Applications of the Propagator in Quantum Statistical Mechanics

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We shall discuss first the basic properties of the propagator and then evaluate some quantities of rather simple quantum mechanical systems.

§ 1. Density Matrix in the Canonical Ensemble[1]

A propagator formalism based on the Bloch equation for the density matrix is presented. The propagator is essentially the density matrix in quantum mechanical terminology. In quantum mechanics, the expectation value of an operator A which acts on a wave function $\psi(\mathbf{r}, t)$ is

$$\bar{A} = (\psi, A\psi). \tag{1}$$

The wave function $\psi(\mathbf{r}, t)$ may be expanded in terms of a complete orthogonal set of functions ϕ_n,

$$\psi(\mathbf{r}, t) = c_n(t)\phi_n(\mathbf{r}), \tag{2}$$

where $\phi_n(\mathbf{r})$ is a function independent of time. Then

$$\bar{A} = \sum_{n,m} c_m^* c_n (n|A|n). \tag{3}$$

We introduce a projection operator P by

$$(n|P|m) = c_n c_m^*, \tag{4}$$

so that

$$\bar{A} = \sum_{n,m} (n|P|m)(m|A|n) = \operatorname{Tr} PA. \tag{5}$$

P has the properties

$$P^2 = P \qquad \text{(idempotent)}, \tag{6}$$

and

$$(n|P|m) = (m|P|n)^* \qquad \text{(Hermitian)}. \tag{7}$$

We define the ensemble average of A by

$$<\bar{A}> = \sum_{n,m} <c_n c_m^*> (m|A|n). \qquad (8)$$

Thus, it is convenient to introduce the density matrix ρ with following elements:

$$(n|\rho|m) = <c_n c_m^*> \qquad (9)$$

and the ensemble average is written as

$$<\bar{A}> = \mathrm{Tr}\,\rho A. \qquad (10)$$

Double averages, quantum mechanical and statistical, both mean essentially the average values, we shall use the notation $<A>$ from now by omitting the bat.

The density matrix has several important properties. First, it is Hermitian, in particular, the diagonal elements are real. and if $A=1$ in Eq. (10),

$$\mathrm{Tr}\,\rho = 1, \qquad (11)$$

which indicates that the diagonal elements $(n|\rho|n)$ of a density matrix give the normalized probability that the state ϕ_n is realized in the ensemble. Second, the averages defined by the density matrices are invariant under unitary transformations.

The time dependence of the wave function is given by the Schrödinger equation

$$-\frac{\hbar}{i} \frac{\partial \psi}{\partial t} = H\psi. \qquad (12)$$

The expansion (2) gives

$$-\frac{\hbar}{i} \sum_n \frac{dc_n}{dt} \phi_n = \sum_n c_n H\phi_n \qquad (13)$$

From (9) and (12), one can derive

$$\frac{d}{dt}(n|P|m) = \frac{i}{\hbar}(n|PH-HP|m). \qquad (14)$$

In terms of the density matrix ρ and the commutator $[\ ,\ ]$ Eq. (14) becomes

$$\frac{\partial \rho}{\partial t} = \frac{i}{\hbar}[\rho, H]. \qquad (15)$$

The formal solution of the Bloch equation (Eq. (15)) for a time independent H is

$$\rho(t) = [\exp(-i\hbar^{-1}Ht)]\rho(0)\exp(i\hbar^{-1}Ht). \qquad (16)$$

From the analogy of classical cases, we introduce a operator

$$\rho = e^{-\beta H} = 1 - \beta H + \frac{1}{2}\beta^2 H^2 - \cdots \qquad (17)$$

as the density matrix for the canonical ensemble, β being $1/kT$.

We are interested in the quantum mechanical systems of N fermions or bosons described by the Hamiltonian H. We shall assume that our system is in equilibrium and the Hamiltonian operator H has the eigenvalues E_n and the eigenfunctions ψ_n:

$$H\psi_n = E_n\psi_n. \tag{18}$$

The partition function of the system is

$$Z_N = \sum_n e^{-E_n/kT}. \tag{19}$$

The Schrödinger equation is not soluble in most cases. Therefore, we try to express the partition function directly in terms of the Hamiltonian H. For this purpose, let us start with the density operator $e^{-\beta H}$ and define

$$\rho(\mathbf{r}'^N, \mathbf{r}^N) = \sum_n \psi_n^*(\mathbf{r}'^N)e^{-\beta E_n}\psi_n(\mathbf{r}^N) = \sum_n \psi_n^*(\mathbf{r}'^N)e^{-\beta H}\psi_n(\mathbf{r}^N), \tag{20}$$

where $\mathbf{r}^N$ represents the coordinates of the N particles. This is the $(\mathbf{r}'^N, \mathbf{r}^N)$ element of the density matrix ρ in the canonical ensemble. The trace of this matrix is simply the partition function:

$$\int \rho(\mathbf{r}'^N, \mathbf{r}^N)\delta(\mathbf{r}'^N, \mathbf{r}^N)d\mathbf{r}'^N d\mathbf{r}^N = \int \rho(\mathbf{r}^N, \mathbf{r}^N)d\mathbf{r}^N = \sum_n e^{-\beta E_n}. \tag{21}$$

In Eq. (20), the density matrix is defined in terms of the energy eigenfunctions. However, it is possible to use orthonormal set of eigenfunctions to express ρ. To show this, we expand the energy eigenfunctions in terms of the orthogonal set $\{\varphi_l\}$:

$$\psi_n = \sum_l c_{nl}\varphi_l, \qquad c_{nl} = \int \psi_n(\mathbf{r}^N)\varphi_l^*(\mathbf{r}^N)d\mathbf{r}^N. \tag{22}$$

Then, using the closure property of ψ_n,

$$\sum_n \psi_n^*(\mathbf{r}'^N)\psi_n(\mathbf{r}^N) = \delta(\mathbf{r}^N - \mathbf{r}'^N), \tag{23}$$

and the orthogonal properties of φ_s, we find

$$\sum_n c_{nl}c_{ns} = \delta_{ls}. \tag{24}$$

Thus, Eq. (20) is reduces to

$$\rho(\mathbf{r}'^N, \mathbf{r}^N) = \sum_l \varphi_l^*(\mathbf{r}'^N)e^{-\beta H}\varphi_l(\mathbf{r}^N). \tag{25}$$

Consequently, the density matrix for thermal equilibrium may be defined in terms of any orthonormal set of functions, and the partition function can be obtained by taking its trace.

On differentiating Eq. (20), we find the Bloch equation

$$\frac{\partial \rho}{\partial \beta} = -H\rho \tag{26}$$

for the equilibrium density matrix. The formal solution can be expressed as

$$\rho = e^{-\beta H}\rho(0), \tag{27}$$

where $\rho(0)$ is the value of ρ at $\beta = 0$.

§ 2. Propagator in the r-β Space[2]

In view of (20), we introduce a new wave function in the $\mathbf{r} - \beta$ space (i.e., space of coordinate and reciprocal thermal energy) by

$$\Psi_n(\mathbf{r}^N, \beta) = e^{-\beta H}\psi_n(\mathbf{r}^N) = e^{-\beta E_n}\psi_n(\mathbf{r}^N). \tag{28}$$

Since H and $e^{-\beta H}$ commute, $\Psi_n(\mathbf{r}^N, \beta)$ satisfies the Bloch equation

$$\frac{\partial \Psi_n}{\partial \beta} = -H\Psi_n \tag{29}$$

The solution of this equation may be obtained by solving the integral equation

$$\Psi_n(\mathbf{r}^N, \beta) = \int K(\mathbf{r}^N\beta, \mathbf{r}'^N\beta')\Psi_n(\mathbf{r}'^N, \beta')d\mathbf{r}'^N, \tag{30}$$

as can easily be verified by differentiating both sides with respect to β. The kernel represents a propagation of the set of coordinates from $(\mathbf{r}'^N, \beta')$ to $(\mathbf{r}^N, \beta)$ and is the propagator. It is mathematically the Green's function satisfying

$$\frac{\partial K(2, 1)}{\partial \beta_2} + H(2)K(2, 1) = \delta(2 - 1). \tag{31}$$

For simplicity, the notation 2 stands for $(\mathbf{r}^N, \beta = \beta_2)$ and 1 for $(\mathbf{r}'^N, \beta = \beta_1)$. Eq. (30) can be written as

$$\psi_n(\mathbf{r}^N) = \{\exp[\beta - \beta']E_n]\}\int K(\mathbf{r}^N\beta, \mathbf{r}'^N\beta')\psi_n(\mathbf{r}'^N)d\mathbf{r}'^N \tag{32}$$

From this expression, we see that $\psi_n(\mathbf{r}^N)$ is an eigenfunction and $\lambda_n = e^{(\beta-\beta')E_n}$ is an eigenvalue of the integral equation (32).

Eq. (31) requires that the kernel be the Green's function belonging to the differential equation (29). The Green's function is subject to the subsidiary condition

$$K(2, 1) \longrightarrow \delta(\mathbf{r}^N - \mathbf{r}'^N) \quad \text{as} \quad \beta_2 \longrightarrow \beta_1 \tag{33}$$

$$= 0 \qquad \qquad \text{if} \quad \beta_2 < \beta_1$$

The kernel may be expanded in terms of the eigenfunctions of the integral equation. From Eq. (32), we have

$$K(2, 1) = \sum_n \frac{\psi_n(\mathbf{r}^N)\psi_n^*(\mathbf{r}'^N)}{\lambda_n}$$

$$= \sum_n \{\exp[-(\beta-\beta')E_n]\}\psi_n(\mathbf{r}^N)\psi_n^*(\mathbf{r}'^N). \tag{34}$$

Equating β' to 0 in Eq. (34), we see that $K(\mathbf{r}^N\beta, \mathbf{r}'^N0)$ reduces the density matrix. We arrive at the relation:

$$Z_N = \int K(\mathbf{r}^N\beta, \mathbf{r}'^N0)d\mathbf{r}^N. \tag{35}$$

We now consider a system with the Hamiltonian

$$H = H_0 + H_1; \quad H_1 = \sum_{i<j=1}^{N} V_{ij}. \tag{36}$$

and the interaction H_1 is small compared to H_0. Corresponding to the above Hamiltonian (Eq. (36)), we put

$$K(2, 1) = K_0(2, 1) + K_1(2, 1) \tag{37}$$

where $K_0(2, 1)$ satisfies

$$\left[\frac{\partial}{\partial\beta_2} + H_0(2)\right]K_0(2, 1) = \delta(2-1). \tag{38}$$

Thus we have

$$\frac{\partial K'}{\partial}\beta_2 + H_0K' = -H_2K. \tag{39}$$

However, since the Green's function belonging to this equation is $K_0(2, 1)$, we obtain

$$K'(2, 1) = -\int_{\beta_1}^{\beta_2}\int_V K_0(2, 3)H(3)K(3, 1)d3, \tag{40}$$

where $d3 = d\mathbf{r}_3d\beta_3$.

Adding $K_0(2, 1)$ to the above equation, we find an integral equation

$$K(2, 1) = K_0(2, 1) - \int K_0(2, 3)H_1(3)K(3, 1)d3 \tag{41}$$

This integral equation can be solved by iteration. We arrived at

$$K(2, 1) = K_0(2, 1) - \int_{\beta_1}^{\beta_2}\int_V K_0(2, 3)H_1(3)K_0(3, 1)d3$$

$$+\int_{\beta_1}^{\beta_2}\int_V\int_{\beta_1}^{\beta_2}\int_V K_0(2, 3)H_1(3)K_0(3, 4)H_1(4)d3d4\ldots \tag{42}$$

§3. Example of a Propagator as an Inverse Operator

From Eq. (35), the partition function is written in the form

$$Z=\int_{-\infty}^{\infty} e^{-\beta E}N(E)dE, \tag{43}$$

where $N(E)$ is the density of states.

Now, the Green's function can be manipulated symbolically as a limit of the resolvent of H, viz,

$$K=\lim_{\varepsilon\in+0} \frac{1}{E-H-i\varepsilon} \tag{44}$$

$|E'>$ being any state, we obviously have

$$(E-H)\frac{1}{E-H-i\varepsilon}|E'> = |E'> + \frac{i\varepsilon}{E-H-i\varepsilon}|E'> \tag{45}$$

The norm of the second term on the right-hand side is

$$N(E)=\varepsilon^2 < E'|\frac{1}{(E-H)^2+\varepsilon^2}|E'>$$

$$=\varepsilon\int < E'|E'>^2\frac{\varepsilon}{(E-E')+\varepsilon^2}\,dE' \tag{46}$$

The second line is obtained by adopting a representation in which H is diagonal; $<E'|E'>^2dE'$ is the norm of the component of $|E'>$. By a known property of the δ function,

$$\delta(E-E')=\frac{1}{\pi}\lim_{\varepsilon\to+0}\frac{\varepsilon}{(E-E')^2+\varepsilon^2} \tag{47}$$

the density of states $N(E)$ is expressed as

$$N(E)=\sum_{E'} <E'|\delta(H-E)|E'>$$

$$=\frac{1}{\pi}\lim_{\varepsilon\to+0}\mathrm{Tr}\Big(\frac{1}{H-E-i\varepsilon}\Big). \tag{48}$$

§4. The Second Virial Coefficient

In the present section the properties of the Laplace transform of $\rho(\beta)$ and tech-

niques for its evaluation are discussed.

For a density matrix $\rho = e^{-\beta H}$ with $H = H_0 + H_1$, define a Laplace transform:

$$\Phi(E) = -\int_0^\infty e^{-\beta H} \rho(\beta) d\beta \tag{49}$$

in the region where E is less than the smallest eigenvalue of H.   Using a boundary condition $\rho(0) = 1$, it was shown[3] that the "Møller wave operator"

$$G(E) = \Phi(E)(E - H_0) \tag{50}$$

satisfies

$$G(E) = 1 + E(-H_0)^{-1} H_1 G(E). \tag{51}$$

This is precisely the familiar stationary state scattering equation in quantum mechanics.

As a preliminary to our subsequent discussion, we define G in terms of the two-body scattering operator t_α by

$$t_\alpha = V_\alpha + V_\alpha (E - H_0)^{-1} t_\alpha \tag{52}$$

where V_α represents the potential of a pair of particles.   Index α runs over all ij pairs of $\frac{1}{2} N(N-1)$.   This is the integral equation for solving the two-body scattering problem.   In terms of the t_α's, an exact expression for G is

$$G(E) = 1 + (E - H_0)^{-1} \sum_\alpha t_\alpha G_\alpha,$$

$$G_\alpha = 1 + (E - H_0)^{-1} \sum_\beta t_\beta G_\beta. \tag{53}$$

By perturbation expansion, Eqs. (53) leads to

$$G(E) = 1 + (E - H_0)^{-1} \sum_\alpha t_\alpha + (E - H_0)^{-1} \sum_\alpha t_\alpha (E - H_0)^{-1} \sum_\beta t_\beta + \cdots. \tag{54}$$

Eq. (53) permit one to evaluate Z in terms of two-body scattering operators for N particles, although it is rather cumbersome if N is large.
For evaluation of the second virial coefficient, $N = 2$ and the sum over pairs has just one term:

$$G = 1 + (E - H_0)^{-1} t \tag{55}$$

The expansion of the equation of state in terms of the inverse volume v^{-1} ($v = V/N$) is

$$\frac{pv}{kT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \cdots, \tag{56}$$

and B is the second virial coefficient.

$$B = -b_2$$

where b_2, the second cluster integral, is given by

$$b_2 = \frac{1}{2V} \iint (<1, 2|e^{-\beta H_2}|1, 2> - <1|e^{-\beta H_1}|1><2|e^{-\beta H_1}|2>)d\mathbf{r}_1 d\mathbf{r}_2 \qquad (57)$$

H_1 and H_2 are, respectively, the Hamiltonians of one particle and of a pair of particles. Then, we have

$$B = -\frac{2\sqrt{2}(2\pi\hbar^2)^{3/2}}{(m\beta)^{3/2}} \int \{<p|\rho(\beta)|p> - \exp(-\beta p^2/m)\}\frac{vd\mathbf{p}}{(2\pi\hbar)^3}$$

$$= -\frac{v}{(\pi m k T)^{3/2}}\frac{1}{2\pi i}\int d\mathbf{p}\int e^{-\beta E}\frac{<p|t|p>}{(E-H_0)^2}dE \qquad (58)$$

From the first line to the second line in the above calculation, the diagonal representation of the density matrix in the following form is used.

$$<p|\rho(\beta)|p> = \frac{1}{2\pi i}\int_C e^{-\beta E}\left[\frac{1}{E-H_0} + \frac{<p|t|p>}{(E-H_0)^2}\right]dE \qquad (59)$$

for the inverse of Eq. (49)

$$\rho(\beta) = \frac{1}{2\pi i}\int_{C+i\infty}^{C-i\infty} e^{-\beta E}\Phi(E)dE \qquad (60)$$

§ 5. The Propagator of a Free Electron in a Homogeneous Magnetic Field

In a uniform magnetic field H along z-axis, a free electron go on a helical path around the z direction, and the projection to the xy-plane perpendicular to H is a uniform circular motion with the Larmor frequency $\omega_L = \frac{eH}{2mc}$. Quantum mechanically the circular motion is equivalent to the 2-dimensional oscillator and the quantized energy of the helical motion is

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega + \frac{p_z^2}{2m}, \qquad \omega = 2\omega_L \qquad (61)$$

and taking account the momentum of a electron in the magnetic field $\mathbf{p} = -\text{grad} - \frac{e}{c}\mathbf{A}$, where $\mathbf{A} = \left(-\frac{1}{2}Hy, \frac{1}{2}Hx, 0\right)$, the wave function is given by

$$\psi_n(r) = (C_n/2\pi)e^{i(p_x x + p_z z)}e_2^{-1 a^2(y-y_0)^2}H_n(a(y-y_0)),$$

$$C_n = [a/\pi^{1/2} 2^n n!]^{1/2}, \quad y_0 = p_x/a^2, \quad a^2 = \frac{eH}{c} = \frac{\omega}{2} \tag{62}$$

For simplicity, we take the units such that $\hbar = 1$ and $2m = 1$ in Eq. (62) and the following. $H_n(y)$ is the hermite polynomial.

The propagator of an electron from $(\mathbf{r}', \beta')$ to $(\mathbf{r}, \beta)$ in the coordinate-reciprocal thermal energy space is given as in Eq. (34) by

$$K(\mathbf{r}\beta, \mathbf{r}'\beta') = \sum_n e^{-(\beta-\beta')E_n} \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}'). \tag{63}$$

Then performing the summation over n and integrating the result over p_x and p_z, we finds

$$K(\mathbf{r}\beta, \mathbf{r}'\beta') = \frac{a^2}{(2\pi)^{5/2}} \frac{\pi}{(\beta-\beta')^{1/2}} [\alpha(\beta, \beta') \sinh(\beta-\beta')\omega]^{-1/2}$$

$$\times \exp\left(-\frac{1}{4}\frac{(z-z')^2}{\beta-\beta'} - \frac{a^2}{4\alpha(\beta, \beta')}[(y-y')^2 + (x-x')^2]\right.$$

$$\left. + i\frac{a}{2}(y+y')(x-x')\right), \tag{64}$$

where

$$\alpha(\beta, \beta') = \tanh[(\beta-\beta')\omega/2].$$

References

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