Density Matrices II

Read CTDL, pages 643-652.

Last time: ψ , $|\ \rangle$, $\boldsymbol{\rho} = |\ \rangle\langle\ |$
* coherent superposition vs. statistical mixture
* $\boldsymbol{\rho}$ can have non-zero off-diagonal elements if it is a statistical mixture, that includes one coherent superposition state.
* populations along diagonal, coherences off-diagonal

$\langle \mathbf{A} \rangle = \text{Trace}(\rho\,\mathbf{A}) = \text{Trace}(\mathbf{A}\,\rho)$

Today: Quantum Beats
prepared state $\boldsymbol{\rho}$
detection as projection operator **D**

What part of **D** samples a specific off-diagonal element of $\boldsymbol{\rho}$?
Optimize the magnitude of quantum beats

"[partial traces]"

* system consisting of 2 parts — e.g. coupled oscillators
* motion in state-space vs. motion in coordinate space.
* "entanglement"

The material on pages 20–2, –3, –5, and –7 is an exact duplication of pages 19–5, –6, –7 and –8.

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Example: Quantum Beats

<u>Preparation</u>, <u>evolution</u>, <u>detection</u>

magically prepare some coherent superposition state $\Psi(t)$

$$\Psi(t) = N \sum_n \underbrace{a_n \psi_n e^{-iE_n t/\hbar}}$$

Several eigenstates of **H**. Evolve freely without any time-dependent intervention

$$\boxed{N = \left[\sum_n |a_n|^2\right]^{-1/2}}$$

normalization

$$\rho(t) = |\Psi(t)\rangle\langle\Psi(t)|$$

Case (1): Detection: only one of the eigenstates, ψ_1, in the superposition is capable of giving fluorescence that our detector can "see".

Thus $$\mathbf{D} = |\psi_1\rangle\langle\psi_1| = \begin{pmatrix} 1 & 0 & \cdots \\ 0 & 0 & 0 \\ \vdots & 0 & 0 \end{pmatrix}$$

a projection operator
(designed to project out only $|\psi_1\rangle$ part of state vector or ρ_{11} part of $\boldsymbol{\rho}$.

$$\rho = N^2 \begin{pmatrix} |a_1|^2 & a_1 a_2^* e^{-i(E_1-E_2)t/\hbar} & & \cdots \\ & |a_2|^2 & & \\ & & |a_3|^2 & \\ & & & \ddots \end{pmatrix}$$

$$\rho_{12} = \langle 1|\Psi\rangle\langle\Psi|2\rangle$$

$$\rho_{12} = N^2 a_1 e^{-iE_1 t/\hbar} a_2^* e^{+iE_2 t/\hbar}$$

D picks out only 1st row of $\boldsymbol{\rho}$.

$$\langle\mathbf{D}\rangle_t = \text{Trace}(\mathbf{D}\rho) = N^2\,\text{Trace}\begin{pmatrix} |a_1|^2 & a_1 a_2^* e^{-i\omega_{12}t} & \text{stuff} & \cdots \\ 0 & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix}$$

$$= N^2 |a_1|^2$$

no time dependence!

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case (2): a particular linear combination of eigenstates is bright: the initial state $2^{-1/2}(\psi_1 + \psi_2)$ has $\langle \mathbf{D} \rangle = 1$.

a projection operator. How much of the original state is present in the evolved state?

$$\mathbf{D} = \frac{1}{2}\left(|\psi_1\rangle + |\psi_2\rangle\right)\left(\langle\psi_1| + \langle\psi_2|\right)$$

$$= \frac{1}{2}\left[|\psi_1\rangle\langle\psi_1| + |\psi_2\rangle\langle\psi_2| + |\psi_1\rangle\langle\psi_2| + |\psi_2\rangle\langle\psi_1|\right]$$

$$= \frac{1}{2}\left[\begin{pmatrix} 1 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \vdots & 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 & \cdots \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \vdots & 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 1 & 0 & \cdots \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \vdots & 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 & \cdots \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \vdots & 0 & 0 & 0 \end{pmatrix}\right]$$

$$\mathbf{D} = \frac{1}{2}\begin{pmatrix} 1 & 1 & 0 & \cdots \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \vdots & 0 & 0 & 0 \end{pmatrix}$$

$$\left[\text{if the bright state had been } 2^{-1/2}(\psi_1 - \psi_2),\ \text{then } \mathbf{D} = \frac{1}{2}\begin{pmatrix} 1 & -1 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}\right]$$

$$\text{Trace}\,(\mathbf{D}\boldsymbol{\rho}) = \frac{1}{2}\mathrm{N}^2 \ \ \text{Trace}\begin{pmatrix} \ \\ \ \end{pmatrix}$$

why do we need to look at only the 1,2 block of $\boldsymbol{\rho}$?

$$(\mathbf{D}\boldsymbol{\rho})_{11} = \frac{1}{2}N^2\left[|a_1|^2 + a_1^* a_2 e^{+i(E_1-E_2)t/\hbar}\right]$$

$$(\mathbf{D}\boldsymbol{\rho})_{22} = \frac{1}{2}N^2\left[|a_2|^2 + a_1 a_2^* e^{-i(E_1-E_2)t/\hbar}\right]$$

$$Trace(\mathbf{D}\boldsymbol{\rho}) = \frac{1}{2}N^2\left[|a_1|^2 + |a_2|^2 + 2\,\mathrm{Re}\left[a_1^* a_2 e^{+i\omega_{12}t}\right]\right]$$

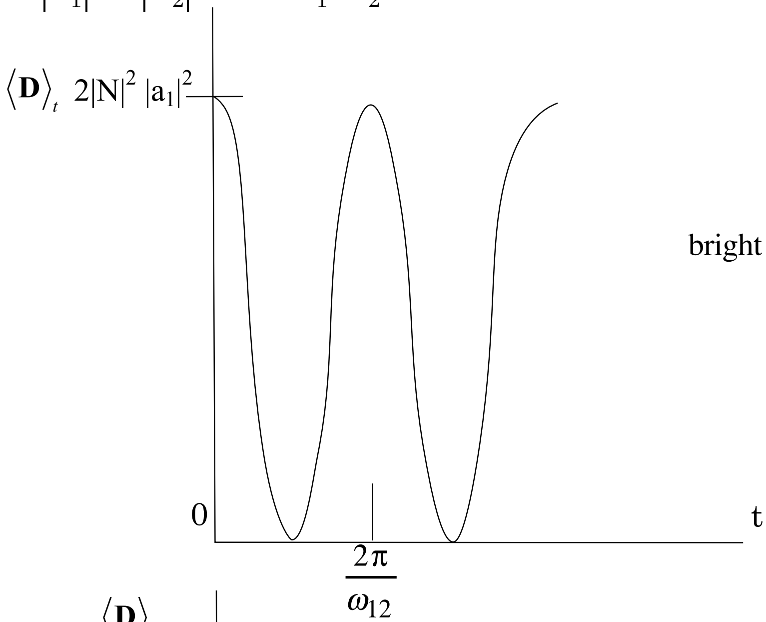
beat note at ω_{12}

[if the bright state had been $2^{-1/2}(\Psi_1 - \Psi_2)$, then $\mathrm{Tr}(\mathbf{D}\,\rho)$ would be the same except for $-2\mathrm{Re}[\quad]$]

$$\text{If } |a_1|^2 = |a_2|^2 \ (\text{and } a_1,\ a_2 \text{ real}),\ \text{Trace}(\mathbf{D}\rho) = \mathrm{N}^2|\mathrm{a}_1|^2\left[1 \pm \cos\omega_{12}t\right] \quad (\mathrm{N}^2 = 1/2)$$

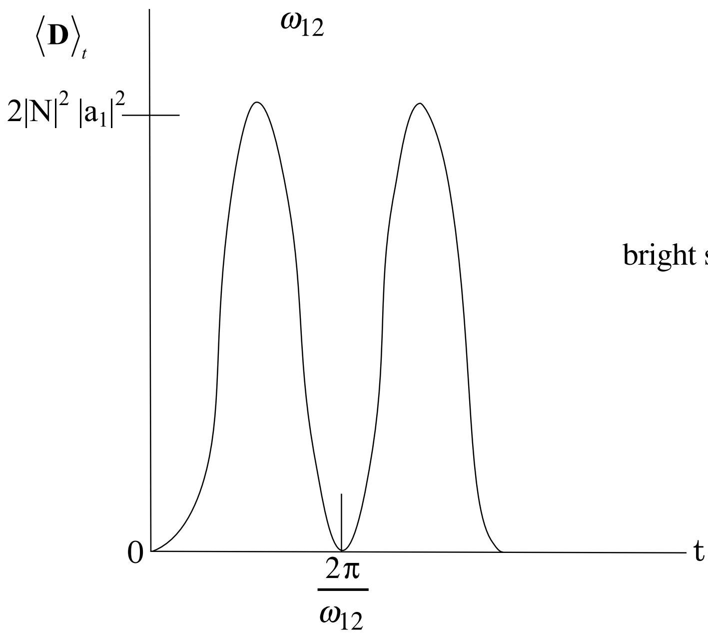
QUANTUM BEAT! 100% modulation!

Either $2\mathrm{N}^2|\mathrm{a}_1|^2$ at t = 0 (+ sign) or 0 at t = 0 (– sign) if $|a_1|^2 = |a_2|^2$ and a_1, a_2 *real*



bright state $2^{-1/2}(\psi_1 + \psi_2)$

$$\mathbf{D} = \begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$



bright state $2^{-1/2}(\psi_1 - \psi_2)$

$$\mathbf{D} = \begin{pmatrix} 1 & -1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Usually $|a_{\mathbf{1}}|_t^{\mathbf{2}} = e^{-t/\tau}$ — exponential decay: we have sinusoidal beats superimposed on exponential decay

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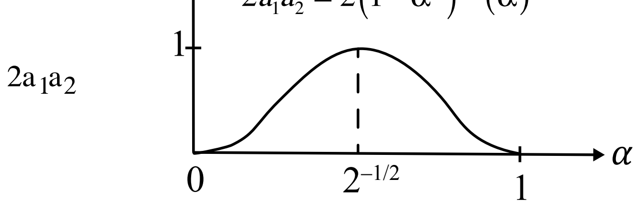
what happens if $|a_1|^2 \neq |a_2|^2$?

try $1-\alpha^2, \alpha^2$ as mixing fractions

$|a_1|^2 + |a_2|^2 = 1$

$2a_1a_2 = 2\left(1-\alpha^2\right)^{1/2}(\alpha)$

Terms in Trace ($\mathbf{D}\boldsymbol{\rho}$)



maximum beat amplitude occurs when $|a_{\mathbf{1}}|^{\mathbf{2}} = |a_{\mathbf{2}}|^{\mathbf{2}}$

So we see that the same Ψ(x,t) or $\boldsymbol{\rho}$(t) can look simple or complicated depending on the nature of the measurement operator! The measurement operator is designed to be sensitive only to specific coherences (i.e. locations in $\boldsymbol{\rho}$) which oscillate at ω_{ij}. THIS IS THE REASON WHY WE CAN SEPARATE PREPARATION AND OBSERVATION SO CLEANLY.

Time evolution of ρ_{nm} and $\langle \mathbf{A} \rangle$

Start with the time-dependent Schrödinger equation:

$$\mathbf{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t} \qquad \begin{cases} \mathbf{H}|\Psi\rangle = i\hbar \dfrac{\partial}{\partial t}|\Psi\rangle \\ \langle \mathbf{H}| H = -i\hbar \dfrac{\partial}{\partial t}\langle \Psi| \end{cases}$$

for time-independent **H** we know $\Psi(t) = \sum_n a_n \psi_n e^{-iE_n t/\hbar}$

1. ρ(t)

$$\boldsymbol{\rho}(t) = |\Psi(t)\rangle\langle\Psi(t)|$$

$$\rho_{nn}(t) = \langle n|\Psi(t)\rangle\langle\Psi(t)|n\rangle = |a_n|^2$$

a time independent "**population**" in state n.

$$\rho_{nm}(t) = a_n a_m^* e^{-i(E_n - E_m)t/\hbar} = a_n a_m^* e^{-i\omega_{nm}t}$$

a "**coherence**" which oscillates at ω_{nm} (eigenstate energy differences /$\hbar$)

2. $\langle \mathbf{A} \rangle_t$

Recall $i\hbar \dfrac{\partial \Psi}{\partial t} = \mathbf{H}\Psi$

$$\frac{\partial}{\partial t}\langle \mathbf{A} \rangle = \left[\frac{\partial}{\partial t}\langle \Psi|\right]\mathbf{A}|\Psi\rangle + \left\langle \Psi\left|\frac{\partial \mathbf{A}}{\partial t}\right|\Psi\right\rangle + \langle\Psi|\mathbf{A}\left[\frac{\partial}{\partial t}|\Psi\rangle\right]$$

$$= \frac{-1}{i\hbar}\left[\langle\Psi|\mathbf{H}\right]\mathbf{A}|\Psi\rangle + \left\langle\frac{\partial \mathbf{A}}{\partial t}\right\rangle + \langle\Psi|\mathbf{A}\left[\frac{1}{i\hbar}\mathbf{H}|\Psi\rangle\right]$$

$$= \frac{i}{\hbar}\langle[\mathbf{H},\mathbf{A}]\rangle + \left\langle\frac{\partial \mathbf{A}}{\partial t}\right\rangle$$

Heisenberg Equation of Motion

This is a scalar equation, not a matrix equation. It tells us about the motion of the "center" of a wavepacket. Note that nothing has been assumed about the time-dependence of **H**. Motion of **A**. Example of one observable quantity.

Nonlecture

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial t}\left[|\Psi\rangle\langle\Psi|\right] = \left[\frac{\partial}{\partial t}|\Psi\rangle\right]\langle\Psi| + |\Psi\rangle\left[\frac{\partial}{\partial t}\langle\Psi|\right]$$

$$= \left[\frac{1}{i\hbar}\mathbf{H}|\Psi\rangle\right]\langle\Psi| + |\Psi\rangle\left[\frac{-1}{i\hbar}\langle\Psi|\mathbf{H}\right]$$

$$= \frac{1}{i\hbar}\left[\mathbf{H}\rho - \rho\mathbf{H}\right]$$

$$i\hbar\frac{\partial \rho}{\partial t} = \left[\mathbf{H},\rho\right]$$

no requirement that **H** be independent of t.

But if **H** is independent of t, then take matrix elements of both sides of equation.

$$i\hbar\dot{\rho}_{jk} = \left\langle j\middle|\mathbf{H}\boldsymbol{\rho} - \boldsymbol{\rho}\mathbf{H}\middle|k\right\rangle$$

$$= E_j\rho_{jk} - \rho_{jk}E_k = \left(E_j - E_k\right)\rho_{jk}$$

$$\dot{\rho}_{jk} = -\frac{i}{\hbar}\left(E_j - E_k\right)\rho_{jk}$$

You already knew this, but not so elegantly.

$$\rho_{jk}(t) = e^{-\frac{i}{\hbar}\left(E_j - E_k\right)t}\rho_{jk}(0)$$

Time evolution of all coherences in the absence of external manipulation!

External manipulation can cause coupling between differential equations.

If **A** commutes with **H** (regardless of whether **H** is time-dependent), there is no dynamics as far as observable **A** is concerned. However, if **A** does not commute with **H**, there can be dynamics of $\langle \mathbf{A} \rangle$ even if both **A** and **H** are time-independent.

Similarly can derive $i\hbar \frac{\partial \rho}{\partial t} = [\mathbf{H}(t), \rho]$ evolution of ρ under **H**(t).

If **H** is time dependent

This is a matrix equation. It specifies the time dependence of each element of $\boldsymbol{\rho}$.

Often we have coupled differential equations where ρ_{ij} is related to ρ_{ii}, ρ_{jj} and perhaps other things too.

<u>Summarize</u>

$$\langle \mathbf{A} \rangle = \mathrm{Tr}(\rho \mathbf{A}) = \mathrm{Tr}(\mathbf{A}\rho)$$

info about quantity being measured

info about state on which measurement is to be made

$$i\hbar \frac{\partial \rho}{\partial t} = [\mathbf{H}, \rho]$$

time evolution

state

initial state : ρ

time evolution of ρ: **H**

observable quantity : **A**

each expressed independently in the form of matrices which can be easily read (or designed!).

NMR pulse gymnastics

<u>statistical mixture states</u> – use the same machinery BUT add the independent ρ_k matrices with weights p_k that correspond to their fractional populations. [Populations have no phase.]

ρ is Hermitian so $\boldsymbol{\rho}$ can be diagonalized by $\mathbf{T}^{\dagger}\boldsymbol{\rho}\mathbf{T} = \tilde{\rho}$. However, if $\boldsymbol{\rho}$ is time-dependent, **T** would have to be time-dependent. This transformation gives a representation without any coherences in $\tilde{\rho}$ even if we started with a coherent superposition state. No problem because this transformation will undiagonalize **H**, thereby reintroducing time dependences.

<u>Systems consisting of 2 parts</u>: method of **partial traces**

e.g. coupled harmonic oscillators

<u>direct product representation</u>

$$\left(\begin{array}{l}\text{recall anharmonically coupled oscillators,} \\ k_{122}q_1q_2^2,\ \psi(q_1,q_2) = \psi_{v_1}(q_1)\psi_{v_2}(q_2)\end{array}\right)$$

$$\psi(x_1,x_2) = \psi_{1,n_1}(x_1)\psi_{2,n_2}(x_2) \qquad\qquad |n_1,n_2\rangle$$

$$\boldsymbol{\rho} = \boldsymbol{\rho}^{(1)} \otimes \boldsymbol{\rho}^{(2)}$$

$\boldsymbol{\rho}$ has 4 indices

$$\rho_{n_1n_2;n_1'n_2'} = \langle n_1|\langle n_2|\psi\rangle\langle\psi|n_2'\rangle|n_1'\rangle$$

It is still a square matrix with $[(n_{1max} + 1)(n_{2max} + 1)]^2$ elements.

We might want to measure the expectation value of an operator that operates on both systems 1 and 2: **A**(1,2)

$$\langle \mathbf{A}\rangle = \mathrm{Trace}(\boldsymbol{\rho}\mathbf{A})$$

$$= \sum_{n_1,n_2} (\boldsymbol{\rho}\mathbf{A})_{n_1n_2;n_1n_2}$$

Alternatively, we might want to measure the expectation value of an operator that operates only on system 1: call it **B**(1).
To use the Trace(ρ **B**) method, need the concept of **partial traces** and need to <u>formally</u> extend **B** so that it acts as a dummy operator on system 2.

$$\tilde{\mathrm{B}}(1) = \mathrm{B}(1) \otimes \mathbf{1}(2)$$

diagonal with respect to n_2

Several types of initial preparation are possible:

1. pure state of $1 \otimes 2$ (a "tensor product" state)
2. statistical mixture in 1, pure state in 2.
3. statistical mixture in both.

Entanglement! Handout from 10/11/02. *Science* **298**, p369 (2002).

Several types of observation are possible:

1. separate observation of subsystem 1 or 2
2. simultaneous measurement of both systems

$$\mathbf{H} = \begin{pmatrix} 0 & 5 & 2 \\ 5 & 2 & 0.5 \\ 2 & 0.5 & 20 \end{pmatrix}$$

This **H** has a 2 × 2 quasi-degenerate block and both members of this block interact weakly with a non-quasi-degenerate remote state.

$$\mathbf{H}^{(0)} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 20 \end{pmatrix}$$

$$\mathbf{H}^{(1)} = \begin{pmatrix} 0 & 5 & 2 \\ 5 & 0 & 0.5 \\ 2 & 0.5 & 0 \end{pmatrix}$$

$$\mathbf{H}^{(2)} = \begin{pmatrix} \frac{2^2}{-20} & \frac{(2)(0.5)}{\frac{0+2}{2}-20} & 0 \\ -\frac{1}{19} & \frac{0.5^2}{-18} & 0 \\ 0 & 0 & \left(\frac{2^2}{20}+\frac{0.5^2}{18}\right) \end{pmatrix}$$

Van Vleck Transformation

$$\underset{\text{in-block}}{H_{nn'}^{(2)}} = \sum_{\substack{k \\ \text{out-of-block}}} \frac{H_{nk}^{(1)} H_{kn'}^{(1)}}{\frac{E_n^{(0)} + E_{n'}^{(0)}}{2} - E_k^{(0)}}$$

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CTDL use this definition of $\tilde{\mathbf{B}}(1)$ (page 306) to prove that

$\langle\tilde{\mathbf{B}}(1)\rangle = \mathrm{Tr}(\boldsymbol{\rho}(1)\mathbf{B}(1))$

calculated as if system 1 were isolated from system 2

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for coupled H–O system

operator of type (1,2) $\mathbf{a}_1^\dagger\mathbf{a}_1\mathbf{a}_2^\dagger\mathbf{a}_2$ (a correlated property of two parts of the system)

type (1) $\mathbf{a}_1^\dagger\mathbf{a}_1$

or type (2) $\mathbf{a}_2^\dagger\mathbf{a}_2$

or type (1 + 2) $\left(\mathbf{a}_1^\dagger\mathbf{a}_1 + \mathbf{a}_2^\dagger\mathbf{a}_2\right)$

See *Chem. Phys. Lett.* **320**, 553 (2000).

Suppose $t = 0$ wavepacket is located at turning point of $v_2 = 5$ in oscillator #2 and at $x_1 = 0$ for oscillator #1

$$\Psi(x_1, x_2, t = 0) = \sum_{n_2=0}^{\infty} a_{n_2} |0, n_2\rangle^{(0)}$$

Discuss inital preparation that gives dynamics within a polyad and between polyads. Diagnostics in state and in configuration space.

suppose we have $\omega_1 = 2\omega_2$ $\quad P = 2n_1 + n_2$ polyads.

and only the $|0,\mathrm{P}\rangle^{(0)}$ state is "bright" (i.e. excitation is initially in oscillator #2)

*n*eed to write $\underbrace{|0,\mathrm{P}\rangle^{(0)}}_{\text{Basis state}}$ as $\displaystyle\sum_{n=0}^{P/2} \mathrm{b}_n \underbrace{|n, P-2n\rangle}_{\text{Eigen state}}$

eigenvectors of $\mathbf{H}(1,2)$ expressed in H–O Basis set

$\mathbf{T}^\dagger\mathbf{H}^P\mathbf{T}$ ($\mathbf{H}^P$ is polyad Hamiltonian)

columns of $\mathbf{T}^\dagger$

The initial state is a coherent superposition of several polyads. Motion occurs in *both* coordinate space and in state space. Each kind of motion is sampled by a different class of diagnostic.

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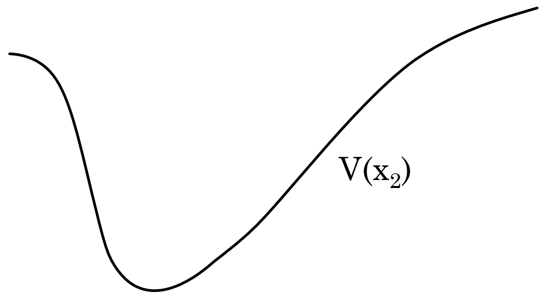
so that we can use $E_{P,n}$ in $e^{-iE_{P,n}t/\hbar}$

to express $\Psi\left(x_1, x_2, t\right)$

get motion of w.p. on



get motion of pieces of state vector within each Polyad P.

Could want expectation values of quantities like $N_1, N_2, P, x_1, x_1 x_2^2$:

$$\left.\begin{aligned}\mathbf{N}_1 &= \mathbf{a}_1^\dagger \mathbf{a}_1 \\ \mathbf{N}_2 &= \mathbf{a}_2^\dagger \mathbf{a}_2\end{aligned}\right\} \text{state space}$$

$$2\mathbf{N}_1(\mathrm{t}) + \mathbf{N}_2(\mathrm{t}) = \mathbf{P}$$

$$\text{coordinate space}\left\{\begin{aligned}\mathbf{x}_1 &= 2^{-1/2}\left(\mathbf{a}_1 + \mathbf{a}_1^\dagger\right) \\ \mathbf{x}_1\mathbf{x}_2^2 &== 2^{-3/2}\left(\mathbf{a}_1 + \mathbf{a}_1^\dagger\right)\left(\mathbf{a}_2 + \mathbf{a}_2^\dagger\right)^2\end{aligned}\right.$$