There's a useful <u>operator formalism</u> applicable to diffusive processes.

Consider a general FP eqn. in 1-d:

$$\frac{\partial f}{\partial t}(x,t) = -\frac{\partial}{\partial x}(af) + \frac{\partial^2}{\partial x^2}(bf) \equiv \hat{\mathcal{L}} f$$

$$a = a(x,t) \sim \text{drift}$$
$$b = b(x,t) \sim \text{diff'n}$$

$$A(x) = \text{some observable} \in \mathbb{R}$$

inner product: $\langle g_1 | g_2 \rangle = \int dx \; g_1^*(x) \, g_2(x)$

$$\langle A \rangle_t \equiv \int dx \; A(x) \, f(x,t)$$

$$\frac{d}{dt}\langle A \rangle_t = \int A \left[-\frac{\partial}{\partial x}(af) + \frac{\partial^2}{\partial x^2}(bf) \right]$$

$$= \int \left[\frac{\partial A}{\partial x} af - \frac{\partial A}{\partial x}\frac{\partial}{\partial x}(bf) \right]$$

$$= \int \left(a \frac{\partial A}{\partial x} + b \frac{\partial^2 A}{\partial x^2} \right) f$$

$$= \int \left(\mathcal{L}^\dagger A \right)(x) \cdot f(x,t)$$

$$\mathcal{L}^\dagger = \text{adjoint of } \mathcal{L} = a \frac{\partial}{\partial x} + b \frac{\partial^2}{\partial x^2}$$

Bra-ket not'n : $\langle A \rangle_t = \langle A | f_t \rangle$

$$\frac{d}{dt} \langle A \rangle_t = \langle A | \hat{\mathcal{L}} f_t \rangle = \langle \hat{\mathcal{L}}^{+} A \,|\, f_t \rangle$$

$$\equiv \langle A | \hat{\mathcal{L}} | f_t \rangle$$ ($\hat{\mathcal{L}}$ acts in either direc'n)

$$|f_t\rangle = e^{\hat{\mathcal{L}} t} |f_0\rangle \equiv \sum_{n=0}^{\infty} \frac{(\hat{\mathcal{L}} t)^n}{n!} |f_0\rangle$$

$f(x,0)$

Convenient to <u>define</u> $A(x,t)$ as follows:

Kolmogorov backward eqn

$$A(x,0) = A(x)$$

$$\frac{\partial A}{\partial t}(x,t) = \hat{\mathcal{L}}^{+} A(x,t) = a \frac{\partial A}{\partial x} + b \frac{\partial^2 A}{\partial x^2}$$

$$\rightarrow \quad |A_t\rangle = e^{\hat{\mathcal{L}}^{+} t} |A_0\rangle$$

$$\langle A \rangle_t = \underbrace{\langle A_0 | e^{\hat{\mathcal{L}} t} f_0 \rangle}_{\langle A_0 | f_t \rangle} = \underbrace{\langle e^{\hat{\mathcal{L}}^{+} t} A_0 | f_0 \rangle}_{\langle A_t | f_0 \rangle}$$

i.e. $$\langle A \rangle_t = \begin{cases} \int A_0(x)\, f(x,t) & \sim \text{Schrö.} \\ \int A(x,t)\, f_0(x) & \sim \text{Heis.} \end{cases}$$

(Recall similar constructions for Hamiltonian dynamics)

Note that in general $\hat{\mathcal{L}}^+ \neq \hat{\mathcal{L}}$, i.e. $\hat{\mathcal{L}}$ is not self-adjoint (~ Hermitian).

As a result, there is relatively little that we can state with confidence about spectral properties of $\hat{\mathcal{L}}$ (existence of eigenvalues & eigenstates, completeness, etc.)

Despite this, let's forge ahead & consider what properties <u>might</u> hold ...
For convenience, let's neglect the time-dependence of ~~$a(x,b)$~~ $a(x,t)$ & $b(x,t)$.
(Focus on 1 instant in time.)

<u>Null eigenstates</u>.

Trivial to see ~~that~~ the constant function $f(x) = 1$ is a null eigstate of $\hat{\mathcal{L}}^+$:

$$\hat{\mathcal{L}}^+ 1 = \left(a \frac{\partial}{\partial x} + b \frac{\partial^2}{\partial x^2} \right) 1 = 0$$

It's also relatively easy to construct $\pi(x)$ s.t. $\hat{\mathcal{L}} \pi = 0$

$$\pi(x) = \frac{1}{b(x)} e^{\varphi(x)} \quad , \quad \varphi(x) = \int_{-\infty}^{x} \frac{a(x')}{b(x')} dx'$$

(The lower bound of integration, $-\infty$, is arbitrary. Choosing a different bound leads to a multiplicative factor that is absorbed into the normaliz'n of π ... which we are ignoring for now.)

<u>But</u>: we have no guarantee that $\pi(x)$ is well-defined everywhere (~~sit~~ suppose $b=0$ for some values of x?) or that it can be normalized.

Let's <u>assume</u> $\pi(x)$ is well-behaved, i.e. well-defined & normalizable.

Then we have a pair of eigenstates associated w/ the eigenvalue 0.

$$\hat{\mathcal{L}}\pi = 0 \quad , \quad \hat{\mathcal{L}}^{+} 1 = 0 \quad .$$

Next, <u>suppose</u> $\hat{\mathcal{L}}\varphi(x) = \lambda\varphi(x)$, $\lambda \neq 0$.

<u>Claim</u>: $\mathrm{Re}(\lambda) \leq 0$.

"Proof". Assume $\varphi(x) \in \mathbb{R}$, hence $\lambda \in \mathbb{R}$ (Leave the generaliz'n to complex fns. as an exercise.)

$$\langle 1 | \hat{\mathcal{L}} | \varphi \rangle = \langle \mathcal{L}^{+} 1 | \varphi \rangle = 0$$

$$\langle 1 | \hat{\mathcal{L}} | \varphi \rangle = \langle 1 | \hat{\mathcal{L}} \varphi \rangle = \lambda \int_{-\infty}^{+\infty} \varphi(x)\, dx$$

$$\therefore \quad \int_{-\infty}^{+\infty} \varphi(x)\, dx = 0$$

i.e. $\varphi(x) > 0$ for some values of x
& $\varphi(x) < 0$ for other values.

Now choose ϵ s.t. $\pi(x) + \epsilon \varphi(x) \geq 0 \quad \forall x$

(Implicit assump'n: $|\varphi| < \infty$, hence $\pi > 0$.)

$f(x,0) = \pi(x) + \epsilon \varphi(x)$ = normalized initi'l prob. dist'n.

$$f(x,t) = e^{\hat{\mathcal{L}} t} f(x,0)$$

$$= \pi(x) + \epsilon e^{\lambda t} \varphi(x)$$

If $\mathrm{Re}\, \lambda \ (= \lambda) > 0$,
then the 2^{nd} term will blow up,
& @ some t we will have
negative values for $f(x,t)$.

"QED"

On general grounds we might expect $\hat{\mathcal{L}}$ & $\hat{\mathcal{L}}^+$ to have the same set of eigenvalues (which come in complex conjugate pairs λ, λ^* when $\lambda \notin \mathbb{R}$). Not sure whether this can be shown rigorously, but let's assume it.

I.e. if $\hat{\mathcal{L}} \varphi(x) = \lambda \varphi(x)$

then $\exists\, \alpha(x)$ s.t. $\hat{\mathcal{L}}^+ \alpha(x) = \lambda^* \alpha(x)$ & v.v.

(Analogous to similar ~~stam~~ statement for real square matrix & its transpose.)

One such pair: $\left.\begin{aligned} \varphi_0(x) &= \pi(x) \\ \alpha_0(x) &= 1 \end{aligned}\right\} \lambda_0 = 0$

Order all others by $\mathrm{Re}(\lambda)$:

$$\lambda_0 = 0 \geq \mathrm{Re}(\lambda_1) \geq \mathrm{Re}(\lambda_2) \geq \cdots$$

$$\hat{\mathcal{L}} \varphi_n(x) = \lambda_n \varphi_n(x)$$
$$\hat{\mathcal{L}}^+ \alpha_n(x) = \lambda_n^* \alpha_n(x)$$

Not'n: $\quad \varphi_n(x) = |n\rangle$
$\qquad\quad \alpha_n^*(x) = \langle n|$

$$\langle m|\hat{\mathcal{L}}|n\rangle = \int \alpha_m^*(x)\left[\hat{\mathcal{L}}\,\varphi_n(x)\right] = \lambda_n \langle m|n\rangle$$

but $$\langle m|\hat{\mathcal{L}}|n\rangle = \int \left[\hat{\mathcal{L}}^\dagger \alpha_m^*(x)\right] \varphi_n(x) = \lambda_m \langle m|n\rangle$$

If we choose m, n s.t. $\lambda_m \neq \lambda_n$,
& if we further assume that $\langle m/n\rangle$
is non-infinite, then we conclude:

$$\langle m/n\rangle \equiv \int \alpha_m^*(x)\, \varphi_n(x) = 0$$
$$\text{if } \lambda_m \neq \lambda_n$$

We've had to make a # of assumptions
to get this far (π, φ well-behaved;
same spectrum of eigvals for $\hat{\mathcal{L}}$, $\hat{\mathcal{L}}^+$;
$|\langle m/n\rangle| < \infty$ when $\lambda_m \neq \lambda_n$).
This is the (steep) price for working w/
non-self-adjoint operators.
Let's make one further assumption:
<u>the φ_n's & α_n's each form a complete
basis set</u>.

Since none of these assumptions can be justified
from 1st principles, let's just say ~~that~~
if the assumptions are satisfied, then
$\hat{\mathcal{L}}$ & $\hat{\mathcal{L}}^+$ are (for our purposes) "well-behaved."

Note: the φ_n's & α_n's are bi-orthogonal, & can be made bi-orthonormal:

$$\langle m | n \rangle = \delta_{mn}$$

(Some care must be taken when $\lambda_m = \lambda_n$.)

Let's express completeness in terms of a sum rule...

$$\text{generic } f(x) = \sum_n c_n \varphi_n(x) = \sum_n c_n | n \rangle = | f \rangle$$

$$\langle n | f \rangle = \int \alpha_n^* \left(\sum_m c_m \varphi_m \right) = \sum_m c_m \delta_{mn} = c_n$$

$$\therefore \quad | f \rangle = \sum_n c_n | n \rangle = \sum_n | n \rangle \langle n | f \rangle$$

$$\therefore \quad \boxed{\sum_n | n \rangle \langle n | = \hat{I}}$$

Equivalently:

$$f(x) = \sum_n | n \rangle \langle n | f \rangle \cancel{= \int \varphi_n(x)}$$

$$= \sum_n \varphi_n(x) \int dx' \, \alpha_n^*(x') f(x')$$

$$= \int dx' \left[\sum_n \alpha_n^*(x') \varphi_n(x) \right] f(x')$$

$$\rightarrow \quad \boxed{\sum_n \alpha_n^*(x') \varphi_n(x) = \delta(x - x')}$$

Assuming $\hat{\mathcal{L}}$ is well-behaved, consider evol'n from init'l dist'n $f(x,0) = f_0(x)$

$$|f_t\rangle = e^{\hat{\mathcal{L}}t}|f_0\rangle$$

$$= \sum_n e^{\hat{\mathcal{L}}t}|n\rangle\langle n|f_0\rangle$$

$$= \sum_n e^{\lambda_n t}|n\rangle\langle n|f_0\rangle$$

$$\xrightarrow{t\to\infty} \sum_{n=0}^{K-1} |n\rangle\langle n|f_0\rangle \equiv \Pi|f_0\rangle$$

where K denotes the degeneracy of the $\lambda=0$ eigenvalue of $\hat{\mathcal{L}}$, & Π is the projector onto the null eigenspace of $\hat{\mathcal{L}}$.

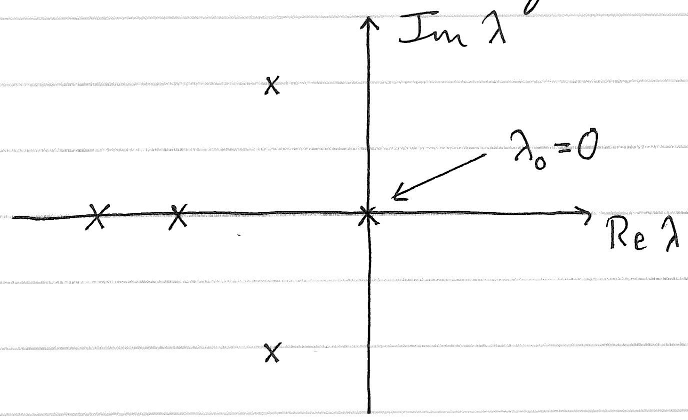
If $K=1$ (i.e. $\lambda=0$ is non-degenerate) then $|f_t\rangle \to |0\rangle\langle 0|f_0\rangle$

But
$$|0\rangle = \pi(x)$$
$$\langle 0| = 1$$
$$\langle 0|f_0\rangle = \int f_0(x) = 1$$

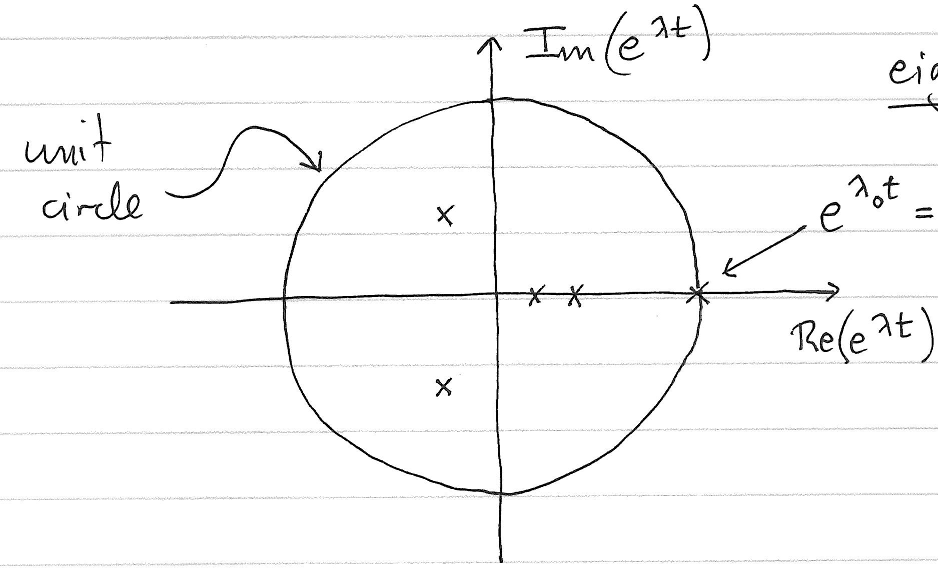
$$\therefore \quad f(x,t) \longrightarrow \pi(x)$$

In this case the prob. dist'n relaxes to the unique stationary dist'n $\pi(x)$.

(When $K>1$, $|f_t\rangle$ relaxes to the stationary distn $\Pi|f_0\rangle$, which is not unique.)



<u>eigvals of $\hat{\mathcal{L}}$</u>



<u>eigvals of $e^{\hat{\mathcal{L}}t}$</u>

$t=0$: all eigvals of $e^{\hat{\mathcal{L}}t}$ start @ 1

$t>0$: they decay or spiral inwards toward zero, except $e^{\lambda_0 t}=1 \;\; \forall t$

Auto-correl'n fns.

Assume $\hat{\mathcal{L}}$ is well-behaved & $K = 0$.

Recall: $A(x,t) = e^{\hat{\mathcal{L}}^+ t} A_0(x)$ ~ Heis.
$f(x,t) = e^{\hat{\mathcal{L}} t} f_0(x)$ ~ Schrö.

$$\langle A \rangle_t = \int A_0(x)\, f(x,t) = \int A(x,t)\, f_0(x)$$

Evaluate these expressions using the kernel (Gn's fn.) $K(x', t \,|\, x, 0)$:

$$\int A_0(x')\, f(x',t)\, dx' = \int dx'\, A_0(x') \left[\int dx\, K(x', t \,|\, x, 0)\, f_0(x) \right]$$

$$= \int dx \left[\int dx'\, A_0(x')\, K(x', t \,|\, x, 0) \right] f_0(x)$$

$$\overset{\text{set}}{=} \int A(x,t)\, f_0(x)$$

$$A(x,t) = \int dx'\, A_0(x')\, K(x', t \,|\, x, 0)$$

$$e^{\hat{\mathcal{L}}^+ t} A_0(x) = \int dx'\, A_0(x')\, K(x', t \,|\, x, 0)$$

[also: $e^{\hat{\mathcal{L}} t} f_0(x') = \int dx\, K(x', t \,|\, x, 0)\, f_0(x)$]

Now choose $A(x)$ s.t. $\int A\pi = 0$.

$t \geq 0$: $C_A(t) = \langle A_0 A_t \rangle$

$$= \int dx' \int dx \; A(x')\, K(x', t | x, 0)\, A(x)\, \pi(x)$$

$$= \int dx \; \left(e^{\hat{\mathcal{L}}^+ t} A_0\right)(x) \cdot A(x)\, \pi(x)$$

$$= \langle e^{\hat{\mathcal{L}}^+ t} A \,|\, A\pi \rangle$$

$$= \langle A | e^{\hat{\mathcal{L}} t} | A\pi \rangle$$

$$= \sum_{mn} \langle A | m \rangle \langle m | e^{\hat{\mathcal{L}} t} | n \rangle \langle n | A\pi \rangle$$

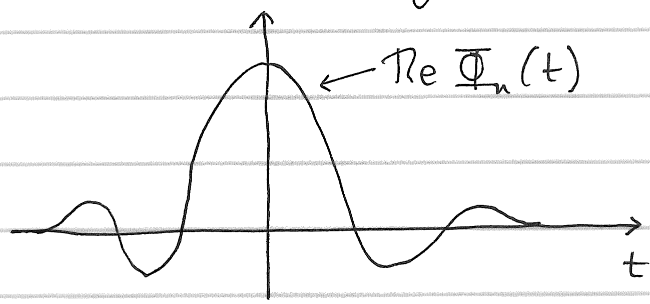
$$= \sum_n \langle A | n \rangle \langle n | A\pi \rangle e^{\lambda_n t} \equiv \sum_n \chi_n^A e^{\lambda_n t}$$

But $C_A(-t) = C_A(t)$ $\therefore$ $\boxed{C_A(t) = \sum_n \chi_n^A e^{\lambda_n |t|}}$

Note that $\chi_0^A = 0$ $\because$ $\langle 0 | A\pi \rangle = \langle A \rangle = 0$

$$C_A(t) = \sum_{n \neq 0} \chi_n^A \underbrace{e^{(\lambda_{nR} + i\lambda_{nI})|t|}}_{\Phi_n(t)}$$

The real part of $\Phi_n(t)$ looks like this:



$|\lambda_{nR}|$ = decay rate

λ_{nI} = oscill'n frequency

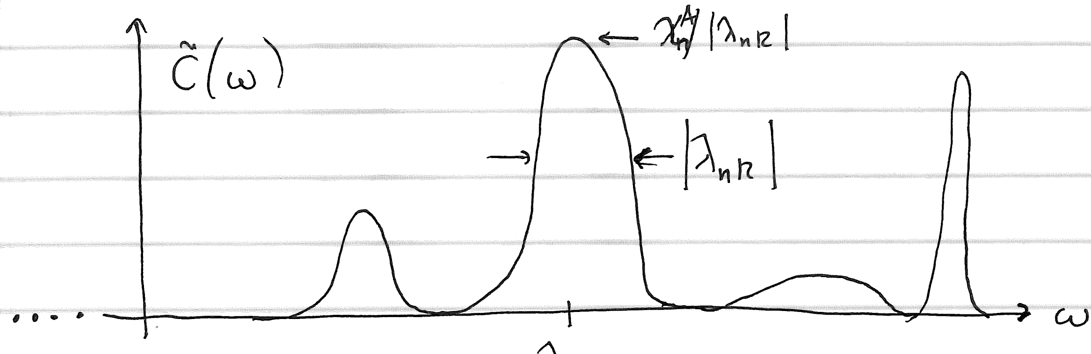
Think of this as a <u>resonance</u>.

$\therefore C_A(t)$ = sum of resonances, w/ weights χ_n^A determined by $A(x)$.

Take all $\chi_n^A \in \mathbb{R}$ for simplicity. Then

$$\tilde{C}_A(\omega) = \int_{-\infty}^{+\infty} C_A(t)\, e^{-i\omega t}\, dt$$

$$= \sum_{n \neq 0} \chi_n^A \cdot \left[\frac{-\lambda_{nR}}{\lambda_{nR}^2 + (\omega - \lambda_{nI})^2} + (\omega \leftarrow -\omega) \right]$$



Weights depend on $A(x)$, locations & widths determined by spectrum of $\mathcal{L}$.

As mentioned earlier, b.c. $\hat{\mathcal{L}}^{+} \neq \hat{\mathcal{L}}$ (in general), it is difficult to say much about the spectral properties of $\hat{\mathcal{L}}$ w/ confidence ... which is why we had to <u>assume</u> well-behaved $\hat{\mathcal{L}}$.

But there is an important case where we can do much better.

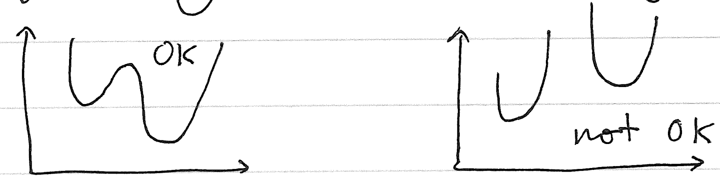
Suppose:

(1) $$\hat{\mathcal{L}} = D \frac{\partial}{\partial x}\left[e^{-\beta V} \frac{\partial}{\partial x}\left(e^{\beta V} f\right)\right] = \overbrace{\frac{1}{\gamma}}^{=\beta D} \frac{\partial}{\partial x}\left(\frac{\partial V}{\partial x} f\right) + D \frac{\partial^2 f}{\partial x^2}$$

$$D = \text{const.}, \quad V = V(x)$$

(2) $$Z \equiv \int dx \; e^{-\beta V} \quad \text{converges}$$

& (3) $\nexists$ infinite barriers in $V(x)$, separating accessible regions



= <u>ergodic</u> <u>assumption</u>

[These assumptions are somewhat stronger than required.]

[As discussed earlier,

$$\pi(x) = \frac{1}{Z} e^{-\beta V(x)}$$

is the unique stationary (equilibrium!) dist'n.]

Now, for $f(x,t)$ obeying $\frac{\partial f}{\partial t} = \hat{\mathcal{L}} f$,
define

$$g(x,t) = \frac{f(x,t)}{\sqrt{\pi(x)}}.$$

Using $\hat{\mathcal{L}} f = D \frac{\partial}{\partial x}\left[\pi \frac{\partial}{\partial x}\left(\frac{f}{\pi}\right)\right]$ we get,
after some tedious algebra,

$$-\frac{\partial g}{\partial t} = -D \frac{\partial^2 g}{\partial x^2} + D V_{eff}\, g \equiv \hat{H} g$$

where

$$V_{eff}(x) = \left(\frac{\beta}{2}\frac{\partial V}{\partial x}\right)^2 - \frac{\beta}{2}\frac{\partial^2 V}{\partial x^2}$$

Now, $\hat{H}$ is essentially the Hamiltonian operator that appears in the Schrö. eqn!
It is known to be self-adjoint,
therefore its eigenstates $\varphi_n(x)$ form
a complete basis:

$$\hat{H}\varphi_n(x) = E_n \varphi_n(x), \quad E_n \in \mathbb{R}$$

(Easy to confirm:
$\psi_0 = \sqrt{\pi}$ is an eigenstate of $\hat{H}$
with eigenvalue $E_0 = 0$.)

$$\hat{\mathcal{L}} f = \frac{\partial f}{\partial t} = \sqrt{\pi}\,\frac{\partial g}{\partial t} = -\sqrt{\pi}\,\hat{H} g$$

Choosing $g = \psi_n$ hence $f = \sqrt{\pi}\cdot\psi_n$:

$$\hat{\mathcal{L}}\left(\sqrt{\pi}\,\psi_n\right) = -\sqrt{\pi}\,\hat{H}\,\psi_n = -E_n\left(\sqrt{\pi}\,\psi_n\right)$$

Thus the eigenstates & eigenvalues of $\hat{\mathcal{L}}$ are:

$$\begin{cases} \varphi_n(x) = \sqrt{\pi}\,\psi_n(x) = e^{-\beta V/2}\,\psi_n(x) \\ \lambda_n = -E_n \in \mathbb{R} \end{cases}$$

We can similarly obtain eigenstates & eigenvalues of $\hat{\mathcal{L}}^{+}$:

$$\begin{cases} \alpha_n(x) = \dfrac{\psi_n(x)}{\sqrt{\pi}} = e^{+\beta V/2}\,\psi_n(x) \\ \lambda_n = -E_n \end{cases}$$

These form complete bases & are bi-orthogonal:

$$\langle m|n\rangle = \delta_{mn} \quad , \quad \sum_n |n\rangle\langle n| = I$$

(after proper normalizn)

These properties of $\{\varphi_n, \alpha_n\}$
follow directly from the orthogonality
& completeness of $\{\varphi_n\}$.

Moreover, for the 1-d Schrö eqn,
the eigenspectrum of $\hat{H}$ is non-degenerate.

We thus reach the following conclusions
for the operator $\hat{\mathcal{L}}$ (given that it
satisfies properties (1) – (3) listed earlier):

- The eigenstates of $\hat{\mathcal{L}}$ & $\hat{\mathcal{L}}^+$ form complete, bi-orthogonal basis sets.

- Their eigenvalues can be arranged as follows:

$$0 = \lambda_0 > \lambda_1 > \lambda_2 > \cdots$$

... which implies (among other things)
that the equil. state

$$\pi = \frac{1}{Z} e^{-\beta V}$$

is the unique stationary soln.,
& $f(x,t) \longrightarrow \pi(x)$ as $t = 0$,
for $\partial f / \partial t = \hat{\mathcal{L}} f$.