You have now reached the End of your Quantum Childhood

It is time for you to graduate from quantum *statics* to quantum *dynamics*

Up to now, all the quantitative calculations have been concerned with the Hamiltonian functions which are independent of time---and therefore with Hamiltonian operators H which are independent of time. In a real sense, all that we have done so far is a mathematical exercise because when the Hamiltonian is time-independent, **nothing observable ever happens.**

It may come as something of a shock to discover, after nine chapters, that we have yet to get down to the business of predicting experiments in a realistic, logically consistent way. Nonetheless, only with a thorough grasp of the formal mathematics of the stationary states can we deal with time varying Hamiltonians. As we shall see, only with the aid of the familiar orthonormal eigenfunctions can the time-dependent wave equation be made tractable.

This textbook seeks primarily to teach what quantum mechanics **is**, and not to explore the intriguing (and very important) byways of philosophical interpretation. We have diverged from this principle here only to highlight the great importance of time-dependent calculations. Even though it comes late in the textbook it is, in a sense, the very heart of the theory. We shall be content to limit time-dependent calculations to only one or two of the theory's most simple applications, since these will suffice to illuminate the important concepts.
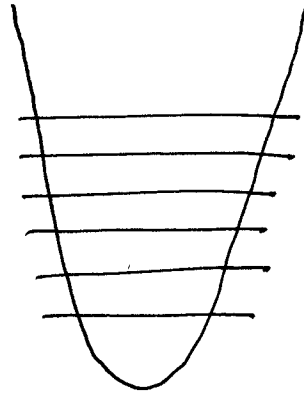
<div align="right">Sherwin 239-241</div>

The probability current ran swiftly out of the heart of quantum mechanics, bearing us down towards observation and measurement with twice the speed of our upward progress .....
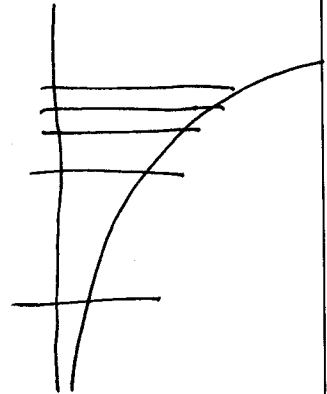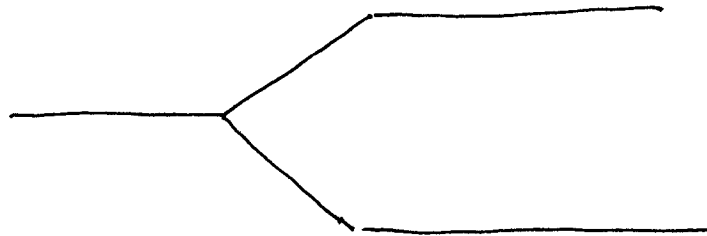
FOUR PARADIGMATIC SYSTEMS
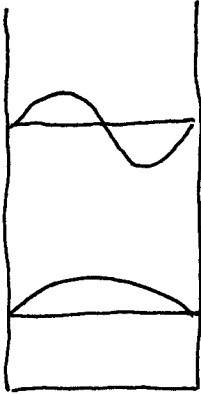
SQUARE

WELL

HARMONIC

OSCILLATOR

HYDROGEN

ATOM

SPIN ½

IF HAMILTONIAN IS TIME-INDEPENDENT,

NO INTERESTING TIME DYNAMICS:

PUT IN AN EXCITED STATE, IT JUST SITS THERE.

PUT IN A COMBINATION OF EXCITED STATES, IT JUST SITS THERE.

REAL SYSTEMS DECAY!

AND, TO OBSERVE, WE MUST PERTURB...

WHAT WE KNOW ABOUT "TIME-DEPENDENCE" IN THE QUANTUM STATICS:

TDSE $\qquad H|\psi(t)\rangle = i\hbar \dfrac{d}{dt}|\psi(t)\rangle$

TISE $\qquad H|m\rangle = E_m|m\rangle$

WHEN H IS INDEPENDENT OF TIME

$$|\psi(t)\rangle = \sum_m |m\rangle \underbrace{\langle m|\psi(0)\rangle}_{a_m} e^{-iE_m t/\hbar}$$

CODIFIED IN WORDS

(1) SOLVE e_v and $e\vec{v}$ PROBLEM

(2) EXPAND $|\psi(0)\rangle$ in $e\vec{v}$ of H

(3) USE TIME-DEPENDENCE OF $e\vec{v}$ TO FIND TIME-DEPENDENCE OF $|\psi\rangle$

Q: WHEN H DEPENDS ON TIME, WHAT CAN WE DO?

FORMALLY: $\quad a_m \longrightarrow a_m(t)$

(1)   SOLVE   TDSE   DIRECTLY.

ALMOST   ALWAYS   TOO   HARD!

FAMOUS   EXCEPTION :   SPIN $\frac{1}{2}$ PROBLEM

TWO-LEVEL   SYSTEM

SAKARAI   QUOTE   p.325

(2)   IF   TIME-DEPENDENT   COMPONENT λH_1 IS   SMALL

COMPARED   TO H_0,   CAN   USE   TDPT

$$H = H_0 + \lambda H_1$$

(i)   SOLVE H_0 ev   and   e$\vec{v}$ PROBLEM

(ii)   EXPAND $|\psi(0)\rangle$ in   e$\vec{v}$ of H_0

(iii)   CALCULATE   TIME-DEPENDENT   CONTRIBUTIONS

IN   POWERS   OF λ

inhomogeneous electric field. Such an electric field separates $|S\rangle$ from $|A\rangle$ in much the same way as the inhomogeneous magnetic field in the Stern-Gerlach experiment separates $|+\rangle$ from $|-\rangle$. A pure beam of $|A\rangle$ then enters a microwave cavity tuned to the energy difference $E_A - E_S$. The dimension of the cavity is such that the time spent by the molecule is just $(\pi/2)\hbar/\gamma$. As a result we stay in the first emission phase of Figure 5.4; we have $|A\rangle$ in and $|S\rangle$ out. The excess energy of $|A\rangle$ is given up to the time-dependent potential as $|A\rangle$ turns into $|S\rangle$ and the radiation (microwave) field gains energy. In this way we obtain Microwave Amplification by Stimulated Emission of Radiation, or MASER.

There are many other applications of the general time-dependent two-state problem, such as the atomic clock and optical pumping. In fact, it is amusing to see that as many as four Nobel Prizes in physics have been awarded to those who exploited time-dependent two-state systems of some form.*

5.6. TIME-DEPENDENT PERTURBATION THEORY

Dyson Series

With the exception of a few problems like the two-level time-dependent problem of the previous section, exact solutions to the differential equation for $c_n(t)$ are usually not available. We must be content with approximate solutions to (5.5.17) obtained by perturbation expansion:

$$c_n(t) = c_n^{(0)} + c_n^{(1)} + c_n^{(2)} + \cdots , \qquad (5.6.1)$$

where $c_n^{(1)}, c_n^{(2)}, \ldots$ signify amplitudes of first order, second order, and so on in the strength parameter of the time-dependent potential. The iteration method used to solve this problem is similar to what we did in time-independent perturbation theory. If initially only the state i is populated, we approximate c_n on the right-hand side of differential equation (5.5.17) by $c_n^{(0)} = \delta_{ni}$ (independent of t) and relate it to the time derivative of $c_n^{(1)}$, integrate the differential equation to obtain $c_n^{(1)}$, plug $c_n^{(1)}$ into the right-hand side [of (5.5.17)] again to obtain the differential equation for $c_n^{(2)}$, and so on. This is how Dirac developed time-dependent perturbation theory in 1927.

Instead of working with $c_n(t)$, we propose to look at the time evolution operator $U_I(t, t_0)$ in the interaction picture, which we will define later. We obtain a perturbation expansion for $U_I(t, t_0)$, and at the very end

---

Nobel Prize winners who took advantage of resonance in the two-level systems are Rabi (1944) on molecular beams and nuclear magnetic resonance; Bloch and Purcell (1952) on **B** field in atomic nuclei and nuclear magnetic moments; Townes, Basov, and Prochorov (1964) on masers, lasers, and quantum optics; and Kastler (1966) on optical pumping.

DERIVATION:

DIRAC   PROC. ROY SOC.   A112   661   (1926)

A114   243   (1927)

$H = H_0 + H_1(t)$

$H_0 |m\rangle = E_m |m\rangle$

BECAUSE H_0 IS   INDEPENDENT   OF   TIME

$\{$ all $|m\rangle \}$ form basis

Have an orthonormal, time-independent basis

$\langle m | m \rangle = \delta_{mm}$

SOLUTION   TO   TDSE   WITH $H_1(t) = 0$ IS

$$|\psi(t)\rangle = \sum_m a_m(0) |m\rangle e^{-iE_m t/\hbar}$$

coeffs are independent of time

WE   WANT   SOLUTION   TO   FULL   TDSE

$$\left(H_0 + H_1(t)\right) |\psi(t)\rangle = i\hbar \frac{d}{dt} |\psi(t)\rangle$$

GENERALIZE $H_1(t) = 0$ SOLUTION TO FIND FULL

SOLUTION

$$| \psi(t) \rangle = \sum_n a_m(t) | m \rangle e^{-iE_m t / \hbar}$$

↑

coeffs are
explicitly
time dependent

COMPLETELY GENERAL SOLUTION

CAN ALWAYS DO THIS SINCE $\{$ all $| m \rangle \}$ is a BASIS

NEED TO SOLVE FOR $a_m(t)$ COEFF'S

PUT TIME - DEPENDENT EXPANSION BACK INTO FULL TDSE:

$$(H_0 + H_1) | \psi(t) \rangle = i \hbar \frac{d}{dt} | \psi(t) \rangle$$

$$(H_0 + H_1) \sum_m a_m(t) | m \rangle e^{-iE_m t / \hbar}$$

$$= i \hbar \frac{d}{dt} \left(\sum_m a_m(t) | m \rangle e^{-iE_m t / \hbar} \right)$$

$$\sum_m (E_m + H_1)\, a_m(t)\, |m\rangle\, e^{-iE_m t/\hbar}$$

$$= \sum_n \left[i\hbar\, \frac{da_m}{dt} + i\hbar \left(-iE_m/\hbar \right) a_m \right] |m\rangle\, e^{-iE_m t/\hbar}$$

INNER PRODUCT WITH $\langle m|$

$$\sum_n \langle m|H_1|m\rangle\, a_m(t)\, e^{-iE_m t/\hbar}$$

$$= \sum_n i\hbar\, \frac{da_m(t)}{dt}\, \langle m|m\rangle\, e^{-iE_m t/\hbar}$$

$$\downarrow$$

$$\delta_{mn}$$

$$\boxed{ i\hbar\, \frac{da_m(t)}{dt} = \sum_n \langle m|H_1|m\rangle\, a_m(t)\, e^{i(E_m - E_n)t/\hbar} }$$

GREAT: INFINITE SET OF ORDINARY FIRST-ORDER

COUPLED DIFF EQS TO SOLVE!

BUT, COMPLETELY EQUIVALENT TO FULL TDSE!

REWRITE

$$i\hbar\,\dot{a}_1 = \langle 1|H_1|1\rangle\, a_1 + \langle 1|H_1|2\rangle\, a_2\, e^{i\omega_{12}t} + \ldots$$

$$i\hbar\,\dot{a}_2 = \langle 2|H_1|1\rangle\, a_1\, e^{i\omega_{21}t} + \ldots$$

.
.
.

$$i\hbar\,\dot{a}_m = \langle m|H_1|1\rangle\, a_1\, e^{i\omega_{m1}t} + \ldots$$

WHERE: $\quad U_{mn} = \langle m|H_1|n\rangle$

$$\omega_{mn} = (E_m - E_n)/\hbar = -\omega_{nm}$$

IN MATRIX FORM:

$$i\hbar\,\frac{d}{dt}\begin{pmatrix} a_1(t) \\ a_2 \\ a_3 \\ a_4 \\ \vdots \end{pmatrix} = \begin{pmatrix} U_{11} & U_{12}\,e^{i\omega_{12}t} & \\ U_{21}\,e^{-i\omega_{12}t} & U_{22} & \cdots \\ \vdots & & \end{pmatrix}\begin{pmatrix} a_1(t) \\ a_2 \\ a_3 \\ a_4 \\ \vdots \end{pmatrix}.$$

CALLED TDPT , BUT ALSO WORKS FOR $H_1(t) = $ CONSTANT

The sum of terms on the extreme left equals, term by term, the sum of terms on the extreme right, so that these two parts of [10–10] cancel. Multiplying the rest of [10–10] by $\Psi_m^0{}^*$, integrating with respect to the spatial coordinates $d\tau$, and using the orthogonality of the Ψ_m^0's,

$$\frac{d}{dt}\,a_m(t) = -\frac{i}{\hbar}\sum_{n=1}^{\infty} a_n(t)\int \Psi_m^0{}^* \, H' \, \Psi_n^0 \, d\tau \qquad \text{[10–11]}$$

where $m = 1, 2, 3, 4, \cdots$.

This is the basic law of time-dependent perturbation theory. It gives the rate of change of the mth component of the expansion [10–9], which describes the true, time-varying wave function of the system. The rate of change of the amplitude a_m depends upon the magnitude of the other amplitudes and also upon a set of matrix elements, $\int \Psi_m^0{}^* H' \Psi_n^0 \, d\tau$, which "connect," by means of H', the pure state Ψ_m^0 with each of the other pure states Ψ_n^0.[3]

We must visualize a vibrating system that has many modes or pure vibrations excited simultaneously. The time-dependent operator H' causes the amplitude of each of the pure vibrations to change in some definite manner. Some will increase with time and others must decrease—since at *all* times $\sum_n a_n^* a_n = 1$, and any amplitude can increase only at the expense of some, or all, of the others.

The fundamental equation [10–11] looks deceptively simple. It stands for a whole set of equations (in general, an infinite set) *each* of which has a large number of terms (in general, an infinite number). We write out these equations (in part) to provide a better appreciation of their nature.

$$-\frac{\hbar}{i}\frac{da_1}{dt} = a_1\int \Psi_1^0{}^* H'\Psi_1^0 d\tau + a_2\int \Psi_1^0{}^* H'\Psi_2^0 d\tau + \cdots + a_k\int \Psi_1^0{}^* H'\Psi_k^0 d\tau + \cdots$$

$$-\frac{\hbar}{i}\frac{da_2}{dt} = a_1\int \Psi_2^0{}^* H'\Psi_1^0 d\tau + a_2\int \Psi_2^0{}^* H'\Psi_2^0 d\tau + \cdots + a_k\int \Psi_2^0{}^* H'\Psi_k^0 d\tau + \cdots$$

$$\vdots$$

$$-\frac{\hbar}{i}\frac{da_k}{dt} = a_1\int \Psi_k^0{}^* H'\Psi_1^0 d\tau + a_2\int \Psi_k^0{}^* H'\Psi_2^0 d\tau + \cdots + a_k\int \Psi_k^0{}^* H'\Psi_k^0 d\tau + \cdots$$

$$\vdots \qquad\qquad \text{[10–12]}$$

---

[3] If, in addition to H^0, H contains a time-independent term H'(space) as well as a time-dependent term H'(space, time), one first applies time-independent perturbation theory to get the corrected wave functions, and then uses these wave functions in the time-dependent theory. This process is illustrated below in Sec. 10.5.

We equate separately each power of λ. For zero order,

$$(d/dt)\, a_1^0 = 0; \quad (d/dt)\, a_2^0 = 0; \quad \cdots \quad ; \quad (d/dt)\, a_k^0 = 0; \quad \cdots \qquad [10\text{--}15$$

That is, if the time-dependent part of the Hamiltonian is zero, then each a_m (which determines the amplitude of the component Ψ_m^0 of the complete wave function Ψ), if determined at one time, is unchanged for any other time. This same result, for the time-independent Hamiltonian, was obtained in Chapter 7.

Equating all terms of λ^1, we have the set of equations

$$-\frac{\hbar}{i}\frac{da_1'}{dt} = a_1^0 \int \Psi_1^{0*} H' \Psi_1^0 d\tau + a_2^0 \int \Psi_1^{0*} H' \Psi_2^0 d\tau + \cdots + a_k^0 \int \Psi_1^{0*} H' \Psi_k^0 d\tau + \cdots$$

$$-\frac{\hbar}{i}\frac{da_2'}{dt} = a_1^0 \int \Psi_2^{0*} H' \Psi_1^0 d\tau + a_2^0 \int \Psi_2^{0*} H' \Psi_2^0 d\tau + \cdots + a_k^0 \int \Psi_2^{0*} H' \Psi_k^0 d\tau + \cdots$$

$$\vdots \qquad\qquad \vdots \qquad\qquad \vdots \qquad\qquad \vdots$$

$$-\frac{\hbar}{i}\frac{da_k'}{dt} = a_1^0 \int \Psi_k^{0*} H' \Psi_1^0 d\tau + a_2^0 \int \Psi_k^{0*} H' \Psi_2^0 d\tau + \cdots + a_k^0 \int \Psi_k^{0*} H' \Psi_k^0 d\tau + \cdots$$

$$\vdots \qquad\qquad \vdots \qquad\qquad \vdots \qquad\qquad \vdots$$

$$[10\text{--}16$$

This set of *approximate* equations differs from the exact set [10–12] by the presence, on the right, of the constant zero-order coefficients a_m^0 and by the presence, on the left, of the *corrections*, a_m', to the zero-order coefficients a_m^0. The a_m^0's are merely the initial conditions. They measure the intensity of vibration of all of the modes of the unperturbed system that are needed to form the actual wave function at $t = t_0$. The equations [10–16] give the growth or decline of the amplitude of vibration of each of the natural modes of the system. Since H' is assumed to be small, the corrections to the amplitudes, a_m', are also small. Thus, although all the vibrations can either grow or decrease as time proceeds, the changes from their initial values will not be very large.

One speaks of a typical mode of vibration, or "proper" vibration (such as that represented by Ψ_1^0, as being "connected," via H', to each of the other modes. The exact equation [10–12] shows that, as time proceeds, the state Ψ_k^0 "feeds amplitude" into the state Ψ_1^0 at a rate given by $a_k \int \Psi_1^{0*} H' \Psi_k^0 d\tau$, and that the reverse process goes on at a rate given by $a_1 \int \Psi_k^{0*} H' \Psi_1^0 d\tau$. This is a completely continuous process. *The perturbation H' acts constantly to reshuffle the degree of excitation of the modes.* If it is suddenly terminated the system remains, thereafter, with exactly constant amplitudes for each proper

SO, HOW CAN WE SOLVE THIS SET OF
COUPLED DIFF EQS?

ZEROTH SOLUTION $\qquad a_m(t) = a_m(0)$

FIRST - ORDER SOLUTION

SOLUTION DEPENDS CRITICALLY ON THE INITIAL CONDITIONS!

ONE CASE OF GREAT INTEREST AND UTILITY IS WHEN
WE START WITH AN $e\vec{v}$ OF H_0

SUPPOSE AT $t=0$, WE ARE IN i^{th} $e\vec{v}$ of H_0

$$\Rightarrow a_m(0) = \delta_{mi} \begin{cases} \ne 1 & \text{if } m=i \\ \ne 0 & \text{if } m \neq i \end{cases}$$

$$i\hbar \frac{d\, a_m(t)}{dt} = \sum_{n} \langle m|H_1|m\rangle \, a_m(t)\, e^{i(E_m - E_n)t/\hbar}$$

FEED IN ZOS ON RHS, INTEGRATE TO GET FOS

FEED IN ℓ^{th} order solution $\qquad\qquad (\ell+1)^{th}$ order
solution

FEED IN ZOS $a_m(t) \approx a_m(0) = \delta_{mi}$

FOR SMALL TIMES

$$i\hbar \, \dot{a}_m = \langle m|H_1|i\rangle \, e^{i(E_m - E_i)t/\hbar}$$

ONLY VALID FOR $a_m(t) \ll a_i(t) \approx 1$.

INTEGRATE

$$\boxed{a_m(t) = \overset{a_m(0)}{\cancel{\delta_{mi}}} - \frac{i}{\hbar} \int_0^t \langle m|H_1|i\rangle \, e^{i(E_m - E_m)t'/\hbar} \, dt'}$$

$$\underset{a_m^{(0)}}{} \qquad \qquad \underset{a_m^{(1)}}{}$$

IF $H_1(t)$ HAS FINITE DURATION, AMPLITUDE OF STATE m IS JUST THE FOURIER COMPONENT OF $\langle m|H_1|i\rangle$ AT FREQUENCY ω_{mi}!

COULD NOW FEED THIS FOS IN, ~~AGA~~ AND INTEGRATE AGAIN TO GET SOS.

only a few cases that get used over and over again!

GENERAL CASE:

ARBITRARY $H_1(t)$

$H_1(t)$

0   t

SPECIAL CASES:

PULSE

HARMONIC

ADIABATIC

SUDDEN

HARMONIC PULSE

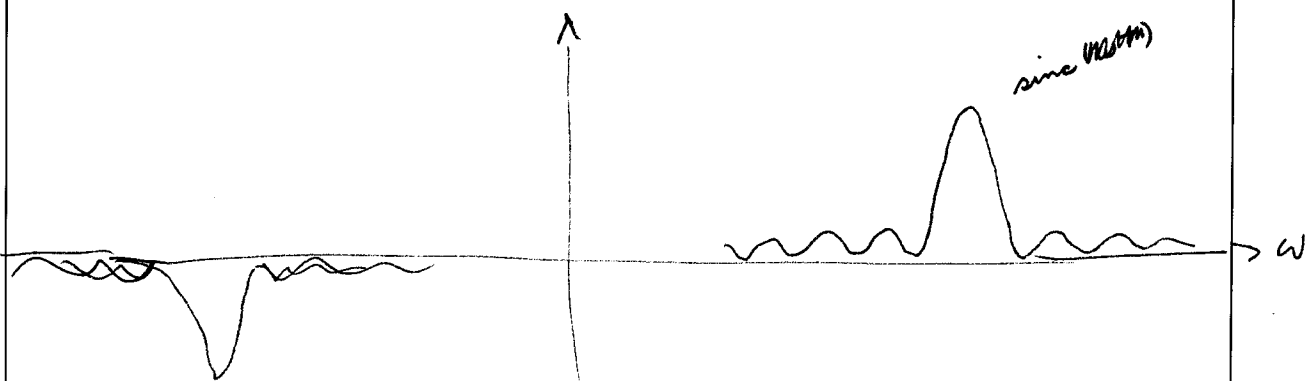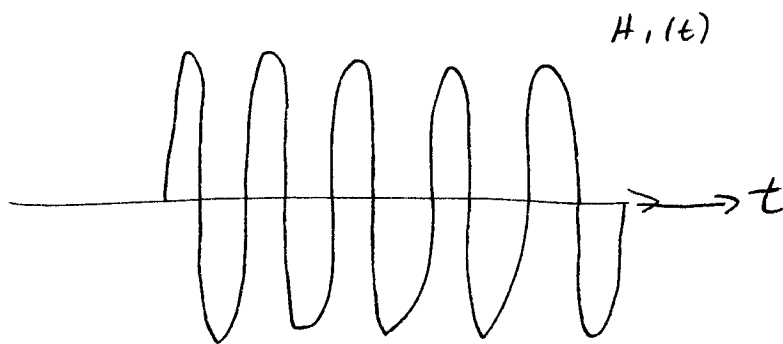ω_2

ω_1
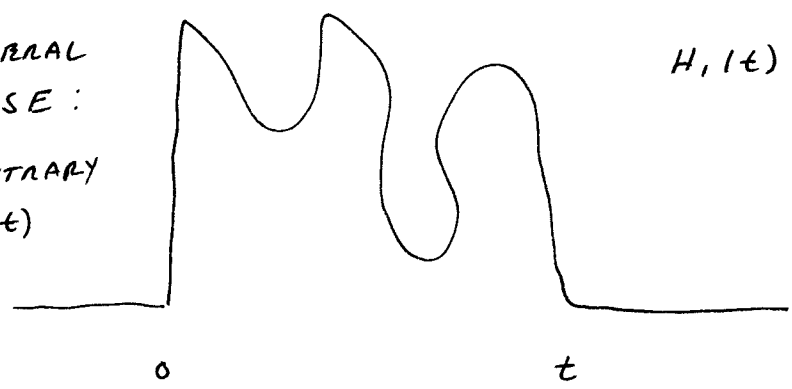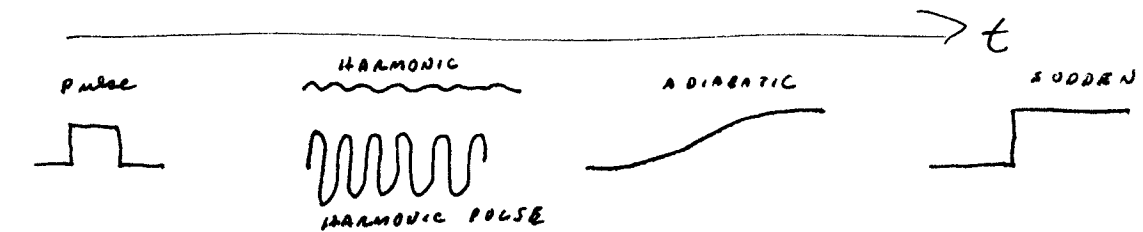
$$\omega_{21} = (E_2 - E_1)/\hbar$$

Fourier components of $H_1(t)$ drive the difference frequencies in the system ...

PICTORAL DICTIONARY OF CASES:
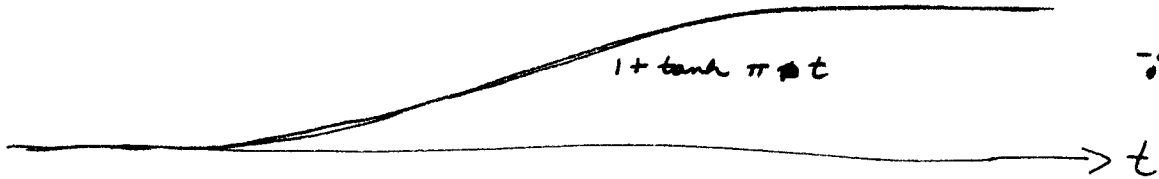
SPECIAL CASE 1: $H_1(t)$ CONSTANT

$$\text{sinc} = \frac{\sin(\tfrac{1}{2}\omega T)}{\tfrac{1}{2}\omega T}$$

SPECIAL CASE 2: $H_1(t)$ SINUSOIDAL

sinc
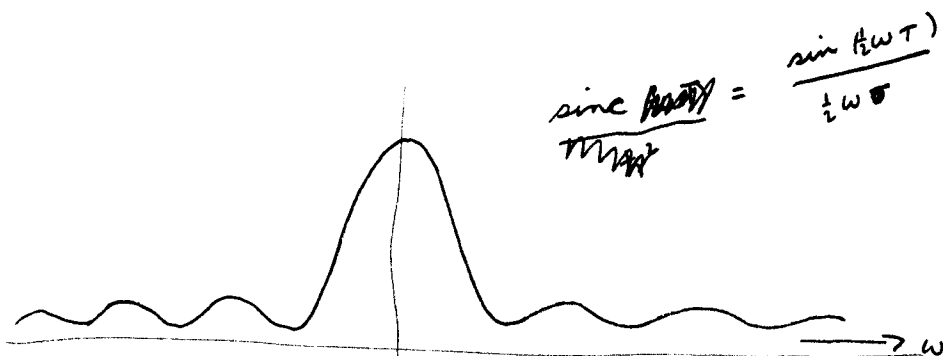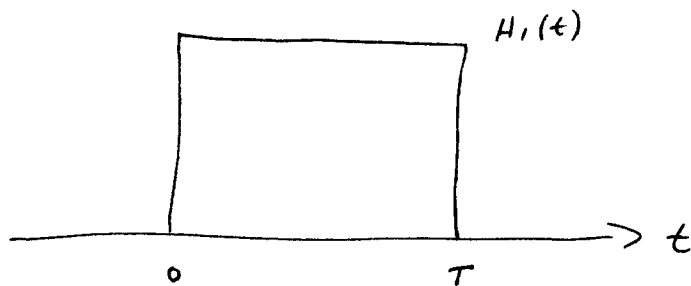
SPECIAL CASE 3:   ADIABATIC

$H_1(t)$

$\delta(\overset{\omega}{})$

$-\frac{i}{}$ cosech$(\pi \frac{}{\omega})$

$1 + $ tanh πt

$\longrightarrow t$

sudden   adiabatic $\longrightarrow$

$v_{welle} \ll v_{particle}$
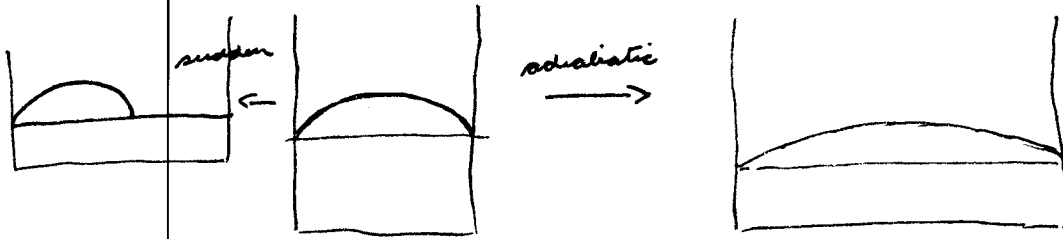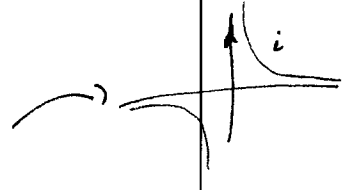
$T \sim \frac{1}{\omega_{MN}} = \frac{\hbar}{E_2 - E_1}$

SPECIAL CASE 4:   SUDDEN

$H_1(t)$

i

$\longrightarrow \omega$

$\frac{1}{2}\delta(\omega)$

0

$|\psi(0^+)\rangle - |\psi(0^-)\rangle = -\frac{i}{\hbar} \int_{-\epsilon/L}^{\epsilon/L} H_1(t') |\psi(t')\rangle \, dt'$

$-\frac{i}{2\pi\omega}$

$= 0$ in limit $\epsilon \to 0$