Chapter 19
Simple Quantum Systems

The time evolution of a quantum system is governed by the time-dependent Schrödinger equation [111]

$$\mathrm{i}\hbar\frac{\partial}{\partial t}|\psi\rangle = H|\psi\rangle \tag{19.1}$$

for the wavefunction ψ. The brackets indicate that $|\psi\rangle$ is a vector in abstract Hilbert space [112]. Vectors can be added

$$|\psi\rangle = |\psi_1\rangle + |\psi_2\rangle = |\psi_1 + \psi_2\rangle \tag{19.2}$$

and can be multiplied with a complex number

$$|\psi\rangle = \lambda|\psi_1\rangle = |\lambda\psi_1\rangle. \tag{19.3}$$

Finally a complex valued scalar product of two vectors is defined[1]

$$C = \langle\psi_1|\psi_2\rangle \tag{19.4}$$

which has the properties

$$\begin{aligned}
&\langle\psi_1|\psi_2\rangle = \langle\psi_2|\psi_1\rangle^* \\
&\langle\psi_1|\lambda\psi_2\rangle = \lambda\langle\psi_1|\psi_2\rangle = \langle\lambda^*\psi_1|\psi_2\rangle \\
&\langle\psi|\psi_1 + \psi_2\rangle = \langle\psi|\psi_1\rangle + \langle\psi|\psi_2\rangle \\
&\langle\psi_1 + \psi_2|\psi\rangle = \langle\psi_1|\psi\rangle + \langle\psi_2|\psi\rangle.
\end{aligned} \tag{19.5}$$

[1] If, for instance, the wavefunction depends on the coordinates of N particles, the scalar product is defined by $\langle\psi_n|\psi_{n'}\rangle = \int \mathrm{d}^3r_1 \cdots \mathrm{d}^3r_N \psi_n^*(r_1 \cdots r_N)\psi_{n'}(r_1 \cdots r_N)$.

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In this chapter we study simple quantum systems like a particle in a one-dimensional potential well $V(x)$ which is described by the partial differential equation [113]

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\psi(x) = H\psi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + V(x)\psi(x), \tag{19.6}$$

or systems which can be approximately described with a finite set of basis states ψ_n, $n = 1 \cdots n_{\max}$. Especially the quantum mechanical two-level system is often used as a simple model for the transition between an initial and a final state due to an external perturbation.[2] It is described by a two-component vector

$$|\psi\rangle = \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} \tag{19.7}$$

and two coupled ordinary differential equations for the amplitudes $C_{1,2}$ of the two states

$$\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix}. \tag{19.8}$$

The two-state model also represents a Qubit, a basic element of a future quantum computer [114]. Whereas a classical bit is in either one of its two states (0 or 1), the wavefunction of a Qubit is generally a superposition of the two states

$$|\psi\rangle = C_0|\psi_0\rangle + C_1|\psi_1\rangle \tag{19.9}$$

and the coefficients $C_{0,1}$ obey an equation similar to (19.8).

19.1 Quantum Particle in a Potential Well

A quantum mechanical particle in a finite[3] potential well, i.e., a potential $V(\mathbf{r})$ which has no upper bound outside a finite interval $a < r < b$ (Fig. 19.1)

$$V(\mathbf{r}) = \infty \quad \text{for} \quad r < a \quad \text{or} \quad r > b \tag{19.10}$$

is described by a complex valued wavefunction

$$\psi(\mathbf{r}) \quad \text{with} \quad \psi(r) = 0 \quad \text{for} \quad r < a \quad \text{or}\, r > b. \tag{19.11}$$

[2] For instance, collisions or the electromagnetic radiation field.

[3] Numerically we can treat only finite systems.

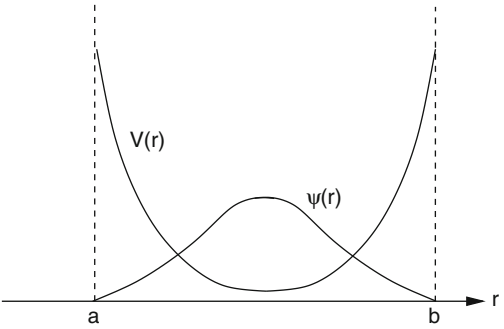

Fig. 19.1 Finite potential well

All observables (quantities which can be measured) of the particle are expectation values with respect to the wavefunction, for instance, its average position is

$$\langle \mathbf{r} \rangle = \langle \psi(\mathbf{r})\, \mathbf{r}\, \psi(\mathbf{r}) \rangle \int \mathrm{d}^3 r\, \psi^*(\mathbf{r}) \mathbf{r} \psi(\mathbf{r}). \tag{19.12}$$

The probability of finding the particle at the position $\mathbf{r_0}$ is given by

$$P(\mathbf{r} = \mathbf{r}_0) = |\psi(\mathbf{r})|^2 . \tag{19.13}$$

In the following we consider a particle in a one-dimensional potential $V(x)$. The Schrödinger equation

$$\mathrm{i}\hbar\dot{\psi} = H\psi = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \psi \tag{19.14}$$

is very similar to a diffusion equation with imaginary diffusion constant. Consider a simple explicit Euler step

$$\psi_{n+1} = (1 - \frac{\mathrm{i}\Delta t}{\hbar} H)\psi_n. \tag{19.15}$$

From the real eigenvalues E of the Hamiltonian we find the eigenvalues of the explicit method

$$\lambda = 1 - \frac{\mathrm{i}\Delta t}{\hbar} E \tag{19.16}$$

which all have absolute values

$$|\lambda| = \sqrt{1 + \frac{\Delta t^2 E^2}{\hbar^2}} > 1. \tag{19.17}$$

Hence the explicit method is not stable. The implicit method

$$\psi_{n+1} = \psi_n - \frac{\mathrm{i}\Delta t}{\hbar} H \psi_{n+1} \tag{19.18}$$

can be rearranged as

$$\psi_{n+1} = \left(1 + \frac{\mathrm{i}\Delta t}{\hbar} H\right)^{-1} \psi_n. \tag{19.19}$$

Here all eigenvalues have absolute values < 1. This method is stable but the norm of the wave function is not conserved. Again combination of implicit and explicit method gives a superior method

$$\psi_{n+1} - \psi_n = -\frac{\mathrm{i}\Delta t}{\hbar} H \left(\frac{\psi_{n+1}}{2} + \frac{\psi_n}{2}\right). \tag{19.20}$$

This equation can be solved for the new value of the wavefunction

$$\psi_{n+1} = \left(1 + \mathrm{i}\frac{\Delta t}{2\hbar} H\right)^{-1} \left(1 - \mathrm{i}\frac{\Delta t}{2\hbar} H\right) \psi_n. \tag{19.21}$$

The eigenvalues of (19.21) all have an absolute value of

$$|\lambda| = \left| \left(1 + \mathrm{i}\frac{E\Delta t}{2\hbar}\right)^{-1} \left(1 - \mathrm{i}\frac{E\Delta t}{2\hbar}\right) \right| = \frac{\sqrt{1 + \frac{E^2\Delta t^2}{4\hbar^2}}}{\sqrt{1 + \frac{E^2\Delta t^2}{4\hbar^2}}} = 1. \tag{19.22}$$

Hence the operator

$$\left(1 + \mathrm{i}\frac{\Delta t}{2\hbar} H\right)^{-1} \left(1 - \mathrm{i}\frac{\Delta t}{2\hbar} H\right) \tag{19.23}$$

is unitary and conserves the norm of the wavefunction. From the Taylor series we find the error order

$$\begin{aligned} &\left(1 + \mathrm{i}\frac{\Delta t}{2\hbar} H\right)^{-1} \left(1 - \mathrm{i}\frac{\Delta t}{2\hbar} H\right) = \left(1 - \mathrm{i}\frac{\Delta t}{2\hbar} H - \frac{\Delta t^2}{4\hbar^2} H^2 + \cdots\right) \left(1 - \mathrm{i}\frac{\Delta t}{2\hbar} H\right) \\ &= 1 - \frac{\mathrm{i}\Delta t}{\hbar} H - \frac{\Delta t^2}{2\hbar^2} H^2 + \cdots = \exp\left(-\frac{i\Delta t}{\hbar} H\right) + O(\Delta t^3). \end{aligned} \tag{19.24}$$

For practical application we rewrite [115]

$$\left(1+\mathrm{i}\frac{\Delta t}{2\hbar}H\right)^{-1}\left(1-\mathrm{i}\frac{\Delta t}{2\hbar}H\right)$$
$$=\left(1+\mathrm{i}\frac{\Delta t}{2\hbar}H\right)^{-1}\left(-1-\mathrm{i}\frac{\Delta t}{2\hbar}H+2\right)=-1+2\left(1+\mathrm{i}\frac{\Delta t}{2\hbar}H\right)^{-1} \tag{19.25}$$

hence

$$\psi_{n+1}=2\left(1+\mathrm{i}\frac{\Delta t}{2\hbar}H\right)^{-1}\psi_n-\psi_n=2\chi-\psi_n. \tag{19.26}$$

ψ_{n+1} is obtained in two steps. First we have to solve

$$\left(1+\mathrm{i}\frac{\Delta t}{2\hbar}H\right)\chi=\psi_n. \tag{19.27}$$

Then ψ_{n+1} is given by

$$\psi_{n+1}=2\chi-\psi_n. \tag{19.28}$$

We introduce a coordinate grid

$$x_j=j\Delta x \qquad j=0\cdots j_{\max} \tag{19.29}$$

and approximate the second derivative by

$$\frac{\partial^2}{\partial x^2}\psi(x_j)=\frac{\psi(x_{j+1})+\psi(x_{j-1})-2\psi(x_j)}{\Delta x^2}. \tag{19.30}$$

Equation (19.27) becomes a system of linear equations

$$A\begin{bmatrix}\chi(x_0)\\ \chi(x_1)\\ \chi(x_2)\\ \vdots\end{bmatrix}=\begin{bmatrix}\psi_n(x_0)\\ \psi_n(x_1)\\ \psi_n(x_2)\\ \vdots\end{bmatrix} \tag{19.31}$$

with a tridiagonal matrix

$$A = 1 + \mathrm{i}\frac{\Delta t}{2\hbar\Delta x^2}\begin{pmatrix} 2 & -1 & & \\ -1 & 2 & -1 & \\ & -1 & 2 & \ddots \\ & & \ddots & \ddots \end{pmatrix} \tag{19.32}$$

$$+\mathrm{i}\frac{\Delta t}{2\hbar}\begin{pmatrix} V(0) & & & \\ & V(\Delta x) & & \\ & & V(2\Delta x) & \\ & & & \ddots \end{pmatrix}. \tag{19.33}$$

The second step (19.28) becomes

$$\begin{bmatrix} \psi_{n+1}(x_0) \\ \psi_{n+1}(x_1) \\ \psi_{n+1}(x_2) \\ \vdots \end{bmatrix} = 2\begin{bmatrix} \chi(x_0) \\ \chi(x_1) \\ \chi(x_2) \\ \vdots \end{bmatrix} - \begin{bmatrix} \psi_n(x_0) \\ \psi_n(x_1) \\ \psi_n(x_2) \\ \vdots \end{bmatrix}. \tag{19.34}$$

19.2 Expansion in a Finite Basis

We consider a quantum system which is described by the wavefunction[4]

$$|\psi(t)\rangle. \tag{19.35}$$

The time-dependent Schrödinger equation is

$$\mathrm{i}\hbar|\dot{\psi}(t)\rangle = H|\psi(t)\rangle. \tag{19.36}$$

The eigenvalues of

$$H|\psi_n\rangle = E_n|\psi_n\rangle \tag{19.37}$$

are the energy values E_n of the stationary states $|\psi_n\rangle$ which are assumed to form an orthonormal basis[5]

[4] In general the wavefunction depends on a large number of variables, for instance, the coordinates and spin variables of N particles.

[5] We assume that the system has a discrete and finite spectrum of eigenvalues, for instance, if the system is bounded by a finite box.

$$\langle \psi_n | \psi_{n'} \rangle = \delta_{n,n'}. \tag{19.38}$$

The general solution of the time-dependent Schrödinger equation can be constructed as a linear combination of the stationary states [113]

$$|\psi(t)\rangle = \sum_n C_n \exp\left\{\frac{E_n}{\mathrm{i}\hbar} t\right\} |\psi_n\rangle. \tag{19.39}$$

The coefficients C_n are determined by the initial values of the wavefunction

$$|\psi(t=0)\rangle = \sum_n C_n |\psi_n> \tag{19.40}$$

and can be obtained from the scalar product

$$\langle \psi_m | \psi(t=0)\rangle = \sum_n C_n \langle \psi_m | \psi_n \rangle = C_m. \tag{19.41}$$

In the following we discuss simple models which approximate the sum over a very large number of eigenstates by the sum over a small number of important states, for instance, an initial and a final state which are coupled by some resonant interaction. Formally we introduce an (incomplete) set of orthonormal states[6]

$$\begin{aligned} &|\phi_1\rangle \cdots |\phi_M\rangle \\ &\langle \phi_i | \phi_j \rangle = \delta_{ij} \end{aligned} \tag{19.42}$$

and approximate the wave function by a linear combination

$$|\psi(t)\rangle \approx \sum_{j=1}^{M} C_j(t) |\phi_j\rangle. \tag{19.43}$$

Inserting into the time-dependent Schrödinger (19.36) equation gives

$$\mathrm{i}\hbar \sum_j \dot{C}_j(t) |\phi_j\rangle = \sum_j C_j(t) H |\phi_j\rangle \tag{19.44}$$

and after taking the scalar product with $|\phi_i\rangle$ we arrive at the system of ordinary differential equations

$$\mathrm{i}\hbar \dot{C}_i = \sum_{j=1}^{M} H_{i,j} C_j(t) \tag{19.45}$$

[6] In general these are linear combinations of the eigenstates.

with the matrix elements of the Hamiltonian

$$H_{i,j} = \langle \phi_i | H | \phi_j \rangle. \tag{19.46}$$

In matrix form (19.45) reads

$$\mathrm{i}\hbar \begin{pmatrix} \dot{C}_1(t) \\ \vdots \\ \dot{C}_M(t) \end{pmatrix} = \begin{pmatrix} H_{1,1} & \cdots & H_{1,M} \\ \vdots & \ddots & \vdots \\ H_{M,1} & \cdots & H_{M,M} \end{pmatrix} \begin{pmatrix} C_1(t) \\ \vdots \\ C_M(t) \end{pmatrix} \tag{19.47}$$

or more symbolically

$$\mathrm{i}\hbar \dot{\mathbf{C}}(t) = \mathbf{H}\mathbf{C}(t). \tag{19.48}$$

19.3 Time-Independent Problems

If the Hamilton operator does not depend explicitly on time ($H = \text{const.}$) the formal solution of (19.48) is given by

$$\mathbf{C} = \exp\left\{\frac{t}{\mathrm{i}\hbar} H\right\} \mathbf{C}(0). \tag{19.49}$$

From the solution of the eigenvalue problem

$$H\mathbf{C}_\lambda = \lambda \mathbf{C}_\lambda \tag{19.50}$$

(eigenvalues λ and corresponding eigenvectors $\mathbf{C}_\lambda$) we build the linear combination

$$\mathbf{C} = \sum_\lambda a_\lambda \mathbf{C}_\lambda \mathrm{e}^{\frac{\lambda}{\mathrm{i}\hbar} t}. \tag{19.51}$$

The amplitudes a_λ can be calculated from the set of linear equations

$$\mathbf{C}(0) = \sum_\lambda a_\lambda \mathbf{C}_\lambda. \tag{19.52}$$

In the following we calculate the time evolution numerically using the fourth-order Runge–Kutta method. This allows also the treatment of a time-dependent Hamiltonian later on.

19.3.1 Simple Two-Level System

The two-level system is the simplest model of interacting states and is very often used in physics (Fig. 19.2).

The interaction matrix of a two-level system is

$$H = \begin{pmatrix} E_1 & V \\ V & E_2 \end{pmatrix} \tag{19.53}$$

and the equations of motion are

$$\begin{aligned} \mathrm{i}\hbar\dot{C}_1 &= E_1 C_1 + V C_2 \\ \mathrm{i}\hbar\dot{C}_2 &= E_2 C_2 + V C_1 \end{aligned}. \tag{19.54}$$

Equations (19.54) can be solved analytically but this involves some lengthy expressions. Let us therefore concentrate on two limiting cases:
(a) For $E_1 = E_2$ we have

$$\ddot{C}_1 = -\frac{V^2}{\hbar^2} C_1 \tag{19.55}$$

which is solved by an oscillating coefficient

$$C_1 = \cos\left(\frac{V}{\hbar} t\right) \tag{19.56}$$

with period

$$T = \frac{2\pi\hbar}{V}. \tag{19.57}$$

(b) For $V \ll |\Delta E| = |E_1 - E_2|$ perturbation theory for the small quantity $V/\Delta E$ gives the following approximations:

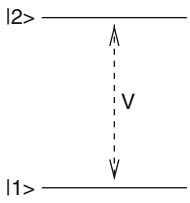

Fig. 19.2 Two level system model

$$\begin{aligned} \lambda_1 &\approx E_1 - \tfrac{V^2}{\Delta E} \\ \lambda_2 &\approx E_2 + \tfrac{V^2}{\Delta E} \end{aligned} \tag{19.58}$$

$$\begin{aligned} \mathbf{C}_1 &\approx \begin{pmatrix} 1 \\ \frac{V}{\Delta E} \end{pmatrix} \\ \mathbf{C}_2 &\approx \begin{pmatrix} \frac{-V}{\Delta E} \\ 1 \end{pmatrix} \end{aligned} . \tag{19.59}$$

For initial values $\mathbf{C}(0) = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ the amplitudes $a_{1,2}$ are calculated from

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} a_1 - a_2 \frac{V}{\Delta E} \\ a_1 \frac{V}{\Delta E} + a_2 \end{pmatrix} \tag{19.60}$$

which gives in lowest order

$$\begin{aligned} a_1 &\approx 1 - \tfrac{V^2}{\Delta E^2} \\ a_2 &\approx \tfrac{V^2}{\Delta E^2} \end{aligned} . \tag{19.61}$$

The approximate solution is

$$\mathbf{C} = \begin{pmatrix} (1 - \frac{V^2}{\Delta E^2}) \mathrm{e}^{\frac{1}{i\hbar}(E_1 - \frac{V^2}{\Delta E^2})t} + \frac{V^2}{\Delta E^2} \mathrm{e}^{\frac{1}{i\hbar}(E_2 + \frac{V^2}{\Delta E^2})t} \\ \frac{V}{\Delta E} \mathrm{e}^{\frac{1}{i\hbar}(E_1 - \frac{V^2}{\Delta E^2})t} - \frac{V}{\Delta E} \mathrm{e}^{\frac{1}{i\hbar}(E_2 + \frac{V^2}{\Delta E^2})t} \end{pmatrix} \tag{19.62}$$

and the occupation probability of the initial state is (Fig. 19.3)

$$|C_1|^2 \approx 1 - 2\frac{V^2}{\Delta E^2} + 2\frac{V^2}{\Delta E^2} \cos\left(\left(\Delta E + 2\frac{V^2}{\Delta E}\right) t\right). \tag{19.63}$$

19.3.2 Three-State Model (Superexchange)

Consider two isoenergetic states i and f which do not interact directly but via coupling to an intermediate state v (Fig. 19.4).
The interaction matrix is

$$H = \begin{pmatrix} 0 & V_1 & 0 \\ V_1 & E_2 & V_2 \\ 0 & V_2 & 0 \end{pmatrix}. \tag{19.64}$$

For simplification we choose $V_1 = V_2$.

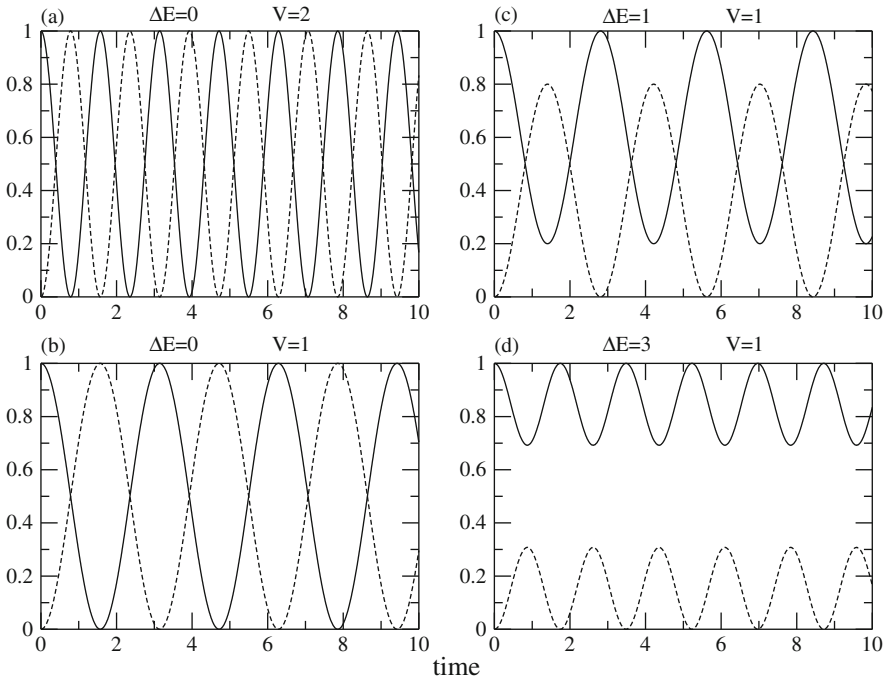

Fig. 19.3 Numerical simulation of a two-level system. The equations of motion of the two-level system (19.54) are integrated with the fourth-order Runge–Kutta method. For two resonant states the occupation probability of the initial state shows oscillations with the period (19.57) proportional to V^{-1}. With increasing energy gap $E_2 - E_1$ the amplitude of the oscillations decreases

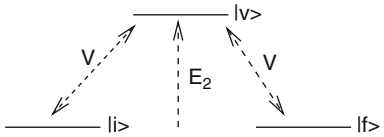

Fig. 19.4 Superexchange model

Let us first consider the special case of a resonant intermediate state $E_2 = 0$:

$$H = \begin{pmatrix} 0 & V & 0 \\ V & 0 & V \\ 0 & V & 0 \end{pmatrix}. \tag{19.65}$$

Obviously one eigenvalue is $\lambda_1 = 0$ and the corresponding eigenvector is

$$\mathbf{C}_1 = \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}. \tag{19.66}$$

The two remaining eigenvalues are solutions of

$$0 = \det \begin{vmatrix} -\lambda & V & 0 \\ V & -\lambda & V \\ 0 & V & -\lambda \end{vmatrix} = \lambda(-\lambda^2 + 2V^2) \tag{19.67}$$

which gives

$$\lambda_{2,3} = \pm\sqrt{2}V. \tag{19.68}$$

The eigenvectors are

$$\mathbf{C}_{2,3} = \begin{pmatrix} 1 \\ \pm\sqrt{2} \\ 1 \end{pmatrix}. \tag{19.69}$$

From the initial values

$$\mathbf{C}(0) = \begin{pmatrix} a_1 + a_2 + a_3 \\ \sqrt{2}a_2 - \sqrt{2}a_3 \\ -a_1 + a_2 + a_3 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \tag{19.70}$$

the amplitudes are calculated as

$$a_1 = \frac{1}{2}\, a_2 = a_3 = \frac{1}{4} \tag{19.71}$$

and finally the solution is

$$\begin{aligned} \mathbf{C} &= \frac{1}{2}\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} + \frac{1}{4}\begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix} \mathrm{e}^{\frac{1}{\mathrm{i}\hbar}\sqrt{2}Vt} + \frac{1}{4}\begin{pmatrix} 1 \\ -\sqrt{2} \\ 1 \end{pmatrix} \mathrm{e}^{-\frac{1}{\mathrm{i}\hbar}\sqrt{2}Vt} \\ &= \begin{pmatrix} \frac{1}{2} + \frac{1}{2}\cos\frac{\sqrt{2}V}{\hbar}t \\ \frac{\sqrt{2}}{2}\mathrm{i}\sin\frac{\sqrt{2}V}{\hbar}t \\ -\frac{1}{2} + \frac{1}{2}\cos\frac{\sqrt{2}V}{\hbar}t \end{pmatrix}. \end{aligned} \tag{19.72}$$

Let us now consider the case of a distant intermediate state $V \ll |E_2|$. $\lambda_1 = 0$ and the corresponding eigenvector still provide one solution. The two other eigenvalues are approximately given by

$$\lambda_{2,3} = \pm\sqrt{\frac{E_2^2}{4} + V^2} + \frac{E_2}{2} \approx \frac{E_2}{2} \pm \frac{E_2}{2}\left(1 + \frac{4V^2}{E_2^2}\right) \tag{19.73}$$

$$\lambda_2 \approx E_2 + \frac{2V^2}{E_2} \quad \lambda_3 \approx -\frac{2V^2}{E_2} \tag{19.74}$$

and the eigenvectors by

$$\mathbf{C}_2 \approx \begin{pmatrix} 1 \\ \frac{E_2}{V} + \frac{2V}{E_2} \\ 1 \end{pmatrix} \qquad \mathbf{C}_3 \approx \begin{pmatrix} 1 \\ -\frac{2V}{E_2} \\ 1 \end{pmatrix}. \tag{19.75}$$

From the initial values

$$\mathbf{C}(0) = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} a_1 + a_2 + a_3 \\ a_2\lambda_2 + a_3\lambda_3 \\ -a_1 + a_2 + a_3 \end{pmatrix} \tag{19.76}$$

we calculate the amplitudes

$$a_1 = \frac{1}{2} \qquad a_2 \approx \frac{V^2}{E_2^2} \qquad a_3 \approx \frac{1}{2}\left(1 - \frac{2V^2}{E_2^2}\right) \tag{19.77}$$

and finally the solution

$$\mathbf{C} \approx \begin{pmatrix} \frac{1}{2}(1 + \mathrm{e}^{-\frac{1}{\mathrm{i}\hbar}\frac{2V^2}{E_2}t}) \\ \frac{V}{E_2}\mathrm{e}^{\frac{1}{\mathrm{i}\hbar}E_2 t} - \frac{2V}{E_2}\mathrm{e}^{-\frac{1}{\mathrm{i}\hbar}\frac{2V^2}{E_2}t} \\ \frac{1}{2}(-1 + \mathrm{e}^{-\frac{1}{\mathrm{i}\hbar}\frac{2V^2}{E_2}t}) \end{pmatrix}. \tag{19.78}$$

The occupation probability of the initial state is

$$|C_1|^2 = \frac{1}{4}|1 + \mathrm{e}^{-\frac{1}{\mathrm{i}\hbar}\frac{2V^2}{E_2}t}|^2 = \cos^2\left(\frac{V^2}{\hbar E_2}t\right) \tag{19.79}$$

which shows that the system behaves like a two-state system with an effective interaction of (Fig. 19.5)

$$V_{\mathrm{eff}} = \frac{V^2}{E_2}. \tag{19.80}$$

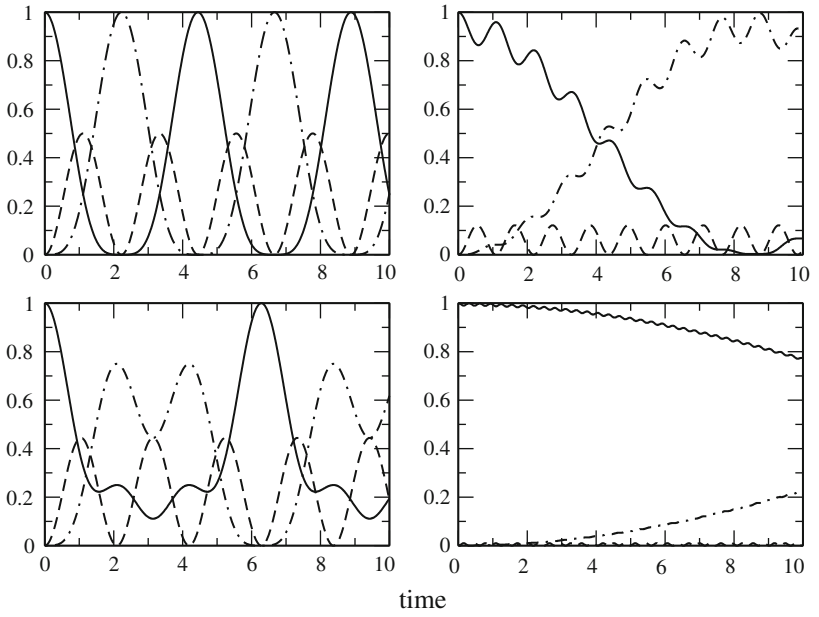

Fig. 19.5 Numerical simulation of the superexchange model. The equations of motion for the model equation (19.64) are solved numerically with the fourth-order Runge–Kutta method. The energy gap is varied to study the transition from the simple oscillation with $\omega = \sqrt{2}V/\hbar$ (19.72) to the effective two-level system with $\omega = V_{\text{eff}}/\hbar$ (19.79). Parameters are $V_1 = V_2 = 1$, $E_1 = E_3 = 0$, $E_2 = 0, 1, 5, 20$. The occupation probability of the initial (*solid curves*), virtual intermediate (*dashed curves*), and final (*dash-dotted curves*) state are shown

19.3.3 Ladder Model for Exponential Decay

We consider now a simple model for exponential decay [116, 117]. State 0 interacts with a manifold of states $(1 \cdots n)$, which do not interact with each other and are equally spaced (Fig. 19.6):

$$H = \begin{pmatrix} 0 & V & \cdots & V \\ V & E_1 & & \\ \vdots & & \ddots & \\ V & & & E_n \end{pmatrix} \qquad E_j = E_1 + (j-1)\Delta E \tag{19.81}$$

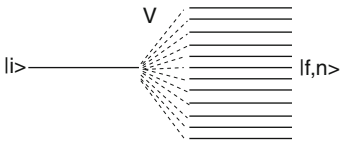

Fig. 19.6 Ladder model

The equations of motion are

$$\begin{aligned} \mathrm{i}\hbar\dot{C}_0 &= V\sum_{j=1}^{n} C_j \\ \mathrm{i}\hbar\dot{C}_j &= E_j C_j + V C_0. \end{aligned} \tag{19.82}$$

For the special case $\Delta E = 0$ we simply have

$$\ddot{C}_0 = -\frac{V^2}{\hbar^2} n C_0 \tag{19.83}$$

with an oscillating solution

$$C_0 \sim \cos\left(\frac{V\sqrt{n}}{\hbar}t\right). \tag{19.84}$$

Here the n states act like one state with an effective coupling of $V\sqrt{n}$.
For the general case $\Delta E \neq 0$ we substitute

$$C_j = u_j \mathrm{e}^{\frac{E_j}{\mathrm{i}\hbar}t} \tag{19.85}$$

and have

$$\mathrm{i}\hbar\dot{u}_j \mathrm{e}^{\frac{E_j}{\mathrm{i}\hbar}t} = V C_0. \tag{19.86}$$

Integration gives

$$u_j = \frac{V}{\mathrm{i}\hbar}\int_{t_0}^{t} \mathrm{e}^{-\frac{E_j}{\mathrm{i}\hbar}t'} C_0(t')\mathrm{d}t' \tag{19.87}$$

and therefore

$$C_j = \frac{V}{\mathrm{i}\hbar}\int_{t_0}^{t} \mathrm{e}^{\mathrm{i}\frac{E_j}{\hbar}(t'-t)} C_0(t')\mathrm{d}t'. \tag{19.88}$$

With the definition

$$E_j = j * \hbar\Delta\omega \tag{19.89}$$

we have

$$\dot{C}_0 = \frac{V}{\mathrm{i}\hbar}\sum_{j=1}^{n} C_j = -\frac{V^2}{\hbar^2}\sum\int_{t_0}^{t} \mathrm{e}^{\mathrm{i}j\Delta\omega(t'-t)} C_0(t')\mathrm{d}t'. \tag{19.90}$$

Replaced the sum by an integral

$$\omega = j\Delta\omega \tag{19.91}$$

and extend the integration range to $-\infty \cdots \infty$. Then the sum becomes approximately a delta function

$$\sum_{j=-\infty}^{\infty} e^{\mathrm{i}j\Delta\omega(t'-t)}\Delta j \to \int_{-\infty}^{\infty} e^{\mathrm{i}\omega(t'-t)}\frac{\mathrm{d}\omega}{\Delta\omega} = \frac{2\pi}{\Delta\omega}\delta(t'-t) \tag{19.92}$$

and hence the result is an exponential decay law (Fig. 19.7)

$$\dot{C}_0 = -\frac{2\pi V^2}{\Delta\omega}C_0 = -\frac{2\pi V^2}{\hbar}\rho(E)C_0 \tag{19.93}$$

with the density of final states

$$\rho(E) = \frac{1}{\hbar\Delta\omega} = \frac{1}{\Delta E}. \tag{19.94}$$

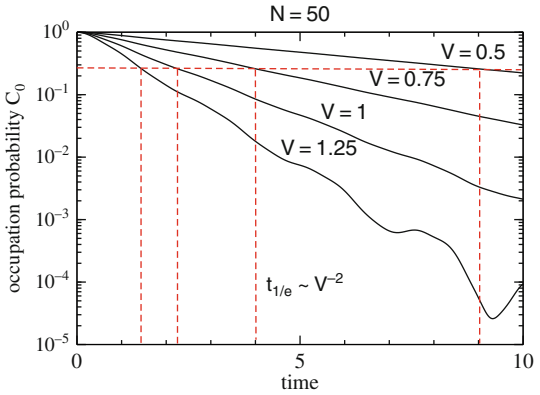

Fig. 19.7 Numerical solution of the ladder model. The time evolution of the ladder model equation (19.82) is calculated with the fourth-order Runge–Kutta method for $N = 50$ states and different values of the coupling V.

19.4 Time-Dependent Models

Now we study models with time-dependent Hamiltonian $H(t)$. Models of this type arise if nuclear motion or external fields are described as classical quantities.

19.4.1 Landau–Zener Model

This model describes crossing of two states, for instance, for colliding atoms or molecules [118, 119]. It is assumed that the interaction V is constant near the crossing point and that the nuclei move classically with constant velocity (Fig. 19.8)

$$H = \begin{pmatrix} 0 & V \\ V & \Delta E(t) \end{pmatrix} \qquad \Delta E(t) = \Delta E_0 + vt. \tag{19.95}$$

For small interaction V or large velocity $\frac{\partial}{\partial t}\Delta E = \dot{Q}\frac{\partial}{\partial Q}\Delta E$ the transition probability can be calculated with perturbation theory to give

$$P = \frac{2\pi V^2}{\hbar \frac{\partial}{\partial t}\Delta E}. \tag{19.96}$$

This expression becomes invalid for small velocities. Here the system stays on the adiabatic potential surface, i.e., $P \to 1$. Landau and Zener found the following expression which is valid in both limits (Fig. 19.9):

$$P_{\mathrm{LZ}} = 1 - \exp\left(-\frac{2\pi V^2}{\hbar \frac{\partial}{\partial t}\Delta E}\right). \tag{19.97}$$

In case of collisions multiple crossing of the interaction region has to be taken into account (Fig. 19.10)

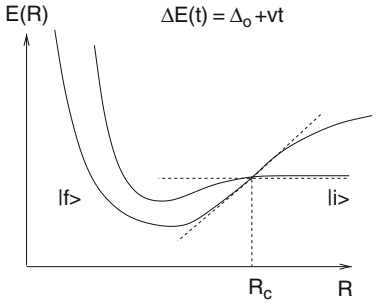

Fig. 19.8 Slow atomic collision

19.4.2 Two-State System with Time-Dependent Perturbation

Consider a two-state system with an oscillating perturbation (for instance, an atom or molecule in a laser field) (Fig. 19.11)

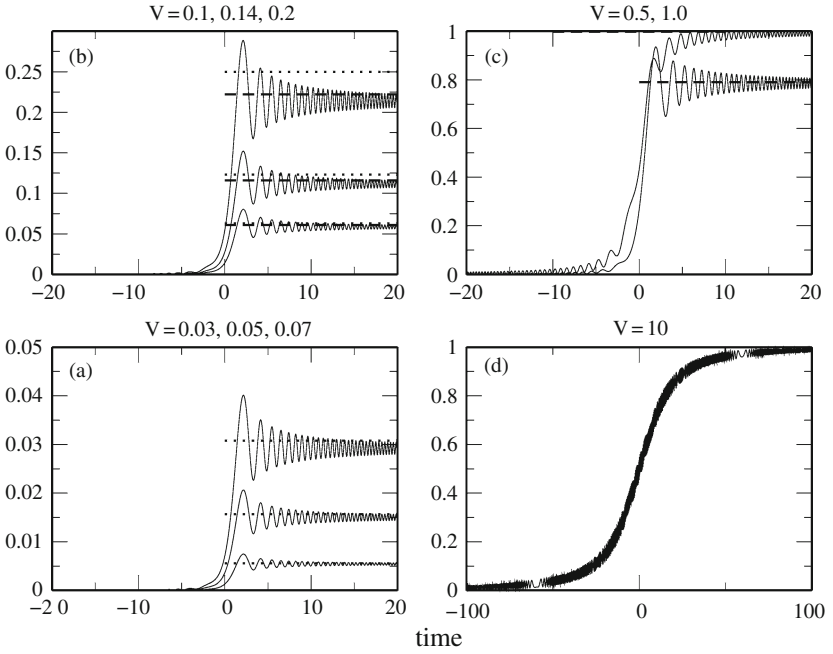

Fig. 19.9 Numerical solution of the Landau–Zener model. Numerical calculations (*solid curves*) are compared with the Landau–Zener probability ((19.97), *dashed lines*) and the approximation ((19.96), *dotted lines*) The velocity is $\mathrm{d}\Delta E/\mathrm{d}t = 1$

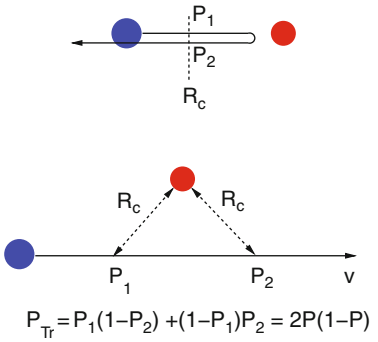

Fig. 19.10 Multiple passage of the interaction region

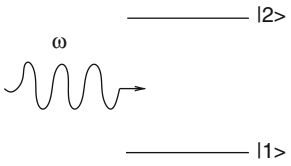

Fig. 19.11 Two-level system in an oscillating field

$$H = \begin{pmatrix} E_1 & V(t) \\ V(t) & E_2 \end{pmatrix} \qquad V(t) = V_0 \cos \omega t. \tag{19.98}$$

The equations of motion are

$$\begin{aligned} \mathrm{i}\hbar \dot{C}_1 &= E_1 C_1 + V(t) C_2 \\ \mathrm{i}\hbar \dot{C}_2 &= V(t) C_1 + E_2 C_2 \end{aligned}. \tag{19.99}$$

After the substitution

$$\begin{aligned} C_1 &= e^{\frac{E_1}{\mathrm{i}\hbar} t} u_1 \\ C_2 &= e^{\frac{E_2}{\mathrm{i}\hbar} t} u_2 \end{aligned} \tag{19.100}$$

they become

$$\begin{aligned} \mathrm{i}\hbar \dot{u}_1 &= V(t) \mathrm{e}^{\frac{E_2 - E_1}{\mathrm{i}\hbar} t} u_2 \\ \mathrm{i}\hbar \dot{u}_2 &= V(t) \mathrm{e}^{\frac{E_1 - E_2}{\mathrm{i}\hbar} t} u_1 \end{aligned}. \tag{19.101}$$

For small times we have approximately

$$u_1 \approx 1 \qquad u_2 \approx 0 \tag{19.102}$$

and with the definition

$$\omega_{21} = \frac{E_2 - E_1}{\hbar} \tag{19.103}$$

we find

$$\dot{u}_2 \approx \frac{V_0}{2\mathrm{i}\hbar} \left(e^{\mathrm{i}\omega t} + e^{-\mathrm{i}\omega t} \right) e^{\mathrm{i}\omega_{21} t}. \tag{19.104}$$

We neglect the fast oscillating term (this is the so-called rotating wave approximation)

$$u_2 \approx \frac{V_0}{2\mathrm{i}\hbar} \frac{e^{\mathrm{i}(\omega_{21} - \omega)t} - 1}{\omega_{21} - \omega} \tag{19.105}$$

and the transition probability

$$|u_2|^2 \approx \frac{V_0^2}{4\hbar^2} \frac{\sin^2 \left(\frac{\omega_{21} - \omega}{2} t \right)}{(\omega_{21} - \omega)^2} \tag{19.106}$$

shows resonance behavior at $\omega = \omega_{21}$. The transition probability per time is approximately given by the Golden rule expression

$$\frac{|u_2(t)|^2}{t} \approx \frac{2\pi}{\hbar}\left(\frac{V_0}{2}\right)^2 \delta(\hbar\omega - \hbar\omega_{21}). \tag{19.107}$$

At larger times the system oscillates between the two states.[7] Applying the random-phase approximation we neglect the perturbation component with positive frequency

$$\mathrm{i}\hbar\dot{u}_1 = V_0 \mathrm{e}^{\mathrm{i}(\omega_{21}-\omega)t} u_2 \tag{19.108}$$

$$\mathrm{i}\hbar\dot{u}_2 = V_0 \mathrm{e}^{-\mathrm{i}(\omega_{21}-\omega)t} u_1 \tag{19.109}$$

and substitute

$$u_1 = a_1 \mathrm{e}^{\mathrm{i}(\omega_{21}-\omega)t} \tag{19.110}$$

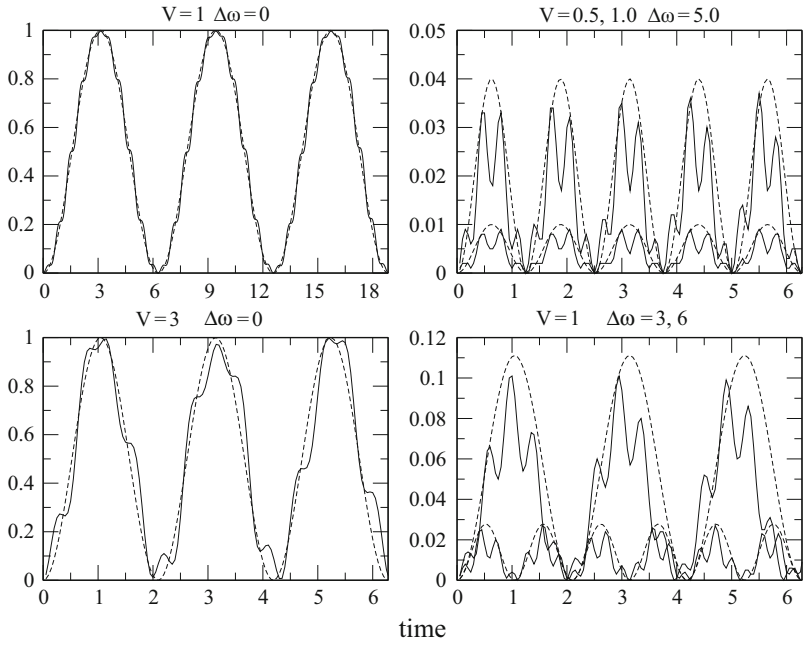

Fig. 19.12 Simulation of a two-state system in an oscillating field. The equations of motion (19.99) are integrated with the fourth-order Runge-Kutta method. At resonance the system oscillates between the two states with the frequency $V/\hbar$. The *dashed curves* show the corresponding solution of a two-level system with constant coupling (Sect. 19.4.2).

[7] These are so-called Rabi oscillations.

to have

$$\mathrm{i}\hbar(\dot{a_1} + a_1\mathrm{i}(\omega_{21} - \omega))\mathrm{e}^{\mathrm{i}(\omega_{21}-\omega)t} = V_0\mathrm{e}^{\mathrm{i}(\omega_{21}-\omega)t}u_2 \tag{19.111}$$

$$\mathrm{i}\hbar\dot{u}_2 = V_0\mathrm{e}^{-\mathrm{i}(\omega_{21}-\omega)t}\mathrm{e}^{\mathrm{i}(\omega_{21}-\omega)t}a_1 \tag{19.112}$$

or

$$\mathrm{i}\hbar\dot{a}_1 = \hbar(\omega_{21} - \omega)a_1 + V_0u_2 \tag{19.113}$$

$$\mathrm{i}\hbar\dot{u}_2 = V_0a_1 \tag{19.114}$$

which shows that the system behaves approximately like a two-level system with a constant interaction V_0 and an energy gap $\hbar(\omega_{12} - \omega) = E_2 - E_1 - \hbar\omega$ (Fig. 19.12).

19.5 Description of a Two-State System with the Density Matrix Formalism

We consider now a two-state system which is coupled to a thermal bath. This model is relevant not only for coherent optical excitation but also for NMR phenomena [120].

19.5.1 Density Matrix Formalism

The density matrix formalism is very suitable for the description of an ensemble of quantum systems or the average evolution of a quantum system in contact with a thermal bath [113].

19.5.1.1 Density Matrix for an Ensemble of Systems

Consider a thermal ensemble of systems. Their wave functions are expanded with respect to basis functions $|\psi_s\rangle$ as

$$|\psi\rangle = \sum C_s|\psi_s\rangle. \tag{19.115}$$

The ensemble average of an operator A is given by

$$\overline{\langle A\rangle} = \overline{\langle\psi A\psi\rangle} = \overline{\langle\sum C_s^*\psi_s A C_{s'}\psi_{s'}\rangle} \tag{19.116}$$

$$= \sum \overline{C_s^*C_{s'}}A_{ss'} = \mathrm{tr}(\rho A) \tag{19.117}$$

with the statistical operator

$$\rho_{s's} = \sum \overline{C_s^*C_{s'}}. \tag{19.118}$$

19.5.1.2 Characterization of the Elements of the Density Matrix

The wave function of a N-state system is a linear combination

$$|\psi\rangle = C_1|\psi_1\rangle + C_2|\psi_2\rangle + \cdots C_N|\psi_N\rangle. \tag{19.119}$$

The diagonal elements of the density matrix are the occupation probabilities

$$\rho_{11} = \overline{|C_1|^2} \qquad \rho_{22} = \overline{|C_2|^2} \cdots \qquad \rho_{NN} = \overline{|C_N|^2}. \tag{19.120}$$

The non-diagonal elements measure the correlation of two states[8]

$$\rho_{12} = \rho_{21}^* = \overline{C_2^* C_1}, \cdots \tag{19.121}$$

19.5.1.3 Equations of Motion for the Density Matrix

The expansion coefficients of

$$|\psi\rangle = \sum C_s|\psi_s\rangle \tag{19.122}$$

can be obtained from the scalar product

$$C_s = \langle\psi_s|\psi\rangle. \tag{19.123}$$

Hence we have

$$C_s^* C_{s'} = \langle\psi|\psi_s\rangle\langle\psi_{s'}|\psi\rangle = \langle\psi_{s'}|\psi\rangle\langle\psi|\psi_s\rangle \tag{19.124}$$

which can be considered to be the s', s matrix element of the operator $|\psi\rangle\langle\psi|$

$$C_s^* C_{s'} = (|\psi\rangle\langle\psi|)_{s's}\,. \tag{19.125}$$

The thermal average is the statistical operator

$$\rho_{s's} = \overline{C_s^* C_{s'}} = \overline{|\psi\rangle\langle\psi|}_{s's} \to \rho = \overline{|\psi\rangle\langle\psi|}. \tag{19.126}$$

From the Schrödinger equation

$$\mathrm{i}\hbar|\dot{\psi}\rangle = H|\psi\rangle \tag{19.127}$$

we find

$$-\mathrm{i}\hbar\langle\dot{\psi}| = \langle H\psi| = \langle\psi|H \tag{19.128}$$

[8] They are often called the "coherence" of the two states.

and hence

$$\mathrm{i}\hbar\dot{\rho} = \mathrm{i}\hbar\left(\overline{|\dot{\psi}\rangle\langle\psi|} + \overline{|\psi\rangle\langle\dot{\psi}|}\right) = \overline{|H\psi\rangle\langle\psi|} - \overline{|\psi\rangle\langle H\psi|}. \tag{19.129}$$

Since the Hamiltonian H is identical for all members of the ensemble we end up with the Liouville–von Neumann equation:

$$\mathrm{i}\hbar\dot{\rho} = H\rho - \rho H = [H, \rho]. \tag{19.130}$$

With respect to a finite basis this becomes explicitly:

$$\mathrm{i}\hbar\dot{\rho}_{ii} = \sum_j H_{ij}\rho_{ji} - \rho_{ij}H_{ji} = \sum_{j\neq i} H_{ij}\rho_{ji} - \rho_{ij}H_{ji} \tag{19.131}$$

$$\begin{aligned}\mathrm{i}\hbar\dot{\rho}_{ik} &= \sum_j H_{ij}\rho_{jk} - \rho_{ij}H_{jk} \\ &= (H_{ii} - H_{kk})\rho_{ik} + H_{ik}(\rho_{kk} - \rho_{ii}) + \sum_{j\neq i,k}(H_{ij}\rho_{jk} - \rho_{ij}H_{jk}).\end{aligned} \tag{19.132}$$

19.5.1.4 Two-State System

Consider a two-state system in a pulsed laser field with Gaussian envelope:

$$H_{12} = \mu E_0 e^{-t^2/t_\mathrm{p}^2}\cos(\omega_L t) \tag{19.133}$$

The equations of motion for the two-state system are

$$\begin{aligned}\mathrm{i}\hbar\dot{\rho}_{11} &= H_{12}\rho_{21} - \rho_{12}H_{21} \\ \mathrm{i}\hbar\dot{\rho}_{22} &= H_{21}\rho_{12} - \rho_{21}H_{12} \\ \mathrm{i}\hbar\dot{\rho}_{12} &= (H_{11} - H_{22})\rho_{12} + H_{12}(\rho_{22} - \rho_{11}) \\ -\mathrm{i}\hbar\dot{\rho}_{21} &= (H_{11} - H_{22})\rho_{21} + H_{21}(\rho_{22} - \rho_{11}).\end{aligned} \tag{19.134}$$

Obviously we have

$$\rho_{11} + \rho_{22} = \text{const} \tag{19.135}$$

and

$$\mathrm{i}\hbar\frac{\partial}{\partial t}(\rho_{11} - \rho_{22}) = 2H_{12}\rho_{21} - 2H_{21}\rho_{12} \tag{19.136}$$

$$\mathrm{i}\hbar\dot{\rho}_{12} = (H_{11} - H_{22})\rho_{12} + H_{12}(\rho_{22} - \rho_{11}) \tag{19.137}$$

$$-\mathrm{i}\hbar\dot{\rho}_{21} = (H_{11} - H_{22})\rho_{21} + H_{21}(\rho_{22} - \rho_{11}). \tag{19.138}$$

The equations of motion can be written as a system of linear equations

$$\mathrm{i}\hbar \begin{pmatrix} \dot{\rho}_{11} \\ \dot{\rho}_{22} \\ \dot{\rho}_{12} \\ \dot{\rho}_{21} \end{pmatrix} = \begin{pmatrix} 0 & 0 & -H_{21} & H_{12} \\ 0 & 0 & H_{21} & -H_{12} \\ -H_{12} & H_{12} & H_{11} - H_{22} & 0 \\ H_{21} & -H_{21} & 0 & H_{22} - H_{11} \end{pmatrix} \begin{pmatrix} \rho_{11} \\ \rho_{22} \\ \rho_{12} \\ \rho_{21} \end{pmatrix} \tag{19.139}$$

or in symbolic form

$$\mathrm{i}\hbar\dot{\rho} = \widehat{L}\rho. \tag{19.140}$$

Hence the same numerical treatment as for the Schrödinger equation can be used (but with larger dimension).

The radiation which is emitted by the two-state system depends on the expectation value of the dipole moment μ and is given by

$$\begin{aligned} \mathrm{Tr}(\rho\mu) &= \mathrm{Tr}\left(\begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} \begin{pmatrix} 0 & \mu \\ \mu & 0 \end{pmatrix} \right) \\ &= \mathrm{Tr} \begin{pmatrix} \mu\rho_{12} & \mu\rho_{11} \\ \mu\rho_{22} & \mu\rho_{21} \end{pmatrix} = \mu(\rho_{12} + \rho_{21}) = \mu x. \end{aligned} \tag{19.141}$$

19.5.2 Analogy to Nuclear MagneticResonance

The time evolution of the two-state system can be alternatively described with three real variables

$$\begin{aligned} x &= 2\Re(\rho_{12}) = \rho_{12} + \rho_{12}^* \\ y &= -2\Im(\rho_{12}) = \tfrac{1}{\mathrm{i}}(\rho_{12}^* - \rho_{12}) \\ z &= \rho_{11} - \rho_{22} \end{aligned} \tag{19.142}$$

which parametrize the density matrix according to[9]

$$\begin{aligned} \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} &= \begin{pmatrix} \frac{1+z}{2} & \frac{x-iy}{2} \\ \frac{x+iy}{2} & \frac{1-z}{2} \end{pmatrix} = \frac{1 + x\sigma_x + y\sigma_y + z\sigma_z}{2} \\ &= \frac{1 + \mathbf{x}\boldsymbol{\sigma}}{2}. \end{aligned} \tag{19.143}$$

The equations of motion for x, y, z are

$$\begin{aligned} \mathrm{i}\hbar\dot{z} &= 2(H_{12}\rho_{21} - H_{21}\rho_{12}) \\ \mathrm{i}\hbar\dot{x} &= (H_{11} - H_{22})(\rho_{12} - \rho_{21}) + (H_{12} - H_{21})(\rho_{22} - \rho_{11}) \\ \mathrm{i}\hbar\dot{y} &= \mathrm{i}(H_{11} - H_{22})(\rho_{12} + \rho_{21}) + \mathrm{i}(H_{12} + H_{21})(\rho_{22} - \rho_{11}) \end{aligned} \tag{19.144}$$

[9] The Pauli matrices $\sigma_{x,y,z}$ are explained in (12.111).

and with the definitions

$$V' = \Re(H_{12}) = \frac{H_{12} + H_{12}^*}{2} \quad V'' = \Im(H_{12}) = \frac{H_{12} - H_{12}^*}{2\mathrm{i}}$$
$$\Delta = H_{11} - H_{22} \tag{19.145}$$

we have finally

$$\begin{pmatrix} \dot{x} \\ \dot{y} \\ \dot{z} \end{pmatrix} = \begin{pmatrix} 0 & -\frac{\Delta}{\hbar} & -2\frac{V''}{\hbar} \\ \frac{\Delta}{\hbar} & 0 & -2\frac{V'}{\hbar} \\ 2\frac{V''}{\hbar} & 2\frac{V'}{\hbar} & 0 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{19.146}$$

which can be written as a vector product

$$\begin{pmatrix} \dot{x} \\ \dot{y} \\ \dot{z} \end{pmatrix} = \begin{pmatrix} \frac{2V'}{\hbar} \\ -\frac{2V''}{\hbar} \\ \frac{\Delta}{\hbar} \end{pmatrix} \times \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \boldsymbol{\omega} \times \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \tag{19.147}$$

For a spin-$\frac{1}{2}$ system we can interpret this equation in the following way: The expectation value of the spin vector is

$$\begin{aligned} \frac{\hbar}{2}\langle\psi|\boldsymbol{\sigma}|\psi\rangle &= \frac{\hbar}{2}\begin{pmatrix} C_1^* & C_2^* \end{pmatrix}\begin{pmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} \\ &= \hbar \begin{pmatrix} \frac{C_1^* C_2 + C_2^* C_1}{2} \\ \frac{C_1^* C_2 - C_2^* C_1}{2i} \\ \frac{|C_1|^2 - |C_2|^2}{2} \end{pmatrix} \end{aligned} \tag{19.148}$$

and for an ensemble of spin-$\frac{1}{2}$ particles the ensemble average is

$$\frac{\hbar}{2}\langle\boldsymbol{\sigma}\rangle = \hbar \begin{pmatrix} \Re(\rho_{12}) \\ -\Im(\rho_{12}) \\ \frac{1}{2}(\rho_{11} - \rho_{22}) \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} x \\ y \\ z \end{pmatrix}. \tag{19.149}$$

Thus $\mathbf{m} = \gamma\frac{\hbar}{2}\begin{pmatrix} x \\ y \\ z \end{pmatrix}$ is the average magnetization vector. The Hamiltonian of a spin-$\frac{1}{2}$ particle in a magnetic field is

$$H = -\gamma\frac{\hbar}{2}\boldsymbol{\sigma}\mathbf{B}. \tag{19.150}$$

Assume a typical NMR experiment with a constant field along the z-axis and a rotating field in the xy-plane

$$\mathbf{B} = \begin{pmatrix} B_1 \cos(\omega_\mathrm{f} t) \\ B_1 \sin(\omega_\mathrm{f} t) \\ B_0 \end{pmatrix}. \tag{19.151}$$

Here the Hamiltonian becomes

$$H = -\gamma \frac{\hbar}{2} \begin{pmatrix} B_0 & B_1 \mathrm{e}^{-\mathrm{i}\omega_\mathrm{f} t} \\ B_1 \mathrm{e}^{\mathrm{i}\omega_\mathrm{f} t} & -B_0 \end{pmatrix} \tag{19.152}$$

and from comparison we find

$$\omega_z = \frac{\Delta}{\hbar} = -\gamma B_0 = -\Omega_0 \tag{19.153}$$

$$H_{12} = V' + \mathrm{i}V'' = -\gamma \frac{\hbar}{2} B_1 \mathrm{e}^{-\mathrm{i}\omega_\mathrm{f} t}. \tag{19.154}$$

The equation of motion for the magnetization is

$$\dot{\mathbf{m}} = \gamma \frac{\hbar}{2} \begin{pmatrix} \dot{x} \\ \dot{y} \\ \dot{z} \end{pmatrix} = \begin{pmatrix} -\gamma B_1 \cos(\omega_\mathrm{f} t) \\ -\gamma B_1 \sin(\omega_\mathrm{f} t) \\ -\gamma B_0 \end{pmatrix} \times \gamma \frac{\hbar}{2} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{19.155}$$

or in the more conventional form

$$\frac{d\mathbf{m}}{dt} = \gamma \mathbf{m} \times \mathbf{B}. \tag{19.156}$$

19.5.3 Relaxation Processes—Bloch Equations

19.5.3.1 Phenomenological Description

Interaction with the environment will be described with phenomenological relaxation terms. Two different contributions have to be considered:

- Dephasing (loss of coherence) $\propto \mathrm{e}^{-t/T_2}$ with a time constant of T_2 (for NMR this is the spin–spin relaxation time)

$$\frac{\mathrm{d}}{\mathrm{d}t}_{|\mathrm{Rel}} \rho_{12} = -\frac{1}{T_2} \rho_{12} \tag{19.157}$$

- Thermalization $\rho_{22} - \rho_{11} \to \rho_{22}^{\mathrm{eq}} - \rho_{11}^{\mathrm{eq}}$ with time constant T_1 (for NMR this is the spin–lattice relaxation time)

$$\frac{\mathrm{d}}{\mathrm{d}t}_{|\mathrm{Rel}}(\rho_{22}-\rho_{11}) = -\frac{1}{T_1}((\rho_{22}-\rho_{11}) - (\rho_{22}^{\mathrm{eq}}-\rho_{11}^{\mathrm{eq}})). \tag{19.158}$$

Within the vector model this gives the Bloch equations [121] which are used to describe NMR phenomena

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \boldsymbol{\omega} \times \begin{pmatrix} x \\ y \\ z \end{pmatrix} - \begin{pmatrix} \frac{x}{T_2} \\ \frac{y}{T_2} \\ \frac{z-z^{\mathrm{eq}}}{T_1} \end{pmatrix} \tag{19.159}$$

or

$$\frac{\mathrm{d}\mathbf{m}}{\mathrm{d}t} = \gamma \mathbf{m} \times \mathbf{B} - \widehat{R}(\mathbf{m}-\mathbf{m}_{\mathrm{eq}}) \qquad \widehat{R} = \begin{pmatrix} \frac{1}{T_2} & 0 & 0 \\ 0 & \frac{1}{T_2} & 0 \\ 0 & 0 & \frac{1}{T_1} \end{pmatrix}. \tag{19.160}$$

More general relaxation processes for systems with many states can be described with a more general relaxation operator

$$\mathrm{i}\hbar\dot{\rho} = [H,\rho] - \mathrm{i}\hbar\widehat{\Gamma}(\rho-\rho_{\mathrm{eq}}). \tag{19.161}$$

19.5.3.2 Free Precession

Consider the special case $B_z = \text{const}\ B_x = B_y = 0$. With $m_\pm = m_x \pm i m_y$ and the Larmor frequency $\Omega_0 = \gamma B_0$ the equations of motion are

$$\begin{aligned} \dot{m}_+ &= -i\Omega_0 m_+ - \tfrac{m_+}{T_2} \\ \dot{m}_z &= -\tfrac{m_z - m_0}{T_1} \end{aligned} \tag{19.162}$$

with the solution

$$\begin{aligned} m_+ &= m_+(0)\mathrm{e}^{-i\Omega_0 t - t/T_2} \\ m_z &= m_0 + (m_z(0)-m_0)\mathrm{e}^{-t/T_1}\,. \end{aligned} \tag{19.163}$$

The corresponding density matrix is diagonal

$$H = \begin{pmatrix} H_{11} & 0 \\ 0 & H_{22} \end{pmatrix} \tag{19.164}$$

and the equations of motion are

$$\begin{aligned} \mathrm{i}\hbar\tfrac{\partial}{\partial t}(\rho_{11}-\rho_{22}) &= -\tfrac{(\rho_{11}-\rho_{22})-(\rho_{11}^{eq}-\rho_{22}^{eq})}{T_1} \\ \mathrm{i}\hbar\tfrac{\partial}{\partial t}\rho_{12} &= \Delta\rho_{12} - \mathrm{i}\hbar\tfrac{1}{T_2}\rho_{12} \end{aligned} \tag{19.165}$$

with the solution

$$\begin{array}{c}(\rho_{11}-\rho_{22}) = (\rho_{11}^{\mathrm{eq}}-\rho_{22}^{\mathrm{eq}}) + [(\rho_{11}(0)-\rho_{22}(0)) - (\rho_{11}^{\mathrm{eq}}-\rho_{22}^{\mathrm{eq}})]\mathrm{e}^{-t/T_1} \\ \rho_{12} = \rho_{12}(0)\mathrm{e}^{-\mathrm{i}\frac{\Delta}{\hbar}t - t/T_2}\end{array} . \quad (19.166)$$

19.5.3.3 Stationary Solution with Monochromatic Excitation

For the monochromatic rotating field

$$\mathbf{B} = \begin{pmatrix} B_1\cos(\omega_\mathrm{f} t) \\ B_1\sin(\omega_\mathrm{f} t) \\ B_0 \end{pmatrix} \quad H_{12} = V_0\mathrm{e}^{-\mathrm{i}\omega_\mathrm{f} t} \quad (19.167)$$

the solution of the Bloch equations

$$\begin{pmatrix} \dot{x} \\ \dot{y} \\ \dot{z} \end{pmatrix} = \boldsymbol{\omega} \times \begin{pmatrix} x \\ y \\ z \end{pmatrix} - \begin{pmatrix} \frac{x}{T_2} \\ \frac{y}{T_2} \\ \frac{z-z^{\mathrm{eq}}}{T_1} \end{pmatrix} \quad (19.168)$$

can be found explicitly. After transforming to a coordinate system which rotates along the z-axis with frequency ω_0

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos(\omega_\mathrm{f} t) & \sin(\omega_\mathrm{f} t) & 0 \\ -\sin(\omega_\mathrm{f} t) & \cos(\omega_\mathrm{f} t) & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad (19.169)$$

the equation of motion simplifies to

$$\begin{pmatrix} \dot{x}' \\ \dot{y}' \\ \dot{z}' \end{pmatrix} = \begin{pmatrix} -\frac{1}{T_2} & \Omega_0-\omega_\mathrm{f} & 0 \\ -\Omega_0+\omega_\mathrm{f} & -\frac{1}{T_2} & -\frac{2V_0}{\hbar} \\ 0 & \frac{2V_0}{\hbar} & -\frac{1}{T_1} \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ \frac{z^{\mathrm{eq}}}{T_1} \end{pmatrix} \quad (19.170)$$

with the stationary solution (Fig. 19.13)

$$\frac{z^{\mathrm{eq}}}{1+4\frac{V_0^2}{\hbar^2}T_1T_2 + T_2^2(\omega_\mathrm{f}-\Omega_0)^2} \begin{pmatrix} 2T_2^2\frac{V_0}{\hbar}(\omega_\mathrm{f}-\Omega_0) \\ -2T_2\frac{V_0}{\hbar} \\ 1+T_2^2(\omega_\mathrm{f}-\Omega_0)^2 \end{pmatrix} . \quad (19.171)$$

Saturation appears for

$$4\frac{V_0^2}{\hbar^2}T_1T_2 \gg 1 + (\omega_\mathrm{f}-\Omega_0)^2T_2^2 . \quad (19.172)$$

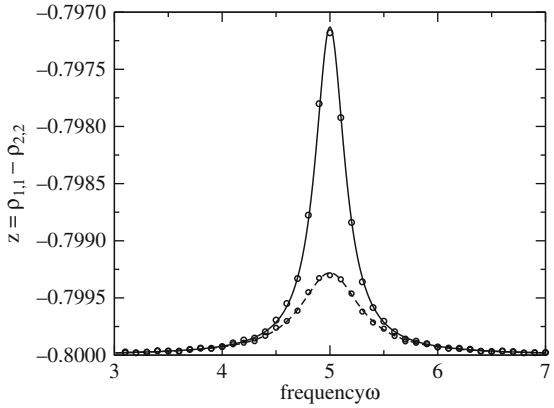

Fig. 19.13 Resonance line. The equations of motion of the two-level system including relaxation terms are integrated with the fourth-order Runge–Kutta until a steady state is reached. Parameters are $\omega_0 = 5, z_{\mathrm{eq}} = -0.8, V = 0.01$, and $T_1 = T_2 = 3.0, 6.9$. The change of the occupation difference is shown as a function of frequency (*circles*) and compared with the steady-state solution (19.171)

The width of the Lorenz line depends on the intensity (saturation broadening) (Fig. 19.14)

$$\Delta\omega = \frac{1}{T_2} \to \frac{1}{T_2}\sqrt{1 + 4\frac{V_0^2}{\hbar^2}T_1T_2}. \tag{19.173}$$

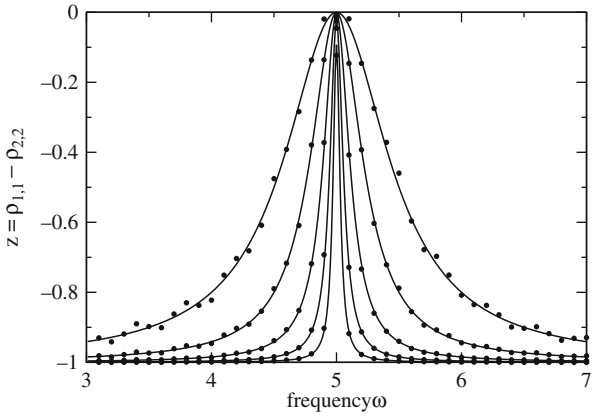

Fig. 19.14 Power saturation and broadening. The resonance line is investigated as a function of the coupling strength V and compared with the stationary solution (19.171) to observe the broadening of the line width (19.173). Parameters are $\omega_0 = 5, z_{\mathrm{eq}} = -1.0, T_1 = T_2 = 100$, and $V = 0.5, 0.25, 0.125, 0.0625, 0.03125$

19.5.3.4 Excitation by a Resonant Pulse

For a resonant pulse $\omega_f = \Omega_0$ with envelope $V_0(t)$ the equation of motion in the rotating system is

$$\begin{pmatrix} \dot{x}' \\ \dot{y}' \\ \dot{z}' \end{pmatrix} = \begin{pmatrix} -\frac{1}{T_2} & 0 & 0 \\ 0 & -\frac{1}{T_2} & -\frac{2V_0(t)}{\hbar} \\ 0 & \frac{2V_0(t)}{\hbar} & -\frac{1}{T_1} \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ \frac{z^{eq}}{T_1} \end{pmatrix}. \tag{19.174}$$

If the relaxation times are large compared to the pulse duration we have the approximate solution

$$x' = x'_0 \tag{19.175}$$

$$y' = \frac{y'_0 + iz'_0}{2} e^{i\Phi} + \frac{y'_0 - iz'_0}{2} e^{-i\Phi} \tag{19.176}$$

$$z' = \frac{z'_0 - ix'_0}{2} e^{i\Phi} + \frac{z'_0 + ix'_0}{2} e^{-i\Phi} \tag{19.177}$$

with the phase angle

$$\Phi = \int_{-\infty}^{t} \frac{2V_0(t')}{\hbar} dt'. \tag{19.178}$$

For a total phase of $\Phi(\infty) = \pi$ (π-pulse) the y- and z-component change their sign. The transition between $z = 1$ and $z = -1$ corresponds to a spin flip. On the other

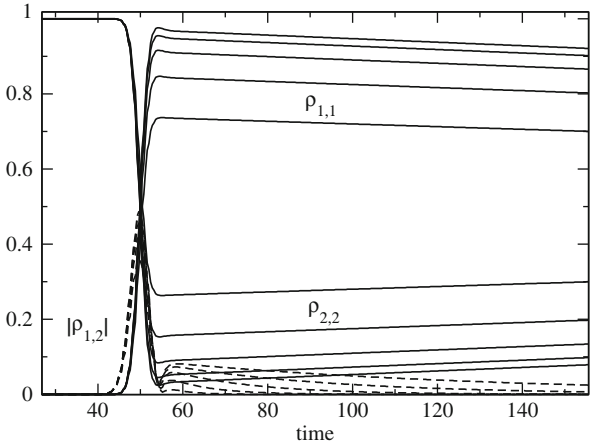

Fig. 19.15 Spin flip by a π-pulse. The equation of motion of the Bloch vector (19.174) is solved with the fourth-order Runge–Kutta for an interaction pulse with a Gaussian shape. The pulse is adjusted to obtain a spin flip, which is a simple model for the invert operation on a Qubit. The influence of dephasing processes is studied. Parameters are $T_1 = 2000, t_p = 3.75, V_0 = 0.5$, and $T_2 = 5, 10, 20, 40, 80$. The occupation probabilities of the two states (*solid curves*) and the coherence (*broken curves*) are shown for several values of the dephasing time

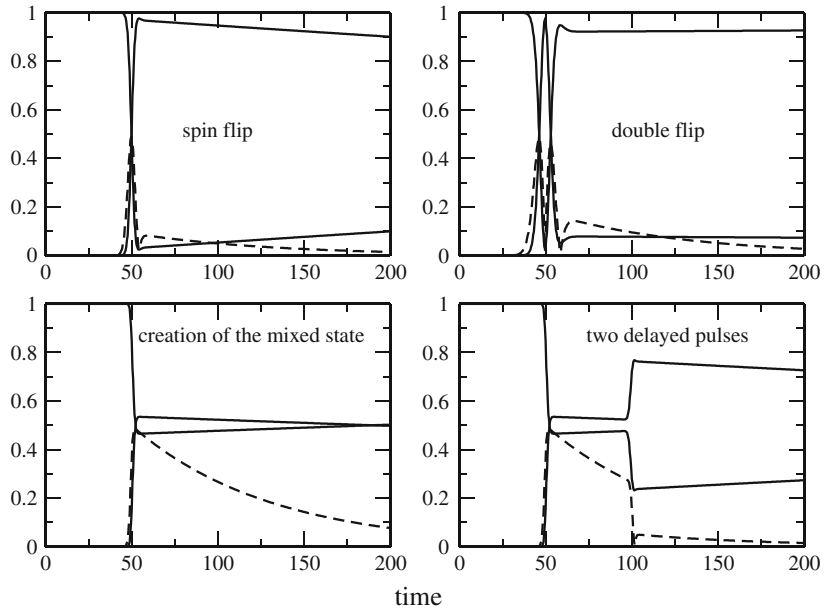

Fig. 19.16 Simulation of $\frac{N}{2}\pi$ pulses. The pulse duration is varied to obtain multiple spin flips or to create the coherently mixed state. Finally a simple measurement of the coherence decay with two delayed π-pulses is simulated, where the first pulse creates the coherently mixed state and the second pulse measures the remaining coherence after a variable delay time

hand a $\frac{\pi}{2}$-pulse converts a pure state into a completely mixed state and vice versa (Figs. 19.15, 19.16).

Problems

Problem 19.1 Schrödinger Equation

In this computer experiment we solve the Schrödinger equation for a particle in the potential $V(x)$ for an initially localized Gaussian wave packet $\psi(t = 0, x) \sim \exp(-a(x - x_0)^2)$. The potential is either a harmonic parabola or a fourth-order double well. The initial width and position of the wave packet can be varied under the constraint $V(x_0) = 0$.

Try to generate the time-independent ground state wave function for the harmonic oscillator

Observe the dispersion of the wave packet for different conditions and try to generate a moving wave packet with little dispersion.

Try to observe tunneling in the double well potential.

Problem 19.2 Two-Level System

In this computer experiment a two-level system is simulated. Amplitude and frequency of an external field can be varied as well as the energy gap between the two levels (see Fig. 19.3).
Compare the time evolution at resonance and away from it.

Problem 19.3 Three-Level System

In this computer experiment a three-level system is simulated.
Verify that the system behaves like an effective two-state system if the intermediate state is higher in energy than initial and final states (see Fig. 19.5).

Problem 19.4 Ladder Model

In this computer experiment the ladder model is simulated. The coupling strength and the spacing of the final states can be varied.
Check the validity of the exponential decay approximation (see Fig. 19.7).

Problem 19.5 Landau–Zener Model

This computer experiment simulates the Landau–Zener model. The coupling strength and the nuclear velocity can be varied (see Fig. 19.9).
Try to find parameters for an efficient crossing of the states.

Problem 19.6 Resonance Line

In this computer experiment a two-level system with damping is simulated. The resonance curve is calculated from the steady-state occupation probabilities (see Figs. 19.13 and 19.14).
Study the dependence of the line width on the intensity (power broadening).

Problem 19.7 Spin Flip

The damped two-level system is now subject to an external pulsed field (see Figs. 19.15 and 19.16).
Try to produce a coherent superposition state ($\pi/2$ pulse) or a spin flip (π pulse).
Investigate the influence of decoherence.