

APAS 5110. Internal Processes in Gases. Fall 1999.
Perturbation Theory

1. TIME-INDEPENDENT PERTURBATION

Suppose that the Hamiltonian H is the sum

$$H = \overset{0}{H} + \epsilon \overset{1}{H} \quad (1.1)$$

of a main part $\overset{0}{H}$ and a small perturbation $\epsilon \overset{1}{H}$, neither of which depend explicitly on time. The aim below is to determine how an eigenfunction $\overset{0}{\phi}(\mathbf{x})$ of the unperturbed Hamiltonian $\overset{0}{H}$, and its corresponding energy $\overset{0}{E}$, is perturbed into an eigenfunction $\phi(\mathbf{x})$ with energy E as a result of the small perturbation $\overset{1}{H}$. An unambiguous correspondence between an unperturbed eigenfunction $\overset{0}{\phi}$ and the perturbed eigenfunction ϕ can be established by imagining turning on the perturbation $\overset{1}{H}$ very slowly, by increasing ϵ gradually from 0 to 1, and watching the eigenfunction and its energy change continuously from the unperturbed to perturbed values.

Expand the eigenfunction $\phi(\mathbf{x})$ and its energy E as series in powers of the parameter ϵ :

$$\phi = \overset{0}{\phi} + \epsilon \overset{1}{\phi} + \epsilon^2 \overset{2}{\phi} + \dots \quad (1.2)$$

$$E = \overset{0}{E} + \epsilon \overset{1}{E} + \epsilon^2 \overset{2}{E} + \dots \quad (1.3)$$

You may think of ϵ as some small parameter, which can be set to one at the end of the calculation. The perturbed and unperturbed eigenfunctions must both be normalized to one,

$$\langle \phi | \phi \rangle = \langle \overset{0}{\phi} | \overset{0}{\phi} \rangle = 1 \quad (1.4)$$

The time-independent Schrödinger equation asserts

$$\begin{aligned} 0 &= (E - H)\phi \\ &= (\overset{0}{E} + \epsilon \overset{1}{E} + \epsilon^2 \overset{2}{E} + \dots - \overset{0}{H} - \epsilon \overset{1}{H})(\overset{0}{\phi} + \epsilon \overset{1}{\phi} + \epsilon^2 \overset{2}{\phi} + \dots) \\ &= (\overset{0}{E} - \overset{0}{H})\overset{0}{\phi} \\ &\quad + \epsilon [(\overset{0}{E} - \overset{0}{H})\overset{1}{\phi} + (\overset{1}{E} - \overset{1}{H})\overset{0}{\phi}] \\ &\quad + \epsilon^2 [(\overset{0}{E} - \overset{0}{H})\overset{2}{\phi} + (\overset{1}{E} - \overset{1}{H})\overset{1}{\phi} + \overset{2}{E}\overset{0}{\phi}] + \dots \end{aligned} \quad (1.5)$$

Since the entire expression (1.5) vanishes identically for all small ϵ , each coefficient of the series expansion in ϵ must vanish separately, yielding successive approximations of perturbation theory.

The zeroth order equation

$$0 = (\overset{0}{E} - \overset{0}{H})\overset{0}{\phi} \quad (1.6)$$

asserts as expected that $\overset{0}{\phi}$ is an eigenfunction of the unperturbed Hamiltonian $\overset{0}{H}$ with energy $\overset{0}{E}$.

The first order perturbation equation

$$0 = (\overset{0}{E} - \overset{0}{H})\overset{1}{\phi} + (\overset{1}{E} - \overset{1}{H})\overset{0}{\phi} \quad (1.7)$$

yields both the first order correction $\overset{1}{E}$ to the energy, and the first order correction $\overset{1}{\phi}$ to the wavefunction, as follows. To obtain the first order correction $\overset{1}{E}$ to the energy, multiply equation (1.7) by $\overset{0}{\phi}^\dagger$ and integrate over all space, giving

$$0 = \langle \overset{0}{\phi} | \overset{0}{E} - \overset{0}{H} | \overset{1}{\phi} \rangle + \langle \overset{0}{\phi} | \overset{1}{E} - \overset{1}{H} | \overset{0}{\phi} \rangle . \quad (1.8)$$

The first term of (1.8) vanishes since $\langle \overset{0}{\phi} | (\overset{0}{E} - \overset{0}{H}) = 0$, and the second term then simplifies to yield

$$\overset{1}{E} = \langle \overset{0}{\phi} | \overset{1}{H} | \overset{0}{\phi} \rangle . \quad (1.9)$$

Equation (1.9) is the desired result for the first order perturbation $\overset{1}{E}$ to the energy.

To obtain the first order correction $\overset{1}{\phi}$ to the wavefunction, expand $\overset{1}{\phi}$ in terms of a complete orthonormal set $\phi_j(\mathbf{x})$ of eigenfunctions of the unperturbed Hamiltonian $\overset{0}{H}$, with energies E_j :

$$\overset{1}{\phi}(\mathbf{x}) = \sum_j \overset{1}{c}_j \phi_j(\mathbf{x}) , \quad (1.10)$$

for some constant coefficients $\overset{1}{c}_j$. Without loss of generality, the unperturbed wavefunction $\overset{0}{\phi}$ can be taken to be the $j = 0$ 'th eigenfunction

$$\overset{0}{\phi}(\mathbf{x}) = \phi_0(\mathbf{x}) , \quad \overset{0}{E} = E_0 . \quad (1.11)$$

Multiplying equation (1.7) by ϕ_j for $j \neq 0$ and integrating over all space gives

$$\begin{aligned} 0 &= \langle \phi_j | \overset{0}{E} - \overset{0}{H} | \overset{1}{\phi} \rangle + \langle \phi_j | \overset{1}{E} - \overset{1}{H} | \overset{0}{\phi} \rangle \\ &= \overset{1}{c}_j (E_0 - E_j) - \langle \phi_j | \overset{1}{H} | \phi_0 \rangle . \end{aligned} \quad (1.12)$$

Thus the first order coefficient $\overset{1}{c}_j$ is

$$\overset{1}{c}_j = \frac{\langle \phi_j | \overset{1}{H} | \phi_0 \rangle}{E_0 - E_j} , \quad (1.13)$$

provided that $E_j \neq E_0$. Equation (1.13) is not valid for $j = 0$; for $\overset{1}{c}_0$, the normalization condition (1.4) ensures that $\overset{1}{c}_0 = 0$. The first order perturbation $\overset{1}{\phi}$ is therefore

$$\overset{1}{\phi} = \sum_{j \neq 0} \frac{\langle \phi_j | \overset{1}{H} | \phi_0 \rangle}{E_0 - E_j} \phi_j , \quad (1.14)$$

where the summation is over all eigenfunctions ϕ_j except the unperturbed eigenfunction ϕ_0 . Equation (1.14) is the desired equation for the first order perturbation $\overset{1}{\phi}$ to the wavefunction.

What if some of the eigenfunctions are degenerate in energy with the unperturbed eigenfunction ϕ_0 ? In that case, if $\overset{0}{\phi}_j$, with $\overset{0}{\phi}_0 = \phi_0$, form a set of eigenfunctions of $\overset{0}{H}$ with

degenerate eigenvalues, $\overset{0}{H}\overset{0}{\phi}_j = E_0\overset{0}{\phi}_j$, then the unperturbed set of eigenfunctions should be chosen so that the perturbed energy matrix is diagonal, as can always be done:

$$\langle \overset{0}{\phi}_j | \overset{1}{H} | \overset{0}{\phi}_i \rangle = \overset{1}{E}_j \delta_{ji} . \quad (1.15)$$

In particular, $\langle \overset{0}{\phi}_j | \overset{1}{H} | \phi_0 \rangle = 0$ for $j \neq 0$. In equation (1.14) for the perturbed wavefunction $\overset{1}{\phi}$, the sum should then exclude the degenerate eigenfunctions $\overset{0}{\phi}_j$ with $E_j = E_0$.

Higher order corrections to the energy and wavefunction can be derived in basically the same way, by multiplying the n 'th order perturbation equation by $\overset{0}{\phi}$ for energy, and by ϕ_j with $j \neq 0$ for the wavefunction, and integrating over all space. Higher order perturbations are of most interest when the first order perturbation vanishes, as for example in the case of the Stark effect, which is the perturbation to the energy levels of an atom when a uniform external electric field is applied.

The second order perturbation $\overset{2}{E}$ to the energy is thus obtained from, equation (1.5),

$$\begin{aligned} 0 &= \langle \overset{0}{\phi} | \overset{0}{E} - \overset{0}{H} | \overset{2}{\phi} \rangle + \langle \overset{0}{\phi} | \overset{1}{E} - \overset{1}{H} | \overset{1}{\phi} \rangle + \langle \overset{0}{\phi} | \overset{2}{E} | \overset{0}{\phi} \rangle \\ &= - \sum_j \overset{1}{c}_j \langle \phi_0 | \overset{1}{H} | \phi_j \rangle + \overset{2}{E} , \end{aligned} \quad (1.16)$$

which with expressions (1.13) for $\overset{1}{c}_j$ gives

$$\overset{2}{E} = \sum_{j \neq 0} \frac{|\langle \phi_j | \overset{1}{H} | \phi_0 \rangle|^2}{E_0 - E_j} . \quad (1.17)$$

Equation (1.17) gives the second order perturbation $\overset{2}{E}$ to the energy.

2. TIME-DEPENDENT PERTURBATION

Consider a situation where the Hamiltonian H is the sum

$$H = \overset{0}{H} + \epsilon \overset{1}{H}(t) \quad (2.1)$$

of a main part $\overset{0}{H}$ which is independent of time, plus a small perturbation $\epsilon \overset{1}{H}(t)$ which may depend on time. Suppose that at time $t = 0$ the wavefunction is in a definite eigenstate $\overset{0}{\psi}$ of the unperturbed Hamiltonian. The aim below is to discover how the wavefunction $\psi(t, \mathbf{x})$ evolves out of this eigenstate as the result of application of the perturbation $\overset{1}{H}(t)$.

Expand the wavefunction $\psi(t, \mathbf{x})$ as a series in powers of the parameter ϵ :

$$\psi = \overset{0}{\psi} + \epsilon \overset{1}{\psi} + \epsilon^2 \overset{2}{\psi} + \dots . \quad (2.2)$$

Schrödinger's equation asserts

$$\begin{aligned}
0 &= (i\hbar\partial/\partial t - H)\psi \\
&= (i\hbar\partial/\partial t - \overset{0}{H} - \epsilon\overset{1}{H})(\overset{0}{\psi} + \epsilon\overset{1}{\psi} + \epsilon^2\overset{2}{\psi} + \dots) \\
&= (i\hbar\partial/\partial t - \overset{0}{H})\overset{0}{\psi} \\
&\quad + \epsilon[(i\hbar\partial/\partial t - \overset{0}{H})\overset{1}{\psi} - \overset{1}{H}\overset{0}{\psi}] \\
&\quad + \epsilon^2[(i\hbar\partial/\partial t - \overset{0}{H})\overset{2}{\psi} - \overset{1}{H}\overset{1}{\psi}] + \dots .
\end{aligned} \tag{2.3}$$

Since the entire expression vanishes identically, each coefficient of the series expansion in ϵ must vanish separately, yielding successive approximations of perturbation theory. The zeroth order equation shows that the unperturbed wavefunction $\overset{0}{\psi}$ must be a solution of the unperturbed Schrödinger equation,

$$(i\hbar\partial/\partial t - \overset{0}{H})\overset{0}{\psi} = 0 , \tag{2.4}$$

as was to be expected. The next order gives the first order perturbation $\overset{1}{\psi}$ to the wavefunction in terms of the unperturbed wavefunction $\overset{0}{\psi}$,

$$(i\hbar\partial/\partial t - \overset{0}{H})\overset{1}{\psi} = \overset{1}{H}\overset{0}{\psi} , \tag{2.5}$$

and subsequent terms yield successively higher perturbations $\overset{n}{\psi}$ to the wavefunction in terms of the previous perturbation $\overset{n-1}{\psi}$

$$(i\hbar\partial/\partial t - \overset{0}{H})\overset{n}{\psi} = \overset{1}{H}\overset{n-1}{\psi} . \tag{2.6}$$

Now let

$$\psi_j(t, \mathbf{x}) = e^{-i\omega_j t} \phi_j(\mathbf{x}) \tag{2.7}$$

denote a complete orthonormal set of eigenfunctions of the unperturbed Hamiltonian $\overset{0}{H}$, with eigenvalues the energies

$$E_j = \hbar\omega_j . \tag{2.8}$$

Without loss of generality, the unperturbed wavefunction $\overset{0}{\psi}$ can be taken to be the $j = 0$ 'th eigenfunction

$$\overset{0}{\psi} = \psi_0 = e^{-i\omega_0 t} \phi_0(\mathbf{x}) . \tag{2.9}$$

The n 'th order perturbation $\overset{n}{\psi}$ can be expanded in terms of the complete set of eigenfunctions of $\overset{0}{H}$

$$\overset{n}{\psi}(t, \mathbf{x}) = \sum_j \overset{n}{c}_j(t) \psi_j(t, \mathbf{x}) \tag{2.10}$$

for some amplitudes $\overset{n}{c}_j(t)$. Since ψ_j are eigenfunctions of $\overset{0}{H}$, it follows that $(i\hbar\partial/\partial t - \overset{0}{H})\psi_j = 0$, so that the left hand side of the perturbation equation (2.6) reduces to $(i\hbar\partial/\partial t - \overset{0}{H})\overset{n}{\psi} =$

$i\hbar \sum_j (d\check{c}_j/dt)\psi_j$. Thus the n 'th order perturbation equation (2.6) becomes

$$i\hbar \sum_j \frac{d\check{c}_j}{dt} \psi_j = \hat{H}^{n-1} \psi. \quad (2.11)$$

Multiplying both sides of equation (2.11) by ψ_j^\dagger and integrating over all space yields

$$\frac{d\check{c}_j}{dt} = \frac{1}{i\hbar} \int \psi_j^\dagger \hat{H}^{n-1} \psi d^3x = \frac{1}{i\hbar} \langle \psi_j | \hat{H}^{n-1} | \psi \rangle. \quad (2.12)$$

The evolution of the amplitudes \check{c}_j follows from integrating equation (2.12) with respect to time:

$$\check{c}_j(t) = \frac{1}{i\hbar} \int_0^t \langle \psi_j | \hat{H}^{n-1} | \psi \rangle dt. \quad (2.13)$$

In particular, the amplitudes \check{c}_j of the first order perturbation are

$$\check{c}_j(t) = \frac{1}{i\hbar} \int_0^t \langle \psi_j | \hat{H} | \psi_0 \rangle dt = \frac{1}{i\hbar} \int_0^t \langle \phi_j | \hat{H} | \phi_0 \rangle e^{i\omega_{j0}t} dt, \quad (2.14)$$

where

$$\omega_{j0} \equiv \omega_j - \omega_0 = (E_j - E_0)/\hbar. \quad (2.15)$$

3. PERIODICALLY VARYING PERTURBATION

Although equation (2.14) is perfectly valid for a general time-varying perturbation $\hat{H}(t)$, it is of particular interest to consider in more detail the case of a periodically varying perturbation, with angular frequency ω say. For example, atoms absorbing or emitting photons of energy $E = \hbar\omega$ can be treated as being subject to a periodically varying electromagnetic field of frequency ω . Since \hat{H} must be Hermitian, $\hat{H}^\dagger = \hat{H}$, the perturbation must take the form

$$\hat{H}(t) = V e^{-i\omega t} + V^\dagger e^{i\omega t}, \quad (3.1)$$

where V is a time-independent operator, and V^\dagger is its Hermitian conjugate. The frequency ω can be taken to be positive, $\omega > 0$, without loss of generality. Below it will become evident that the negative frequency ($\propto e^{-i\omega t}$) term of equation (3.1) represents absorption of a quantum of energy with $E = \hbar\omega$, a transition from a lower to a higher energy state, while the positive frequency term, which looks like a time-reversed version of the negative frequency term, represents emission, a transition from a higher to lower energy state.

Consider first just the negative frequency $V e^{-i\omega t}$ absorption term. The amplitudes \check{c}_j of the first order perturbed wavefunction, equation (2.14), are, for the negative frequency perturbation,

$$\check{c}_j(t) = \frac{1}{i\hbar} \int_0^t \langle \phi_j | V | \phi_0 \rangle e^{i(\omega_{j0}-\omega)t} dt, \quad (3.2)$$

where $\omega_{j0} \equiv \omega_j - \omega_0$ is the frequency difference between state j and the unperturbed state 0. Equation (3.2) integrates to give the absorption amplitude

$$\check{c}_j(t) = \frac{1}{\hbar} \langle \phi_j | V | \phi_0 \rangle \frac{1 - e^{i(\omega_{j0}-\omega)t}}{\omega_{j0} - \omega}. \quad (3.3)$$

The probability of being in state j at time t is the absolute value squared of the amplitude $\overset{1}{c}_j$, the absorption probability

$$|\overset{1}{c}_j(t)|^2 = \frac{1}{\hbar^2} |\langle \phi_j | V | \phi_0 \rangle|^2 \left(\frac{\sin [(\omega_{j0} - \omega)t/2]}{(\omega_{j0} - \omega)/2} \right)^2. \quad (3.4)$$

For perturbation theory to be applicable, the probabilities $|\overset{1}{c}_j|^2$ should be small for small times t , so the relevant regime of equation (3.4) is for large times t . As time t becomes large, the factor $(\sin [(\omega_{j0} - \omega)t/2] / (\omega_{j0} - \omega)/2)^2$ in equation (3.4), regarded as a function of $\omega_{j0} - \omega$, becomes sharply peaked about $\omega_{j0} - \omega = 0$, tending to infinity at $\omega_{j0} - \omega = 0$, and falling off sharply away from $\omega_{j0} - \omega = 0$. In the limit as t goes to infinity, the factor tends to a Dirac delta-function

$$\left(\frac{\sin [(\omega_{j0} - \omega)t/2]}{(\omega_{j0} - \omega)/2} \right)^2 \rightarrow 2\pi t \delta(\omega_{j0} - \omega) = 2\pi \hbar t \delta(E_{j0} - E) \quad (t \rightarrow \infty), \quad (3.5)$$

where the coefficient of the delta-function follows from $\int_{-\infty}^{\infty} \sin^2 x x^{-2} dx = \pi$. Equation (3.5) substituted in (3.4) shows that the absorption probability $|\overset{1}{c}_j|^2$ grows linearly with time t at large times t . The probability divided by the time t can be interpreted as the transition probability $P(j \leftarrow 0)$ per unit time out of state 0 into state j

$$P(j \leftarrow 0) \equiv \frac{|\overset{1}{c}_j(t)|^2}{t} = \frac{2\pi}{\hbar} |\langle \phi_j | V | \phi_0 \rangle|^2 \delta(E_{j0} - E). \quad (3.6)$$

The Dirac delta-function $\delta(E_{j0} - E)$ in the transition probability (3.6) represents energy conservation: the energy $E = \hbar\omega$ of the transition equals the energy difference $E_{j0} \equiv E_j - E_0$ between the states. The fact that the delta-function is achieved only asymptotically as $t \rightarrow \infty$, according to equation (3.5), reflects the uncertainty principle: exact energy conservation applies only in the limit of long times. Since the frequency ω is being assumed to be positive, the final state j has energy above the initial state 0, and the transition described by equation (3.6) then evidently represents absorption of a quantum $E = \hbar\omega$ of energy.

The delta-function in the transition probability (3.6) enforces energy conservation, but it is evident that this can only work if the final state j has just the right energy. On closer examination, one realizes the replacement (3.5) of the expression in square brackets in (3.4) by a delta-function is valid only if there is a continuum of final states j that are smoothly distributed over an interval of energy broad compared to the width of the delta-function. Thus the transition probability per unit time (3.6) should properly be integrated over the number dN_j of final states j

$$\begin{aligned} P(j \leftarrow 0) &= \frac{2\pi}{\hbar} \int |\langle \phi_j | V | \phi_0 \rangle|^2 \delta(E_{j0} - E) dN_j \\ &= \frac{2\pi}{\hbar} |\langle \phi_j | V | \phi_0 \rangle|^2 \frac{dN_j}{dE}, \end{aligned} \quad (3.7)$$

where dN_j/dE is the density of final states at the energy E_j satisfying energy conservation $E_{j0} = E$. Equation (3.7) is called **Fermi's Golden Rule**. In general, when considering transitions from one set of states to another set, one should *average* over initial states and *sum* over final states.

According to the Hermitian property (3.1) of the perturbation Hamiltonian $\overset{1}{H}$, there should also be a positive frequency part of the perturbation. Repeating the above analysis, one concludes that the positive frequency part must correspond to a downward transition, with emission of a quantum $E = \hbar\omega$ of energy. In the case considered above, the eigenstate j lay above the eigenstate 0 by $E_{j0} = E$ in energy, so the transition must be from the upper state j to the lower state 0. Thus the probability per unit time for a transition from j to 0 is

$$P(0 \leftarrow j) = \frac{2\pi}{\hbar} |\langle \phi_j | V | \phi_0 \rangle|^2 \frac{dN_0}{dE}, \quad (3.8)$$

which is the same as equation (3.7) apart from the factor for the density of final states.

To obtain the number of transitions per unit time which occur in an actual case, the transition probability $P(j \leftarrow 0)$ of equation (3.7) should be multiplied by the number of particles in state j , and likewise the inverse transition probability $P(0 \leftarrow j)$ of equation (3.8) should be multiplied by the number of particles in state 0.

4. SCATTERING MATRIX

A standard problem in quantum mechanics is to calculate the probability that a particle with some initial wavefunction $\psi_i(t, \mathbf{x})$ will be scattered into some final wavefunction $\psi_f(t, \mathbf{x})$ as the result of scattering off some (possibly time-dependent) potential V . If the potential V is suitably weak, then this problem can be treated as a standard application of time-dependent perturbation theory, §2. However, it is helpful to explore the problem in a little more detail by deriving an exact expression for the scattering matrix S_{fi} , equation (4.9). This expression reduces to the perturbation theory result (2.14) in the case of a weak potential.

In the commonest case, the potential V is supposed to be localized in space (or time), so that the initial and final wavefunctions ψ_i and ψ_f can be taken to be eigenfunctions of the free Hamiltonian. The perturbation theory result for the scattering amplitude in this case is called the **Born approximation**. Here the Hamiltonian is split into a sum of the free Hamiltonian $p^2/2m$ and the (possibly time-dependent) potential V :

$$H = \overset{0}{H} + \overset{1}{H}, \quad (4.1)$$

with

$$\overset{0}{H} = \frac{p^2}{2m}, \quad \overset{1}{H} = V. \quad (4.2)$$

The eigenfunctions $\psi_{\mathbf{k}}$ of the free Hamiltonian,

$$i\hbar \frac{\partial \psi_{\mathbf{k}}}{\partial t} = \overset{0}{H} \psi_{\mathbf{k}} = E \psi_{\mathbf{k}}, \quad (4.3)$$

are free wavefunctions $\psi_{\mathbf{k}} = (2\pi)^{-3/2} e^{-i\omega t + i\mathbf{k} \cdot \mathbf{x}}$ with eigenvalues $E = \hbar\omega = (\hbar\mathbf{k})^2/2m$.

It is also possible to consider more complicated situations. In scattering off charged ions, for example, the potential V falls off rather slowly, as $1/r$, at long range. In this case a better perturbation approximation is to incorporate the long range part of the potential into $\overset{0}{H}$, and to take the initial and final wavefunctions ψ_i and ψ_f to be Coulomb wavefunctions. The perturbation theory result for the scattering amplitude in this case is called the **Coulomb-Born approximation**.

Suppose that $\Psi(t, \mathbf{x})$ is the exact solution for the particle wavefunction

$$i\hbar \frac{\partial}{\partial t} \Psi = H \Psi \quad (4.4)$$

subject to the boundary condition that

$$\Psi(t, \mathbf{x}) \rightarrow \psi_i(t, \mathbf{x}) \quad (4.5)$$

as $t \rightarrow -\infty$ (to apply this boundary condition strictly, one needs to consider wave packets of large but finite spatial extent formed out of superpositions of plane waves of nearly equal momenta). At time t , the amplitude for the particle to be in the state ψ_f is

$$\langle \psi_f | \Psi \rangle = \int \psi_f^\dagger(t, \mathbf{x}) \Psi(t, \mathbf{x}) d^3x . \quad (4.6)$$

The boundary condition on Ψ can be stated as

$$\lim_{t \rightarrow -\infty} \int \psi_f^\dagger(t, \mathbf{x}) \Psi(t, \mathbf{x}) d^3x = \delta_{fi} . \quad (4.7)$$

The scattering matrix (or S-matrix) S_{fi} is defined to be the scattering amplitude (4.6) in the limit $t \rightarrow \infty$,

$$S_{fi} \equiv \lim_{t \rightarrow \infty} \int \psi_f^\dagger(t, \mathbf{x}) \Psi(t, \mathbf{x}) d^3x . \quad (4.8)$$

Thus the scattering matrix S_{fi} is given by

$$\begin{aligned} S_{fi} - \delta_{fi} &= \left[\int \psi_f^\dagger(t, \mathbf{x}) \Psi(t, \mathbf{x}) d^3x \right]_{t=-\infty}^{\infty} \\ &= \int_{-\infty}^{\infty} \frac{\partial}{\partial t} \left(\int \psi_f^\dagger \Psi d^3x \right) dt \\ &= \int_{-\infty}^{\infty} \int \left(\psi_f^\dagger \frac{\partial \Psi}{\partial t} + \frac{\partial \psi_f^\dagger}{\partial t} \Psi \right) d^3x dt \\ &= \int_{-\infty}^{\infty} \int \frac{1}{i\hbar} (\psi_f^\dagger H \Psi - \psi_f^\dagger \overset{0}{H} \Psi) d^3x dt \\ &= \frac{1}{i\hbar} \int_{-\infty}^{\infty} \int \psi_f^\dagger \overset{1}{H} \Psi d^3x dt . \end{aligned} \quad (4.9)$$

Equation (4.9) says that the scattering matrix is

$$S_{fi} = \delta_{fi} + \frac{1}{i\hbar} \int_{-\infty}^{\infty} \int \psi_f^\dagger \overset{1}{H} \Psi d^3x dt . \quad (4.10)$$

The probability that the particle will be scattered from the initial state ψ_i into the final state ψ_f is the square of the scattering matrix

$$\text{probability}(f \leftarrow i) = |S_{fi}|^2 . \quad (4.11)$$

If the scattering potential $\overset{1}{H}$ is sufficiently weak, then the incident wavefunction Ψ is hardly affected, and one can approximate $\Psi \approx \psi_i$. This leads to the first order perturbation

expression for the scattering matrix

$$S_{fi}(\text{perturbation theory}) = \delta_{fi} + \frac{1}{i\hbar} \int_{-\infty}^{\infty} \int \psi_f^\dagger \hat{H} \psi_i d^3x dt . \quad (4.12)$$

Equation (4.12) is the same as equation (2.14), with the initial wavefunction being taken to be ψ_i at $t \rightarrow -\infty$ instead of ψ_0 at $t = 0$, and the final wavefunction being taken to be ψ_f at $t \rightarrow \infty$ instead of ψ_j at time t . If the initial and final wavefunctions ψ_i and ψ_f are free wavefunctions, then equation (4.12) is the Born approximation.

The expression (4.12) for the perturbative scattering amplitude is notable because it involves an integral not only over all space but also over all time. Such scattering amplitudes are a precursor of the Feynman diagrams of relativistic quantum field theory, where space and time appear in a manifestly Lorentz covariant fashion.