Solutions Manual

Chapter 2

(1) The problem on the transmission and scattering matrix

(a) The wavefunction is written as

$$\psi(x) = \begin{cases} Ae^{ik_L x} + Be^{-ik_L x} & (x < 0) \\ Ce^{ik_R x} + De^{-ik_R x} & (x > 0), \end{cases}$$

where $\hbar k_L = \sqrt{2m(\epsilon - V_L)}$ and $\hbar k_R = \sqrt{2m(\epsilon - V_R)}$. From the boundary condition at $x = 0$, we have

$$\begin{pmatrix} A \\ B \end{pmatrix} = \frac{1}{2k_L} \begin{pmatrix} k_L + k_R & k_L - k_R \\ k_L - k_R & k_L + k_R \end{pmatrix} \begin{pmatrix} C \\ D \end{pmatrix} = M \begin{pmatrix} C \\ D \end{pmatrix}.$$

Here, $M = M(L \leftarrow R)$ is the transfer matrix. A particular solution is obtained by letting $D = 0$, which represents a wave incident from the left and transmits through the potential barrier to the right.

We calculate

$$\mathcal{R}(\epsilon) = \frac{|B|^2}{|A|^2} = \frac{(k_L - k_R)^2}{(k_L + k_R)^2}$$

$$\mathcal{T}(\epsilon) = \frac{k_R}{k_L} \frac{|C|^2}{|A|^2} = \frac{4k_L k_R}{(k_L + k_R)^2},$$

where the relation $\mathcal{R}(\epsilon) + \mathcal{T}(\epsilon) = 1$ should be noted. The current density j is obtained from

$$j = \begin{cases} \dfrac{\hbar k_L}{m} \left(|A|^2 - |B|^2\right) & (x < 0) \\ \dfrac{\hbar k_R}{m} |C|^2 & (x > 0). \end{cases}$$

The current conservation requires the relation

$$\frac{|B|^2}{|A|^2} + \frac{k_R}{k_L} \frac{|C|^2}{|A|^2} = 1,$$

which corresponds to the relation of $\mathcal{R}(\epsilon) + \mathcal{T}(\epsilon) = 1$.

(b) In the same way as (a), the wavefunction is written as

$$\psi(x)=\begin{cases} Ae^{ikx}+Be^{-ikx} & (x<-a)\\ Ce^{-\kappa x}+De^{\kappa x} & (-a<x<a),\\ Ee^{ikx}+Fe^{-ikx} & (x>a)\end{cases}$$

where $\hbar k=\sqrt{2m\epsilon}$ and $\hbar\kappa=\sqrt{2m(V_0-\epsilon)}$.
From the boundary conditions at $x=-a$ and $x=a$, we have the relation for the transfer matrix $M=M(L\leftarrow C)M(C\leftarrow R)$ as

$$\begin{pmatrix} A\\ B\end{pmatrix}=\begin{pmatrix} (\cosh 2\kappa a+i(\xi/2)\sinh 2\kappa a)\,e^{2ika} & (i\eta/2)\sinh 2\kappa a\\ -(i\eta/2)\sinh 2\kappa a & (\cosh 2\kappa a-i(\xi/2)\sinh 2\kappa a)\,e^{-2ika}\end{pmatrix}\begin{pmatrix} E\\ F\end{pmatrix},$$

where we abbreviate the parameters with $\xi=\kappa/k-k/\kappa$ and $\eta=\kappa/k+k/\kappa$.
A particular solution is obtained by letting $F=0$ as

$$\frac{E}{A}=\frac{e^{-2ika}}{\cosh 2\kappa a+i(\xi/2)\sinh 2\kappa a}.$$

Then the transmission becomes

$$\mathcal{T}(\epsilon)=\frac{|E|^2}{|A|^2}\approx 16e^{-4\kappa a}\left(\frac{k\kappa}{k^2+\kappa^2}\right)^2,$$

where we use $\cosh 2\kappa a\approx\sinh 2\kappa a\approx e^{2\kappa a}/2$ for $\kappa a\gg 1$.

(c) The transfer matrix M and the S matrix are defined as

$$\begin{pmatrix} A\\ B\end{pmatrix}=\begin{pmatrix} M_{11} & M_{12}\\ M_{21} & M_{22}\end{pmatrix}\begin{pmatrix} E\\ F\end{pmatrix},$$

and

$$\begin{pmatrix} B\\ E\end{pmatrix}=\begin{pmatrix} S_{11} & S_{12}\\ S_{21} & S_{22}\end{pmatrix}\begin{pmatrix} A\\ F\end{pmatrix},$$

where the coefficients B and E represent the *outgoing* waves in terms of the coefficients A and F of the *incoming* waves. The matrices S and M are related to each other with the condition of the conservation of the current density probability as

$$|B|^2+|E|^2=|A|^2+|F|^2,$$

which produces the unitarity condition of the S matrix as $S^\dagger S = I$. Here, $S^\dagger$ is the Hermitian conjugate matrix of S and has the constraints as

$$|S_{11}| = |S_{22}|, \quad |S_{12}| = |S_{21}|,$$
$$|S_{11}|^2 + |S_{12}|^2 = 1, \quad S_{11}S_{12}^* + S_{21}S_{22}^* = 0.$$

When the Schrödinger equation has a solution with time-reversal symmetry as in (b), there is a symmetric condition expressed by $S^*S = I$. When the S matrix is unitary and symmetric, the transfer matrix M is expressed using the S matrix as

$$M = \begin{pmatrix} 1/S_{12} & S_{11}^*/S_{12}^* \\ S_{11}/S_{12} & 1/S_{12}^* \end{pmatrix}$$

with

$$\det M = (1 - |S_{11}|^2)/|S_{12}|^2 = 1.$$

The direct calculations of the transfer matrices M in (a) and (b) show that M in (b) with time-reversal symmetry satisfies these conditions, while that in (a) does not. The transmission coefficient $\mathcal{T}(\epsilon)$ is given by $|E|^2/|A|^2$ with $F = 0$ as

$$\mathcal{T}(\epsilon) = \frac{1}{|M_{11}|^2} = |S_{12}|^2.$$

(2) The problem on the thermoelectric transport relations

(a) In metallic systems, we neglect the lattice contribution to thermal conductivity. The Boltzmann equation in the relaxation time approximation becomes

$$f = f_0 - \tau\left(v_x \frac{\partial f_0}{\partial x} + \frac{eE}{m}\frac{\partial f_0}{\partial v_x}\right)$$

and electric and thermal current densities are defined by

$$j = \frac{2}{(2\pi)^3}\iiint e v_x f dk_x dk_y dk_z$$
$$j_q = \frac{1}{(2\pi)^3}\iiint \epsilon v_x f dk_x dk_y dk_z.$$

Using the following relations for the Fermi–Dirac distribution function $f_0 = 1/(e^{(\epsilon-\mu)/k_BT)} + 1)$

$$\frac{\partial f_0}{\partial v_x} = mv_x \frac{\partial f_0}{\partial \epsilon}$$

$$\frac{\partial f_0}{\partial x} = -\frac{\partial f_0}{\partial \epsilon} \left\{ \frac{\epsilon}{T} \frac{\partial T}{\partial x} + T \frac{\partial}{\partial x} \left(\frac{\mu}{T} \right) \right\},$$

j and j_q are calculated as

$$\begin{aligned} j &= \frac{2}{(2\pi)^3} \iiint \tau \left(-ev_x^2 \frac{\partial f_0}{\partial x} - \frac{e^2 E}{m} v_x \frac{\partial f_0}{\partial v_x} \right) dk_x dk_y dk_z \\ &= \mathcal{K}_0 \left\{ e^2 E - eT \frac{\partial}{\partial x} \left(\frac{\mu}{T} \right) \right\} - \mathcal{K}_1 \frac{e}{T} \frac{\partial T}{\partial x} \\ j_q &= \frac{2}{(2\pi)^3} \iiint \tau\epsilon \left(-v_x^2 \frac{\partial f_0}{\partial x} - \frac{eE}{m} v_x \frac{\partial f_0}{\partial v_x} \right) dk_x dk_y dk_z \\ &= \mathcal{K}_1 \left\{ eE - T \frac{\partial}{\partial x} \left(\frac{\mu}{T} \right) \right\} - \mathcal{K}_2 \frac{1}{T} \frac{\partial T}{\partial x}, \end{aligned}$$

where the coefficients $\mathcal{K}_n$ $(n = 0, 1, 2)$ are given by

$$\begin{aligned} \mathcal{K}_n &= \frac{2}{(2\pi)^3} \iiint \left(-\frac{\partial f_0}{\partial \epsilon} \right) \tau v_x^2 \epsilon^n dk_x dk_y dk_z \\ &= \frac{2\sqrt{2m}}{3\pi^2 \hbar^3} \int_0^\infty \left(-\frac{\partial f_0}{\partial \epsilon} \right) \tau \epsilon^{n+3/2} d\epsilon \end{aligned}$$

Note that

$$\frac{\partial}{\partial x} \left(\frac{\mu}{T} \right) = \frac{\partial}{\partial T} \left(\frac{\mu}{T} \right) \frac{\partial T}{\partial x}.$$

(b) The electric conductivity σ is obtained with the condition of $\partial T/\partial x = 0$ in j and the Seebeck coefficient S is obtained with the condition of $j = 0$ and $\partial(\mu/T)/\partial x = 0$ as

$$\sigma = \frac{j}{E} = e^2 \mathcal{K}_0, \quad S = \frac{\partial V}{\partial T} = E \frac{\partial x}{\partial T} = \frac{1}{eT} \frac{K_1}{K_0},$$

while the thermal conductivity κ is obtained with the condition of $j = 0$ as

$$\kappa = \frac{j_q}{-\partial T/\partial x} = \frac{\mathcal{K}_0 \mathcal{K}_2 - \mathcal{K}_1^2}{\mathcal{K}_0 T}.$$

For the Fermi–Dirac distribution function in the metallic systems, since $-\partial f_0/\partial \epsilon \approx \delta(\epsilon - \epsilon_F)$, we have

$$\sigma = \frac{ne^2 \tau}{m}, \qquad \kappa = \frac{\pi^2}{3} \frac{n\tau}{m} k_B^2 T,$$

where the density n is $n = (1/3\pi^2)(2m/\hbar^2)^{3/2}\epsilon_F^{3/2}$.
We note that in the present free electron metallic systems,

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 (= 2.45 \times 10^{-8}[\mathrm{W}\cdot\Omega/K^2])$$

takes a constant value, which is called the Wiedemann–Franz law.

(c) Rewriting the equations for j and j_q in (a) as

$$E = \frac{j}{\sigma} + \frac{T}{e}\frac{\partial}{\partial x}\left(\frac{\mu}{T}\right) - \frac{T}{e}\frac{\mathcal{K}_1}{\mathcal{K}_0}\frac{\partial}{\partial x}\left(\frac{1}{T}\right)$$
$$j_q = -\kappa\frac{\partial T}{\partial x} + j\frac{e}{\sigma}K_1,$$

and putting them into the formula for heat transfer density

$$Q = jE + \frac{\partial j_q}{\partial x},$$

we obtain

$$Q = \frac{j^2}{\sigma} - \frac{\partial}{\partial x}\left(\kappa\frac{\partial T}{\partial x}\right) - j\frac{T}{e}\frac{\partial}{\partial x}\left(\frac{\mathcal{K}_1 - \mu\mathcal{K}_0}{\mathcal{K}_0 T}\right).$$

The first term is the usual Joule heat density and the second term is the heat density due to the thermal transport. The third term $Q_T = -\xi j(\partial T/\partial x)$ expresses the heat density, which appears when both the current density j and the gradient of temperature $\partial T/\partial x$ are present. Here, the term Q_T is the Thomson heat density and $\xi = (T/e)d((\mathcal{K}_1 - \mu\mathcal{K}_0)/\mathcal{K}_0 T)/dT$ is the Thomson coefficient.

(3) The problem on the derivation of Kubo formula

(a) We evaluate P within the lowest order perturbation theory

$$P = \sum_{\alpha\beta} \left(\epsilon_\beta - \epsilon_\alpha\right) \left(P_{\alpha\beta} - P_{\beta\alpha}\right),$$

where the probability is

$$P_{\alpha\beta} = f(\epsilon_\alpha)\left(1 - f(\epsilon_\beta)\right) W_{\alpha\beta}$$

with the Fermi–Dirac distribution function $f(\epsilon)$. Using Fermi golden rule for the perturbation $V = eEz$, the transition rate $W_{\alpha\beta}$ is obtained as

$$W_{\alpha\beta} = \frac{2\pi}{\hbar} e^2 |E|^2 |\langle\alpha|z|\beta\rangle|^2 \delta\left(\hbar\omega - (\epsilon_\beta - \epsilon_\alpha)\right).$$

(b) Combining the result in (a) with the formula

$$P = \langle \mathbf{E}\cdot\mathbf{J}\rangle = \lim_{\omega\to 0} \mathrm{Re}\left[\sigma(\omega)\right] |E|^2,$$

we obtain the conductivity

$$\lim_{\omega\to 0} \mathrm{Re}\left[\sigma(\omega)\right] = \lim_{\omega\to 0} \frac{2\pi e^2}{\hbar} \sum_{\alpha\beta} |\langle\alpha|z|\beta\rangle|^2 \left(\epsilon_\beta - \epsilon_\alpha\right)$$
$$\times \left(f(\epsilon_\alpha) - f(\epsilon_\beta)\right) \delta\left(\hbar\omega - (\epsilon_\beta - \epsilon_\alpha)\right).$$

This expression is rewritten in terms of the momentum operator by using the relation

$$\langle\alpha|p_z|\beta\rangle = -\frac{i}{\hbar} m \left(\epsilon_\beta - \epsilon_\alpha\right) \langle\alpha|z|\beta\rangle,$$

which is obtained from

$$p_z = m\frac{dz}{dt} = -\frac{i}{\hbar} m \left[zH - Hz\right].$$

Therefore, in the limit $\omega \to 0$ the conductivity is written as

$$\sigma = 2\pi\hbar \left(\frac{e}{m}\right)^2 \int \sum_{\alpha\beta} |\langle\alpha|p_z|\beta\rangle|^2$$
$$\times \left(-\frac{\partial f}{\partial \epsilon}\right) \delta\left(\epsilon - \epsilon_\alpha\right) \delta\left(\epsilon - \epsilon_\beta\right) d\epsilon.$$

This is the Kubo formula for the conductivity. Note that in the above derivation the linear response is included through Fermi golden rule for the electronic transitions induced by an applied field.

(4) The problem on the friction coupled to heat bath

(a) From the equations of motion by $\dot{x} = dH/dp$, $\dot{p} = -dH/dq$, we have

$$\dot{x} = \frac{p}{m}, \quad \dot{p} = -\frac{dV(x)}{dx} + \sum_i \gamma_i \left(x_i - \frac{\gamma_i}{m_i \omega_i^2} x \right)$$
$$\dot{x}_i = \frac{p_i}{m_i}, \quad \dot{p}_i = -m_i \omega_i^2 x_i + \gamma_i x,$$

which are reduced to

$$m\ddot{x} = -\frac{dV(x)}{dx} + \sum_i \gamma_i x_i - \sum_i \frac{\gamma_i^2}{m_i \omega_i^2} x$$
$$m_i \ddot{x}_i = -m_i \omega_i^2 x_i + \gamma_i x.$$

These equations express the time evolutions of a system coupled to a heat bath.

(b) With initial conditions, we have the solution for the motion of the heat bath oscillators $x_i(t)$ as

$$x_i(t) = x_i(0)\cos(\omega_i t) + \frac{p_i(0)}{m_i \omega_i} \sin(\omega_i t)$$
$$+ \frac{\gamma_i}{m_i \omega_i} \int_0^t \sin\left[\omega_i (t - t')\right] x(t') dt'.$$

(c) Integrating the third term by parts, we have

$$x_i(t) - \frac{\gamma_i}{m_i \omega_i^2} x(t) = \left(x_i(0) - \frac{\gamma_i}{m_i \omega_i^2} x(0) \right) \cos(\omega_i t)$$
$$+ \frac{p_i(0)}{m_i \omega_i} \sin(\omega_i t) - \frac{\gamma_i}{m_i \omega_i^2} \int_0^t \cos\left[\omega_i (t - t')\right] \frac{p(t')}{m} dt'.$$

Then substituting this into the equation of $\dot{p}$, we have

$$m\frac{dv(t)}{dt} + \frac{dV(x)}{dx} + \sum_i \frac{\gamma_i^2}{m_i \omega_i^2} \int_0^t \cos\left[\omega_i (t - t')\right] v(t') dt'$$
$$= \sum_i \gamma_i \left[\left(x_i(0) - \frac{\gamma_i}{m_i \omega_i^2} x(0) \right) \cos(\omega_i t) + \frac{p_i(0)}{m_i \omega_i} \sin(\omega_i t) \right].$$

Therefore, we have the generalized Langevin equation as

$$m\frac{dv(t)}{dt} = -m \int_{-\infty}^t \gamma(t - t') v(t') dt' + \eta(t) + F$$

where $F = -dV(x)/dx$, $\gamma(t)$ and $\eta(t)$ are expressed by

$$\gamma(t) = \Theta(t)\frac{1}{m}\sum_i \frac{\gamma_i^2}{m_i\omega_i^2}\cos(\omega_i t),$$

$$\eta(t) = \sum_i \gamma_i \left[\left(x_i(0) - \frac{\gamma_i}{m_i\omega_i^2}x(0)\right)\cos(\omega_i t) + \frac{p_i(0)}{m\omega_i}\sin(\omega_i t)\right].$$

This shows that friction function $\gamma(t)$ has a memory effect. When the spectrum of ω_i is continuous, we replace the sum into the integral as $\int_0^\infty g(\omega)d\omega$ where $g(\omega)$ is the DOS for the harmonic oscillators. If the DOS is quadratic as $g(\omega_i) \propto \omega_i^2$, then $\gamma(t)$ is proportional to $\delta(t)$ and the Langevin equation becomes Markovian.

(d) Fluctuating force $\eta(t)$ is determined from the initial positions and momenta of the oscillators. When the initial distribution is in thermal equilibrium as $f_{\mathrm{eq}} = \exp(-H_B^{(0)}/k_B T)$, we have

$$\left\langle x_i(0) - \frac{\gamma_i^2}{m_i\omega_i^2}x(0)\right\rangle = 0, \quad \langle p_i(0)\rangle = 0$$

and the second moments become

$$\left\langle \left(x_i(0) - \frac{\gamma_i^2}{m_i\omega_i^2}x(0)\right)^2 \right\rangle = 0, \quad \left\langle \frac{p_i(0)^2}{m_i}\right\rangle = k_B T.$$

These provide the fluctuation–dissipation relation

$$\langle\eta(t)\rangle = 0, \quad \langle\eta(t)\eta(t')\rangle = mk_B T\gamma(t-t').$$

This is equivalent to the Caldeira–Leggett model describing the irreversible process due to macroscopic friction by introducing the Lagrangian as follows:

$$L = \frac{1}{2}m\dot{x}^2 - V(x) + \sum_i \gamma_i x_i x + \sum_i \left[\frac{1}{2}m_i\dot{x}_i{}^2 - \frac{1}{2}m_i\omega_i^2\dot{x}_i{}^2\right] - \sum_i \frac{\gamma_i^2}{2m_i\omega_i^2}x_i^2.$$

We note that the bath term $x_i(\omega)$ in the Fourier space

$$x_i(\omega) = \frac{\gamma_i x(\omega)}{m_i(\omega_i^2 - \omega^2)},$$

cancels the second and third friction term of $x(\omega)$ in $m\ddot{x} = -dV(x)/dx + \sum_i \gamma_i x_i - \sum_i \left(\gamma_i^2/m_i\omega_i^2\right) x$ at $\omega = 0$.

(5) The problem on the relaxation of distribution function

(a) Changing the continuous master equation as

$$\frac{\partial P(v,t)}{\partial t} = -\int W(v \to v+r)P(v,t)dr + \int W(v-r \to v)P(v-r,t)dr$$

and using the general relation of

$$f(v-r,t) = f(v,t) - r\frac{\partial}{\partial x} f(v,t) + \cdots = e^{-r\partial/\partial v} f(v,t),$$

the continuous master equation is written as

$$\frac{\partial P(v,t)}{\partial t} = -\int \left(1 - e^{-r\partial/\partial v}\right) W(v \to v+r)P(v,t)dr$$
$$= \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \left(\frac{\partial}{\partial v}\right)^n \int W(v \to v+r) r^n P(v,t)dr.$$

This shows that the coefficients $C_n(v)$ is expressed as

$$C_{n\geq 1}(v) = \int W(v \to v+r) r^n dr, \quad C_0(v) = 0.$$

Since $W(v \to v+r)\Delta t$ is the probability $v \to v+r$ in Δt,

$$\int W(v \to v+r) r^n dr = \lim_{\Delta t \to 0} \left\langle \frac{(v(t+\Delta t) - v(t))^n}{\Delta t} \right\rangle.$$

For the Langevin equation without external force ($\mathbf{F} = 0$),

$$C_1(v) = \frac{\langle \Delta v(t) \rangle}{\Delta t} = -\gamma v, \quad C_{n\geq 3} = \frac{\langle \Delta v(t)^n \rangle}{\Delta t} = 0,$$
$$C_2(v) = \frac{\langle \Delta v(t)^2 \rangle}{\Delta t} = \frac{1}{\Delta t} \int_t^{t+\Delta t} \frac{\langle \eta(t)\eta(t') \rangle}{m^2} dt dt' = \frac{2k_B T \gamma}{m}.$$

Then we obtain the Fokker–Planck equation as

$$\frac{\partial P(v,t)}{\partial t} = \left(\frac{\partial}{\partial v}\gamma v + \frac{k_B T \gamma}{m} \frac{\partial^2}{\partial v^2}\right) P(v,t).$$

For the steady state with $\partial P(v,t)/\partial t = 0$, we have $P_{eq}(v) = \exp(-mv^2/2k_B T)$, showing $P(v,t)$ approaches the Maxwell–Boltzmann distribution in the long time.

(b) In the presence of external force, the Langevin equation is

$$m\frac{dv}{dt} = -\frac{\partial V}{\partial x} - m\gamma v + \eta(t), \quad \langle \eta(t)\eta(t')\rangle = 2mk_B T\gamma\delta(t-t').$$

When we consider the large friction for γ, since $d\mathbf{v}/dt$ becomes 0 for a short time, $v = (-dV/dx + \eta(t))/m\gamma$. Then

$$C_1(v) = -\frac{1}{m\gamma}\frac{dV}{dx}, \quad C_2(v) = \frac{2k_B T}{m\gamma}, \quad C_{n\geq 3}(v) = 0,$$

and we have the Fokker–Planck equation as

$$\frac{\partial P(v,t)}{\partial t} = \frac{1}{m\gamma}\frac{\partial}{\partial x}\left[\frac{\partial V}{\partial x} + k_B T\frac{\partial}{\partial x}\right] P(v,t),$$

which is known as the Smoluchowski equation.

Since the diffusion constant is given by $D = k_B T/m\gamma$, the first term of this equation expresses the drift nature by an external potential and the second term reveals the diffusive nature. When the probability current J is defined by $\partial P/\partial t = -\partial J/\partial x$, we have

$$\begin{aligned} J &= -\frac{1}{m\gamma}\left(\frac{\partial V}{\partial x} + k_B T\frac{\partial}{\partial x}\right) P(v,t). \\ &= -\frac{k_B T}{m\gamma} e^{-V/k_B T}\frac{\partial}{\partial x}\left[e^{V/k_B T} P(v,t)\right]. \end{aligned}$$

The steady-state $\partial P/\partial t = 0$ is achieved for $J = \text{const.}$ Especially for $J = 0$, we have the Boltzmann distribution

$$P(v,t) \propto e^{-V/k_B T}.$$

Let us obtain the nonequilibrium probability current J. Integrating from $x = A$ to $x = B$ (we assume $P(B) = 0$)

$$m\gamma J \int_A^B e^{V/k_B T} dx = -k_B T\left[e^{V/k_B T} P\right]_A^B,$$

we have the probability current as

$$J = \frac{k_B T\, P(A) e^{V(A)/k_B T}}{m\gamma \int_A^B e^{V/k_B T} dx}.$$

Evaluating the potential curve V at the saddle point C by $V = V(C) - K_C(x - x_C)^2/2 + \cdots$ and using the relation

$$\int_A^B e^{(V - V(C))/k_B T} dx \simeq \int_{-\infty}^{\infty} e^{-\frac{K_C(x-x_C)^2}{2k_B T}} dx = \sqrt{\frac{2\pi k_B T}{K_C}},$$

we have the Arrhenius-type of the probability current

$$\tilde{J} = \frac{J}{P(A)} = \frac{1}{m\gamma}\sqrt{\frac{K_C k_B T}{2\pi}} e^{-Q/k_B T}$$

where $Q = V(C) - V(A)$ is the activation energy.

Chapter 3

(1) The problem on the representations

(a) For $\hat{H} = \hat{H}_0 + \hat{V}(t)$, the equations of motion become

(1) Schrödinger representation:

$$i\hbar \frac{\partial \hat{\psi}_S(t)}{\partial t} = \hat{H}\hat{\psi}_S(t)$$

(2) Heisenberg representation:

$$i\hbar \frac{\partial \hat{A}_H(t)}{\partial t} = \left[\hat{A}_H(t), \hat{H}\right]$$

with the Heisenberg operator as

$$\hat{A}_H(t) = e^{i\hat{H}t/\hbar}\hat{A}e^{-i\hat{H}t/\hbar}.$$

(3) Interaction representation:

$$i\hbar \frac{\partial \hat{\psi}_I(t)}{\partial t} = \hat{V}(t)\hat{\psi}_I(t)$$

with the Interaction operators as

$$\hat{A}_I(t) = e^{i\hat{H}_0 t/\hbar}\hat{A}e^{-i\hat{H}_0 t/\hbar}$$
$$\hat{\psi}_I(t) = e^{i\hat{H}_0 t/\hbar}e^{-i\hat{H}t/\hbar}\hat{\psi}(0) = \hat{S}(t, 0)\hat{\psi}(0).$$

(b) The expectation values of the operator $\langle \hat{A} \rangle$ are

(1) Schödinger representation:

$$\begin{aligned}\langle \hat{A}(t) \rangle &= \langle \hat{\psi}_S(t)|\hat{A}|\hat{\psi}_S(t)\rangle \\ &= \langle \hat{\psi}(0)|e^{i\hat{H}t/\hbar}\hat{A}e^{-i\hat{H}t/\hbar}|\hat{\psi}(0)\rangle.\end{aligned}$$

(2) Heisenberg representation:

$$\begin{aligned}\langle \hat{A}(t) \rangle &= \langle \hat{\psi}(0)|\hat{A}_H(t)|\hat{\psi}(0)\rangle \\ &= \langle \hat{\psi}(0)|e^{i\hat{H}t/\hbar}\hat{A}e^{-i\hat{H}t/\hbar}|\hat{\psi}(0)\rangle.\end{aligned}$$

(3) Interaction representation:

$$\begin{aligned}\langle \hat{A}(t) \rangle &= \langle \hat{\psi}_I(t)|\hat{A}_I(t)|\hat{\psi}_I(t)\rangle \\ &= \langle \hat{\psi}_I(t)|e^{i\hat{H}_0 t/\hbar}\hat{A}e^{-i\hat{H}_0 t/\hbar}|\hat{\psi}_I(t)\rangle. \\ &= \langle \hat{\psi}(0)|e^{i\hat{H}t/\hbar}\hat{A}e^{-i\hat{H}t/\hbar}|\hat{\psi}(0)\rangle.\end{aligned}$$

Thus, $\langle \hat{A}(t) \rangle$ does not depend on the representations.

(2) The problem on the onset of magnetic moment

(a) Let us consider the Anderson model within the Hartree–Fock approximation as

$$\hat{H} = \sum_{k\sigma} \left(\epsilon_{k\sigma} \hat{c}^{\dagger}_{k\sigma} \hat{c}_{k\sigma} + V_k \hat{c}^{\dagger}_{k\sigma} \hat{d}_{\sigma} + V_k^* \hat{d}^{\dagger}_{\sigma} \hat{c}_{k\sigma} \right) + \sum_{\sigma} \epsilon_d \hat{d}^{\dagger}_{\sigma} \hat{d}_{\sigma}$$
$$+ U \sum_{\sigma} \langle \hat{n}_{\bar{\sigma}} \rangle \hat{n}_{\sigma} - U \langle \hat{n}_{\uparrow} \rangle \langle \hat{n}_{\downarrow} \rangle,$$

with $\hat{n}_{d\sigma} = \hat{d}^{\dagger}_{\sigma} \hat{d}_{\sigma}$ and U is the Coulomb interaction. This Hamiltonian has the same form for the non-interacting case by $\epsilon_d \to \epsilon_d + U \langle \hat{n}_{\bar{\sigma}} \rangle$. Therefore, we have Green's function $G^r_{\sigma}(t) = -(i/\hbar)\theta(t)\langle [\hat{d}_{\sigma}(t), \hat{d}^{\dagger}_{\sigma}(0)] \rangle$ as

$$G^r_{\sigma}(\epsilon) = \frac{1}{\epsilon - \epsilon_d - U \langle \hat{n}_{\bar{\sigma}} \rangle - \Sigma^r(\epsilon)},$$

with the self-energy of $\Sigma^r(\epsilon) = \sum_{k\sigma} |V_k|^2/(\epsilon - \epsilon_{k\sigma} + i0^+)$. The occupation $\langle \hat{n}_{\sigma} \rangle$ for each spin σ is obtained from the self-consistent calculation of

$$\langle \hat{n}_{\sigma} \rangle = \int_{-\infty}^{\epsilon_F} \left(-\frac{1}{\pi} \mathrm{Im}[G^r_{\sigma}(\epsilon)] \right) d\epsilon$$
$$= \frac{1}{\pi} \left(\frac{\pi}{2} + \tan^{-1} \frac{\epsilon_F - \epsilon_d - U \langle \hat{n}_{\bar{\sigma}} \rangle}{\Gamma/2} \right)$$

where $\Gamma = 2\pi \sum_{k\sigma} |V_k|^2 \delta(\epsilon - \epsilon_{k\sigma})$.

(b) For the symmetric case $\epsilon_F = \epsilon_d + U/2$, we have

$$y \cot(\pi \langle \hat{n}_{\sigma} \rangle) = \left(\langle \hat{n}_{\bar{\sigma}} \rangle - \frac{1}{2} \right) \pi$$

with a spin-unpolarized solution with $\langle \hat{n}_{\sigma} \rangle = \langle \hat{n}_{\bar{\sigma}} \rangle = 1/2$. Here, we put $y = \pi\Gamma/2U$. To find the spin-polarized solution with $\langle \hat{n}_{\sigma} \rangle \neq \langle \hat{n}_{\bar{\sigma}} \rangle$, we consider the energy when the electronic state at ϵ_F is modified by $n_{\sigma,\hat{\sigma}} = 1/2 \pm \delta n$. Since the increase of total energy becomes $\delta n \delta\epsilon - U(\delta n)^2$ with $\delta n = \nu(\epsilon_F)\delta\epsilon$, the condition for the appearance of the spin-polarized state becomes $U\nu(\epsilon_F) > 1$, which is called the Stoner criterion. Then for the symmetric case, we have

$$y > y^2 + \left(\langle \hat{n}_{\sigma} \rangle - \frac{1}{2} \right)^2 \pi^2,$$

which is reduced to

$$y < 1, \qquad \text{that is} \quad U > \frac{\pi\Gamma}{2}.$$