-\frac{ie}{\hbar}\oint\vec{A}\cdot\mathrm{d}\vec{l}}=A_+e^{-\frac{ie}{\hbar}\iint\vec{B}\cdot\mathrm{d}\vec{S}}=A_+e^{-\frac{ie}{\hbar}\Phi}$,$A_-\to A_-e^{\frac{ie}{\hbar}\Phi}=A_-e^{i2\pi\Phi/(2\Phi_0)}(\Phi_0=\frac{h}{2e})$,$P=2A^2\left[1+\cos^2\left(2\pi\frac{\Phi}{\Phi_0}\right)\right]\leq4A^2$

输运现象温度:$\vec{J}_Q=-\kappa\nabla T$;浓度:$\vec{J}_Q=-D\nabla n$;电势:$\vec{J}_e=-\sigma\nabla\varphi$ **(1)非平衡分布函数**:$f_n(\vec{r},\vec{k},t)\frac{\mathrm{d}\vec{r}\mathrm{d}\vec{k}}{(2\pi)^3}$(单位体积材料中,在$t$的第$n$能带中,在$\left(\vec{r},\vec{k}\right)$处单位体积$\mathrm{d}\vec{r}\mathrm{d}\vec{k}$某自旋的平均电子数)**(2)非平衡电流**$\vec{J}_e=-en(\vec{r},t)\vec{v}_d=-\frac{2}{(2\pi)^3}\int e\vec{v}_{\vec{k}}f\left(\vec{r},\vec{k},t\right)\mathrm{d}\vec{k}$ **(3)平衡**:$\vec{J}=-\frac{2}{(2\pi)^3}\int e\vec{v}_{\vec{k}}f_0\mathrm{d}\vec{k}=0$**(4)从平衡到非平衡**:$\frac{\mathrm{d}\vec{k}}{\mathrm{d}t}=-\frac{e\vec{E}}{\hbar},\vec{J}=-\frac{2}{(2\pi)^3}\int e\vec{v}_{\vec{k}}f\mathrm{d}\vec{k}\neq0$**(5)玻尔兹曼方程**$\frac{\partial f}{\partial t}=\left(\frac{\partial f}{\partial t}\right)_{\text{漂移}}+\left(\frac{\partial f}{\partial t}\right)_{\text{碰撞}}$(I)漂移无碰撞:$f\left(\vec{r},\vec{k},\vec{t}\right)=f\left(\vec{r}-\frac{\mathrm{d}\vec{r}}{\mathrm{d}t}\mathrm{d}t,\vec{k}-\frac{\mathrm{d}\vec{k}}{\mathrm{d}t}\mathrm{d}t,t-\mathrm{d}t\right)$ (II)碰撞+漂移:$f\left(\vec{r},\vec{k},\vec{t}\right)=f\left(\vec{r}-\frac{\mathrm{d}\vec{r}}{\mathrm{d}t}\mathrm{d}t,\vec{k}-\frac{\mathrm{d}\vec{k}}{\mathrm{d}t}\mathrm{d}t,t-\mathrm{d}t\right)+\left(\frac{\partial f}{\partial t}\right)_{\text{碰撞}}\mathrm{d}t$.稳态玻尔兹曼方程($\partial_tf=0$)$\dot{\vec{k}}\cdot\frac{\partial f}{\partial\vec{k}}+\dot{\vec{r}}\cdot\frac{\partial f}{\partial\vec{r}}=\left(\frac{\partial f}{\partial t}\right)_{\text{碰撞}}$. 近似条件:$f=f_0+f_1(f_1\ll f_0)$,$\left(\frac{\partial f}{\partial t}\right)=\frac{f_0-f}{\tau}=-\frac{f_1}{\tau}$. 近似玻尔兹曼方程:$\dot{\vec{k}}\cdot\frac{\partial f_0}{\partial\vec{k}}+\dot{\vec{r}}\cdot\frac{\partial f_0}{\partial\vec{r}}=-\frac{f_1}{\tau}$ (III)直流电导率.仅$\vec{E}$下:$-\frac{e\vec{E}}{\hbar}\cdot\frac{\partial f_0}{\partial\vec{k}}=-\frac{f_1}{\tau}$,$\vec{J}_e=-\frac{2e}{(2\pi)^3}\int f\vec{v}_{\vec{k}}\mathrm{d}\vec{k}=-\frac{e}{4\pi^3}\int(f_0+f_1)\vec{v}_{\vec{k}}\mathrm{d}\vec{k}=-\frac{e}{4\pi^3}\int f_1\vec{v}_{\vec{k}}\mathrm{d}\vec{k}$.已知$f_1=\frac{e\tau\vec{E}}{\hbar}\cdot\frac{\partial f_0}{\partial\vec{k}}$;$\frac{\partial f_0}{\partial\vec{k}}=\frac{\partial f_0}{\partial\epsilon}\cdot\frac{\partial\epsilon}{\partial\vec{k}}$;$\vec{k}=\frac{1}{\hbar}\frac{\partial\epsilon}{\partial\vec{k}}$,$\vec{J}_e=\frac{e^2}{4\pi^3}\int\tau\frac{\partial f_0}{\partial\epsilon}\vec{k}_{\vec{k}}(\vec{v}_{\vec{k}}\cdot\vec{E})\mathrm{d}\vec{k}=\frac{e^2}{4\pi^3}\int\tau\frac{\vec{v}_{\vec{k}}(\vec{v}_{\vec{k}}\cdot\vec{E})}{\hbar v_k}\left(-\frac{\partial f_0}{\partial\epsilon}\right)\mathrm{d}S\mathrm{d}\epsilon=\frac{e^2}{4\pi^3\hbar}\int\tau\frac{\vec{v}_k(\vec{v}_{\vec{k}}\cdot\vec{E})}{v_k}\mathrm{d}S_F$,$\vec{J}_e=\left[\frac{e^2}{4\pi^3\hbar}\int\tau\frac{\vec{v}_{\vec{k}}\vec{v}_{\vec{k}}}{v_k}\mathrm{d}S_F\right]\cdot\vec{E}=\overleftrightarrow{\sigma}\cdot\vec{E}$ [例]立方晶系:$\sigma=\sigma_{xx}=\sigma_{yy}=\sigma_{zz}=\frac{(\sigma_{xx}+\sigma_{yy}+\sigma_{zz})}{3}=\frac{e^2}{4\pi^3\hbar}\int\tau\frac{v_{k_x}^2}{v_k}\mathrm{d}S_F=\frac{1}{12\pi^3}\frac{e^2}{\hbar}\int\tau v_k\mathrm{d}S_F$. 若$m^*,\tau$ 各向同性:$\sigma=\frac{\tau}{12\pi^3}\frac{e^2}{m^*}\int k_F\mathrm{d}S_F$.球面费米面:$\sigma=\frac{\tau}{3\pi^2}\frac{e^2k_F^3}{m^*}=\frac{ne^2\tau_{E_F}}{m^*}$**(6)热电势**.$T,\mu$因素:$\frac{\partial f_0}{\partial T}=-\frac{\partial f_0}{\partial\epsilon}\cdot\frac{\epsilon-\mu}{T}$,$\frac{\partial f_0}{\partial\mu}=-\frac{\partial f_0}{\partial\epsilon}$, 无电场方程:$-\frac{\partial f_0}{\partial\epsilon}\vec{v}_{\vec{k}}\cdot\left[\frac{\epsilon_k-\mu}{T}\nabla T+\nabla\mu\right]=-\frac{f_1}{\tau}$. 电流密度:$\vec{J}_e=\frac{e}{4\pi^3}\int\tau\frac{(\vec{v}_{\vec{k}}\vec{v}_{\vec{k}})\cdot\nabla\mu}{\hbar v_k}\left(-\frac{\partial f_0}{\partial\epsilon}\right)\mathrm{d}S\mathrm{d}\epsilon$ +

$\frac{e}{4\pi^3}\int\tau\frac{(\vec{v}_{\vec{k}}\vec{v}_{\vec{k}})\cdot\nabla T}{\hbar v_k}\left(\frac{\epsilon-\mu}{T}\right)\left(-\frac{\partial f_0}{\partial\epsilon}\right)\mathrm{d}S\mathrm{d}\epsilon$.化学势梯度$\frac{\nabla\mu}{e}$与外场电场$\vec{E}$等价.**(7)热流类比电流**$\vec{J}_e = \frac{e^2}{4\pi^3}\int\tau\frac{(\vec{v}_{\vec{k}}\vec{v}_{\vec{k}})\cdot\left(\vec{E}+\frac{\nabla\mu}{e}\right)}{\hbar v_k}\left(-\frac{\partial f_0}{\partial\epsilon}\right)\mathrm{d}S\mathrm{d}\epsilon + \frac{e}{4\pi^3}\int\tau\frac{(\vec{v}_{\vec{k}}\vec{v}_{\vec{k}})\cdot\nabla T}{\hbar v_k}\left(\frac{\epsilon-\mu}{T}\right)\left(-\frac{\partial f_0}{\partial\epsilon}\right)\mathrm{d}S\mathrm{d}\epsilon$,定义热流:$\vec{J}_Q = \frac{1}{4\pi^3}\int(\epsilon_k-\mu)\vec{v}_kf_1\mathrm{d}\vec{k} = -\frac{e}{4\pi^3}\int\vec{E}\cdot[\tau\frac{(\vec{v}_{\vec{k}}\vec{v}_{\vec{k}})(\epsilon_k-\mu)}{\hbar v_k}(-\frac{\partial f_0}{\partial\epsilon})\mathrm{d}S\mathrm{d}\epsilon] - \frac{1}{4\pi^3}\int\nabla T\cdot[\tau\frac{(\vec{v}_{\vec{k}}\vec{v}_{\vec{k}})}{\hbar v_k}\frac{(\epsilon-\mu)^2}{T}(-\frac{\partial f_0}{\partial\epsilon})\mathrm{d}S\mathrm{d}\epsilon]$.设$\zeta_n = \frac{\tau}{12\pi^3\hbar}\int v_k(\epsilon_k-\mu)^n\left(-\frac{\partial f_0}{\partial\epsilon}\right)\mathrm{d}S\mathrm{d}\epsilon$,则$\vec{J}_e = e^2\zeta_0\vec{E} - \frac{e}{T}\zeta_1(-\nabla T), \vec{J}_Q = -e\zeta_1\vec{E}+\frac{1}{T}\zeta_2(-\nabla T)$.无外加$\vec{E}: \vec{J}_e = 0 \Rightarrow e^2\zeta_0\vec{E} - \frac{e}{T}\zeta_1(-\nabla T) = 0, \vec{E} = \frac{1}{eT}\frac{\zeta_1}{\zeta_0}(-\nabla T)$,热流密度:$\vec{J}_Q = \frac{1}{T}\left(\zeta_2-\frac{\zeta_1^2}{\zeta_0}\right)(-\nabla T)$,热导率:$\kappa = \frac{1}{T}\left(\zeta_2-\frac{\zeta_1^2}{\zeta_0}\right)$,电导率:$\sigma = e^2\zeta_0$.**(8)补充:热电势**热电场:$\vec{E} = \frac{1}{eT}\frac{\zeta_1}{\zeta_0}(-\nabla T)$,热电系数(单位温度差下材料中电势差的变化量):$S = -\frac{1}{eT}\frac{\zeta_1}{\zeta_0} = -\frac{\pi^3}{3}\frac{k_B^2T}{e}\left[\frac{\partial\ln\sigma}{\partial\epsilon}\right]_{E_F} \propto T\left(\frac{\partial\ln\langle\tau\rangle}{\partial\epsilon}+\frac{\partial\ln\langle v_k\rangle}{\partial\epsilon}+\frac{\partial\ln S}{\partial\epsilon}\right)_{E_F}$

多电子(0)原始哈密顿量:$\hat{H}_T = \sum_i\frac{|\vec{p_i}|^2}{2m} + \sum_n\frac{|\vec{p_n}|^2}{2M_n} + \frac{1}{2}\sum_{ij}'\frac{e^2}{|\vec{r_i}-\vec{r_j}|} + \frac{1}{2}\sum_{nn'}'\frac{Z_nZ_{n'}e^2}{|\vec{R_n}-\vec{R_{n'}}|} + \sum_{n,i}V_n(\vec{r_i}-\vec{R_n}) + \hat{H}_R$(价电子动能,原子实动能,电子间库伦势,原子实间库伦势,电子和原子实之间,相对论修正)**(1)B-O绝热近似**.(I)电子:$\hat{H}_e = \sum_i\left[\frac{|\vec{p_i}|^2}{2m}+\sum_nV_n(\vec{r_i}-\vec{R_n})\right] + \frac{1}{2}\sum_{ij}'\frac{e^2}{|\vec{r_i}-\vec{r_j}|} + \hat{H}_R$,原子实:$\hat{H}_c = \sum_n\frac{|\vec{p_n}|^2}{2M_n} + \frac{1}{2}\sum_{nn'}'\frac{Z_nZ_{n'}e^2}{|\vec{R_n}-\vec{R_{n'}}|} + V_{\mathrm{ec}}(\{\vec{R_n}\})(II)\{-\frac{\hbar^2}{2m}\sum_j\nabla_j^2 - \sum_{j,l}\frac{Z_le^2}{|r_j-R_l|} + \frac{1}{2}\sum_{j\neq j'}\frac{e^2}{|r_j-r_{j'}|} - E\}\Psi(r_1,r_2,\cdots,r_N) = 0, \hat{P}_{jj'}\Psi = -\Psi, .n(r) = n(r;R_1,\ldots,R_{\mathcal{N}}), E = E(R_1,\ldots,R_{\mathcal{N}})$**(2)$H_2$Model**:(I)HL:$\Psi_{HL} = A[\varphi_H(r_1-R_1)\varphi_H(r_2-R_2)+\varphi_H(r_1-R_2)\varphi_H(r_2-R_1)]\chi_0$(HL = Heitler-London).$\varphi_H(r)$是电子轨道在基态的波函数; χ_0 代表自旋单子波函数.(II)Mullikan Ansatz:$\Psi_{\mathrm{HF}} = \frac{1}{\sqrt{2}}\mathrm{Det}[\varphi_m(r_1)\alpha(1)\varphi_m(r_2)\beta(2)]$(HF = Hatree-Fock).(III)JC:$\Psi_{JC} = \Psi(r_1,r_2)\chi_0$**(III)Hartree-Fock**对e:$\hat{H} = -\sum_i\frac{\hbar^2}{2m_e}\nabla_{\vec{r_i}}^2 + \sum_iV_{\mathrm{ion}}(\vec{r_i}) + \frac{e^2}{2}\sum_{(i\neq j)}\frac{1}{|\vec{r_i}-\vec{r_j}|}$,多体态:$\Psi^H(\{\vec{r_i}\}) = \phi_1(\vec{r_1})\ldots\phi_N(\vec{r_N}),\ E^H = \langle\Psi^H|\hat{H}|\Psi^H\rangle = \sum_i\langle\phi_i|\frac{-\hbar^2\nabla_{\vec{r}}^2}{2m_e} + V_{\mathrm{ion}}(\vec{r})|\phi_i\rangle + \frac{e^2}{2}\sum_{ij(i\neq j)}\langle\phi_i\phi_j|\frac{1}{|\vec{r}-\vec{r}'|}|\phi_i\phi_j\rangle$, $\delta[E^H-\sum_i\epsilon_i(\langle\phi_i|\phi_i\rangle-1)] = 0, \langle\delta\phi_i| - \frac{\hbar^2\nabla_{\vec{r}}^2}{2m_e} + V_{\mathrm{ion}}(\vec{r})|\phi_i\rangle + e^2\sum_{i\neq j}\langle\delta\phi_i\phi_j|\frac{1}{|\vec{r}-\vec{r}'|}|\phi_i\phi_j\rangle - \epsilon_i\langle\delta\phi_i|\phi_i\rangle = \langle\delta\phi_i|[-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m_e} + V_{\mathrm{ion}} + e^2\sum_{i\neq j}\langle\phi_j|\frac{1}{|\vec{r}-\vec{r}'|}|\phi_j\rangle - \epsilon]|\phi_i\rangle = 0$.Hatree:$[-\frac{\hbar^2\nabla\vec{r}^2}{2m_e} + V_{\mathrm{ion}}(\vec{r}) + e^2\sum_{j\neq i}\langle\phi_j|\frac{1}{|\vec{r}-\vec{r}'|}|\phi_i\rangle]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r})$,Hatree势:$V_i^H(\vec{r}) = e^2\sum_{i\neq j}\langle\phi_j|\frac{1}{|\vec{r}-\vec{r}'|}|\phi_j\rangle$.平均场近似:Hatree-Fock多体态:$\Psi^{\mathrm{HF}}(\{\vec{r_i}\}) = \frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_1(\vec{r}_1) & \cdots & \phi_1(\vec{r}_N)\\ \vdots & \ddots & \vdots\\ \phi_N(\vec{r}_1) & \cdots & \phi_N(\vec{r}_N)\end{vmatrix}$.$(\phi_i(\vec{r}) \approx \psi_i(\vec{r})\chi_i(\sigma))$,总能量:$E^{\mathrm{HF}} = \langle\Psi^{\mathrm{HF}}|\hat{H}|\Psi^{\mathrm{HF}}\rangle = \sum_i\langle\phi_i|\frac{-\hbar^2\nabla_{\vec{r}}^2}{2m_e} + V_{\mathrm{ion}}(\vec{r})|\phi_i\rangle + \frac{e^2}{2}\sum_{ij(i\neq j)}\langle\phi_i\phi_j|\frac{1}{|\vec{r}-\vec{r}'|}|\phi_i\phi_j\rangle - \frac{e^2}{2}\sum_{ij(i\neq j)}\langle\phi_i\phi_j|\frac{1}{|\vec{r}-\vec{r}'|}|\phi_j\phi_i\rangle$,$[\frac{-\hbar^2\nabla_{\vec{r}}^2}{2m_e} + V_{\mathrm{ion}} + V_i^H(\vec{r})]\phi_i(\vec{r}) - e^2\sum_{j\neq i}\langle\phi_j|\frac{1}{|\vec{r}-\vec{r}'|}|\phi_i\rangle\phi_j(\vec{r}) = \epsilon_i\phi_i(\vec{r})$.密度:$\rho_i(\vec{r}) = |\phi_i(\vec{r})|^2, \rho(\vec{r}) = \sum_i\rho_i(\vec{r}); V_i^H(\vec{r}) = e^2\sum_{j\neq i}\int\frac{\rho_j(\vec{r}')}{|\vec{r}-\vec{r}'|}\mathrm{d}\vec{r}' = e^2\int\frac{\rho(\vec{r}')-\rho_i(\vec{r}')}{|\vec{r}-\vec{r}'|}\mathrm{d}\vec{r}'$;**单粒子交换密度:**$\rho_i^X(\vec{r},\vec{r}') = \sum_{j\neq i}\frac{\phi_i(\vec{r}')\phi_i^*(\vec{r})\phi_j(\vec{r})\phi_j^*(\vec{r}')}{\phi_i(\vec{r})\phi_i^*(\vec{r})}$;HF势:$V_i^{HF}(\vec{r}) = e^2\int\frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}\mathrm{d}\vec{r}' - e^2\int\frac{\rho_i(\vec{r}')+\rho_i^X(\vec{r},\vec{r}')}{|\vec{r}-\vec{r}'|}\mathrm{d}\vec{r}'$,单HF:$[\frac{-\hbar^2\nabla_{\vec{r}}^2}{2m_e} + V_{ion}(\vec{r}) + V_i^{HF}(\vec{r})]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r})$.**(IV)Jellium Model(均匀电子气)**$\phi_i(\vec{r}) = \frac{e^{i\vec{k}_i\cdot\vec{r}}}{\sqrt{\Omega}}$($\Omega$为晶胞体积.均匀电子气的波矢的数值范围为$k\in[0,k_F]$).$\frac{4\pi}{3}r_s = \frac{\Omega}{N} = n^{-1} = \frac{3\pi^2}{k_F^3}, \frac{\hbar^2}{2m_ea_0^2} = \frac{e^2}{2a_0} = 1$Ry.态方程$[-\frac{\hbar^2\nabla_{\vec{r}}^2}{2m_e} - e^2\int\frac{\rho_{\vec{k}}^{HF}(\vec{r},\vec{r}')}{|\vec{r}-\vec{r}'|}\mathrm{d}\vec{r}']\phi_{\vec{k}}(\vec{r}) = \epsilon_{\vec{k}}\phi_{\vec{k}}(\vec{r})$.平面波证明:$-\frac{\hbar^2\nabla^2}{2m_e}\frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{\Omega}} = \frac{\hbar^2\hat{k}^2}{2m_e}\frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{\Omega}}, e^2[\int\frac{\rho_{\vec{k}}^{HF}(\vec{r},\vec{r}')}{|\vec{r}-\vec{r}'|}\mathrm{d}\vec{r}']\phi_{\vec{k}}(\vec{r}) = \frac{-e^2}{\sqrt{\Omega}}\int\frac{\rho_{\vec{k}}^{HF}(\vec{r},\vec{r}')}{|\vec{r}-\vec{r}'|}\mathrm{d}\vec{r}'e^{i\vec{k}\cdot\vec{r}} = \frac{-e^2}{\sqrt{\Omega}}\sum_{\vec{k}'}\int\frac{\phi_{\vec{k}}(\vec{r}')\phi_{\vec{k}}^*(\vec{r})\phi_{\vec{k}'}(\vec{r})\phi_{\vec{k}'}^*(\vec{r}')}{\phi_{\vec{k}}(\vec{r})\phi_{\vec{k}}^*(\vec{r})}\frac{1}{|\vec{r}-\vec{r}'|}\mathrm{d}\vec{r}'e^{i\vec{k}\cdot\vec{r}} = \frac{-e^2}{\sqrt{\Omega}}\sum_{\vec{k}'}\int\frac{e^{-i(\vec{k}-\vec{k}')\cdot(\vec{r}-\vec{r}')}}{\Omega}\frac{\mathrm{d}\vec{r}'e^{i\vec{k}\cdot\vec{r}}}{|\vec{r}-\vec{r}'|}$,$(\int\frac{1}{r}e^{i\vec{k}\cdot\vec{r}}\mathrm{d}\vec{r} = \frac{4\pi^2}{k^2}, \sum_{\vec{k}}f(\vec{k}) = \frac{\Omega}{(2\pi)^3}\int f(\vec{k})\mathrm{d}\vec{k}), \frac{-4\pi^2}{\sqrt{\Omega}}[\int_{k'<k_F}\frac{\mathrm{d}\vec{k}'}{(2\pi)^3}\frac{1}{|\vec{k}-\vec{k}'|^2}]e^{i\vec{k}\cdot\vec{r}} = -\frac{e^2}{\pi}k_FF(\frac{k}{k_F})\frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{\Omega}}.(F(x) = 1 + \frac{1-x^2}{2x}\ln|\frac{1+x}{1-x}|)$.(II)$\phi_{\vec{k}}(\vec{r})$能量:$\epsilon_{\vec{k}} = \frac{\hbar^2k^2}{2m_e} - \frac{e^2}{\pi}k_FF(\frac{k}{k_F})$,总能量$E^{HF} = 2\sum_{k<k_F}\frac{\hbar^2|\vec{k}|^2}{2m_e} - \frac{e^2k_F^2}{\pi}\sum_{k<k_F}\left[1+\frac{k_F^2-k^2}{2kk_F}\ln\left|\frac{k_F+k}{k_F-k}\right|\right]$.平均能:$\frac{E^{HF}}{N} = \frac{3}{5}\epsilon_F - \frac{3}{4}\frac{e^2k_F}{\pi} = \left[\frac{2.21}{(r_s/a_0)^2}-\frac{0.916}{(r_s/a_0)}\right]$Ry.交换能:$\frac{E^X}{N} = -\frac{3e^2}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}n^{\frac{1}{3}} = -1.447(a_0^3n)^{\frac{1}{3}}$Ry;高密度极限:$\frac{E}{N} = \left[\frac{2.21}{(r_s/a_0)^2}-\frac{0.916}{(r_s/a_0)}+0.0622\ln\frac{r_s}{a_0}-0.096+\mathcal{O}\left(\frac{r_s}{a_0}\right)\right]$

DFT(1)$\mathcal{H} = -\sum_i\frac{\hbar^2}{2m_e}\nabla_{\vec{r}_i}^2 + \sum_iV_{\mathrm{ion}}(\vec{r_i}) + \frac{e^2}{2}\sum_{ij(j\neq i)}\frac{1}{|\vec{r_i}-\vec{r_j}|} = T + W + V$.DF:$F[n(r)] = \langle\Psi|T+W|\Psi\rangle = F[n(\vec{r})] = T^S[n(\vec{r})] + \frac{e^2}{2}\iint\frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|}\mathrm{d}\vec{r}\mathrm{d}\vec{r}' + E^{XC}[n(\vec{r})], E[n(\vec{r})] = \langle\Psi|\mathcal{H}|\Psi\rangle = F[n(\vec{r})] + \int V(\vec{r})n(\vec{r})\mathrm{d}\vec{r}$,变分:$\delta n(\vec{r}) = \delta\phi_i(\vec{r})\phi_i(\vec{r})$,约束$\int\delta n(\vec{r})\mathrm{d}\vec{r} = \int\delta\phi_i(\vec{r})\phi_i(\vec{r})\mathrm{d}\tilde{r} = 0$,Kohn-Sham:$\left[-\frac{\hbar^2}{2m_e}\nabla_{\vec{r}}^2 + V^{\mathrm{eff}}(\vec{r},n(\vec{r}))\right]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r})(V^{\mathrm{eff}}(\vec{r},n(\vec{r})) = V(\vec{r}) + e^2\int\frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|}\mathrm{d}\vec{r}' + \frac{\delta E^{XC}[n(\vec{r})]}{\delta n(\vec{r})})$.$E^{XC}[n(\vec{r})] = \int n(\vec{r})\epsilon^{XC}([n],\vec{r})\mathrm{d}\vec{r}$.LDA:$E_{\mathrm{LDA}}^{XC} = \int\epsilon^{XC}[n(\vec{r})]n(\vec{r})\mathrm{d}\vec{r}$;GGA:$E_{\mathrm{GGA}}^{XC} = \int\epsilon^{XC}[n(\vec{r}),|\nabla n(\vec{r})|]n(\vec{r})\mathrm{d}\vec{r}$.