

# **Time-Variable Perturbation**

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Chapter 18 treats the case of weak or off-resonant fields for which a perturbation approach to field-stimulated transitions gives an accurate picture of their dynamics. Perturbation may be regarded as an iterative process and is simple when only the first iteration is needed. Several famous results come from such an approximation. These include Fermi's Golden Rule, the TRK-oscillator strength-sum rule, and virial identities. Relations between  $E \cdot r$  and  $A \cdot p$  approaches are seen, too.

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**CHAPTER 18 INTRODUCTION TO TIME-VARIABLE PERTURBATION..... 1**

**18.1 Time Dependent Potential..... 1**

    (a) Perturbation approximations..... 1

    (b) Iterative perturbation expansion ..... 3

**18.2 First-Order Perturbation Theory and Fermi-Golden-Rule..... 4**

    (a) First order iteration of dipole approximation ..... 4

    (b) The spectral intensity function and energy-time uncertainty..... 6

    (c) Fermi's "Golden Rule"..... 8

**18.3 Classical Lorentz vs. Quantum Oscillator response..... 11**

    (a) Classical Lorentz response ..... 11

    (b) First-order semi-classical response..... 11

    (c) Oscillator strength..... 12

        (1) Harmonic oscillator..... 13

    (d) Thomas-Reiche-Kuhn sum and virial identities..... 13

    (e)  $A \cdot P$  interaction again ..... 15

**Problems for Chapter 18..... 17**

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## Chapter 18 Introduction to Time-Variable Perturbation

### 18.1 Time Dependent Potential

The following is an analysis of time dependent perturbations like  $E \cdot r$  in (17.1.20) and more general perturbations  $V(t)$  that are arbitrary functions of time. Perturbation theory attempts to give solutions to the time Schrodinger equation (17.2.1b) with an explicitly time-dependent (non-autonomous) Hamiltonian.

$$\mathbf{H}(t) = \mathbf{H}_0 + \mathbf{V}(t) = \mathbf{H}_0 + \mathbf{H}_I \quad (18.1.1a)$$

A non-autonomous Schrodinger equation is generated by the total Hamiltonian  $\mathbf{H}(t)$ .

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \mathbf{H}(t) |\Psi(t)\rangle = (\mathbf{H}_0 + \mathbf{V}(t)) |\Psi(t)\rangle \quad (18.1.1b)$$

We represent it using a basis  $\{|\epsilon_1\rangle, |\epsilon_2\rangle, \dots\}$  of eigenstates of the unperturbed part  $\mathbf{H}_0$  of the Hamiltonian.

$$\mathbf{H}_0 |\epsilon_k\rangle = \epsilon_k |\epsilon_k\rangle = \hbar \omega_k |\epsilon_k\rangle \quad (18.1.3)$$

This is the same as (17.2.2) as is the expansion (17.2.5a) repeated here of the initial state in this basis.

$$|\Psi(0)\rangle = \sum_k |\epsilon_k\rangle \langle \epsilon_k | \Psi(0)\rangle = \sum_k |\epsilon_k\rangle c_k \quad (18.1.4)$$

#### (a) Perturbation approximations

The next steps involve the art of a particular approximation and differ from the time-independent formulation of (17.2.5). First, definition (17.2.5b) has variable  $c_k(t)$  replacing constant  $c_k$ .

$$|\Psi(t)\rangle = \sum_k e^{-i\omega_k t} |\epsilon_k\rangle c_k(t) \quad (18.1.5)$$

The idea is that a small varying  $V(t)$  will cause a slow variation of the otherwise constant  $|\epsilon_k\rangle$ -expansion coefficients  $c_k(t)$  of the initial state. The comparatively rapid phase oscillation frequencies  $\omega_k$  of the unperturbed  $\epsilon$ -states are assumed constant; the comparatively slow variation of the state is to be entirely accounted for by  $c_k(t)$ .

While the  $|\epsilon_k\rangle$  and  $\epsilon_k$  are rarely eigenkets or eigenvalues of the total Hamiltonian  $\mathbf{H}_0 + \mathbf{H}_I$ , they do constitute a complete set of eigensolutions of the unperturbed Hamiltonian  $\mathbf{H}_0$  and therefore able to make an arbitrary state  $|\Psi(t)\rangle$  at any time. This approximation does not try to adjust either the eigenvectors or the eigenvalues to be instantaneous eigensolutions of the total Hamiltonian  $\mathbf{H}(t)$ . That adjustment is entirely made up by the coefficients  $c_k(t)$  for which an approximate solution will now be derived.

Assumed state  $|\Psi(t)\rangle$  obeys Schrodinger equation (18.1.1b). The left hand side is a time derivative.

$$\begin{aligned}
 i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle &= i\hbar \frac{\partial}{\partial t} \sum_k e^{-i\omega_k t} |\varepsilon_k\rangle c_k(t) \\
 &= i\hbar \sum_k \frac{\partial e^{-i\omega_k t}}{\partial t} |\varepsilon_k\rangle c_k(t) + i\hbar \sum_k e^{-i\omega_k t} |\varepsilon_k\rangle \frac{\partial c_k(t)}{\partial t} \\
 &= \sum_k \hbar\omega_k e^{-i\omega_k t} |\varepsilon_k\rangle c_k(t) + i\hbar \sum_k e^{-i\omega_k t} |\varepsilon_k\rangle \frac{\partial c_k(t)}{\partial t}
 \end{aligned} \tag{18.1.6}$$

Schrodinger equation (18.1.1) is rewritten in (18.1.7) below. It may be subtracted from (18.1.6) to cancel the left hand time derivatives and first sum on the right hand side since  $\mathbf{H}_0|\varepsilon_k\rangle$  equals  $\hbar\omega_k|\varepsilon_k\rangle$  by (18.1.3).

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \sum_{k'} e^{-i\omega_{k'} t} \mathbf{H}_0 |\varepsilon_{k'}\rangle c_{k'}(t) + \sum_{k'} e^{-i\omega_{k'} t} \mathbf{V}(t) |\varepsilon_{k'}\rangle c_{k'}(t) \tag{18.1.7}$$

So, the second sum with the  $c_k(t)$  derivative in (18.1.6) equals the second sum in (18.1.7).

$$i\hbar \sum_k e^{-i\omega_k t} |\varepsilon_k\rangle \frac{\partial c_k(t)}{\partial t} = \sum_{k'} e^{-i\omega_{k'} t} \mathbf{V}(t) |\varepsilon_{k'}\rangle c_{k'}(t) \tag{18.1.8}$$

Using eigenstate orthonormality ( $\langle \varepsilon_j | \varepsilon_k \rangle = \delta_{jk}$ ) gives a Schrodinger-like equation for coefficients  $c_k(t)$ .

$$i\hbar \frac{\partial c_k(t)}{\partial t} = \sum_{k'} e^{i\omega_k t} e^{-i\omega_{k'} t} \langle \varepsilon_k | \mathbf{V}(t) | \varepsilon_{k'} \rangle c_{k'}(t) \tag{18.1.9}$$

The equation has oscillatory coupling involving perturbation matrix elements  $\langle \varepsilon_j | \mathbf{V}(t) | \varepsilon_k \rangle$  and  $e^{i(\omega_j - \omega_k)t}$ .

$$i\hbar \frac{\partial c_j(t)}{\partial t} = \sum_k e^{i(\omega_j - \omega_k)t} \langle \varepsilon_j | \mathbf{V}(t) | \varepsilon_k \rangle c_k(t) = \sum_k V_{jk}(t) c_k(t) \tag{18.1.10a}$$

Each coupling component has a phase factor oscillating at a beat or transition frequency  $\Omega_{jk} = \omega_j - \omega_k$ .

$$i\hbar \frac{\partial c_j(t)}{\partial t} = \sum_k e^{i(\omega_j - \omega_k)t} \langle \varepsilon_j | \mathbf{V}(t) | \varepsilon_k \rangle c_k(t) = \sum_k V_{jk}(t) c_k(t) \tag{18.1.10b}$$

The  $(j,k)$ -coupling time dependence is a modulation by  $\langle \varepsilon_j | \mathbf{V}(t) | \varepsilon_k \rangle$  of the transition beat phasor  $e^{i\Omega_{jk}t}$ .

$$V_{jk}(t) = e^{i\Omega_{jk}t} \langle \varepsilon_j | \mathbf{V}(t) | \varepsilon_k \rangle = e^{i(\omega_j - \omega_k)t} \langle \varepsilon_j | \mathbf{V}(t) | \varepsilon_k \rangle \tag{18.1.10c}$$

The time variation of the state amplitude of general state  $|\Psi(t)\rangle$  in (18.1.5) is

$$\langle \varepsilon_k | \Psi(t) \rangle = e^{-i\omega_k t} c_k(t) . \tag{18.1.10d}$$

Apart from its phase factor,  $\langle \varepsilon_k | \Psi(t) \rangle$  varies only if the coefficient  $c_k(t)$  varies and that happens only if the perturbation  $\mathbf{V}(t)$  is non-zero. But, no matter what  $\mathbf{V}(t)$  does, the  $\mathbf{H}_0$  eigenstates  $|\varepsilon_k\rangle$  and their eigenvalues  $\varepsilon_k = \hbar\omega_k$  are assumed constant. Only  $c_k(t)$  is influenced by  $\mathbf{V}(t)$ .

### (b) Iterative perturbation expansion

To begin solving (18.1.10a) assume the initial state is a pure  $\mathbf{H}_0$  eigenstate  $|\varepsilon_k\rangle=|\varepsilon_I\rangle$ , that is,

$$c_k(0)=\delta_{kI}=c_k^{(0)}. \quad (18.1.11)$$

Then coupled equations (18.1.10a) simplify for a short time ( $t \sim 0$ ). The first approximation is

$$i\hbar \frac{\partial c_j^{(1)}(t)}{\partial t} = \sum_k V_{jk}(t)c_k^{(0)}(t) = \sum_k V_{jk}(t)\delta_{kI} = V_{jI}(t). \quad (18.1.12)$$

The first approximation for each coefficient is given by a single integral of the perturbation component.

$$c_j^{(1)}(t) = \delta_{jI} + \frac{1}{i\hbar} \int_0^t dt_1 V_{jI}(t_1) \quad (18.1.13)$$

The second approximation to (18.1.10a) uses the first approximation as a starting point.

$$\begin{aligned} i\hbar \frac{\partial c_j^{(2)}(t)}{\partial t} &= \sum_k V_{jk}(t)c_k^{(1)}(t) = \sum_k V_{jk}(t) \left[ \delta_{kI} + \frac{1}{i\hbar} \int_0^t dt_1 V_{kI}(t_1) \right] \\ &= V_{jI}(t) + \frac{1}{i\hbar} \sum_k V_{jk}(t) \int_0^t dt_1 V_{kI}(t_1) \end{aligned} \quad (18.1.14a)$$

Integrating with initial value (18.1.11) gives the second iterate of each coefficient.

$$c_j^{(2)}(t) = \delta_{jI} + \frac{1}{i\hbar} \int_0^t dt_1 V_{jI}(t_1) + \frac{1}{(i\hbar)^2} \sum_k \int_0^t dt_2 V_{jk}(t_2) \int_0^{t_2} dt_1 V_{kI}(t_1) \quad (18.1.14b)$$

The third approximate iteration is done similarly and so on for each higher one.

$$c_j^{(3)}(t) = c_j^{(2)}(t) + \frac{1}{(i\hbar)^3} \sum_{k,k'} \int_0^t dt_3 V_{jk'}(t_3) \int_0^{t_3} dt_2 V_{k'k}(t_2) \int_0^{t_2} dt_1 V_{kI}(t_1) \quad (18.1.15)$$

The complexity of each iterative contribution increases rapidly. The situation is reminiscent of the matrix perturbation expansion outlined in Ch. 3 by equation (3.2.5). Carrying (18.1.15) out means summing all possible sequences between two state-1 and state-j while (3.2.5) sums all path sequences between state-1 and itself. For a constant perturbation operator  $\mathbf{V}(t)=\mathbf{V}$  the integrals in (18.1.15) produce energy denominators which are similar to those in (3.2.5).

## 18.2 First-Order Perturbation Theory and Fermi-Golden-Rule

Much of quantum transition theory is based on first order approximations. These are described in this section in a way that can be compared and improved with better approximations in later Chapters.

### (a) First order iteration of dipole approximation

As is the case for matrix perturbation, time dependent perturbation gets the most mileage from its simplest approximation, the first iteration (18.1.13). Consider a perturbation with a single time Fourier component: a charge  $q$  sitting at point  $\mathbf{r}$  in an x-polarized plane wave electric field  $\mathbf{E}(t) = \mathbf{e}_x E_o e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t+\phi)}$ .

$$\mathbf{V}^-(t) = -q \mathbf{E}(t) \cdot \mathbf{r} = -q \mathbf{r} \cdot \mathbf{e}_x E_o e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t+\phi)} \sim -q E_o e^{-i(\omega t-\phi)} \mathbf{r} \cdot \mathbf{e}_x \quad (18.2.1)$$

If the charge is an electron ( $q=-|e|=1.6E-19 C$ ) in an atom whose radius ( $\sim 0.5 A=0.5E-10m$ ) is ten thousand times smaller than optical wavelength ( $0.5\mu m=0.5E-6m$ ) then it is convenient to invoke the *dipole approximation* (mentioned after (17.1.20a)) ignoring the small  $k$ -dependency of the plane wave.

$$e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} \sim e^{-i\omega t} \quad (\text{for negligible } \mathbf{k}\cdot\mathbf{r})$$

The dipole approximation reduces the perturbation to an  $\mathbf{x}$ -operator with an oscillating phase factor.

$$\mathbf{V}^-(t) \sim -q E_o e^{-i(\omega t-\phi)} \mathbf{r} \cdot \mathbf{e}_x = -q E_o e^{-i(\omega t-\phi)} \mathbf{x} \quad (18.2.2a)$$

Let us define a positive frequency  $\mathbf{V}^+(t)$  that is the complex conjugate of  $\mathbf{V}^-(t)$ . ( $E_o$  is real here.)

$$\mathbf{V}^+(t) \sim -q E_o e^{+i(\omega t-\phi)} \mathbf{r} \cdot \mathbf{e}_x = -q E_o e^{+i(\omega t-\phi)} \mathbf{x} \quad (18.2.2b)$$

A real standing cosine potential  $\mathbf{V}^c(t)$  is a sum of  $\mathbf{V}^+(t)$  and  $\mathbf{V}^-(t)$ .

$$\mathbf{V}^c(t) = [\mathbf{V}^+(t) + \mathbf{V}^-(t)]/2 \sim -q E_o \mathbf{r} \cdot \mathbf{e}_x \cos(\omega t - \phi) = -q E_o \mathbf{x} \cos(\omega t - \phi) \quad (18.2.2c)$$

A vector potential which would give the same field  $\mathbf{E} = -\partial\mathbf{A}/\partial t$  is the following. (Recall (17.1.12).)

$$\begin{aligned} \mathbf{A} &= \mathbf{e}_x 2|a| \sin(kx - \omega t - \phi) \sim \mathbf{e}_x 2|a| \sin(\omega t - \phi) = \mathbf{e}_x |a| (-ie^{-i(\omega t - \phi)} + ie^{+i(\omega t - \phi)}) \\ &= \mathbf{e}_x (ae^{-i\omega t} + a^* e^{+i\omega t}) \end{aligned}$$

$\mathbf{E}$ -field magnitude  $E_o$  is given in terms of a complex  $\mathbf{A}$  amplitude  $a$  and  $\phi$  is initial cosine phase of  $\mathbf{E}$ .

$$E_o = 2|a|\omega \quad \text{where: } a = -i|a| e^{i\phi}, \quad (18.2.3a)$$

This is for later comparison with quantum fields. The corresponding  $\mathbf{A}\cdot\mathbf{P}$  interaction term would be

$$-(q/M)\mathbf{A}\cdot\mathbf{P} \sim 2(q/M)|a| \sin(\omega t - \phi) \mathbf{P} \cdot \mathbf{e}_x = \mathbf{P}_x (-q/M)(ae^{-i\omega t} + a^* e^{+i\omega t}). \quad (18.2.3b)$$

Let the  $\mathbf{E}\cdot\mathbf{r}$  interaction  $\mathbf{V}^c(t)$  be given in terms of  $a = -i|a| e^{i\phi}$ .

$$\mathbf{V}^c(t) \sim -2q\omega|a| \cos(\omega t - \phi) \mathbf{r} \cdot \mathbf{e}_x = -\mathbf{x} q (i\omega ae^{-i\omega t} - i\omega a^* e^{+i\omega t}). \quad (18.2.4)$$

Consider now, first-order amplitudes  $c_j^{(1)}(t)$  from (18.1.13) of eigenstate  $|\epsilon_j\rangle$  for a system starting out in state  $|\epsilon_1\rangle$  at  $t=0$  and perturbed by a cosine potential  $\mathbf{V}^c(t)$  in (18.2.4) above.

$$c_j^{(1)}(t) = \delta_{j1} + \frac{1}{i\hbar} \int_0^t dt_I V_{j1}^c(t_I) = \delta_{j1} + \frac{1}{i\hbar} \int_0^t dt_I e^{i\Omega_{j1} t_I} \langle \varepsilon_j | \mathbf{V}^c(t_I) | \varepsilon_1 \rangle \quad (18.2.5a)$$

The key quantities are the beats or  $(j \leftarrow 1)$ -transition frequencies  $\Omega_{j1}$  and  $(j \leftarrow 1)$ -dipole matrix elements  $r_{j1}$ .

$$\Omega_{j1} = \omega_j - \omega_1, \quad r_{j1} = \mathbf{e} \cdot \langle j | \mathbf{r} | 1 \rangle \quad (18.2.5b)$$

The three components of a dipole are labeled  $(x, y, z)$ . Each are treated equivalently.

$$x_{j1} = \mathbf{e}_x \cdot \langle j | \mathbf{r} | 1 \rangle = \langle j | \mathbf{x} | 1 \rangle, \quad y_{j1} = \mathbf{e}_y \cdot \langle j | \mathbf{r} | 1 \rangle = \langle j | \mathbf{y} | 1 \rangle, \quad z_{j1} = \mathbf{e}_z \cdot \langle j | \mathbf{r} | 1 \rangle = \langle j | \mathbf{z} | 1 \rangle$$

Using  $\mathbf{V}^c(t)$  from (18.2.3) gives the amplitude integral expressions.

$$c_j^{(1)}(t) = \delta_{j1} + q \frac{r_{j1}}{\hbar} \int_0^t dt_1 \left( -\omega a e^{i(\Omega_{j1} - \omega)t_1} + \omega a^* e^{i(\Omega_{j1} + \omega)t_1} \right) \quad (18.2.5c)$$

Carrying out the integrals and inserting the amplitude  $a = -i|a| e^{i\phi}$  gives the following.

$$\begin{aligned} c_j^{(1)}(t) &= \delta_{j1} + q \frac{r_{j1}}{\hbar} \left( i\omega a \frac{e^{i(\Omega_{j1} - \omega)t} - 1}{\Omega_{j1} - \omega} - i\omega a^* \frac{e^{i(\Omega_{j1} + \omega)t} - 1}{\Omega_{j1} + \omega} \right) \\ &= \delta_{j1} + q \frac{r_{j1}\omega|a|}{\hbar} \left( e^{i\phi} \frac{e^{i(\Omega_{j1} - \omega)t} - 1}{\Omega_{j1} - \omega} + e^{-i\phi} \frac{e^{i(\Omega_{j1} + \omega)t} - 1}{\Omega_{j1} + \omega} \right) \end{aligned} \quad (18.2.5d)$$

It is helpful to rewrite the amplitudes  $c_j^{(1)}(t)$  as follows (Here:  $E_0 = 2|a|\omega$  appears again.)

$$c_j^{(1)}(t) = \delta_{j1} + \frac{q r_{j1} E_0}{2\hbar} \left[ e^{i\phi} S(\Delta^\uparrow, t) + e^{-i\phi} S(\Delta^\downarrow, t) \right], \quad (18.2.5e)$$

using an important *spectral amplitude function*  $S(\Delta, t)$  of an angular frequency *detuning parameter*  $\Delta$

$$S(\Delta, t) = \int_0^t d\tau e^{i\tau\Delta} = \frac{e^{it\Delta/2} \sin(t\Delta/2)}{\Delta/2}. \quad (18.2.5f)$$

$S$  maximizes for  $\Delta = \Delta^\uparrow = 0$  if  $\omega$  excites an energy increase ( $\omega_j > \omega_1$ ) or for  $\Delta^\downarrow = 0$  if energy drops ( $\omega_j < \omega_1$ ).

$$\Delta^\uparrow = \Omega_{j1} - \omega : (\text{excitation: } \varepsilon_1 \rightarrow \varepsilon_j > \varepsilon_1) \quad \Delta^\downarrow = \Omega_{j1} + \omega : (\text{de-excitation: } \varepsilon_1 \rightarrow \varepsilon_j < \varepsilon_1) \quad (18.2.5g)$$

## (b) The spectral intensity function and energy-time uncertainty

It is important to visualize the spectral function  $S(\Delta, t)$  since it appears repeatedly in quantum theory, spectroscopy, acoustics, optics, and practically any subject with oscillation.  $S(\Delta, t)$  first appears in this book in connection with pulse trains in Fig. 5.3.2 and wavepacket revivals in Fig. 12.2.5 to Fig. 12.2.7.

One may view  $S(\Delta, t)$  as a function  $S_t(\Delta)$  of frequency  $\Delta$  for a fixed time parameter  $t$  or *vice-versa* as a time function  $S_\Delta(t)$  for a fixed frequency  $\Delta$ .  $S(\Delta, t) = S_t(\Delta)$  is the Fourier  $\Delta$ -spectrum of a "box-car" function  $x(t)$  that is constant  $x(\tau) = I$  between time  $\tau = 0$  and time  $\tau = t$  but zero ( $x = 0$ ) before or after.  $S(\Delta, t) = S_\Delta(t)$  is the zero-frequency spectral component at time  $t$  of a pure single frequency  $\Delta$  turned on at time  $t = 0$ .

Amplitude-square  $|c_j^{(1)}(t)|^2$  is a probability which includes *spectral intensity functions*  $I(\Delta, t)$

$$I(\Delta, t) = |S(\Delta, t)|^2 = \frac{\sin^2(t\Delta/2)}{(\Delta/2)^2}. \quad (18.2.6a)$$

The spectral intensity function  $I(\Delta, t)$  is plotted versus detuning  $\Delta$  and time  $t$  in Fig. 18.2.1. Its most notable feature is a peak at zero detuning ( $\Delta = 0$ ) soaring up as the square ( $I = t^2$ ) of time.

$$\lim_{\Delta \rightarrow 0} I(\Delta, t) = \lim_{\Delta \rightarrow 0} \frac{\sin^2(t\Delta/2)}{(\Delta/2)^2} = t^2. \quad (18.2.6b)$$

Off the main peak, at non-zero- $\Delta$ , are lesser  $4/\Delta^2$ -high peaks whose  $2/\Delta$ -amplitudes oscillate or "beat" at frequency  $\Delta/2$ . (Note  $t \cdot \Delta = \pm 3\pi, \pm 5\pi, \dots$  peaks of diminishing heights  $4/\Delta^2 = 4t^2/9\pi^2, 4t^2/25\pi^2, \dots$  in Fig. 18.2.1) The central  $t^2$ -peak is the biggest of these beats, but unlike its companion "beatlets", the ( $\Delta = 0$ )-peak has *zero* beat frequency and *infinite* amplitude. It just keeps on climbing and *never* comes back down!

The  $\Delta/2$  frequency of each "beatlet" might be a source of worry since we have noted generally that a system with two states  $|\epsilon_1\rangle$  and  $|\epsilon_j\rangle$  with frequency  $\omega_1$  and  $\omega_j$ , respectively, would beat at frequency  $\Omega_{j1} = \omega_j - \omega_1 = \Delta$ , not at  $\Delta/2$ . But, as should be the case,  $\Omega_{j1} = \Delta$  is the frequency of the *probability*

$$|c_j(t)|^2 \sim \sin^2(t\Delta/2) = (1 - \cos(t\Delta))/2. \quad (18.2.7)$$

Meanwhile the *amplitude*  $c_j(t) \sim \sin(t\Delta/2)$  has the half-frequency  $\Delta/2$ . Recall (2.3.14) for similar situations.

Infinite or near infinite amplitudes are a bigger source of worry here. No probability value  $|c_j(t)|^2$  should exceed 100% or unity ( $c_j(t) \leq 1$ ) let alone approach infinity! Indeed, the  $|c_j^{(1)}(t)|^2$  values are only the first order approximate iteration (18.2.5). Low- $\Delta$ -high- $t$  amplitudes  $c_j^{(1)}(t)$  need to be fixed by (at least) higher order approximations  $c_j^{(2)}(t), c_j^{(3)}(t), \dots$  in order to make accurate predictions for longer time or finer detuning frequency  $\Delta$ . However, as we've noted before, perturbation theory often becomes a doomed enterprise of dark arts and crafts. An alternative quasi-exact solution will be discussed in Chapter 19. (Compare Fig. 18.2.1 with a deceptively similar Fig. 19.1.4)



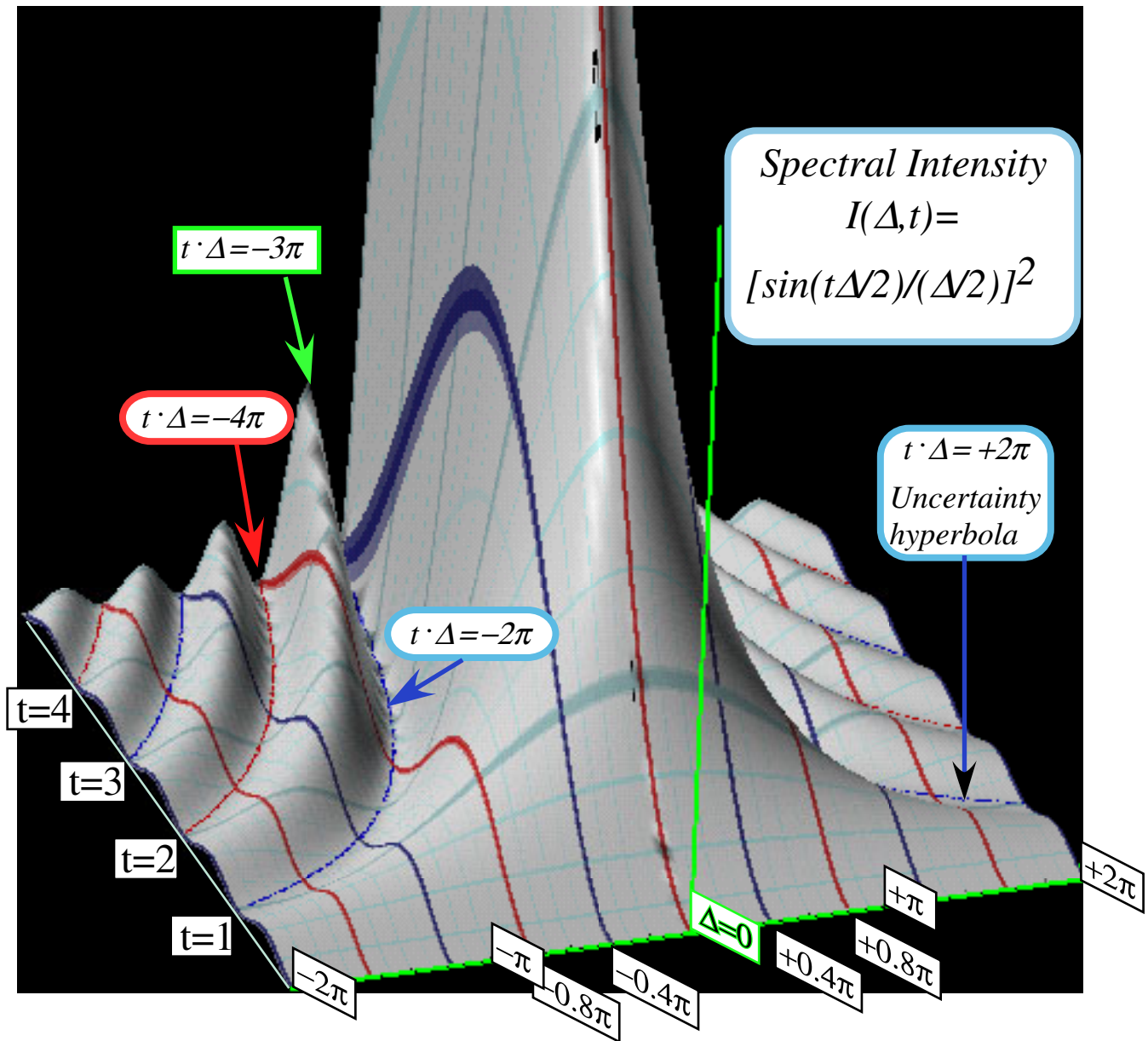


Fig. 18.2.1 Spectral intensity function  $I(\Delta, t)$  for first order iterate.

The zeros of  $I(\Delta, t)$  nearest to  $\Delta=0$  are at  $t\Delta/2 = \pm\pi$  and define a *time-frequency uncertainty relation*

$$t \cdot \Delta = (\Delta\tau) \cdot (\Delta\omega) = \pm 2\pi . \tag{18.2.8}$$

The longer time  $t=\Delta\tau$  that the perturbation acts, the less the width  $\Delta=\Delta\omega$  of the main peak. From Planck's energy-frequency axiom  $E=\hbar\omega$  arises the *Heisenberg time-energy uncertainty relation*

$$\Delta\tau \cdot \Delta E = \pm 2\pi\hbar = \pm h . \tag{18.2.9}$$

The longer the time  $t=\Delta\tau$  allowed for a transition, the smaller the tolerance  $\Delta E$  for  $\omega$ -deviation or "non-conservation" of energy. Extremely short times yield a broad energy spectral peak whose bounding zeros at

$\Delta = \pm 2\pi/t$  will, as time  $t$  advances, converge as they follow a pair of hyperbolas asymptotic to the  $t$ -axis and  $\Delta=0$  line in Fig. 18.2.1. The hyperbolas appear to "squeeze" or focus the peak.

The fringe "beatlet" peaks on either side of the main one are left out of this uncertainty relation. They are a small but non-zero part of the total probability spectrum. However, the fringes are an artifact of the "sharp-turn-on" of the perturbation  $V(t)$  at initial time  $t=0$ . They are analogous to the ringing fringes of the  $\sin(K_{cut}x)/x$  wave in Fig. 12.2.2 associated with a sharp cut-off of the energy spectrum. Fringes go away for more realistic cut-off that are more gradual as was seen by comparing the ringing fringes of a "box-car" spectrum in Fig. 12.2.7 with a smooth Gaussian spectrum in Fig. 12.2.8 which has no fringes.

### (c) Fermi's "Golden Rule"

It is interesting to note that, for short time ( $t \sim 0$ ) intensity rises as  $I=t^2$  for a range of  $\Delta$  inside a pair of uncertainty hyperbolas ( $-2\pi/t < \Delta < \pm 2\pi/t$ ). All energy states get an initial " $t^2$ -jolt" no matter how far they are detuned from resonance, another artifact of a diabatic or "sudden" turn-on. As shown in Fig. 18.2.2, the  $t^2$ -rise continues for a decreasing range around  $\Delta=0$  since greater- $|\Delta|$  amplitudes succumb more quickly to their assigned  $\Delta$ -beating. This leaves a decreasing number  $2\pi/t$  of peak  $\Delta$ -values still on a  $t^2$ -rise. So  $I$ -peak area in Fig. 18.2.2 varies as the product of its squeezing base  $\Delta=2\pi/t$  and soaring height  $t^2$  increasing linearly something like  $2\pi t$ . So does *total transition probability*  $\Sigma(t)$  according to famous "golden-rules" of atomic transitions. Such rules are quantified by investigating the frequency  $\Delta$ -integral  $\Sigma(t)$  of  $I(\Delta, t)$ .

$$\Sigma(t) = \int_{-\infty}^{\infty} d\Delta |S(\Delta, t)|^2 = \int_{-\infty}^{\infty} d\Delta \frac{\sin^2(t\Delta/2)}{(\Delta/2)^2}. \quad (18.2.10a)$$

The time derivative of the frequency integral  $\Sigma(t)$  is more calculus-friendly.

$$\frac{d\Sigma(\Delta, t)}{dt} = \int_{-\infty}^{\infty} d\Delta \frac{2\sin(t\Delta/2)\cos(t\Delta/2)}{(\Delta/2)^2} \Delta/2 = \int_{-\infty}^{\infty} d\Delta \frac{2\sin(t\Delta)}{\Delta}. \quad (18.2.10b)$$

This is reduced to contour integrals and evaluated using Cauchy's theorem  $f(a) = \frac{1}{2\pi i} \oint \frac{f(z)}{z-a} dz$ . (See exercise.)

$$\frac{d\Sigma(\Delta, t)}{dt} = \frac{1}{i} \oint_{C_1} dz \frac{e^{itz}}{z} - \frac{1}{i} \oint_{C_2} dz \frac{e^{-itz}}{z} = 2\pi. \quad (18.2.10c)$$

This gives the mathematical basis for *Fermi's golden rule for constant transition rates*.

$$\Sigma(t) = \int_{-\infty}^{\infty} d\Delta |S(\Delta, t)|^2 = 2\pi \cdot t \quad (18.2.10d)$$

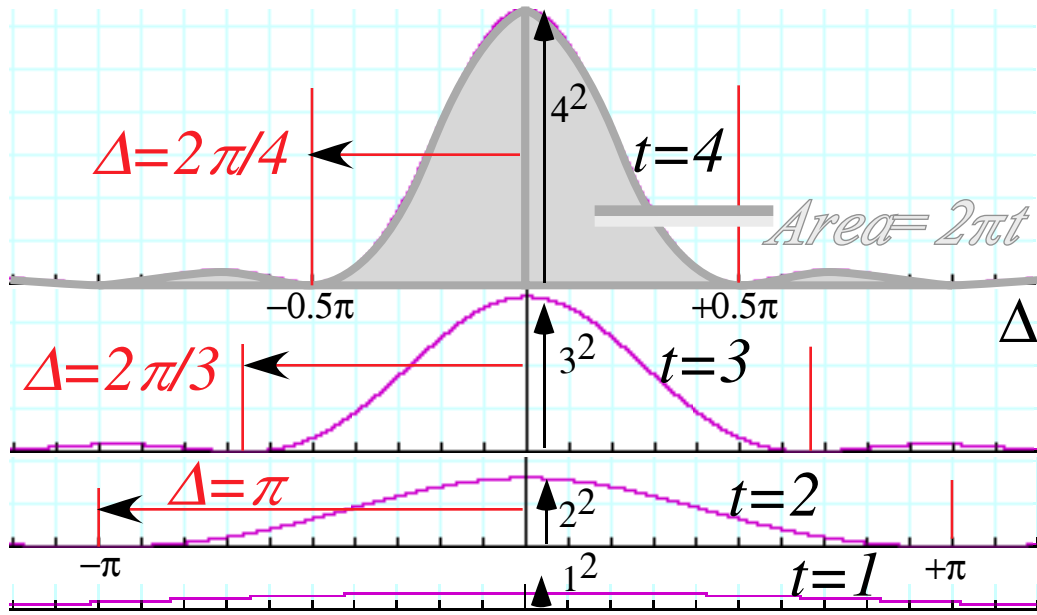


Fig. 18.2.2 Time dependence of spectral intensity function and area.

Only one  $S$ -term of (18.2.5e) can resonate. The  $S(\Delta^\uparrow, t)$ -term peaks at  $\omega = \omega_j - \omega_1$  when  $\Delta^\uparrow = \omega_j - \omega_1 - \omega$  is zero as it must be for upward ( $\omega_j > \omega_1$ ) transitions. For downward ( $\omega_j < \omega_1$ ) transitions, the  $S(\Delta^\downarrow, t)$ -term peaks at  $\Delta^\downarrow = \omega_j - \omega_1 + \omega = 0$  or  $\omega = \omega_1 - \omega_j$ . The latter follows a golden rule if sum  $\Sigma_j = \Sigma_j \Delta n_j$  over final states- $j$  finds uniform energy state density  $dn_j/d\Delta$  near  $\Delta \sim 0$ . Then total transition rate  $R$  is  $d\Sigma(t)/dt = 2\pi$  times a constant which is a product of  $r_{j1}$  and  $dn_j/d\Delta$  evaluated near the resonant  $S(0, t)$  peak at  $\omega = \Omega_{j1} = \omega_1 - \omega_j$ .

$$R = \frac{d}{dt} \sum_j |c_j^{(1)}(t)|^2 = \frac{d}{dt} \int_{-\infty}^{\infty} d\Delta |c_j^{(1)}(t)|^2 \frac{dn_j}{d\Delta} = \left| \frac{q r_{j1} E_0}{2\hbar} \right|^2 \frac{dn_j}{d\Delta} \frac{d\Sigma(t)}{dt} = (\text{const.}) \quad (18.2.11a)$$

Upward rates are golden if perturbation  $E_0(\omega)$  has a uniform spectrum near a resonance  $\omega = \Omega_{j1} = \omega_j - \omega_1$ .

$$R_{j \leftarrow 1} = \frac{d}{dt} \int_{-\infty}^{\infty} d\Delta |c_j^{(1)}(t)|^2 = \left| \frac{q r_{j1} E_0(\Omega_{j1})}{2\hbar} \right|^2 \frac{d\Sigma(t)}{dt} = (\text{const.}) \quad (18.2.11b)$$

Rate constancy needs some sort of quasi-continuous spectrum so the many beats will cancel each other and not contribute spurious coherent oscillation.

Constant rate  $R$  means constant drainage out an initial state  $|\epsilon_1\rangle$  through matrix element  $r_{j1}$  to a final state  $|\epsilon_j\rangle$  as long as the perturbation is in effect. So if, for example, the rate  $R$  is one transition per  $10^6$  seconds for each atom, a bottle of  $N(0) = 10^6$  atoms would make a quantum counter go "click.click...click. click ...click.." at the average rate of one click per second whenever the perturbation is turned on. That is an

average rate. Don't try to set a clock using quantum clicks unless you are willing to average over an enormous number of them. Each click only comes when it's good and ready to come!

But if the perturbation is left on the click rate must go down as the population 'dies off.' Only if one somehow replaces the "live" states will the observed rate remain constant. More precisely,  $N(0)$  atoms in state  $|\epsilon_1\rangle$  at  $t=0$  leaves  $N(t)=N(0)e^{-Rt}$  atoms in state  $|\epsilon_1\rangle$  at time  $t$  with an instantaneous "click" rate of  $N(t)R=N(0)Re^{-Rt}$ . A constant *relative* rate  $R$  gives pure  $e^{-Rt}$  exponential decay rate in a decay experiment.

### 18.3 Classical Lorentz vs. Quantum Oscillator response

It is instructive to compare classical and quantum-semi-classical oscillator response to harmonic perturbation. This tests  $\mathbf{E} \cdot \mathbf{r}$  versus  $\mathbf{A} \cdot \mathbf{p}$  interactions and shows what are the classical correspondences of amplitude  $c_j^{(1)}(t)$  and the beat frequency  $\Omega_{j1} = \omega_j - \omega_1$ . We also see how the multiplicative or parametric resonance of quantum theory yields the additive or linear (Lorentz) resonance of classical oscillation.

#### (a) Classical Lorentz response

The following is a classical equation for a charge- $q$  and mass- $M$  harmonic oscillator of natural frequency  $\omega_0$  stimulated by an E-field of frequency  $\omega_S$ .

$$\ddot{x} + \omega_0^2 x = \frac{qE_0}{M} \cos(\omega_S t) \quad (18.3.1a)$$

The solution to this equation for zero initial position or velocity ( $x(0) = 0 = v(0)$ ) is as follows.

$$x_{\text{classical}}(t) = \frac{qE_0}{M} \frac{\cos \omega_S t - \cos \omega_0 t}{\omega_0^2 - \omega_S^2} \quad (18.3.1b)$$

Now this is compared with the corresponding quantum physics of harmonic resonance due to a field

$$\mathbf{V}^c(t) = -qE_0 \cos(\omega t - \phi) \mathbf{x}. \quad (18.2.2b)_{\text{repeated}}$$

#### (b) First-order semi-classical response

The general perturbed state (18.1.5) is repeated below and expanded to first order for  $c_1^{(1)}(t) = 1$ .

$$|\Psi(t)\rangle = \sum_j e^{-i\omega_j t} |\varepsilon_j\rangle c_j(t) \quad (18.1.5)_{\text{repeated}}$$

$$\cong e^{-i\omega_1 t} \left( |\varepsilon_1\rangle + \sum_{j \neq 1} e^{-i\Omega_{j1} t} c_j(t) |\varepsilon_j\rangle \right), \text{ where: } \Omega_{j1} = \omega_j - \omega_1 \quad (18.3.2)$$

The first order iterate for a harmonic perturbation of frequency  $\omega$  is given by (18.2.5d) repeated here.

$$c_j^{(1)}(t) = \delta_{j1} + q \frac{r_{j1} \omega |a|}{\hbar} \left( e^{i\phi} \frac{e^{i(\Omega_{j1} - \omega)t} - 1}{\Omega_{j1} - \omega} + e^{-i\phi} \frac{e^{i(\Omega_{j1} + \omega)t} - 1}{\Omega_{j1} + \omega} \right) \quad (18.2.5d)_{\text{repeated}}$$

$$= \delta_{j1} + q \frac{r_{j1} E_0}{2\hbar} \left( \frac{e^{i(\Omega_{j1} - \omega)t} - 1}{\Omega_{j1} - \omega} + \frac{e^{i(\Omega_{j1} + \omega)t} - 1}{\Omega_{j1} + \omega} \right) \quad (18.3.2)$$

Then  $E_0 = 2|a|\omega$  from (18.2.3b) is used with  $\phi = 0$  to match the E-field of (18.2.2b) to (18.3.1a) above. The preceding two approximations are now used to estimate the coordinate expectation value  $\langle \Psi | \mathbf{x} | \Psi \rangle$ .

$$\langle x \rangle = \langle \Psi | \mathbf{x} | \Psi \rangle = \sum_{j \neq 1} e^{-i\Omega_{j1}t} c_j(t) r_{1j} + \sum_{j' \neq 1} e^{+i\Omega_{j'1}t} c_{j'}^*(t) r_{1j'}^* = 2\text{Re} \sum_{j \neq 1} e^{-i\Omega_{j1}t} c_j(t) r_{1j}$$

$$\text{where: } \langle j | \mathbf{x} | 1 \rangle = r_{j1} = r_{1j}^* \quad \text{and: } \Omega_{j1} = \omega_j - \omega_1 \quad (18.3.3)$$

We assume a zero initial (ground state-|1>) position value. ( $\langle 1 | \mathbf{x} | 1 \rangle = 0$ ) Also, we neglect second order terms  $c_j(t)c_{j'}^*(t)r_{j'j}$  in a first order calculation. Putting  $c_1^{(1)}(t)$  from (18.3.2) in the  $\langle x \rangle$  expression gives

$$\begin{aligned} \langle x \rangle &= 2\text{Re} \sum_{j \neq 1} e^{-i\Omega_{j1}t} c_j^{(1)}(t) r_{1j} \\ &= 2\text{Re} \frac{q r_{j1} r_{1j} E_0}{2\hbar} \left( \frac{e^{-i\omega t} - e^{-i\Omega_{j1}t}}{\Omega_{j1} - \omega} + \frac{e^{i\omega t} - e^{-i\Omega_{j1}t}}{\Omega_{j1} + \omega} \right) \end{aligned} \quad (18.3.4a)$$

This resembles the classical response equation (18.3.1b). Sum restriction  $j \neq 1$  is automatic since  $\Omega_{11} = 0$ .

$$\begin{aligned} \langle x \rangle &= \sum_{j \neq 1} \frac{q |r_{j1}|^2 E_0}{\hbar} \text{Re} \left( \frac{(\Omega_{j1} + \omega)(e^{-i\omega t} - e^{-i\Omega_{j1}t}) + (\Omega_{j1} - \omega)(e^{i\omega t} - e^{-i\Omega_{j1}t})}{\Omega_{j1}^2 - \omega^2} \right) \\ &= \sum_{j=1} \frac{2\Omega_{j1} q |r_{j1}|^2 E_0}{\hbar} \left( \frac{\cos \omega t - \cos \Omega_{j1} t}{\Omega_{j1}^2 - \omega^2} \right) \end{aligned} \quad (18.3.4b)$$

### (c) Oscillator strength

Factors of the corresponding  $x_{classical}$  in (18.3.1b) and quantum  $\langle x \rangle$  above are isolated.

$$\begin{aligned} \langle x \rangle &= \sum_{j=1} \frac{2\Omega_{j1} |r_{j1}|^2 M}{\hbar} \left( \frac{q E_0 \cos \omega t - \cos \Omega_{j1} t}{M \Omega_{j1}^2 - \omega^2} \right) \\ &= \sum_{j=1} f_{j1} \cdot x_{classical} \end{aligned} \quad (18.3.5a)$$

Each classical response term has a natural frequency  $\omega_0$  that is the *Lorentz-atomic-oscillator* frequency

$$\omega_0 = \Omega_{j1} = \omega_j - \omega_1. \quad (18.3.5b)$$

This is the *(j←1)-transition frequency*  $\Omega_{j1}$  or quantum beat. Each is driven by stimulus frequency  $\omega_S$ .

$$\omega_S = \omega. \quad (18.3.5c)$$

Each Lorentz oscillator responds with a certain *(j←1)-oscillator strength*  $f_{j1}$  defined here.

$$f_{j1} = \frac{2\Omega_{j1} |r_{j1}|^2 M}{\hbar} \quad (18.3.5d)$$

(1) *Harmonic oscillator*

The following uses some facts about the quantum 1D-harmonic oscillator which are derived in Chapter 20. For a harmonic oscillator potential ( $V(r)=1/2\omega^2r^2$ ) the only  $f_{j1}$  arising from the ( $j=1$ )-state  $|\nu=0\rangle$  is from ( $j=2$ )-state, that is, the first excited state  $|\nu=1\rangle$ . The oscillator dipole matrix is derived in (20.3.8).

$$r_{\nu 0} = \langle \nu | x | 0 \rangle = \langle \nu | a + a^\dagger | 0 \rangle \sqrt{\frac{\hbar}{2M\omega}} = \delta_{\nu 1} \sqrt{\frac{\hbar}{2M\Omega_{0,1}}} \quad , \quad \text{So: } f_{\nu,0} = \delta_{\nu,1} \quad (18.3.6)$$

Therefore (18.3.5a) for ground state excitation reduces to a single ( $f_{1,0}=1$ )-term ( $j=1$  means  $\nu=0$  and  $j=2$  means  $\nu=1$ .) equal to the classical response, that is,  $\langle x \rangle = x_{classical}$  is true exactly.

The quantum result is exactly the classical one despite the fact that it is based on a first order  $c_j^{(1)}(t)$  approximation! We know that the  $c_j^{(1)}(t)$  approximation is wrong near its central peak since it blows up. How can such an untrustworthy quantum result come up with an exact classical one?

The classical result blows up at resonance ( $\omega_S = \omega$ ) but legitimately so. To approximate near-resonance behavior of any quantum system one needs higher-than-first-order approximations. This is particularly the case for a harmonic oscillator whose quantum ( $\nu+1 \leftarrow \nu$ ) transitions all have the same frequency ( $\omega = \Omega_{\nu+1 \leftarrow \nu}$ ) and therefore are all in resonance at once. After the first excited state  $|\nu=1\rangle$  acquires an amplitude from the ground state  $|\nu=0\rangle$  there will begin a transition to  $|\nu=2\rangle$ , then  $|\nu=3\rangle$ , and so on, as each ( $\nu+1 \leftarrow \nu$ ) pair contributes oscillator strength to the  $\langle x \rangle$ -value near resonance ( $\omega_S = \omega$ ).

No such problem arises if the stimulus is far enough from resonance. The first order theory accounts for the beats, which for a cold oscillator, consist solely of the ( $1 \leftarrow 0$ ) beats plotted in Fig. 18.2.1.

While an oscillator potential  $1/2\omega^2r^2$  restricts oscillator strength to ( $\nu+1 \leftarrow \nu$ )-transitions between neighboring pairs of levels, other potentials  $V(r)$  may have strength in general ( $k \leftarrow j$ )-transitions. If so, the first order response (18.3.5a) has multiple interfering terms contributing to  $\langle x \rangle$ . Even so, if the stimulus  $\omega$  is close to a particular resonance  $\Omega_{j1}$  with a non-zero oscillator strength  $f_{j1}$  (but not close enough to ruin the first-order approximation) then the  $f_{j1}$ -term in the sum will dominate as  $1/(\Omega_{j1}^2 - \omega_1^2)$  blows up.

**(d) Thomas-Reiche-Kuhn sum and virial identities**

It turns out that a sum of oscillator strengths is invariant to choice of potential. The sum is  $\sum_j f_{j1} = 1$  for an oscillator by (18.3.6). The general sum in question is like the one in (18.3.5a) sans  $x_{classical}$ .

$$\sum_{j=1} f_{j1} = \sum_{j=1} 2\Omega_{j1} r_{j1}^* M / \hbar = \sum_{j=1} 2\Omega_{j1} \langle 1 | \mathbf{x} | j \rangle \langle j | \mathbf{x} | 1 \rangle M / \hbar \quad (18.3.7)$$

An  $\mathbf{x}$ -matrix element is related to a  $\mathbf{p}$ -matrix element using commutation  $[\mathbf{p}, \mathbf{x}] = \hbar/i$  with  $\mathbf{H}_0 = \mathbf{p}^2/2M + V(\mathbf{x})$ .

$$[\mathbf{H}_0, \mathbf{x}] = [\mathbf{p}^2, \mathbf{x}] / 2M = \hbar \mathbf{p} / Mi \quad (18.3.8)$$

Now the definitions  $\mathbf{H}_0 |j\rangle = \hbar\omega_j \mathbf{H}_0 |j\rangle$  and  $\Omega_{j1} = \omega_j - \omega_1$  are used with this commutation.

$$\langle j | \mathbf{p} | 1 \rangle = Mi \langle j | [\mathbf{H}_0, \mathbf{x}] | 1 \rangle / \hbar = Mi (\omega_j - \omega_1) \langle j | \mathbf{x} | 1 \rangle = Mi \Omega_{j1} r_{j1}$$

The resulting replacements

$$\langle j | \mathbf{x} | 1 \rangle = \langle j | \mathbf{p} | 1 \rangle / (Mi \Omega_{j1}) \quad \text{or:} \quad \langle 1 | \mathbf{x} | j \rangle = \langle 1 | \mathbf{p} | j \rangle / (Mi \Omega_{1j}) = -\langle 1 | \mathbf{p} | j \rangle / (Mi \Omega_{j1}) \quad (18.3.9)$$

then yield the *Thomas-Reiche-Kuhn sum rule for oscillator strength*. This holds for any  $\mathbf{H}_0$  eigenstate  $|1\rangle$ .

$$\sum_{j=1} f_{j1} = \sum_{j=1} 2 \langle 1 | \mathbf{x} | j \rangle \langle j | \mathbf{p} | 1 \rangle / \hbar i = 2 \langle 1 | \mathbf{x} \mathbf{p} | 1 \rangle / \hbar i = -2 \langle 1 | \mathbf{p} \mathbf{x} | 1 \rangle / \hbar i = 1 \quad (18.3.10a)$$

A corollary of the TRK rule is the *virial identity* that also holds for any  $\mathbf{H}_0$  eigenstate  $|m\rangle$ .

$$\langle m | \mathbf{x} \mathbf{p} | m \rangle = \hbar i / 2 = -\langle m | \mathbf{p} \mathbf{x} | m \rangle \quad (18.3.10b)$$

The time derivative of the virial matrix element is zero. Schrodinger's equation  $|\dot{m}\rangle = -i / \hbar \mathbf{H} |m\rangle$  gives

$$0 = \frac{\partial}{\partial t} \langle m | \mathbf{x} \mathbf{p} | m \rangle = \langle \dot{m} | \mathbf{x} \mathbf{p} | m \rangle + \langle m | \mathbf{x} \mathbf{p} | \dot{m} \rangle = \frac{i}{\hbar} \langle m | \mathbf{H} \mathbf{x} \mathbf{p} | m \rangle - \frac{i}{\hbar} \langle m | \mathbf{x} \mathbf{p} \mathbf{H} | m \rangle = \frac{i}{\hbar} \langle m | [\mathbf{H}, \mathbf{x} \mathbf{p}] | m \rangle$$

For a power-law-potential Hamiltonian  $\mathbf{H} = \mathbf{p}^2/2M + V \cdot \mathbf{x}^P$  the commutation reduces as follows.

$$0 = \frac{i}{\hbar} \langle m | \left[ \frac{\mathbf{p}^2}{2M}, \mathbf{x} \mathbf{p} \right] | m \rangle - \frac{i}{\hbar} \langle m | \left[ V \cdot \mathbf{x}^P, \mathbf{x} \mathbf{p} \right] | m \rangle = \langle m | \frac{\mathbf{p}^2}{M} | m \rangle - P \langle m | V \cdot \mathbf{x}^P | m \rangle$$

From this follows a *quantum eigenstate virial theorem* which is similar to the classical virial theorem.

$$\langle KE \rangle = \langle m | \frac{\mathbf{p}^2}{2M} | m \rangle = \frac{P}{2} \langle m | V \cdot \mathbf{x}^P | m \rangle = \frac{P}{2} \langle PE \rangle \quad (18.3.10c)$$

Interference terms  $a_m^* a_n \langle m | \mathbf{H} | n \rangle$  in  $\langle \Psi | \mathbf{H} | \Psi \rangle$  matrices for mixed state  $|\Psi\rangle = \sum a_m |m\rangle$  give beating  $\langle KE(t) \rangle$  and  $\langle PE(t) \rangle$  which disobey the virial theorem. However, if averages of  $a_m^* a_n$  may be assumed to be zero for  $m \neq n$  this leaves only the diagonal probabilities  $P(n) = a_n^* a_n = |a_n|^2$ . Then an *averaged virial theorem* still holds for a randomized ensemble of mixed states, and the classical result is recovered.

$$\overline{\langle KE \rangle} = \overline{\langle \Psi | \frac{\mathbf{p}^2}{2M} | \Psi \rangle} = \frac{P}{2} \overline{\langle \Psi | V \cdot \mathbf{x}^P | \Psi \rangle} = \frac{P}{2} \overline{\langle PE \rangle} \quad (18.3.10d)$$

For the harmonic oscillator ( $P=2$ ), average kinetic energy  $\langle KE \rangle$  average potential energy  $\langle PE \rangle$  are equal.



**(e) A•P interaction again**

One might inquire what the oscillator response  $\langle x \rangle$  would be if the  $-q\mathbf{A}\cdot\mathbf{P}/M$  perturbation from (17.1.21a) is substituted for the  $-q\mathbf{E}\cdot\mathbf{r}$  interaction of (17.1.21b) used in the preceding equation (18.2.5). We have been using (18.2.4) which is repeated below. (Recall amplitude definition:  $\omega a = -i\omega |a| e^{i\phi}$  )

$$-q\mathbf{E}\cdot\mathbf{r} \sim -2q\omega |a| \mathbf{r}\cdot\mathbf{e}_x \cos(\omega t - \phi) = \mathbf{x} q (i\omega a e^{-i\omega t} - i\omega a^* e^{+i\omega t}). \quad (18.2.4)_{repeated}$$

to derive the following dipole interaction matrix element which then was used to calculate response.

$$-\langle j|q\mathbf{E}\cdot\mathbf{r}|1\rangle = \langle j|\mathbf{x}|1\rangle q (-i\omega a e^{-i\omega t} + i\omega a^* e^{+i\omega t}). \quad (18.3.11)$$

Instead, for the same electromagnetic field  $\mathbf{E} = -\partial\mathbf{A}/\partial t$ , consider using the following interaction

$$-(q/M)\mathbf{A}\cdot\mathbf{P} \sim 2(q/M)|a| \mathbf{P}\cdot\mathbf{e}_x \sin(\omega t - \phi) = \mathbf{P}_x (-q/M)(a e^{-i\omega t} + a^* e^{+i\omega t}), \quad (18.2.3b)_{repeated}$$

which gives the following dipole interaction matrix element.

$$-\langle j|(q/M)\mathbf{A}\cdot\mathbf{P}|1\rangle = \langle j|\mathbf{P}_x|1\rangle (q/M)(-a e^{-i\omega t} - a^* e^{+i\omega t}) \quad (18.3.12a)$$

The momentum matrix can be related to the position dipole using  $\langle j|\mathbf{p}|1\rangle = Mi\Omega_{j1}\langle j|\mathbf{x}|1\rangle$  from (18.3.9).

$$-\langle j|(q/M)\mathbf{A}\cdot\mathbf{P}|1\rangle = \langle j|\mathbf{X}|1\rangle (qi\Omega_{j1})(-a e^{-i\omega t} - a^* e^{+i\omega t}) \quad (18.3.12b)$$

$$= \langle j|\mathbf{X}|1\rangle q(-i\Omega_{j1}a e^{-i\omega t} - i\Omega_{j1}a^* e^{+i\omega t}) \quad (18.3.12c)$$

Comparison of (18.3.11) to (18.3.12c) reveals a discrepancy in factors of the form  $\pm\omega/\Omega_{j1}$  and dispels any notion that  $-q\mathbf{E}\cdot\mathbf{r}$  and  $-q\mathbf{A}\cdot\mathbf{P}/M$  are equal. However, for an excitation resonance ( $\omega = \Omega_{j1}$ ) the first terms will match and for a de-excitation resonance ( $\omega = \Omega_{1j} = -\Omega_{j1}$ ) the second terms will match. So golden rule rates, which are insensitive to coherence between the terms, might incorrectly suggest equality of  $-q\mathbf{E}\cdot\mathbf{r}$  and  $-q\mathbf{A}\cdot\mathbf{P}/M$ . Such a coincidence sets a trap into which many have fallen, but attempts to use  $-q\mathbf{A}\cdot\mathbf{P}/M$  to derive coherent response fails if the  $(\mathbf{X},\mathbf{P}) \rightarrow (\mathbf{x},\mathbf{p})$  transformation (6.2.21) is ignored.

For convenience we collect here a summary of classical dipole fields  $\mathbf{E} = -\partial\mathbf{A}/\partial t$ :

$$\mathbf{E} = 2\omega |a| \mathbf{e}_x \cos(\omega t - \phi) = (i\omega a e^{-i\omega t} - i\omega a^* e^{+i\omega t}) \mathbf{e}_x \quad \text{where: } \omega a = -i\omega |a| e^{i\phi} = -iE_0/2 e^{i\phi}$$

$$\mathbf{A} = -2|a| \mathbf{e}_x \sin(\omega t - \phi) = (a e^{-i\omega t} + a^* e^{+i\omega t}) \mathbf{e}_x \quad (18.3.13)$$

This will be compared to very similar looking expressions for quantum fields in which the amplitudes  $\mathbf{E}$ ,  $\mathbf{A}$ , and  $a$  are replaced by operators. Sometimes such a replacement is given an oxymoronic label of *second quantization*. This is a result of the long history of semi-classical treatments of particles (quantized nuclei, atoms, molecules, solids, etc.) in fields (classical electromagnetic fields) which has been so useful. The idea is that a “second coming” is needed to “fix up” the field, too. This is ironic in

light of the fact that quantum theory owes its very existence to Planck's hypothesis of *electromagnetic* quanta.

As we will see, one needs to regard the particles and field as a single spacetime quantum system. Classical reductionism goes only so far before it becomes misleading and paradoxical. A first step toward such a re-en"light"enment is a non-perturbative treatment of a radiation field interacting with just two levels of an atom, molecule, or a single spin-1/2 of an electron, nucleon, atom, molecule, solid, etc.

In the next section we revisit the *ABCD* formulation from Chapters 9 and 10 of two-level  $U(2)$  quantum states. The difference now will be that one or more of those *A*, *B*, *C*, or *D* parameters can wiggle in time and even be controlled from the outside. Indeed, it's more semi-classical theory but one with a twist!

## Problems for Chapter 18.

### Golden Cauchy Potato

18.2.1 Use Cauchy's theorem to verify the Fermi Golden Rule (18.2.10) for constant transition rates. Show relevant integration contours and explain your steps.

### Beat to death

- (a) Compare the relative heights of  $0^{th}$ ,  $1^{st}$ ,  $2^{nd}$ , ...,  $N^{th}$  beat probability peaks in Fig. 18.2.1.
- (b) Use whatever means to deduce the probability versus time to be under the  $0^{th}$  beat peak in Fig. 18.2.1. (Only numbers and time  $t$  are allowed in your answer!)
- (a) Compare the relative probabilities under  $0^{th}$ ,  $1^{st}$ ,  $2^{nd}$ ,  $3^{rd}$  beat peaks in Fig. 18.2.1. How does that relative distribution vary with time?

### Jailhouse Rock 'round the Clock

18.3.1 In Problem 18.1.1 (*Jailhouse Rock 'n Roll*) prisoner- $M$  is in the infinite-well maximum security prison of Chapter 12 suffering from an Earthquake (caused perhaps by a heavy-metal rock band) that seems to go on forever.  $M$  remains in any of its eigenstates only in the absence of perturbations. But now the prison floor tilt angle varies:  $\phi = \phi^{limit} \sin(\omega_{rock}t)$  giving  $V_{rock'n roll}(x)$  of Problem 18.1.1. Use that here.

Discuss transition from the ground state  $|\epsilon_1\rangle$  to  $|\epsilon_m\rangle$  stimulated by frequency  $\omega_{rock}$  of amplitude  $\phi^{limit} = \pi/10$ . Consider cases:  $\omega_{rock} = \epsilon_1$  ( $=I$  in theorist  $\hbar=I$  units),  $2 \epsilon_1$ ,  $3 \epsilon_1$ ,  $4 \epsilon_1$ .

- (a) Using only the first term in  $V_{rock'n roll}(x)$ , derive first order transition amplitudes  $c_m^{(1)}$ .
- (b) Derive the resulting expectation value  $\langle x \rangle$  of position if  $M$  is "waked up" from its ground state.
- (c) Derive the resulting expectation value  $\langle p \rangle$  of momentum if  $M$  is "waked up" from its ground state.
- (d) Discuss the Thomas-Reiche-Kuhn sum rule and the Virial Theorem for the prison.

