

ETH/PSI LECTURES 2

Quantum Transitions S and T Matrices

General Goals:
Answer the following questions.

How does one formulate a
nonperturbative problem in quantum
mechanics?

How does this differ from standard
approaches in quantum mechanics?

OUTLINE

- General transition amplitude
- S matrix history
- Derivation of S matrix
- Direct/Time-reversed; Post/Prior; In-states/Out-states
- Green's function method
- Lippmann-Schwinger equation
- Perturbation expansion
- Relativistic formalism
- T matrix
- Nonperturbative Fermi Golden Rule
- Gauge transformations
- Misperceptions in the AMO community

TRANSITION AMPLITUDE REQUIREMENTS

Transition amplitudes for processes caused by an electromagnetic field cannot be expressed by perturbation theory if the field strength is too large.

That is, there exists a radius of convergence for perturbation theory that is intensity-dependent. [HRR, J Math Phys **3**, 387 (1962)].

Textbooks on quantum mechanics generally do not discuss a suitable general method that is applicable for fields that surpass the radius of convergence of perturbation theory.

The theory presented here is based on scattering methods, but it was realized in the 1960s that it could be extended to all types of processes, not just scattering. [HRR, PRA **1**, 803 (1970)].

Note Kroll & Watson (1973) citation of a new approach to S matrices.

BRIEF HISTORY OF S MATRICES

Introduced for use in scattering problems; hence the letter **S**.

J. A. Wheeler, Phys. Rev. **52**, 1107 (1937).

W. Heisenberg, Z. Physik **120**, 513, 673 (1943).

E. C. G. Stückelberg, Helv. Phys. Acta **17**, 3 (1943); **18**, 21, 195 (1945).

In a search for a general nonperturbative formalism to use for strong-field problems, it was shown that the S-matrix formalism can be employed for *any* quantum process:

free-free (scattering)

bound-free (ionization, photodetachment)

free-bound (recombination)

bound-bound (excitation, de-excitation)

HRR, Phys. Rev. A **1**, 803 (1970).

RIGOROUS DERIVATION OF AN S MATRIX

Basic requirement: The transition-causing interaction occurs only within a domain bounded in space and time. Example: transitions in the focus of a pulsed laser.

(The RFBeta problem will be treated separately.)

Important properties of an S matrix as derived here:

- ***It can be formulated entirely in terms of quantities measurable in the laboratory.***
- ***It does not require that dynamics be tracked over time. Equations of motion are incorporated in the S matrix.***
- ***There is no need for “adiabatic decoupling”.***
- ***It gives unambiguous rules for gauge transformations.***
- ***It can be applied to any process as long as the space-time domain of the interaction region is bounded.***

The general problem is evoked of an atomic electron subjected to a pulsed, focused laser beam. This is a convenience, not a requirement.

There will be a complete set of states $\{\Psi_n\}$ that satisfy the Schrödinger equation describing the atomic electron that may be undisturbed or in interaction with a laser beam:

$$i\partial_t\Psi = H\Psi = (H_0 + H_I)\Psi$$

The outcome of any experiment will be measured by laboratory instruments that never experience a laser field. As far as the laboratory instruments are concerned, there is a complete set of states $\{\Phi_n\}$ that satisfy the Schrödinger equation describing an atomic electron that does **NOT** experience the laser field:

$$i\partial_t\Phi = H_0\Phi$$

By hypothesis, the laser pulse is finite, so

$$\lim_{t \rightarrow \pm\infty} [H(t) - H_0] = 0$$

The two complete sets of Φ states and Ψ states can be organized so that they correspond at $t \rightarrow -\infty$:

$$\lim_{t \rightarrow -\infty} [\Phi_n(t) - \Psi_n(t)] = 0$$

After the laser interaction has occurred, the only way for the laboratory instruments to discover what has happened is to form overlaps of all possible final Φ_f states with the state that began as a particular Ψ_i state. This is the S matrix:

$$S_{fi} = \lim_{t \rightarrow +\infty} (\Phi_f, \Psi_i)$$

Subtract the amplitude that no transition has occurred. This is the transition amplitude:

$$M_{fi} \equiv (S - 1)_{fi} = \lim_{t \rightarrow +\infty} (\Phi_f, \Psi_i) - \lim_{t \rightarrow -\infty} (\Phi_f, \Psi_i)$$

This is now in the form of an exact differential:

$$M_{fi} = \int_{-\infty}^{+\infty} dt \frac{\partial}{\partial t} (\Phi_f, \Psi_i)$$

$$M_{fi} = \int_{-\infty}^{+\infty} dt \left[(\partial_t \Phi_f, \Psi_i) + (\Phi_f, \partial_t \Psi_i) \right]$$

$$i\partial_t \Phi = H_0 \Phi \Rightarrow \partial_t \Phi = -iH_0 \Phi$$

$$i\partial_t \Psi = (H_0 + H_I) \Psi \Rightarrow \partial_t \Psi = -i(H_0 + H_I) \Psi$$

\Rightarrow

$$M_{fi} = -i \int_{-\infty}^{+\infty} dt (\Phi_f, H_I \Psi_i)$$

An alternative form is especially useful for strong-field problems. Instead of making a one-to-one correspondence of Φ and Ψ states at $t \rightarrow -\infty$, do it at $t \rightarrow +\infty$ and then look for the probabilities that particular initial states could have led to this final result. The result is:

$$M_{fi} = -i \int_{-\infty}^{+\infty} dt (\Psi_f, H_I \Phi_i)$$

Footnotes:

Using two sets of states : $\{\Phi\}$ and $\{\Psi\}$ makes it unnecessary to consider how the interaction turns off at $t \rightarrow \pm \infty$.

That is, “adiabatic decoupling” is never necessary.

It is also unnecessary to use “time-development operators” or “propagators” to follow the progress in time of the system. Equations of motion are incorporated in the derivation of the transition amplitude.

This approach is now standard in the atom-atom and atom-ion scattering community.

IN-STATES / OUT-STATES

When Ψ states are correlated with Φ states at $t \rightarrow -\infty$ they are called in-states and are designated $\Psi^{(+)}$.

When Ψ states are correlated with Φ states at $t \rightarrow +\infty$ they are called out-states and are designated $\Psi^{(-)}$.

The two standard S matrices are often seen written as

$$(S - 1)_{fi} = -i \int dt \left(\Phi_f, H_I \Psi_i^{(+)} \right)$$

$$(S - 1)_{fi} = -i \int dt \left(\Psi_f^{(-)}, H_I \Phi_i \right)$$

TERMINOLOGY

The two alternative forms are known as:

Direct-time

Time-reversed

Or as:

Post

Prior

Or as:

In-state

Out-state

The last alternative is the most common, but it has the confusing terminology that in a simple scattering problem the *in-state* treatment will have *outgoing spherical waves*, and the *out-state* treatment will have *incoming spherical waves*.

GREEN'S FUNCTION / GREEN'S OPERATOR METHOD

Another approach:

Start with the same Schrödinger equations for Φ and Ψ and the same definition of the S matrix as before. Then introduce the Green's operators (or Green's functions) defined by:

$$(i\partial_t - H_0) G^{(\pm)}(t, t_0) = \delta(t - t_0)$$

They propagate solutions forward or backward in time:

$$G^{(+)}(t, t_0) \Phi(t_0) = -i\theta(t - t_0) \Phi(t)$$

$$G^{(-)}(t, t_0) \Phi(t_0) = i\theta(t_0 - t) \Phi(t)$$

where $\theta(x)$ is the standard unit step function

$$\theta(x) = \begin{cases} 1, & x > 0 \\ 0, & x < 0 \end{cases}$$

Then a formal solution of the complete Schrödinger equation

$$(i\partial_t - H) \Psi = 0$$

is given by

$$\Psi^{(\pm)}(t) = \Phi(t) + \int dt_1 G^{(\pm)}(t, t_1) H_I(t_1) \Psi^{(\pm)}(t_1)$$

as can be verified by direct substitution. Then substitute (for example) the in-state solution into the S matrix:

$$S_{fi} = \lim_{t \rightarrow +\infty} \left(\Phi_f(t), \Psi_i^{(+)}(t) \right)$$

$$S_{fi} = \lim_{t \rightarrow +\infty} \left(\Phi_f, \Phi_i \right) + \lim_{t \rightarrow +\infty} \int dt_1 \left(\Phi_f(t), G^{(+)}(t, t_1) H_I(t_1) \Psi_i^{(+)}(t_1) \right)$$

$$= \delta_{fi} + \lim_{t \rightarrow +\infty} \int dt_1 \left(G^{(-)}(t_1, t) \Phi_f(t), H_I(t_1) \Psi_i^{(+)}(t_1) \right)$$

$$(S - 1)_{fi} = -i \int dt \left(\Phi_f, H_I \Psi_i^{(+)} \right).$$

The properties have been used that

$$G^{(-)}(t, t_0) = G^{(+)\dagger}(t_0, t)$$

$$\lim_{t \rightarrow +\infty} \theta(t - t_1) = 1.$$

SYMBOLIC OPERATOR METHOD LIPPMANN-SCHWINGER EQUATION

The symbolic operator method is a very extensive subject.
A simple case will be treated here to give a sample of the techniques.

Consider a Hamiltonian that is time-independent, so that there are energy eigenvalues.

Operator forms for the Schrödinger equations are:

$$(H_0 - E) \Psi = -H_I \Psi$$

$$(H_0 - E) \Phi = 0$$

$$(H_0 - E) G = -1$$

The Green's function can be written as an inverse operator:

$$G = \frac{1}{E - H_0}, \quad \frac{1}{E - H_0} \equiv (E - H_0)^{-1}$$

The formal solution is

$$\Psi = \Phi + \frac{1}{E - H_0} H_I \Psi$$

The singularity in the inverse operation can be regularized by infinitesimal offsets. These distinguish the in- and out-states.

$$G^{(\pm)} = \lim_{\epsilon \rightarrow 0^+} \frac{1}{E - H_0 \pm i\epsilon}$$
$$\Psi^{(\pm)} = \Phi + G^{(\pm)} H_I \Psi^{(\pm)}$$
$$= \Phi + \lim_{\epsilon \rightarrow 0^+} \frac{1}{E - H_0 \pm i\epsilon} H_I \Psi^{(\pm)}$$

This is the famous Lippmann-Schwinger equation.

It represented the start of operator techniques.

Lippmann & Schwinger, Phys Rev **79**, 469 (1950).

The Lippmann-Schwinger equation is an implicit solution for $\Psi^{(\pm)}$ because it appears on both sides of the equation. This expression is generally used as a starting point for generating a perturbation expansion. That is, make the right side definite by using Φ in place of $\Psi^{(\pm)}$, then use the new approximation in place of $\Psi^{(\pm)}$ on the right-hand side, and so on ...

There is another procedure using the complete Green's function.

$$H = H_0 + H_I$$

$$(H - E) \Psi = 0$$

$$(H - E) \Phi = H_I \Phi$$

$$(H - E) \mathcal{G} = -1$$

$$\mathcal{G} = \frac{1}{E - H}$$

$$\frac{1}{E - H} \equiv (E - H)^{-1}$$

$$\Phi = \Psi - \mathcal{G}H_I\Phi$$

$$\Psi = \Phi + \frac{1}{E - H}\Phi$$

$$\Psi^{(\pm)} = \Phi + \lim_{\epsilon \rightarrow 0^+} \frac{1}{E - H \pm i\epsilon}\Phi$$

This is now an *explicit* solution for $\Psi^{(\pm)}$. The price paid for this is the difficult-to-find complete Green's function

$$\mathcal{G} = \frac{1}{E - H}$$

It is now elementary to develop a perturbation expansion by using the operator theorem

$$\frac{1}{A + B} = \frac{1}{A} - \frac{1}{A}B\frac{1}{A} + \frac{1}{A}B\frac{1}{A}B\frac{1}{A} - \dots$$

A proof of this expression is simple: $(A+B)$ is distributive even though $1/(A+B)$ is not.

$$\begin{aligned}
 (A + B) \frac{1}{A + B} &= A \frac{1}{A + B} + B \frac{1}{A + B} \\
 A \frac{1}{A + B} &= 1 - B \frac{1}{A} + B \frac{1}{A} B \frac{1}{A} - \dots \\
 B \frac{1}{A + B} &= B \frac{1}{A} - B \frac{1}{A} B \frac{1}{A} + \dots \\
 (A + B) \frac{1}{A + B} &= 1
 \end{aligned}$$

With the substitutions

$$\begin{aligned}
 A &= E - H_0 \pm i\epsilon \\
 B &= -H_i
 \end{aligned}$$

The perturbation expansion is arrived at directly:

$$\Psi^{(\pm)} = \Phi + \frac{1}{E - H_0 \pm i\epsilon} H_I \Phi + \frac{1}{E - H_0 \pm i\epsilon} H_I \frac{1}{E - H_0 \pm i\epsilon} H_I \Phi + \dots$$

GENERAL APPRAISAL

The symbolic methods disguise the actual complexity of the problem. When specific representations are introduced in place of the operators, much of the apparent simplicity vanishes.

Apart from the first S-matrix approach, all the other methods suffer from complications in the formal structure. The most prominent is the “*adiabatic decoupling*” problem, where it must be specified how the interaction-causing mechanism is turned on and off.

The “operational” (or “observability” or “Machian”) definition of the S-matrix formalism as derived here avoids the decoupling problem. The specific means by which the interaction is turned on or off is not observable and never enters the problem.

KLEIN-GORDON RELATIVISTIC S MATRIX

The Klein-Gordon equation applies to spin-zero particles rather than spin-1/2 particles like the electron or the nucleons.

Spinor space is not required so the problem is much simplified and can be used as a way of accessing relativistic properties simply.

See HRR, PRA **42**, 1476 (1990) for derivation of the Klein-Gordon S matrix.

DIRAC-RELATIVISTIC S MATRIX

The starting point is exactly the same as the nonrelativistic case:

- There are noninteracting states Φ and interacting states Ψ .
- The two sets of states are correlated at $t \rightarrow -\infty$.
- The S matrix is determined by overlaps at $t \rightarrow +\infty$ of the evolved initial Ψ state with all possible Φ states.
- Subtraction of the amplitude for no transition then gives the transition amplitude:

$$M_{fi} \equiv (S - 1)_{fi} = \lim_{t \rightarrow +\infty} (\Phi_f, \Psi_i) - \lim_{t \rightarrow -\infty} (\Phi_f, \Psi_i)$$

The difference comes from how an inner product or “overlap” is formed relativistically as compared to nonrelativistically, and from the fact that Φ and Ψ are now spinors in a 4-dimensional Dirac spinor space.

DIRAC SPACE

Nonrelativistically, $(\Phi, \Psi) = \int d^3r \Phi^\dagger \Psi$

Relativistically: $(\Phi, \Psi) = \int d^3r \Phi^\dagger \Psi = \int d^3r \bar{\Phi} \gamma^0 \Psi$

where Φ, Ψ are now 4-spinors and $\bar{\Phi}$ is the Dirac adjoint spinor.

The Dirac adjoint spinor has the properties $\bar{\Psi} \Psi = \text{Lorentz scalar}$,
 $\bar{\Psi} \gamma^\mu \Psi = \text{Lorentz vector}$, and so on ...

Following the nonrelativistic procedure, the S matrix satisfies

$(S - 1)_{fi} = \lim_{t \rightarrow +\infty} (\Phi_f, \Psi_i) - \lim_{t \rightarrow -\infty} (\Phi_f, \Psi_i)$ In the Dirac space, this can be converted to a surface integral in space-time and, using the 4-space divergence theorem it can also be converted to $\int d^4x \dots$

See HRR, Prog Quant Elex **16**, 1 (1992).

Even the 4-space volume can be made covariant.

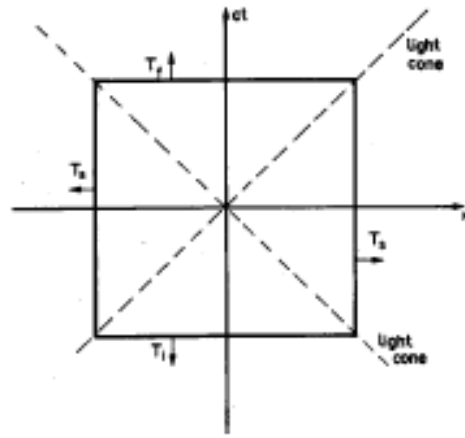


FIG. 1. Surface of integration in space-time represented in Eqn. (56) for use in the integration in Eqn. (57).

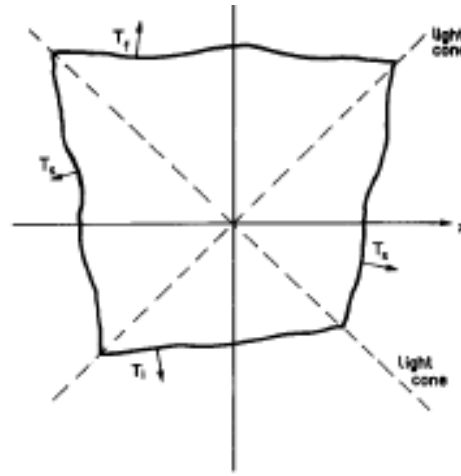


FIG. 2. Covariant generalization of the surface of integration shown in Fig. 1. This is the surface employed in Eqn. (59).

of these hypersurfaces constitutes a closed surface Σ with outwardly directed normal everywhere, i.e.

$$\Sigma = \tau_t \cup \tau_x \cup \tau_s. \quad (56)$$

If the time associated with τ_t approaches $+\infty$ (so that the time on τ_t approaches $-\infty$), then the surface τ_x will approach an infinite spacelike distance from the origin, i.e., from the quantum transition event. The state vectors can then be taken to approach zero on τ_x . Hence the right-hand side of Eqn. (55) can be rewritten as the surface integral in four-space

$$\lim_{t \rightarrow +\infty} \int d^3r \bar{\Phi}_t \gamma^0 \Psi_t^{(+)} - \lim_{t \rightarrow -\infty} \int d^3r \bar{\Phi}_t \gamma^0 \Psi_t^{(+)} = \oint_{\Sigma} d\sigma_{\mu} \bar{\Phi}_t \gamma^{\mu} \Psi_t^{(+)}. \quad (57)$$

The scalar product of two four-vectors employed in Eqn. (57) is given in general by

$$a_{\mu} b^{\mu} = a^{\mu} b_{\mu} = a^0 b^0 - \mathbf{a} \cdot \mathbf{b}. \quad (58)$$

That is, the conventions used in Bjorken and Drell⁽⁷⁴⁾ continue to be employed. The surface Σ of Eqn. (56) may now be generalized so that the surfaces τ_t , τ_x are no longer flat, although their normals must still everywhere be timelike; and the surface τ_s is now no longer perfectly a hypercircular cylinder, although its normal must still everywhere be spacelike. This generalization of Fig. 1 is rendered in Fig. 2 with one spatial dimension. With this generalized notion of Σ , the Lorentz-covariant statement of the S matrix is

$$(S - 1)_k = \oint_{\Sigma} d\sigma_{\mu} \bar{\Phi}_t \gamma^{\mu} \Psi_t^{(+)}. \quad (59)$$

The γ^{μ} in Eqn. (59) are the Dirac matrices $\gamma^0, \gamma^1, \gamma^2, \gamma^3$ employed with the conventions adopted by Bjorken and Drell.⁽⁷⁶⁾ Equation (59) is in a form in which the divergence theorem in four-space can be directly applied, leading to

$$(S - 1)_k = \int d^4x \partial_{\mu} (\bar{\Phi}_t \gamma^{\mu} \Psi_t^{(+)}). \quad (60)$$

T MATRIX & FERMI'S GOLDEN RULE

Start with the simplest case: *nonrelativistic, time-independent*.

Use complete units.

$$(S - 1)_{fi} = -\frac{i}{\hbar} \int dt (\Phi_f, V \Psi_i)$$

$$\Phi_f = \phi_f(\vec{r}) \exp\left(-\frac{i}{\hbar} E_f t\right), \quad \Psi_i = \psi_i(\vec{r}) \exp\left(-\frac{i}{\hbar} E_i t\right)$$

$$\int dt \exp\left[i \frac{(E_f - E_i)t}{\hbar}\right] = 2\pi\hbar \delta(E_f - E_i)$$

$$(S - 1)_{fi} = -2\pi i \delta(E_f - E_i) T_{fi}, \quad \text{where}$$

$$T_{fi} = (\phi_f, V \psi_i)$$

This defines the T matrix in terms of $(S-1)$.

(V and H_I are equivalent.)

$(S-1)_{fi}$ is a transition amplitude. The transition probability per unit time is

$$w = \lim_{\tau \rightarrow \infty} \frac{|(S-1)_{fi}|^2}{\tau} = \lim_{\tau \rightarrow \infty} \frac{2\pi\delta(E_f - E_i)2\pi\delta(0)}{\tau} |T_{fi}|^2$$

$$2\pi\delta(E_f - E_i) = \lim_{\tau \rightarrow \infty} \int_{-\tau/2}^{\tau/2} dt \frac{1}{\hbar} \exp\left[i \frac{(E_f - E_i)t}{\hbar} \right]$$

$$2\pi\delta(0) = \lim_{\tau \rightarrow \infty} \int_{-\tau/2}^{\tau/2} dt \frac{1}{\hbar} = \frac{\tau}{\hbar}$$

$$w = \left(\frac{2\pi}{\hbar} \right) \delta(E_f - E_i) |T_{fi}|^2$$

For transitions into a continuum of final states, the total transition rate is

$$W = \frac{2\pi}{\hbar} \int_{E_f - \Delta E/2}^{E_f + \Delta E/2} dE \delta(E_f - E_i) |T_{fi}|^2 \rho(E)$$

$$W = \frac{2\pi}{\hbar} |T_{fi}|^2 \rho(E)$$

where $\rho(E)$ is the density of final states.

The last result is Fermi's Golden Rule, usually derived in a perturbation-theory context, where

$$T_{fi} = (\phi_f, H_I \psi_i) \rightarrow (\phi_f, V \phi_i)$$

is the first-order perturbation-theory matrix element.

Starting from the time-reversed matrix element, the relevant T matrix would be

$$T_{fi} = (\psi_f, H_I \phi_i) \rightarrow (\phi_f, V \phi_i)$$

IMPORTANT: In both cases the complete T matrix contains one interacting ψ state and one non-interacting ϕ state.

A common error found in the literature is that the nonperturbative result is assumed to have an interacting ψ state in both locations in the matrix element.

FERMI'S GOLDEN RULE FOR THE TIME-DEPENDENT SINGLE-FREQUENCY MULTIPHOTON CASE

The result is:

$$(S - 1)_{fi} = -2\pi i \sum_n \delta(\Delta E - n\hbar\omega) T_{fi}^{(n)}$$

$$\Delta E = E_f - E_i + U_p$$

$$\begin{aligned} w &= \lim_{\tau \rightarrow \infty} \frac{|(S - 1)_{fi}|^2}{\tau} = \sum_n \frac{2\pi\delta(\Delta E - n\hbar\omega) 2\pi\delta(0)}{\tau} |T_{fi}^{(n)}|^2 \\ &= \frac{2\pi}{\hbar} \sum_n \delta(\Delta E - n\hbar\omega) |T_{fi}^{(n)}|^2 \end{aligned}$$

The total transition rate comes from integration over the final phase space.

This structure, with “sideband” states spaced $\hbar\omega$ apart is called *Floquet behavior*.

GAUGE TRANSFORMATIONS

The S-matrix approach makes it obvious how a gauge transformation should be done. Starting with the form

$$(S - 1)_{fi} = -i \int dt (\Phi_f, H_I \Psi_i)$$

it is clear that **Ψ , and H_I will change, but not Φ_f .**

In this form, or in the time-reversed form, there is always a state vector that is independent of the field. That is, there will be an element of the reference states $\{\Phi\}$ in every matrix element. The gauge-transformed S matrix is therefore

$$(S - 1)'_{fi} = -i \int dt (\Phi_f, H'_I \Psi'_i) \neq (S - 1)_{fi}$$

A gauge transformation has a nontrivial effect on transition matrix elements.

MISPERCEPTIONS IN THE AMO COMMUNITY

Since a 1952 paper by Willis Lamb there has been a conviction in a substantial (large majority?) part of the AMO community that the “length gauge” with the interaction $-\mathbf{r} \cdot \mathbf{E}$ is the fundamental gauge. This misconception persists to the present day, where lasers are the dominant source of electromagnetic fields. It should be clear that a vector field cannot adequately be represented by a scalar potential, but the mistake persists.

Added to this basic mistake is the assumption (almost universally unrecognized) that any matrix element is automatically gauge-invariant:

$$(S - 1)'_{fi} = -i \int dt (\Phi'_f, H'_I \Psi'_i) = -i \int dt (U \Phi_f, (U H_I U^{-1}) U \Psi_i) = (S - 1)_{fi}$$

This is the property of a picture transformation, not a gauge transformation.

S MATRIX IN THE RFBeta PROBLEM

The RF field is always on; CW (continuous wave) operation is assumed.

Asymptotic states *include* the effects of the RF field.

Transitions are caused by the *weak interaction* that is responsible for beta decay in general.

The S matrix is therefore simply a lowest-order perturbation-theory transition amplitude:

H_I is the weak interaction, and the Φ states include the RF field.

NEXT LECTURE

The RFBeta problem:

- Beta decay coupling
- S matrix
- Volkov solution
- Selection rules
- Evaluation of modified beta decay