Resonance Operators: Equation of Motion

Last time: tools for describing a pump/probe wavepacket experiment

* $\boldsymbol{\rho}(t \le 0)$ incoherent, populations on diagonal

* $\mathbf{E}(0)$ excitation matrix. Transforms initial state into coherent superposition: for electronic transition get $\left|g, v''_g\right\rangle$ translated vertically onto upper potential surface

* $\mathbf{U}(t,0) = e^{-i\mathbf{H}t/\hbar}$ time evolution of $t = 0$ prepared wavepacket. If $\boldsymbol{\rho}(0) = \mathbf{E}(0)\boldsymbol{\rho}(t \le 0)\mathbf{E}^{\dagger}$ is expressed in the eigenbasis, $\mathbf{U}$ has simple diagonal form. Otherwise need to express everything in zero-order basis and transform.
  Why? The pluck is almost always a simple zero-order non-eigenstate.

$$\boldsymbol{\rho}(\mathrm{t}) = \mathbf{U}(t,0)\mathbf{E}(0)\boldsymbol{\rho}(t \le 0)\mathbf{E}^{\dagger}(0)\mathbf{U}^{\dagger}(t,0)$$

* Now describe the specific nature of the detection operation

$$\mathrm{I}(t) = \mathrm{Trace}(\mathbf{D}\boldsymbol{\rho})$$

If you want to sample the $\boldsymbol{\rho}_{\mathrm{ij}}(t)$ element of $\boldsymbol{\rho}(t)$, you want a detection matrix with non-zero $\mathbf{D}_{\mathrm{ji}}$ element.

Often we observe something in an experiment like

$$\left\langle \mathbf{a}_i^{\dagger}\mathbf{a}_i \right\rangle$$
$$\langle \mathbf{Q}_i \rangle, \langle \mathbf{P}_i \rangle$$
$$\left\langle \frac{\mathbf{P}_i^2}{2m} \right\rangle$$
$$\langle V \rangle$$
$$\left|\langle \Psi(t) | \Psi \rangle\right|^2$$

and we would like to understand what this implies about the dynamical mechanism
where does it start?
how fast does it leave?
why?
where does it go next?
why?
how fast does it go there? why?
what fraction gets to the target state? why?

We build a toy model $\mathbf{H}^{\mathrm{eff}}$ with the goal of reproducing the early time dynamics. We want to be able to look at the toy model and identify the most important dynamical features of that model.

dynamical feature$\leftrightarrow$model parameter, dynamical mechanism

Tools for computing dynamics from $\mathbf{H}^{\mathrm{model}}$! or constructing $\mathbf{H}^{\mathrm{model}}$ from expt.

<u>Today</u>: useful ways of monitoring and describing the mechanism of the dynamics encoded in $\boldsymbol{\rho}(t)$.

What do I mean by encoded? N × N $\boldsymbol{\rho}(t)$ matrix. Since $\boldsymbol{\rho}$ is Hermitian, there are $\frac{N^2 - N}{2} + N = \frac{N(N+1)}{2}$ independent t-dependent elements. Too much information.

Some useful relationships.

$$\langle \mathbf{A} \rangle_t = \mathrm{Trace}\big(\mathbf{A}\boldsymbol{\rho}(t)\big)$$

$$\text{if } \mathbf{A} = \mathbf{ab}, \text{ then } \langle \mathbf{A} \rangle_t = \mathrm{Trace}(\mathbf{ab}\boldsymbol{\rho}) = \sum_i \sum_{j,k} a_{ij} b_{jk} \rho_{ki}$$

$$= \sum_{ijk} b_{jk} \rho_{ki} a_{ij}$$

$$= \mathrm{Trace}(\mathbf{b}\boldsymbol{\rho}\mathbf{a})$$

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

Ehrenfest's Theorem There are many ways to replace $\frac{d}{dt}\langle \mathbf{A} \rangle$ by something that gives more insight.

$$i\hbar \dot{\boldsymbol{\rho}}(t) = \big[\mathbf{H}, \boldsymbol{\rho}(t)\big]$$

* opposite sign of commutator with respect to Ehrenfest

* This is a relationship between matrix elements, not expectation values

Ehrenfest's Theorem gives us a quantum mechanical form of classical equations of motion

Newton's

$$\frac{d\vec{r}}{dt} = \frac{1}{m}\vec{p}$$

$$\frac{d\vec{p}}{dt} = -\nabla V(\vec{r})$$

Hamilton's

$$\dot{Q}_i = \frac{\partial \mathcal{H}}{\partial P_i}$$

$$\dot{P}_i = -\frac{\partial \mathcal{H}}{\partial Q_i}$$

where P_i, Q_i are conjugate observables (page 718, of HLB-RWF. Poisson's bracket) Return to these at the end of 5.74.

We *say* that the center of a wavepacket follows Newton's equations.

This is not quite true.

We would like to say

$$\frac{d}{dt}\langle \mathbf{q} \rangle = \frac{1}{m}\langle \mathbf{p} \rangle$$

$$\frac{d}{dt}\langle \mathbf{p} \rangle = -\nabla V(\mathbf{q})\Big|_{q=\langle q \rangle}$$

but this is not quite true

$$\mathbf{H} = \frac{\mathbf{p}^2}{2m} + \mathbf{V}(\mathbf{q})$$

Ehrenfest:

$$i\hbar \frac{d}{dt}\langle \mathbf{q} \rangle_t = \langle [\mathbf{q},\mathbf{H}] \rangle_t$$

$$[\mathbf{q},\mathbf{H}] = \frac{1}{2m}\left[\mathbf{q},\mathbf{p}^2\right] = \frac{2i\hbar}{2m}\mathbf{p}$$

Thus $\frac{d}{dt}\langle q \rangle_t = \frac{1}{m}\langle p \rangle_t$. This is what we wanted. This relates the motion of the coordinate-center of the wavepacket to the momentum-center of the wavepacket. Recall that even if we write $\Psi(0)$ as $\sum_i \mathbf{a}_i \psi_i(\mathbf{q})$, we still specify $\langle \mathbf{p} \rangle$.

$$i\hbar \frac{d}{dt}\langle \mathbf{p} \rangle = \langle [\mathbf{p},\mathbf{H}] \rangle_t$$

$$[\mathbf{p},\mathbf{H}] = \frac{\hbar}{i}\left[\frac{\partial}{\partial \mathbf{q}}, \mathbf{V}(\mathbf{q})\right] = -i\hbar \nabla \mathbf{V}(\mathbf{q})$$

$$\text{Thus } \frac{d}{dt}\langle \mathbf{p} \rangle = -\langle \nabla \mathbf{V}(\mathbf{q}) \rangle \neq -\underbrace{\nabla \mathbf{V}(\langle \mathbf{q} \rangle)}_{\boxed{\text{This is a gradient of } V \text{ at the center of the wavepacket}}}$$

How large an error do we make if we pretend that

$$\frac{d}{dt}\langle\mathbf{p}\rangle = -\nabla\mathbf{V}\big(\langle\mathbf{q}\rangle\big)?$$

Expand $\mathbf{V(q)}$ in power series:

$$V(q) = V\big(\langle\mathbf{q}\rangle_t\big) + \left.\frac{dV}{dq}\right|_{q=\langle\mathbf{q}\rangle_t}\big(\mathbf{q}-\langle\mathbf{q}\rangle\big) + \frac{1}{2}\left.\frac{d^2V}{dq^2}\right|_{q=\langle q\rangle_t}\big(\mathbf{q}=\langle\mathbf{q}\rangle_t\big)^2$$

Thus

$$\langle\mathbf{V(q)}\rangle = V\big(\langle\mathbf{q}\rangle_t\big) + \left.\frac{dV}{dq}\right|_{q=\langle\mathbf{q}\rangle_t}\cancelto{0}{\big(\langle\mathbf{q}\rangle_t-\langle\mathbf{q}\rangle_t\big)}$$

$$+\frac{1}{2}\frac{d^2V}{dq^2}\Big(\langle\mathbf{q}^2\rangle_t - 2\langle\mathbf{q}\rangle_t^2 + \langle\mathbf{q}\rangle_t^2\Big)$$

$$\langle\mathbf{V(q)}\rangle - V\big(\langle\mathbf{q}\rangle_t\big) = \frac{1}{2}\left.\frac{d^2V}{dq^2}\right|_{q=\langle\mathbf{q}\rangle_t}\underbrace{\Big(\langle\mathbf{q}^2\rangle - \langle\mathbf{q}\rangle_t^2\Big)}_{\sigma_q}$$

The error one makes in predicting $\langle\mathbf{V(q)}\rangle$ by pretending that Newton's equations apply to the center of the wavepacket is proportional to

$$\underbrace{\left.\frac{d^2V}{dq^2}\right|_{q=\langle\mathbf{q}\rangle}}_{\boxed{\text{curvature of potential}}}\qquad\underbrace{\sigma_q}_{\boxed{\text{width of wavepacket}}}$$

(no curvature, no error)

So there are many situations where we can make this useful particle-like approximation even when $|\Psi(q)|^2$ has lost any resemblance to a particle-like state.

Similarly, by expanding $\frac{dV}{dq}$ (which is what we need for $\langle \nabla \mathbf{V}(\mathbf{q})\rangle$)about $q = \langle \mathbf{q}\rangle$

$$\left\langle \frac{d\mathbf{V}}{d\mathbf{q}} \right\rangle_t - \left.\frac{dV}{dq}\right|_{q=\langle \mathbf{q}\rangle_t} = \frac{1}{2}\left.\frac{d^3V}{dq^3}\right|_{q=\langle \mathbf{q}\rangle_t} \sigma_q$$

Ehrenfest's Theorem also allows us to describe (and simplify) the dynamics in "state space" rather than coordinate-momentum space. This can be very useful.

Suppose we can write $\mathbf{H} = \sum_j \mathbf{h}_j + \sum_{j\neq k} \mathbf{h}_{jk}$

$\mathbf{h}_j$ describes isolated sub-systems. It is the basis for a choice of $\mathbf{H}^{(0)} = \sum_j \mathbf{h}_j$ that defines basis states as $|1,n_1\rangle\,|2,n_2\rangle \ldots |N,n_N\rangle$. Simple (and convenient) product basis (there are often several useful choices, e.g. normal vs. local modes of vibration).

$\mathbf{h}_{jk}$ describes couplings between subsystems. It is responsible for dynamics if the pluck produces a single product basis (non-eigen) state.

For example,

$$\mathbf{H} = \frac{\hbar\omega_1}{2}\left(\mathbf{a}_1^\dagger\mathbf{a}_1 + \mathbf{a}_1\mathbf{a}_1^\dagger\right) + \frac{\hbar\omega_2}{2}\left(\mathbf{a}_2^\dagger\mathbf{a}_2 + \mathbf{a}_2\mathbf{a}_2^\dagger\right)$$
$$+ k_{122}\left(\mathbf{a}_1^\dagger\mathbf{a}_2\mathbf{a}_2 + \mathbf{a}_1\mathbf{a}_2^\dagger\mathbf{a}_2^\dagger\right)$$

a 1:2 anharmonically coupled pair of harmonic oscillators.

Recall:

$$\mathbf{a}_1|n_1\rangle = n_1^{1/2}|n_1 - 1\rangle \qquad \text{annihilation}$$

$$\mathbf{a}_1^\dagger|n_1\rangle = (n_1+1)^{1/2}|n_1+1\rangle \qquad \text{creation}$$

$$\mathbf{N}_1 = \mathbf{a}_1^\dagger\mathbf{a}_1 \qquad \left[\mathbf{a}_i,\mathbf{a}_i^\dagger\right] = 1 \qquad \left[\mathbf{a}_i,\mathbf{a}_j^\dagger\right] = 0$$

Ehrenfest tells us to evaluate some interesting commutators:
[$\mathbf{h}_{12}$,$\mathbf{H}$] = … do this second

$$\left[\mathbf{N}_1,\mathbf{H}\right]=\left[\mathbf{a}_1^{\dagger}\mathbf{a}_1,\mathbf{h}_1\right]+\left[\mathbf{a}_1^{\dagger}\mathbf{a}_1,\mathbf{h}_2\right]$$
$$+\left[\mathbf{a}_1^{\dagger}\mathbf{a}_1,\mathbf{h}_{12}\right]$$

any operator commutes with itself

$$\left[\mathbf{a}_1^{\dagger}\mathbf{a}_1,\frac{\hbar\omega_1}{2}\left(\mathbf{a}_1^{\dagger}\mathbf{a}_1+\mathbf{a}_1\mathbf{a}_1^{\dagger}\right)\right]=\frac{\hbar\omega_1}{2}\underbrace{\left[\mathbf{a}_1^{\dagger}\mathbf{a}_1,\mathbf{a}_1^{\dagger}\mathbf{a}_1\right]}_{0}$$
$$+\frac{\hbar\omega_1}{2}\left[\mathbf{a}_1^{\dagger}\mathbf{a}_1,\mathbf{a}_1\mathbf{a}_1^{\dagger}\right]$$

$$\mathbf{a}_1\mathbf{a}_1^{\dagger}=\underbrace{\left[\mathbf{a}_1,\mathbf{a}_1^{\dagger}\right]}_{\substack{=1\\ \text{1 commutes}\\ \text{with anything}}}+\underbrace{\mathbf{a}_1^{\dagger}\mathbf{a}_1}_{\text{commutes with itself}}$$

Thus $\left[\mathbf{a}_1^{\dagger}\mathbf{a}_1,\mathbf{h}_1\right]=0$
$\left[\mathbf{a}_1^{\dagger}\mathbf{a}_1,\mathbf{h}_2\right]=0$ $\quad$ $\mathbf{a}_1\mathbf{a}_1^{\dagger}$ do not operate on $\mathbf{h}_2$

Finally,

$$\left[\mathbf{a}_1^{\dagger}\mathbf{a}_1,k_{122}\mathbf{a}_1^{\dagger}\mathbf{a}_2\mathbf{a}_2\right]+\left[\mathbf{a}_1^{\dagger}\mathbf{a}_1,k_{122}\mathbf{a}_1\mathbf{a}_2^{\dagger}\mathbf{a}_2^{\dagger}\right]$$
$$=k_{122}\left(\mathbf{a}_2\mathbf{a}_2\underbrace{\left[\mathbf{a}_1^{\dagger}\mathbf{a}_1,\mathbf{a}_1^{\dagger}\right]}_{\mathbf{a}_1^{\dagger}}+\mathbf{a}_2^{\dagger}\mathbf{a}_2^{\dagger}\underbrace{\left[\mathbf{a}_1^{\dagger}\mathbf{a}_1,\mathbf{a}_1\right]}_{-\mathbf{a}_1}\right)$$
$$=k_{122}\left(\mathbf{a}_1^{\dagger}\mathbf{a}_2\mathbf{a}_2-\mathbf{a}_1\mathbf{a}_2^{\dagger}\mathbf{a}_2^{\dagger}\right)$$

Now look at the other interesting commutator

$$
\begin{aligned}
\left[\mathbf{h}_{12},\mathbf{H}\right] &= \frac{\hbar\omega_1}{2}\left[\mathbf{h}_{12},\mathbf{N}_1\right] + \frac{\hbar\omega_2}{2}\left[\mathbf{h}_{12},\mathbf{N}_2\right] + \cancelto{0}{\left[\mathbf{h}_{12},\mathbf{h}_{12}\right]} \\
&= \frac{\hbar\omega_1 k_{122}}{2}\left(\left[\mathbf{a}_1\mathbf{a}_2^\dagger\mathbf{a}_2^\dagger,\mathbf{a}_1^\dagger\mathbf{a}_1\right] + \left[\mathbf{a}_1^\dagger\mathbf{a}_2\mathbf{a}_2,\mathbf{a}_1^\dagger\mathbf{a}_1\right]\right) \\
&\quad + \frac{\hbar\omega_2 k_{122}}{2}\left(\left[\mathbf{a}_1\mathbf{a}_2^\dagger\mathbf{a}_2^\dagger,\mathbf{a}_2^\dagger\mathbf{a}_2\right] + \left[\mathbf{a}_1^\dagger\mathbf{a}_2\mathbf{a}_2,\mathbf{a}_2^\dagger\mathbf{a}_2\right]\right) \\
&= \frac{\hbar\omega_1 k_{122}}{2}\left(\mathbf{a}_1\mathbf{a}_2^\dagger\mathbf{a}_2^\dagger - \mathbf{a}_1^\dagger\mathbf{a}_2\mathbf{a}_2\right) \\
&\quad + \frac{\hbar\omega_2 k_{122}}{2}\left(\mathbf{a}_1\mathbf{a}_2^\dagger\underbrace{\left[\mathbf{a}_2^\dagger\mathbf{a}_2^\dagger,\mathbf{a}_2\right]}_{\boxed{-2\mathbf{a}_2^\dagger}} + \mathbf{a}_1^\dagger\mathbf{a}_2\underbrace{\left[\mathbf{a}_2\mathbf{a}_2,\mathbf{a}_2^\dagger\right]}_{\boxed{2\mathbf{a}_2}}\right) \\
&= \left(\frac{\hbar\omega_1 - 2\hbar\omega_2}{2}\right)k_{122}\left(\mathbf{a}_1\mathbf{a}_2^\dagger\mathbf{a}_2^\dagger - \mathbf{a}_1^\dagger\mathbf{a}_2\mathbf{a}_2\right)
\end{aligned}
$$

Change notation

$$\Omega = k_{122}\mathbf{a}_1^\dagger\mathbf{a}_2\mathbf{a}_2$$
$$\Omega^\dagger = k_{122}\mathbf{a}_1\mathbf{a}_2^\dagger\mathbf{a}_2^\dagger$$

$\mathbf{h}_{12} = \Omega + \Omega^\dagger$ resonance operator. $\mathbf{h}_{12}$ is Hermitian so $\langle\Omega+\Omega^\dagger\rangle$ is real

$[\mathbf{N}_1, \mathbf{H}] = \Omega - \Omega^\dagger$ rate of change operator

see
this

$$[\mathbf{h}_{12},\mathbf{H}] = \frac{\hbar(\omega_1 - 2\omega_2)}{2}\ (\Omega^\dagger - \Omega)$$

$\underbrace{i\hbar\frac{d}{dt}}_{\text{real}}\langle\mathbf{N}_1\rangle = \langle\Omega - \Omega^\dagger\rangle$ pure imaginary

$$i\hbar\frac{d}{dt}\langle\mathbf{h}_{12}\rangle = \hbar(\omega_1 - 2\omega_2)\langle\Omega^\dagger - \Omega\rangle$$

$\mathbf{\Omega} + \mathbf{\Omega}^\dagger$

Thus $\frac{d}{dt}\langle \mathbf{N}_1 \rangle = \frac{-\frac{d}{dt}\langle \mathbf{h}_{12} \rangle}{\hbar(\omega_1 - 2\omega_2)/2}$.

It is also easy to derive

$$\frac{d}{dt}\langle \mathbf{N}_1 \rangle = -\frac{1}{2}\frac{d}{dt}\langle \mathbf{N}_2 \rangle.$$

Conserved quantity: $2\langle \mathbf{N}_1 \rangle_t + \langle \mathbf{N}_2 \rangle_t = 2\langle \mathbf{N}_1 \rangle_0 + \langle \mathbf{N}_2 \rangle_0$ (polyad quantum number)

The rate of change of population in mode 1 is proportional to

* k_{122} strength of coupling
* $\frac{1}{\omega_1 - 2\omega_2}$. closeness to "resonance"

This algebra is especially useful when there are several different resonance operators.

This algebra allows us to ask what is the fractional importance of each resonance operator for the dynamics of any conceivable pluck. See page 649 of HLB-RWF.