The Path Integral Formulation of Quantum and Statistical Mechanics

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I. Foundations

THE QUANTUM MECHANICAL PROPAGATOR

$$\langle x | \Psi(t)\rangle = \langle x | e^{-iHt/\hbar} | \Psi(0)\rangle$$

$$= \int dx_0 \underbrace{\boxed{\langle x | e^{-iHt/\hbar} | x_0\rangle}}_{\text{propagator}} \langle x_0 | \Psi(0)\rangle$$

Propagator for a free particle:

$$\langle x_f | e^{-iH_0 t/\hbar} | x_0\rangle = \langle x_f | e^{-ip^2 t/2m\hbar} | x_0\rangle$$

$$= \int dp \ \langle x_f | e^{-ip^2 t/2m\hbar} | p\rangle\langle p | x_0\rangle$$

$$= (2\pi\hbar)^{-1} \int dp \ e^{-ip^2 t/2m\hbar} \ e^{ip(x_f - x_0)/\hbar}$$

$$= \left(\frac{m}{2\pi i\hbar t}\right)^{1/2} \exp \frac{i}{\hbar}\frac{m}{2t}(x_f - x_0)^2$$

Remarks :

$$\left| \langle x_f | e^{-iH_0 t/\hbar} | x_0 \rangle \right|^2 = \frac{m}{2\pi\hbar t},$$ independent of x_f, x_0.

$$\frac{m}{2t}(x_f - x_0)^2 = \frac{1}{2} m \left(\frac{x_f - x_0}{t} \right)^2 \cdot t = S(x_0, 0; x_f, t)$$ action

Propagator for a particle in a one-dim. potential:

We need to split the time evolution operator.

$$e^{\hat{A}+\hat{B}} = e^{\hat{A}} e^{\hat{B}} e^{-\frac{1}{2}[\hat{A},\hat{B}]} + \cdots \qquad \text{Weyl identity}$$

If $[\hat{A},\hat{B}]$ is small,

$$e^{\hat{A}+\hat{B}} \simeq e^{\hat{A}} e^{\hat{B}} \left\{ 1 - \frac{1}{2}[\hat{A},\hat{B}] + \cdots \right\} = e^{\hat{A}} e^{\hat{B}} + \mathcal{O}([\hat{A},\hat{B}])$$

Use this with $\hat{A} = -\frac{i}{\hbar}\hat{T}t \quad (\hat{T} = \hat{p}^2/2m)$, $\hat{B} = -\frac{i}{\hbar}\hat{V}t$:

$$[\hat{A},\hat{B}] = -\frac{1}{\hbar^2}[\hat{T},\hat{V}]\,t^2 \qquad \text{small if } t \to 0 .$$

$$\therefore \quad e^{-iHt/\hbar} \underset{t\to 0}{\simeq} e^{-\frac{i}{\hbar}\hat{T}t} e^{-\frac{i}{\hbar}\hat{V}t} + \mathcal{O}\left(t^2[\hat{T},\hat{V}]\right)$$

Trotter product rule

More accurate expression: split symmetrically

$$e^{-iHt/\hbar} \underset{t\to 0}{\simeq} e^{-\frac{i}{\hbar}\hat{T}\frac{t}{2}} \, e^{-\frac{i}{\hbar}\hat{V}t} \, e^{-\frac{i}{\hbar}\hat{T}\frac{t}{2}} + \mathcal{O}(t^3 [\hat{T},\hat{V}])$$

Long time propagator:

$$e^{-\frac{i}{\hbar}Ht} = \underbrace{e^{-\frac{i}{\hbar}H\cdot\Delta t} \, e^{-\frac{i}{\hbar}H\cdot\Delta t} \cdots e^{-\frac{i}{\hbar}H\cdot\Delta t}}_{N \text{ factors}}$$

$$\Delta t \equiv t/N$$

THE PATH INTEGRAL

$$\langle x_f | e^{-iHt/\hbar} | x_0 \rangle = \langle x_f | e^{-iH\Delta t/\hbar} \underset{\int dx_{N-1}\, |x_{N-1}\rangle\langle x_{N-1}|}{\uparrow} e^{-iH\Delta t/\hbar} \cdots \underset{\int dx_1\, |x_1\rangle\langle x_1|}{\uparrow} e^{-iH\Delta t/\hbar} | x_0 \rangle$$

$$\boxed{\langle x_f | e^{-iHt/\hbar} | x_0 \rangle = \int dx_{N-1} \cdots \int dx_1 \, \langle x_f | e^{-iH\Delta t/\hbar} | x_{N-1} \rangle \cdots \langle x_1 | e^{-iH\Delta t/\hbar} | x_0 \rangle}$$

Substituting the Trotter expression for the short time propagator,

$$\boxed{\langle x_f | e^{-iHt/\hbar} | x_0 \rangle = \left(\frac{m}{2\pi i \hbar \Delta t} \right)^{N/2} \int dx_{N-1} \cdots \int dx_1 \cdot \exp \frac{i}{\hbar} \sum_{k=1}^{N} \left[\frac{m}{2\Delta t} (x_k - x_{k-1})^2 - \Delta t \, V(x_k) \right]}$$

discretized path integral – exact for $N \to \infty$

Interpretation :

$x_k \to x(t_k)$, $t_k = k\Delta t$. In the limit $N \to \infty$,

$$\frac{1}{2\Delta t}\sum_{k=1}^{N}(x_k - x_{k-1})^2 = \frac{\Delta t}{2}\sum_{k=1}^{N}\left(\frac{x(t_k)-x(t_{k-1})}{\Delta t}\right)^2 = \int_0^t \frac{1}{2}\dot{x}(t')^2 dt'$$

$$\Delta t \sum_{k=1}^{N} V(x_k) = \Delta t \sum_{k=1}^{N} V(x(t_k)) = \int_0^t V(x(t'))\,dt'$$

The exponent becomes $\displaystyle\int_0^t dt'\left(\frac{\dot{x}^2}{2} - V(x(t'))\right) = \underbrace{\int_0^t dt'\, L(t')dt'}_{\text{classical action}}$

$$\boxed{\langle x_f | e^{-iHt/\hbar} | x_0 \rangle = \int \mathcal{D}x(t') \exp \frac{i}{\hbar} S[x(t')]}$$

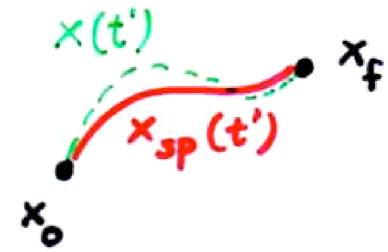
- sum over paths
- functional integral

THE SEMICLASSICAL LIMIT

Note : $\exp \frac{i}{\hbar} S$ has an essential singularity at $\hbar = 0$. We can only take $\hbar \to 0$.

Apply the stationary phase approximation to the functional integral

$$x(t') = x_{sp}(t') + \delta x(t')$$



$\uparrow$ stationary phase path

$$S[x(t')] = S[x_{sp}(t') + \delta x(t')]$$

$$= \int_0^t dt' \left\{ \frac{m}{2} \left[\dot{x}_{sp}(t') + \delta \dot{x}(t') \right]^2 - V\left(x_{sp}(t') + \delta x(t')\right) \right\}$$

To 1st order in $\delta x(t')$,

$$S[x(t')] = S[x_{sp}(t')] + \delta S$$

$$\delta S = \int_0^t dt' \left\{ m\,\delta\dot{x}(t')\,\dot{x}_{sp}(t') - V'(x_{sp}(t'))\,\delta x(t') \right\}$$

Integrating by parts,

$$\delta S = \underbrace{m\,\delta x(t')\,\dot{x}_{sp}(t')\Big|_0^t}_{\text{vanishes}} - \int_0^t dt'\,\delta x(t')\left\{ m\,\ddot{x}_{sp}(t') + V'(x_{sp}(t')) \right\}$$

We have $\delta S = 0$ if

$$\boxed{m\,\ddot{x}_{sp}(t') + V'(x_{sp}(t')) = 0}$$ Euler-Lagrange equation

... Result:

$$\langle x_f | e^{-iHt/\hbar} | x_0 \rangle \underset{\hbar\to 0}{=} \sum_{x_{cl}(t')} (2\pi\hbar)^{-1/2} \left| \frac{\partial^2 S}{\partial x_0 \partial x_f} \right|^{1/2} e^{iS[x_{cl}]/\hbar - i\mu\pi/2}$$

THE SCHRÖDINGER EQUATION FROM THE PATH INTEGRAL

Postulates:

1) $\psi(x_2;t_2) = \int dx_1 \; K(x_2,t_2;x_1,t_1)\,\psi(x_1,t_1)$

$$K(x_2,t_2;x_1,t_1) \equiv \langle x_2|\exp\left\{-\frac{i}{\hbar}H(t_2-t_1)\right\}|x_1\rangle$$

$$= \int dx_3 \; K(x_2,t_2;x_3,t_3)\,K(x_3,t_3;x_1,t_1)$$

2) $K(x_2,t_2;x_1,t_1) = \int_{x_1(t_1)}^{x_2(t_2)} \mathcal{D}x(t)\,\exp\frac{i}{\hbar}S[x(t)]$

We will use these postulates to evolve a wavefunction by $\Delta t \to 0$ and show that the wfn satisfies the TDSE.

Proof:

$$S = \int_t^{t+\Delta t} L\,dt = \frac{m}{2\Delta t}(x-x_0)^2 - \frac{\Delta t}{2}[V(x)+V(x_0)]$$

with $\quad x_0(t)\,, \quad x(t+\Delta t)$

$$\Psi(x;t+\Delta t) = \left(\frac{m}{2\pi i\hbar\Delta t}\right)^{1/2}\int dx_0\, e^{\frac{i}{\hbar}\int_t^{t+\Delta t} L\,dt'}\,\Psi(x_0;t)$$

$$= \left(\frac{m}{2\pi i\hbar\Delta t}\right)^{1/2}\int dx_0\, \exp\left\{\frac{i}{\hbar}\,\frac{m}{2\Delta t}(x-x_0)^2 - \frac{\Delta t}{2}\left(V(x)+V(x_0)\right)\right\}\Psi(x_0;t)$$

Setting $\quad x_0 \equiv x+y\,,$

$$\Psi(x;t+\Delta t) = \left(\frac{m}{2\pi i\hbar\Delta t}\right)^{1/2}\int dy\, e^{\frac{i}{\hbar}\left\{\frac{m}{2\Delta t}y^2 - \frac{\Delta t}{2}[V(x)+V(x+y)]\right\}}\,\Psi(x+y;t)$$

Expand in powers of Δt through 1st order.

Note the dominant contribution to the integral comes from $y \sim \mathcal{O}(\Delta t^{1/2})$, so we keep terms up to 2nd order in y.

$$\Psi(x;t+\Delta t) \simeq \Psi(x;t) + \Delta t \frac{\partial\Psi}{\partial t}$$

$$= \left(\frac{m}{2\pi i\hbar\Delta t}\right)^{1/2} \int dy \; \exp\left\{\frac{im}{2\hbar\Delta t} y^2\right\} \cdot \left\{1 - \frac{i}{\hbar}\frac{\Delta t}{2}\left[V(x) + V(x) + yV'(x) + \dots\right]\right\} \cdot \left[\Psi(x;t) + y\Psi'(x;t) + \frac{y^2}{2}\Psi''(x;t)\right]$$

Integral: $$\int_{-\infty}^{\infty} y^2 e^{\frac{im}{2\hbar\Delta t}y^2} dy = \frac{\sqrt{\pi}}{2}\left(\frac{-im}{2\hbar\Delta t}\right)^{-3/2}$$

Multiplying this by the $\Delta t^{-1/2}$ prefactor, we see that the terms containing y^2 will contribute terms proportional to Δt. We therefore drop the y^2 terms from the expansion of V but keep them in the expansion of ψ. Therefore

$$\psi(x;t) + \Delta t \frac{\partial \psi}{\partial t}$$

$$= \left(\frac{m}{2\pi i \hbar \Delta t}\right)^{1/2} \left[1 - \frac{i}{\hbar} \Delta t\, V(x)\right] \int dy\; e^{\frac{i}{\hbar}\frac{m}{2\Delta t} y^2} \left[\psi(x;t) + \frac{y^2}{2} \psi''(x;t)\right]$$

$$= \left(\frac{m}{2\pi i \hbar \Delta t}\right)^{1/2} \left[1 - \frac{i}{\hbar} \Delta t\, V(x)\right] \left\{ \left(\frac{2\pi \hbar \Delta t}{-im}\right)^{1/2} \psi(x;t) \right.$$

$$\left. + \frac{1}{2} \frac{\sqrt{\pi}}{2} \left(\frac{-im}{2\hbar \Delta t}\right)^{-3/2} \psi''(x;t) \right. \quad \Rightarrow$$

$$\psi(x;t) + \Delta t \frac{\partial \psi}{\partial t} = \left[1 - \frac{i}{\hbar} \Delta t\, V(x)\right] \psi(x;t) + \frac{i\hbar}{2m} \psi''(x;t) \Delta t + \mathcal{O}(\Delta t^2)$$

$$\Rightarrow \qquad i\hbar \frac{\partial \psi(x;t)}{\partial t} = -\frac{\hbar^2}{2m} \psi''(x;t) + V(x)\, \psi(x;t)$$

SYSTEMS OF MANY DEGREES OF FREEDOM

$$H = \frac{p_x^2}{2m_x} + \frac{p_y^2}{2m_y} + V(x,y)$$

$$\langle x_f\, y_f |\, e^{-iHt/\hbar}\, | x_0\, y_0 \rangle = \int_{x_0}^{x_f} \mathcal{D}x(t) \int_{y_0}^{y_f} \mathcal{D}y(t)\; e^{\frac{i}{\hbar} S[x(t),\, y(t)]}$$

Separable systems: if $V(x,y) = V_1(x) + V_2(y)$,

$$K(x_f\, y_f, t;\, x_0\, y_0, 0) = K_1(x_f, t;\, x_0, 0)\, K_2(y_f, t;\, y_0, 0)$$

Identical particles: the short time propagator is

$$\langle x_1 x_2 | \exp(-iH\Delta t/\hbar) | x_1' x_2' \rangle$$

$$= K(x_1, x_2, x_1' x_2'; \Delta t) \pm K(x_1, x_2, x_2' x_1'; \Delta t)$$

where K is the propagator for distinguishable particles.

bosons: +
fermions: −

Exchange effects in fermions: terms of alternating sign

"sign problem"

even in imaginary time!

QUADRATIC LAGRANGIANS

$$L = a(t)\dot{x}^2 + b(t)\dot{x}x + c(t)x^2 + d(t)\dot{x} + e(t)x + f(t)$$

$$K(x_2, t_2; x_1, t_1) = \int \mathcal{D}x(t) \exp \frac{i}{\hbar} S[x(t)]$$

Expand $x(t)$ about the classical path $x_{cl}(t)$:

$$x(t) = x_{cl}(t) + \underset{\substack{\uparrow \\ \text{not necessarily small}}}{u(t)}$$

$$S[x(t)] = \int_{t_1}^{t_2} dt \left\{ a(t)\left[\dot{x}_{cl}(t)^2 + \dot{u}(t)^2 + 2\dot{x}_{cl}(t)\dot{u}(t)\right] + \dots \right\}$$

All terms linear in $u(t)$ or $\dot{u}(t)$ vanish because the 1st variation of the action is zero along the classical path. Collecting the remaining terms,

$$S[x(t)] = S[x_{cl}(t)] + \int_{t_1}^{t_2} dt \left\{ a(t)\dot{u}(t)^2 + b(t)\dot{u}(t)u(t) + c(t)\,u(t)^2 \right\}$$

and the propagator is

$$K(x_2,t_2;x_1,t_1) = e^{\frac{i}{\hbar}S[x_{cl}(t)]} \int_0^0 \mathcal{D}u(t)\ \exp \frac{i}{\hbar}\int_{t_1}^{t_2} dt \left\{ a(t)\dot{u}(t)^2 + \cdots \right\}$$

Since all $u(t)$ start from and return to zero, the integral over paths can be a function only of times at the end points:

$$K(x_2,t_2;x_1,t_1) = e^{\frac{i}{\hbar}S[x_{cl}(t)]} \cdot F(t_1,t_2)$$

INFLUENCE FUNCTIONAL FORMALISM

Hamiltonian:

$$H = \underbrace{H_0(s, p_s)}_{\text{observable system}} + \underbrace{H_b(\{x_i, p_i\}, s)}_{\text{environment ("bath") + interaction}}$$

Reduced density operator:

$$\tilde{\rho}(t) \equiv \mathrm{Tr}_b\left(e^{-iHt/\hbar}\rho(0)\, e^{iHt/\hbar}\right)$$

Path integral representation:

$$\langle s''|\tilde{\rho}(t)|s'\rangle = \int d\vec{x}\ \langle s''\vec{x}|\, e^{-iHt/\hbar}\rho(0)\, e^{iHt/\hbar}\,|s'\vec{x}\rangle$$

$$= \int d\vec{x} \int ds_0^+ \int d\vec{x}_0^+ \int ds_0^- \int d\vec{x}_0^-\ \langle s''\vec{x}|\, e^{-iHt/\hbar}\,|s_0^+\vec{x}_0^+\rangle$$

$$\cdot \langle s_0^+\vec{x}_0^+|\rho(0)|s_0^-\vec{x}_0^-\rangle\ \langle s_0^-\vec{x}_0^-|\, e^{iHt/\hbar}\,|s'\vec{x}\rangle$$

$$= \int d\vec{x} \int ds_0^+ \int ds_0^- \int d\vec{x}_0^+ \int d\vec{x}_0^- \int \mathcal{D}s_+ \int \mathcal{D}s_- \int \mathcal{D}\vec{x}_+ \int \mathcal{D}\vec{x}_-$$

$$\exp \frac{i}{\hbar}\left\{\mathcal{S}_0[s_+] + \mathcal{S}_b[s_+,\vec{x}_+]\right\} \cdot \langle s_0^+\vec{x}_0^+|\rho(0)|s_0^-\vec{x}_0^-\rangle$$

$$\cdot \exp -\frac{i}{\hbar}\left\{\mathcal{S}_0[s_-] + \mathcal{S}_b[s_-,\vec{x}_-]\right\} \qquad \Rightarrow$$

$$\langle s''|\tilde{\rho}(t)|s'\rangle = \int ds_0^+ \int ds_0^- \int \mathcal{D}s_+ \int \mathcal{D}s_-\ e^{\frac{i}{\hbar}\left(\mathcal{S}_0[s_+]-\mathcal{S}_0[s_-]\right)}$$

$$\cdot F[s_+, s_-]$$

Influence functional:

$$F[s_+, s_-] \equiv \int d\vec{x} \int d\vec{x}_0^+ \int d\vec{x}_0^- \int \mathcal{D}\vec{x}_+ \int \mathcal{D}\vec{x}_- \langle s_0^+ \vec{x}_0^+ | \rho(0) | s_0^- \vec{x}_0^- \rangle$$

$$\cdot \exp \frac{i}{\hbar} \left\{ S_b[s_+, \vec{x}_+] - S_b[s_-, \vec{x}_-] \right\}$$

or, resumming the paths,

$$F[s_+, s_-] = \mathrm{Tr}_b \left\{ U_b[s_+] \, \rho(0) \, U_b^{-1}[s_-] \right\}$$

where U_b is the time evolution operator for the bath Hamiltonian which is now time-dependent because of the time dependence of $s_\pm(t')$:

$$H_b\left(\vec{x}, s_\pm(t')\right)$$

Harmonic bath :

$$H_b = \sum_i \frac{p_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 x_i^2 - c_i s x_i$$

If $\quad \rho(0) = \rho_s(0)\, e^{-\beta H_b^0}$, then

$$F[s_+, s_-] = \langle s_0^+ | \rho_s(0) | s_0^- \rangle$$ ← independent of bath

$$\exp -\frac{1}{\hbar} \int_0^t dt' \int_0^{t'} dt'' \left[s_+(t') - s_-(t') \right]$$

$$\cdot \left[\alpha(t'-t'') s_+(t'') - \alpha^*(t'-t'') s_-(t'') \right]$$

HARMONIC BATH MODELS

$$H = \underbrace{\frac{p_s^2}{2m_0} + V_0(s)}_{H_0 \ (\text{system})} + \sum_j \left\{ \frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 \left(x_j - \frac{c_j s}{m_j \omega_j^2} \right)^2 \right\}$$

Classical mechanics:

$$m\ddot{s}(t) = -V_0'(s) + \sum_j c_j x_j(t) - \frac{c_j^2 s(t)}{m_j \omega_j^2}$$

$$m_j \ddot{x}_j(t) = -m_j \omega_j^2 \left(x_j(t) - \frac{c_j s(t)}{m_j \omega_j^2} \right)$$

Solution :

$$x_j(t) = x_j(0)\cos\omega_j t + \frac{p_j(0)}{m_j\omega_j}\sin\omega_j t$$
$$+ \frac{c_j}{m_j\omega_j}\int_0^t dt'\, s(t')\sin\omega_j(t-t')$$

↑ integrate by parts ⇒

$$m\ddot{s}(t) + V_0'(s(t)) - \sum_j\left(c_j x_j(0)\cos\omega_j t + c_j\frac{p_j(0)}{m_j\omega_j^2}\sin\omega_j t\right)$$
$$- \sum_j\left(\frac{c_j^2}{m_j\omega_j^2}s(0)\cos\omega_j t + \frac{c_j^2}{m_j\omega_j^2}\int_0^t dt'\,\dot{s}(t')\cos\omega_j(t-t')\right)$$
$$= 0$$

Define

$$J(\omega) \equiv \frac{\pi}{2} \sum_j \frac{c_j^{\,2}}{m_j \omega_j} \delta(\omega - \omega_j)$$ "spectral density"

$$\eta(t) \equiv \frac{2}{\pi} \int_{-\infty}^{\infty} d\omega \, \frac{J(\omega)}{\omega} \cos \omega t$$ "friction"

$$= \sum_j \frac{c_j^{\,2}}{m_j \omega_j^{\,2}} \cos \omega_j t$$

$$F(t) \equiv \sum_j c_j \left\{ \left(x_j(0) - \frac{c_j}{m_j \omega_j^{\,2}} s(0) \right) \cos \omega_j t + \frac{p_j(0)}{m_j \omega_j} \sin \omega_j t \right\}$$ "force"

$$\Rightarrow \qquad m\ddot{s}(t) + V_0'(s(t)) + \int_0^t dt'\, \eta(t-t')\,\dot{s}(t') = F(t)$$

generalized Langevin equation (GLE)

- dissipation
- memory
- $\langle F(t) F(t') \rangle = \frac{1}{\beta}\,\eta(t-t')$

Quantum mechanics:

Propagator for forced harmonic oscillator: Gaussian

Influence functional: if $\rho(0) = \rho_S(0)\, e^{-\beta H_b^0}$,

$$F[s_+, s_-] = \langle s_0^+ | \rho_S(0) | s_0^- \rangle \leftarrow \text{absorb in "system" part}$$

$$\cdot \exp\left\{ -\frac{1}{\hbar} \int_0^t dt' \int_0^{t'} dt'' \, [s_+(t') - s_-(t')] \cdot [\alpha(t'-t'')\, s_+(t'') - \alpha^*(t'-t'')\, s_-(t'')] \right\}$$

$$\alpha(t-t') = \frac{1}{\hbar} \sum_j c_j^2 \langle x_j(t')\, x_j(t) \rangle_\beta \qquad \text{(complex)}$$

force autocorrelation function

- Nonlocal couplings (memory)