ETH LECTURES 1

15 November 2011

QUANTUM MECHANICS *WITHOUT* PERTURBATION THEORY

General Goals

Answer the following questions:

How does one formulate nonperturbative problems in quantum mechanics?

How does this differ from standard approaches in quantum mechanics?

Have perturbative viewpoints created problems?

OUTLINE

- Limits on perturbation theory
- Brief S matrix history
- Derivation of S matrix (see also ETH Spring 2010 lectures)
- Terminology: Direct/Time-reversed; Post/Prior; In-states/Out-states
- Green's function method (see Spring 2010 for more detail)
- Symbolic methods: Lippmann-Schwinger equation
- Perturbation expansion
- Relativistic formalism (abbreviated; see Spring 2010)
- T matrix
- Nonperturbative Fermi Golden Rule
- Gauge transformations (a basic result only; more later)
- Misperceptions in the AMO community

LIMITS ON PERTURBATION THEORY

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 do not even discuss intensity limits on perturbation theory.

Also: There exists confusion between “multiphoton” and “nonperturbative”. They are different concepts.

Multiphoton:

If the energy requirements to meet threshold conditions for any given transition exceed the $\hbar\omega$ energy of a single photon, then the minimum required photon order is greater than one. This will be a multiphoton process whether it is perturbative or not.

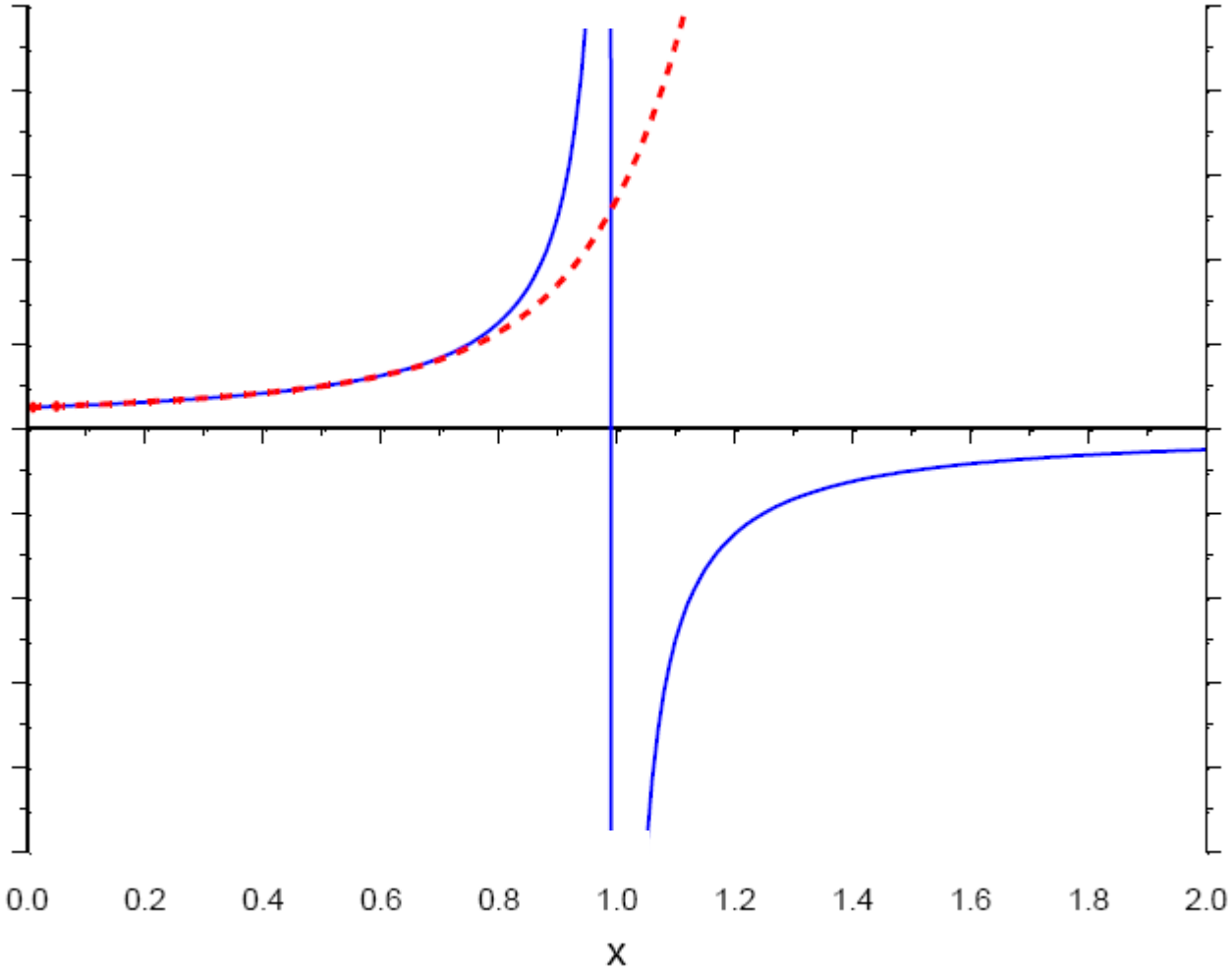
Nonperturbative:

If the intensity is larger than that at which a perturbation expansion is convergent, then perturbation theory will fail. This is sometimes difficult to determine, since perturbation theory can give a plausible-appearing result even if it is actually meaningless.

An elementary example of the hazards of ignoring a radius of convergence: The power series expansion of *1/(1-x)* is a sum of positive terms for $x \geq 0$, but the exact expression becomes negative. The radius of convergence of the series is $|x| < 1$.

The blue line is the exact result; the red dashed line is the series summed to fourth order.

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + \ldots$$
$$|x| < 1$$



The mathematics of the radius of convergence of perturbation theory is messy, but the result for an upper limit is very simple and very physical:

Perturbation theory fails before the first channel closing occurs.

Must explain:

- What is a channel closing?
- Why does it depend on the field intensity?

The answer to these questions requires a knowledge of the ***ponderomotive energy*** also known as ***ponderomotive potential*** -- a more revealing name.

PONDEROMOTIVE POTENTIAL

Consider atomic ionization in a strong laser field:

At threshold, the photoelectron is free of the atom, but it must exist as a free, charged particle in the presence of a strong field to which it is coupled.

At threshold, the kinetic energy of the photoelectron is **zero**, but if it migrates outside the laser field, the potential energy of the interaction of the free electron is converted to a kinetic energy. This is called the *quiver energy* because the electron will oscillate in the field.

There is widespread confusion on this issue: many people think of the electron as "quivering" when it is first ionized. NOT TRUE! The field interaction energy is a ***potential energy*** that becomes manifest only when the particle leaves the field and potential energy is converted to kinetic energy.

Corollary:

If the laser pulse is short, the field vanishes before the photoelectron can retrieve the ponderomotive energy.

At 800 nm, this transfer might not be complete even at 1 ps.

In femtosecond pulses (100 fs or less), none of the ponderomotive energy is returned to the photoelectron.

Energy conservation at ionization requires a contribution of U_p by the field at ionization to provide the required potential energy, but that amount of energy is not returned to the electron as the field turns off. *The field itself is classical, and regarded as a limitless source or sink of photons.*

Evidence for this is clear: if the laser pulse is short enough that there is not time for the conversion of potential energy into kinetic energy, then there is no recovery of the potential energy and photoelectron spectra can start at zero energy. If photoelectrons were "quivering" at the time of ionization, photoelectron spectra would show the quiver energy as the minimum of a spectrum.

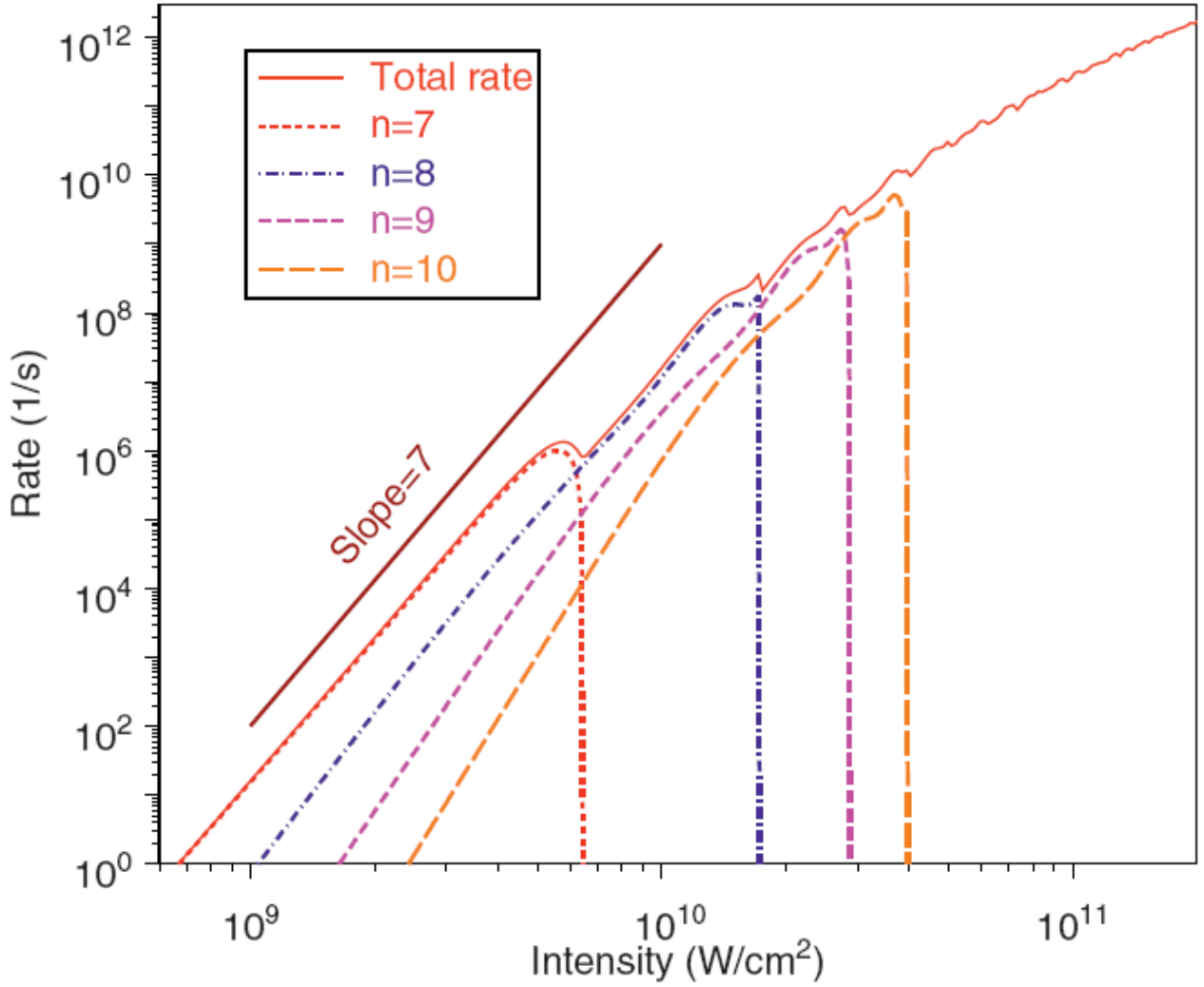
The potential energy of the interaction of a free charged particle in a plane-wave field is the ***ponderomotive energy*** U_p.

U_p is intensity-dependent: $U_p = \frac{I}{4\omega^2}$ in atomic units; I = intensity.

At threshold the field must supply binding energy E_B (or *IP* or I_p) + U_p

If n_0 photons are required at some intensity, and intensity is increased so that $n_0 + 1$ becomes the minimum, this is a ***channel closing.***

Example: PHOTODETACHMENT OF H^- BY 10 μm LASER



Upper limit for convergence of perturbation theory is the channel closing at 6 x 10^9 W/cm^2 . (Focal averaging gives a smooth total rate curve.)

Were the process perturbative, the rate curve would increase as I^{n_0} where n_0 is the lowest order allowed by energy conservation. This appears as a line of slope n_0 in a log-log plot of rate vs. intensity.

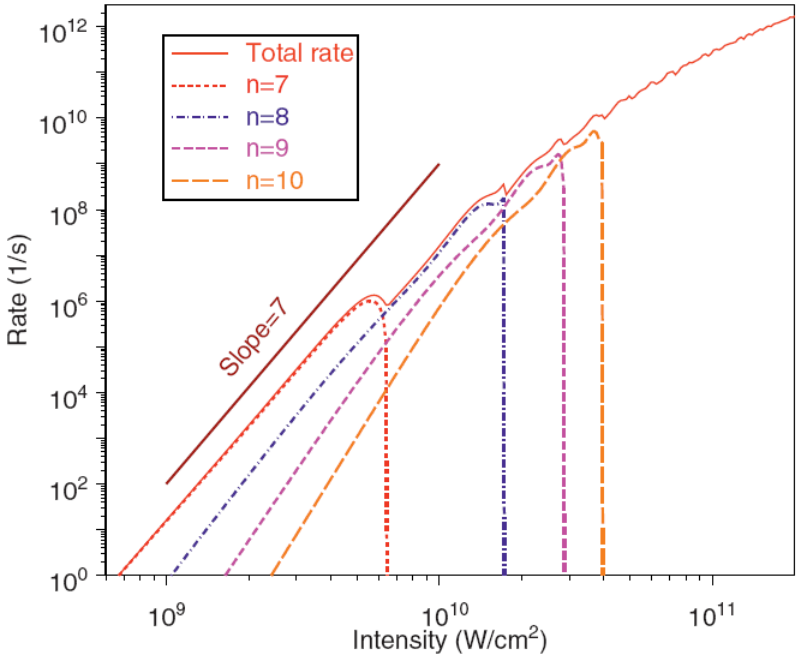
For photodetachment of a negative hydrogen ion by a *10 μm* laser:

$$\lambda = 10\ \mu\text{m}, \quad \omega = 4.56\times10^{-3}\ a.u.$$

$$E_B = 0.754\ eV = 0.02772\ a.u.$$

$$n_0 = \left\lceil \frac{E_B}{\omega} \right\rceil = \lceil 6.1 \rceil = 7$$

Where $\lceil .. \rceil$ is the *ceiling function*; the smallest integer containing the quantity within the brackets.



Major qualitative features of this diagram:

- Even well below the intensity for channel closing, orders highest than the minimum possible order make important contributions.
- The slope on this log-log plot never exceeds 7 even as channels close and the lowest order indexes up to 8, 9, 10, …
- That is, the slope is never as large as 8 even when that is the lowest allowed order.
- The process is nonperturbative throughout the intensity range shown; the first channel closing is only an ***upper limit*** on perturbation theory. The actual limit could be at a much lower intensity.

Calculation of **quantitative** results is done with S-matrix theory.

Now we turn 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).
(Note remarks by Kroll & Watson, 1973.)

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.

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

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

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

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

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:

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

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

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

This is now in the form of an exact differential:

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

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

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

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

$$\Rightarrow$$

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

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

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

Footnotes:

Using two sets of states : $\{\Phi\}$ and $\{\Psi\}$ makes it unnecessary to consider *how* the interaction turns off at $t \to \pm\infty$.
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 $t \to -\infty$ they are called in-states and are designated $\Psi^{(+)}$.
When Ψ states are correlated with Φ states at $t \to +\infty$ 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*.

A brief survey of elaborations and alternative approaches follows.

(Verification of some of the steps are optional exercises for the listener.)

GREEN'S FUNCTION / GREEN'S OPERATOR METHOD

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:

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

They propagate solutions forward or backward in time:

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

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

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

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

$$\frac{d}{dx}\theta\left(x\right) = \delta\left(x\right)$$

A formal solution of the complete Schrödinger equation

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

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:

$$\begin{aligned}
S_{fi} &= \lim_{t\to+\infty} \left(\Phi_f(t), \Psi_i^{(+)}(t)\right) \\
S_{fi} &= \lim_{t\to+\infty} (\Phi_f, \Phi_i) + \lim_{t\to+\infty} \int dt_1 \left(\Phi_f(t), G^{(+)}(t, t_1) H_I(t_1) \Psi_i^{(+)}(t_1)\right) \\
&= \delta_{fi} + \lim_{t\to+\infty} \int dt_1 \left(G^{(-)}(t_1, t) \Phi_f(t), H_I(t_1) \Psi_i^{(+)}(t_1)\right) \\
(S-1)_{fi} &= -i \int dt \left(\Phi_f, H_I \Psi_i^{(+)}\right).
\end{aligned}$$

The properties have been used that

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

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

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:

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

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.

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

$$\begin{aligned} \Psi^{(\pm)} &= \Phi + G^{(\pm)} H_I \Psi^{(\pm)} \\ &= \Phi + \lim_{\epsilon \to 0+} \frac{1}{E - H_0 \pm i\epsilon} H_I \Psi^{(\pm)} \end{aligned}$$

This is the famous Lippmann-Schwinger equation.

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* $\mathcal{G}$.

$$H = H_0 + H_I$$

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

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

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

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

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

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

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

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

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

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

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

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

$$(A+B)\frac{1}{A+B} = A\frac{1}{A+B} + B\frac{1}{A+B}$$

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

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

$$(A+B)\frac{1}{A+B} = 1$$

With the substitutions

$$A = E - H_0 \pm i\epsilon$$

$$B = -H_i$$

The perturbation expansion is arrived at directly:

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

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. Nevertheless, the formal simplicity is an aid to understanding and insight.

Alternatives to our S-matrix approach, used in some formal field theory and in particle physics, uses only the Ψ solutions that have to approach free Φ solutions at $t \to \pm\infty$. This leads to 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.

RETURN TO THE STRONG-FIELD PROBLEM

Remark: High-energy FELs (100 eV, 1 keV, …) produce environments that can be treated with perturbation theory. They are not true strong-field problems.

Nonperturbative methods will be used exclusively.

There is a rationale for formulating everything relativistically, and then going to the nonrelativistic limit when it is justified.

The reason for this point of view:

When the laser fields are very strong, then properties of the laser field can be more important than properties of the target materials being studied. Photon fields propagate at the speed of light, which then argues for a fully relativistic treatment.

[This point of view resolves the $A^2\,(t)$ problem.]

The formalism for this exists, but it has largely been ignored.
It is mentioned here, but not developed.

RELATIVISTIC S MATRICES

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

The KG equation is the relativistic extension of the Schrödinger equation.

The Dirac equation applies to spin-1/2 particles and requires 4-component spinors.

The Dirac equation is the relativistic extension of the Pauli (or Pauli-Schrödinger) equation that uses 2-component spinors.

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

KLEIN-GORDON S MATRIX

Only basic results are given here. If time permits, this topic will be developed more fully in a later lecture. A complete development is given in HRR, PRA **42**, 1476 (1990).

The KG equation (suggested in a footnote in the original Schrödinger paper) for a free particle in a plane-wave electromagnetic field A^μ is:

$$\{[i\partial_\mu - eA_\mu(x)][i\partial^\mu - eA^\mu(x)] - m^2\}\Psi(x) = 0$$

where

$$\partial^\mu \equiv \frac{\partial}{\partial x_\mu}, \quad \partial_\mu \equiv \frac{\partial}{\partial x^\mu}$$

are, respectively, the *contravariant* and *covariant* differential operators.

As used here, contra- and covariance refer to how quantities transform under coordinate transformations.

Covariance is also used to mean that every element in an expression transforms the same way under a Lorentz transformation. For example, if $\pi^\mu = p^\mu - eA^\mu$ is the kinetic 4-momentum, each of the terms in the expression is a "Lorentz 4-vector". The scalar product of two 4-vectors is a Lorentz scalar. The KG equation above is a covariant expression because each of the terms is a Lorentz scalar.

If a static binding potential (for example, a Coulomb potential) is added

$$A^{\mu} \rightarrow A^{\mu} + g^{\mu 0} V(\mathbf{r})$$

covariance is lost. The KG equation can be written in two forms:

$$[(i\partial_{\mu} - eA_{\mu})(i\partial^{\mu} - eA^{\mu}) - m^2 - \mathcal{V}^A]\Psi(x) = 0$$

$$\mathcal{V}^A = i\partial_0 V + V i\partial_0 - V^2$$

$$[(i\partial_{\mu} - Vg_{\mu 0})(i\partial^{\mu} - Vg^{\mu 0}) - m^2 - \mathcal{V}^F]\Psi(x) = 0$$

$$\mathcal{V}^F = i\partial_{\mu} eA^{\mu} + eA^{\mu} i\partial_{\mu} - e^2 A^{\mu} A_{\mu}$$

In conventional perturbation theory, $\mathcal{V}^F$ would be regarded as small; in a strong-field theory, $\mathcal{V}^A$ would be the small quantity.

In the Strong-Field Approximation, $\mathcal{V}^A$ is dropped altogether:

$$(\underline{S} - \underline{1})_{fi}^{\mathrm{SFA}} = -i \int d^4x \, \Psi_f^{(-)F*} \mathcal{V}^F \Phi_i$$

DIRAC S MATRIX

A full discussion here requires a lot of introductory material.
A complete description can be found in HRR, J. Opt. Soc. B **7**, 574 (1990).

The Dirac equation is:

$$(i\gamma^{\mu}\partial_{\mu} - e\gamma^{\mu}A_{\mu} - \gamma^{0}V - m)\Psi = 0$$

The Dirac S matrix is:

$$(S-1)_{fi} = -i\int \mathrm{d}^4x\bar{\Psi}_f^{(-)}eA^{\mu}\gamma_{\mu}\Phi_i$$

The Ψ and Φ functions are Dirac 4-spinors, and the γ^{μ} are the Dirac matrices.

After this brief excursion into relativistic formalism, return to the nonrelativistic problem.

T MATRIX & FERMI'S GOLDEN RULE

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

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

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

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

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

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

This defines the *T* matrix in terms of *(S-1)*.
(*V* is an alternative notation for H_I.)

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

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

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

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

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

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

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

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

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:

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

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

$$w = \lim_{\tau\to\infty} \frac{\left|\left(S-1\right)_{fi}\right|^2}{\tau} = \sum_n \frac{2\pi\delta\left(\Delta E - n\hbar\omega\right)2\pi\delta\left(0\right)}{\tau}\left|T_{fi}^{(n)}\right|^2$$

$$= \frac{2\pi}{\hbar}\sum_n \delta\left(\Delta E - n\hbar\omega\right)\left|T_{fi}^{(n)}\right|^2$$

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_I and H_I will change because they depend on how the field is represented, but Φ_f does not depend on the field and will not change.**

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 $-\boldsymbol{r}\cdot\boldsymbol{E}$ 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:

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

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

A look ahead …

Gauge transformations, widely regarded as formalities that are inessential, become fundamental when strong fields are present. This is an essential consideration at low frequencies.

The subject of gauges will be raised again with important new results that have not been discussed previously.

Relativistic considerations become important at low frequencies, so relativistic topics will be revisited.