5 Perturbations and Approximation Methods

In this chapter we study methods of approximation frequently used to solve quantum mechanical problems that are too difficult (or impossible) to solve analytically. We will cover both stationary (i.e., time-independent) and time-dependent perturbation techniques involving perturbations of small enough amplitude compared to the unperturbed Hamiltonian of such systems.

Some of the material presented in this chapter is taken from Auletta, Fortunato and Parisi, Chap. 10 and Cohen-Tannoudji, Diu and Laloë, Vol. II, Chaps. XI and XIII.

5.1 The Theory of Stationary Perturbations

It is very often the case in quantum mechanics that the Hamiltonian of a system is not explicitly a function of time. These are cases where we need to solve the time-independent form of the Schrödinger equation (see equation (1.56) in Chapter 1). Unfortunately, in most cases it is not possible to solve Schrödinger equation exactly to obtain analytical solutions. Physicists must then resort to methods of approximations in order to develop solutions of increasing accuracy by considering higher orders of perturbations.

We consider the case of a quantum mechanical system with an Hamiltonian such that

$$\hat{H} = \hat{H}_0 + \hat{W}', \tag{5.1}$$

where $\hat{H}_0$ is the unperturbed Hamiltonian, for which we know the eigenvectors and eigenvalues, and $\hat{W}$ is a perturbation such that $\hat{W}' \ll \hat{H}_0$ (but see below). We assume that both $\hat{H}_0$ and $\hat{W}'$ are independent of time. This lack of dependence on time and the difference in importance between the two components of the Hamiltonian is the basis for the ***theory of stationary perturbations***.

Given the relative smallness of the perturbation we normalize it in relation to $\hat{H}_0$ and introduce a real parameter $\lambda \ll 1$ such that

$$\hat{W}' = \lambda \hat{W} \tag{5.2}$$

and

$$\hat{H}(\lambda) = \hat{H}_0 + \lambda \hat{W}. \tag{5.3}$$

We will assume that the unperturbed Hamiltonian $\hat{H}_0$ possesses a set of eigenvectors $\left\{ \left| u_n^i \right\rangle \right\}$, which also forms a basis (i.e, $\left\langle u_n^i \middle| u_m^j \right\rangle = \delta_{nm}\delta_{ij}$ and $\sum_{n,i} \left| u_n^i \right\rangle\!\left\langle u_n^i \right|$), and associated eigenvalues E_n^0, where $i = 1, \ldots, g_n$ stands for the potential degeneracy of the corresponding energy levels. The problem consists in finding the new (perturbed) eigenvectors $|\psi(\lambda)\rangle$ and energies $E(\lambda)$ corresponding to equation (5.3) for the perturbed Hamiltonian. We propose to achieve this through a power series expansion for these quantities. More precisely, our new eigenvalue problem is defined by

$$\hat{H}(\lambda)|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle, \tag{5.4}$$

with

$$\begin{aligned} |\psi(\lambda)\rangle &= \sum_{j=0}^{\infty} \lambda^j |j\rangle \qquad (5.5) \\ E(\lambda) &= \sum_{j=0}^{\infty} \lambda^j \varepsilon_j, \qquad (5.6) \end{aligned}$$

where $|j\rangle$ and ε_j are to be evaluated in terms of $|u_n^i\rangle$ and E_n^0. We also require that $\langle\psi(\lambda)\,|\,\psi(\lambda)\rangle = 1$. It is important to realize that the normalization condition only defines $|\psi(\lambda)\rangle$ up to a global phase factor. That is, if $|\psi(\lambda)\rangle$ is a suitable expansion, then so is $e^{i\phi}|\psi(\lambda)\rangle$, with ϕ an arbitrary phase parameter. We will therefore fix the global phase by choosing $\langle 0\,|\,\psi(\lambda)\rangle$ to be a real quantity. Furthermore, since λ is also chosen to be real, it follows from this phase condition and equation (5.5) that $\langle 0\,|\,j\rangle$ must be real for all j.

We now insert equations (5.5)-(5.6) into equation (5.4) to get

$$\begin{aligned} \left(\hat{H}_0 + \lambda\hat{W}\right)\left(\sum_{j=0}^{\infty}\lambda^j|j\rangle\right) &= \left(\sum_{k=0}^{\infty}\lambda^k\varepsilon_k\right)\left(\sum_{j=0}^{\infty}\lambda^j|j\rangle\right) \\ &= \sum_{j,k=0}^{\infty}\lambda^{j+k}\varepsilon_k|j\rangle, \qquad (5.7) \end{aligned}$$

which can be transformed to

$$\sum_{j=0}^{\infty}\lambda^j\left[\left(\hat{H}_0 - \varepsilon_0\right)|j\rangle + \left(\hat{W} - \varepsilon_1\right)|j-1\rangle - \sum_{k=2}^{\infty}\varepsilon_k|j-k\rangle\right] = 0 \tag{5.8}$$

with the understanding that $|m\rangle = 0$ for $m < 0$. Since this equation must be verified for any value of λ, it must be that all terms in equation (5.8) (i.e., for any order j) vanish. We therefore find that for the term of order j

$$\left(\hat{H}_0 - \varepsilon_0\right)|j\rangle + \left(\hat{W} - \varepsilon_1\right)|j-1\rangle - \varepsilon_2|j-2\rangle - \ldots - \varepsilon_j|0\rangle = 0. \tag{5.9}$$

However, these equations cannot be solved independently since they are constrained by the aforementioned normalization condition of the ket $|\psi(\lambda)\rangle$. That is,

$$\begin{aligned}
\langle \psi(\lambda) \,|\, \psi(\lambda) \rangle &= \sum_{j,k=0}^{\infty} \lambda^{j+k} \langle j \,|\, k \rangle \\
&= \sum_{m=0}^{\infty} \lambda^{m} \left(\sum_{n=0}^{m} \langle m-n \,|\, n \rangle \right) \\
&= 1 \qquad (5.10)
\end{aligned}$$

Again, this equation cannot depend on λ and we must have

$$\sum_{n=0}^{m} \langle m-n \,|\, n \rangle = 0. \qquad (5.11)$$

For example, up to order 2 equation (5.10) yields

$$\langle 0 \,|\, 0 \rangle + \lambda \left(\langle 1 \,|\, 0 \rangle + \langle 0 \,|\, 1 \rangle \right) + \lambda^2 \left(\langle 2 \,|\, 0 \rangle + \langle 1 \,|\, 1 \rangle + \langle 0 \,|\, 2 \rangle \right) = 1, \qquad (5.12)$$

or

$$\begin{aligned}
\langle 0 \,|\, 0 \rangle &= 1 \qquad (5.13) \\
\langle 1 \,|\, 0 \rangle + \langle 0 \,|\, 1 \rangle &= 0 \qquad (5.14) \\
\langle 2 \,|\, 0 \rangle + \langle 1 \,|\, 1 \rangle + \langle 0 \,|\, 2 \rangle &= 0. \qquad (5.15)
\end{aligned}$$

But our choice for the phase condition (i.e, $\langle 0 \,|\, j \rangle$ is real) implies that $\langle 0 \,|\, j \rangle = \langle j \,|\, 0 \rangle$, and therefore

$$\begin{aligned}
\langle 1 \,|\, 0 \rangle &= \langle 0 \,|\, 1 \rangle \\
&= 0 \qquad (5.16) \\
\langle 2 \,|\, 0 \rangle &= \langle 0 \,|\, 2 \rangle \\
&= -\frac{1}{2} \langle 1 \,|\, 1 \rangle . \qquad (5.17)
\end{aligned}$$

More generally, it is easy to see from equation (5.11) that for the term of order j

$$\begin{aligned}
\langle j \,|\, 0 \rangle &= \langle 0 \,|\, j \rangle \\
&= -\frac{1}{2} \sum_{n=1}^{m-1} \langle m-n \,|\, n \rangle \\
&= -\frac{1}{2} \left(\langle j-1 \,|\, 1 \rangle + \langle j-2 \,|\, 2 \rangle + \ldots + \langle 2 \,|\, j-2 \rangle + \langle 1 \,|\, j-1 \rangle \right). \qquad (5.18)
\end{aligned}$$

Returning to our example for calculations up to the second order, equation (5.9) yields

$$\begin{aligned}
\hat{H}_0 \left|0\right\rangle - \varepsilon_0 \left|0\right\rangle &= 0 & (5.19)\\
\left(\hat{H}_0 - \varepsilon_0\right) \left|1\right\rangle + \left(\hat{W} - \varepsilon_1\right) \left|0\right\rangle &= 0 & (5.20)\\
\left(\hat{H}_0 - \varepsilon_0\right) \left|2\right\rangle + \left(\hat{W} - \varepsilon_1\right) \left|1\right\rangle - \varepsilon_2 \left|0\right\rangle &= 0. & (5.21)
\end{aligned}$$

The first of these relations makes it clear that ε_0 is an eigenvalue of $\hat{H}_0$, which we are free to choose. The complexity of the analysis will vary depending on whether this eigenvalue is degenerate or not.

5.1.1 Perturbation of a Non-degenerate Energy Level

For a non-degenerate energy level, say, E_n^0, is associated only one ket $\left|u_n\right\rangle$ and we write

$$\begin{aligned}
\varepsilon_0 &= E_n^0 & (5.22)\\
\left|0\right\rangle &= \left|u_n\right\rangle. & (5.23)
\end{aligned}$$

This is, evidently, the energy associated to the unperturbed system. The first order correction to this value is obtained by projecting equation (5.20) on $\left|u_n\right\rangle = \left|0\right\rangle$

$$\begin{aligned}
\left\langle u_n \middle| \left(\hat{H}_0 - E_n^0\right) \middle| 1\right\rangle + \left\langle u_n \middle| \left(\hat{W} - \varepsilon_1\right) \middle| u_n\right\rangle &= \left\langle u_n \middle| \left(\hat{W} - \varepsilon_1\right) \middle| u_n\right\rangle\\
&= 0, & (5.24)
\end{aligned}$$

since $\left\langle u_n\right| \hat{H}_0 = \left\langle u_n\right| E_n^0$, and we thus find that

$$\varepsilon_1 = \left\langle u_n \middle| \hat{W} \middle| u_n\right\rangle. \tag{5.25}$$

If we next consider another eigenvector $\left|u_m^i\right\rangle$ (i.e., $m \neq n$), potentially of a degenerate subspace, of $\hat{H}_0$, we can calculate through another projection of equation (5.20)

$$\begin{aligned}
\left\langle u_m^i \middle| \left(\hat{H}_0 - E_n^0\right) \middle| 1\right\rangle + \left\langle u_m^i \middle| \left(\hat{W} - \varepsilon_1\right) \middle| u_n\right\rangle &= \left(E_m^0 - E_n^0\right) \left\langle u_m^i \middle| 1\right\rangle\\
&\quad + \left\langle u_m^i \middle| \hat{W} \middle| u_n\right\rangle\\
&= 0, & (5.26)
\end{aligned}$$

since $\left\langle u_m^i \middle| u_n\right\rangle = 0$, or

$$\left\langle u_m^i \middle| 1\right\rangle = \frac{1}{E_n^0 - E_m^0} \left\langle u_m^i \middle| \hat{W} \middle| u_n\right\rangle. \tag{5.27}$$

Combining all such coefficients with equation (5.14) we can write

$$|1\rangle = \sum_{m\neq n}\sum_{i=1}^{g_m} \frac{\left\langle u_m^i \middle| \hat{W} \middle| u_n \right\rangle}{E_n^0 - E_m^0} \left|u_m^i\right\rangle . \tag{5.28}$$

We can use a similar technique to determine the second order correction. We first calculate ε_2 by projecting equation (5.21) on $|u_n\rangle = |0\rangle$

$$\left\langle u_n \middle| \left(\hat{H}_0 - E_n^0\right) \middle| 2 \right\rangle + \left\langle u_n \middle| \left(\hat{W} - \varepsilon_1\right) \middle| 1 \right\rangle - \varepsilon_2 \left\langle u_n \,\middle|\, u_n \right\rangle = 0, \tag{5.29}$$

from which we get (remember that $\langle u_n \,|\, 1\rangle = 0$ from equation (5.14))

$$\begin{aligned} \varepsilon_2 &= \left\langle u_n \middle| \hat{W} \middle| 1 \right\rangle \\ &= \sum_{m\neq n}\sum_{i=1}^{g_m} \frac{\left|\left\langle u_m^i \middle| \hat{W} \middle| u_n \right\rangle\right|^2}{E_n^0 - E_m^0}. \end{aligned} \tag{5.30}$$

The energy $E_n(\lambda)$ of the perturbed system, approximate to the second order, is thus given by

$$E_n(\lambda) \simeq E_n^0 + \left\langle u_n \middle| \hat{W}' \middle| u_n \right\rangle + \sum_{m\neq n}\sum_{i=1}^{g_m} \frac{\left|\left\langle u_m^i \middle| \hat{W}' \middle| u_n \right\rangle\right|^2}{E_n^0 - E_m^0}. \tag{5.31}$$

Finally, we project equation (5.21) on $\left|u_m^i\right\rangle$, still with $m \neq n$, such that

$$\left\langle u_m^i \middle| \left(\hat{H}_0 - E_n^0\right) \middle| 2 \right\rangle + \left\langle u_m^i \middle| \left(\hat{W} - \varepsilon_1\right) \middle| 1 \right\rangle - \varepsilon_2 \left\langle u_m^i \,\middle|\, u_n \right\rangle \;=\; 0. \tag{5.32}$$

Using $\left\langle u_m^i \,\middle|\, u_n \right\rangle = 0$ for $m \neq n$, and equations (5.25) and (5.28), this relation is transformed to

$$\begin{aligned} \left\langle u_m^i \,\middle|\, 2 \right\rangle &= \frac{1}{E_n^0 - E_m^0}\left(\left\langle u_m^i \middle| \hat{W} \middle| 1 \right\rangle - \varepsilon_1 \left\langle u_m^i \,\middle|\, 1 \right\rangle\right) \\ &= \frac{1}{E_n^0 - E_m^0} \sum_{p\neq n}\sum_{j=1}^{g_p} \frac{\left\langle u_p^j \middle| \hat{W} \middle| u_n \right\rangle}{E_n^0 - E_p^0} \left(\left\langle u_m^i \middle| \hat{W} \middle| u_p^j \right\rangle - \left\langle u_n \middle| \hat{W} \middle| u_n \right\rangle \left\langle u_m^i \,\middle|\, u_p^j \right\rangle\right) \\ &= \frac{1}{E_n^0 - E_m^0} \sum_{p\neq n}\sum_{j=1}^{g_p} \frac{\left\langle u_p^j \middle| \hat{W} \middle| u_n \right\rangle}{E_n^0 - E_p^0} \left(\left\langle u_m^i \middle| \hat{W} \middle| u_p^j \right\rangle - \left\langle u_n \middle| \hat{W} \middle| u_n \right\rangle \delta_{mp}\delta_{ij}\right). \end{aligned} \tag{5.33}$$

Combining equations (5.23), (5.28) and (5.33) we then find that, to the second order,

$$\begin{aligned} |\psi(\lambda)\rangle &\simeq |u_n\rangle \\ &\quad + \sum_{m\neq n}\sum_{i=1}^{g_m} \frac{\left\langle u_m^i \middle| \hat{W}' \middle| u_n \right\rangle}{E_n^0 - E_m^0} \left|u_m^i\right\rangle \end{aligned}$$

$$+\sum_{m\neq n}\sum_{i=1}^{g_m}\left[\frac{1}{E_n^0-E_m^0}\sum_{p\neq n}\sum_{j=1}^{g_p}\frac{\left\langle u_p^j\middle|\hat{W}'\middle|u_n\right\rangle}{E_n^0-E_p^0}\left(\left\langle u_m^i\middle|\hat{W}'\middle|u_p^j\right\rangle-\left\langle u_n\middle|\hat{W}'\middle|u_n\right\rangle\delta_{mp}\delta_{ij}\right)\right]\left|u_m^i\right\rangle, \tag{5.34}$$

where the expansion was written with increasing order of approximation on successive lines.

Equations (5.31) and (5.34) are the result of our stationary perturbations approximation to the order 2. We note the following facts: *i)* our earlier condition that $\hat{W}'\ll\hat{H}_0$ is necessary but insufficient since it is the smallness of the matrix elements $\left\langle u_m^i\middle|\hat{W}'\middle|u_n\right\rangle$ of the Hamiltonian perturbation relative to the differences between E_n^0 and the other energy levels E_m^i that matters (i.e., we need $\left\langle u_m^i\middle|\hat{W}'\middle|u_n\right\rangle\ll E_n^0-E_m^0$), and *ii)* the unperturbed eigenvectors $|u_n\rangle$ and eigenvalues E_n will only be affected by the perturbation if it couples $|u_n\rangle$ to $\left|u_m^i\right\rangle$ (i.e., $\left\langle u_m^i\middle|\hat{W}'\middle|u_n\right\rangle\neq 0$).

5.1.2 Perturbation of a Degenerate Energy Level

In cases where we choose a level $\varepsilon_0=E_n^0$ that is degenerate, i.e., there are several eigenvectors $\left|u_n^i\right\rangle$ $(i=1,2,\ldots,g_n)$ of the unperturbed Hamiltonian $\hat{H}_0$ sharing this eigenvalue, and equation (5.19)

$$\hat{H}_0\left|0\right\rangle=\varepsilon_0\left|0\right\rangle \tag{5.35}$$

is not sufficient to uniquely determine $|0\rangle$. This is because any of the kets $\left|u_n^i\right\rangle$ or their linear combinations will verify this equation. Here, we will solve this problem by limiting ourselves to the first order for the energies and zeroth order for the eigenvectors of $\hat{H}$.

We first project equations (5.20) on one of the eigenvectors $\left|u_n^i\right\rangle$

$$\left\langle u_n^i\middle|\left(\hat{H}_0-E_n^0\right)\middle|1\right\rangle+\left\langle u_n^i\middle|\left(\hat{W}-\varepsilon_1\right)\middle|0\right\rangle=0 \tag{5.36}$$

or

$$\left\langle u_n^i\middle|\hat{W}\middle|0\right\rangle=\varepsilon_1\left\langle u_n^i\middle|0\right\rangle. \tag{5.37}$$

We now make use of the projector associated with the subspace of energy E_n^0, i.e., $\sum_{j=1}^{g_n}\left|u_n^j\right\rangle\left\langle u_n^j\right|$, and insert it on the left-hand side of equation (5.36) to get

$$\sum_{j=1}^{g_n}\left\langle u_n^i\middle|\hat{W}\middle|u_n^j\right\rangle\left\langle u_n^j\middle|0\right\rangle=\varepsilon_1\left\langle u_n^i\middle|0\right\rangle. \tag{5.38}$$

Evidently the quantities $\left\langle u_n^i\middle|\hat{W}\middle|u_n^j\right\rangle$ are the elements of the $g_n\times g_n$ (sub)matrix associated to the subspace of E_n^0, and $\left\langle u_n^j\middle|0\right\rangle$ are the elements of vector $|0\rangle$ also limited to that subspace. If we define these quantities with $W_{n,ij}\equiv\left\langle u_n^i\middle|\hat{W}\middle|u_n^j\right\rangle$ and $c_j\equiv\left\langle u_n^j\middle|0\right\rangle$, then this equation can be written as

$$\sum_{j=1}^{g_n} \left(W_{n,ij} - \varepsilon_1 \delta_{ij}\right) c_j = 0. \tag{5.39}$$

Equation (5.39) is clearly that of an eigenvalue problem. It follows that to determine the eigenvectors to order 0 and eigenvalues to order 1 for the unperturbed vectors $\left|u_n^i\right\rangle$ and energy level E_n^0 of the Hamiltonian $\hat{H}$, we simply need to diagonalize the matrix of elements $W_{n,ij} \equiv \left\langle u_n^i \middle| \hat{W} \middle| u_n^j \right\rangle$. For example, in the case where E_n^0 is twice degenerate the formalism presented in Section 1.6 of Chapter 1 can be used.

Exercise 5.1. We consider the case of two spin-1/2 particules of spin $\hat{\mathbf{S}}_1$ and $\hat{\mathbf{S}}_2$ subjected to external magnetic field $\mathbf{B} = B_0 \mathbf{e}_z$. Treat B_0 as a classical quantity and assume that the particles are fixed in space.

a) Calculate the Hamiltonian $\hat{H}_0$ resulting from the interaction of the particles with the external magnetic field, as well as from the interaction Hamiltonian $\hat{W}$ between them.

b) Assuming that the particles have different gyromagnetic ratios (i.e., $\gamma_1 \neq \gamma_2$), calculate the different states and energy levels due to $\hat{H}_0$, and the first order corrections brought about by $\hat{W}$ to the energy levels and to the state with of lowest energy.

c) Now assume that $\gamma_1 = \gamma_2$ and calculate the first order corrections brought about by $\hat{W}$ to the energy levels.

Solution.

a) The unperturbed Hamiltonian $\hat{H}_0$ is easily calculated through the magnetic dipole interaction between the external magnetic field and the particles' spins. That is, with $\hat{\mathbf{M}}_j$ the magnetic dipole moment of particle j,

$$\begin{aligned} \hat{H}_0 &= -\left(\hat{\mathbf{M}}_1 + \hat{\mathbf{M}}_2\right) \cdot \mathbf{B} \\ &= -\left(\gamma_1 \hat{\mathbf{S}}_1 + \gamma_2 \hat{\mathbf{S}}_2\right) \cdot \mathbf{B} \\ &= \omega_1 \hat{S}_{1z} + \omega_2 \hat{S}_{2z}, \end{aligned} \tag{5.40}$$

where $\omega_j = -\gamma_j B_0$. The magnetic field due to a magnetic dipole at a distance r is given by

$$\hat{\mathbf{B}}_j = \frac{\mu_0}{4\pi r^3} \left[3\mathbf{n}\left(\mathbf{n} \cdot \hat{\mathbf{M}}_j\right) - \hat{\mathbf{M}}_j\right], \tag{5.41}$$

with $\mathbf{n} = \mathbf{r}/r$. The interaction Hamiltonian between the two spins is therefore

$$\begin{aligned} \hat{W} &= -\gamma_1 \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{B}}_2 \\ &= -\gamma_2 \hat{\mathbf{S}}_2 \cdot \hat{\mathbf{B}}_1 \\ &= \frac{\mu_0}{4\pi r^3} \gamma_1 \gamma_2 \left[\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 - 3\left(\hat{\mathbf{S}}_1 \cdot \mathbf{n}\right)\left(\hat{\mathbf{S}}_2 \cdot \mathbf{n}\right)\right] \\ &= \xi(r)\left(T_0 + T_0' + T_1 + T_{-1} + T_2 + T_{-2}\right), \end{aligned} \tag{5.42}$$

with $\xi(r) = -\gamma_1\gamma_2\mu_0/\left(4\pi r^3\right)$ and, if we define $\mathbf{n} = \sin(\theta)\cos(\phi)\,\mathbf{e}_x + \sin(\theta)\sin(\phi)\,\mathbf{e}_y + \cos(\theta)\,\mathbf{e}_z$,

$$\begin{aligned}
\hat{T}_0 &= \left[3\cos^2(\theta) - 1\right]\hat{S}_{1z}\hat{S}_{2z} &(5.43)\\
\hat{T}_0' &= -\frac{1}{4}\left[3\cos^2(\theta) - 1\right]\left(\hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+}\right) &(5.44)\\
\hat{T}_1 &= \frac{3}{2}\sin(\theta)\cos(\theta)\,e^{-i\phi}\left(\hat{S}_{1z}\hat{S}_{2+} + \hat{S}_{1+}\hat{S}_{2z}\right) &(5.45)\\
\hat{T}_{-1} &= \frac{3}{2}\sin(\theta)\cos(\theta)\,e^{i\phi}\left(\hat{S}_{1z}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2z}\right) &(5.46)\\
\hat{T}_2 &= \frac{3}{4}\sin^2(\theta)\,e^{-i2\phi}\hat{S}_{1+}\hat{S}_{2+} &(5.47)\\
\hat{T}_{-2} &= \frac{3}{4}\sin^2(\theta)\,e^{i2\phi}\hat{S}_{1-}\hat{S}_{2-}. &(5.48)
\end{aligned}$$

These equations were derived using

$$\begin{aligned}
\hat{S}_{jx} &= \frac{1}{2}\left(\hat{S}_{j+} + \hat{S}_{j-}\right) &(5.49)\\
\hat{S}_{jy} &= \frac{i}{2}\left(\hat{S}_{j-} - \hat{S}_{j+}\right). &(5.50)
\end{aligned}$$

b) The different spin states of the system are given by the four different kets $|\varepsilon_1, \varepsilon_2\rangle$, with $\varepsilon_1, \varepsilon_2 = \pm$. The time-independent Schrödinger equation for the unperturbed Hamiltonian is

$$\begin{aligned}
\hat{H}_0\,|\varepsilon_1, \varepsilon_2\rangle &= \left(\omega_1\hat{S}_{1z} + \omega_2\hat{S}_{2z}\right)|\varepsilon_1, \varepsilon_2\rangle\\
&= \frac{\hbar}{2}\left(\varepsilon_1\omega_1 + \varepsilon_2\omega_2\right)|\varepsilon_1, \varepsilon_2\rangle. &(5.51)
\end{aligned}$$

The four energy levels are therefore

$$\begin{aligned}
E^0_{-,-} &= -\frac{\hbar}{2}\left(\omega_1 + \omega_2\right) &(5.52)\\
E^0_{-,+} &= -\frac{\hbar}{2}\left(\omega_1 - \omega_2\right) &(5.53)\\
E^0_{+,-} &= \frac{\hbar}{2}\left(\omega_1 - \omega_2\right) &(5.54)\\
E^0_{+,+} &= \frac{\hbar}{2}\left(\omega_1 + \omega_2\right). &(5.55)
\end{aligned}$$

We know from equation (5.31) that the first order correction to the energies are given by $\left\langle \varepsilon_1, \varepsilon_2 \middle| \hat{W} \middle| \varepsilon_1, \varepsilon_2 \right\rangle$. Since we are looking for the diagonal matrix elements of $\hat{W}$, we need to find the terms in equations (5.43)-(5.48) that do not cause a transition between two different states. Because of this we choose any operator that do not depend on $\hat{S}_{j\pm}$; $\hat{T}_0$ is the only such operator. Defining $\Omega = \xi(r)\left[3\cos^2(\theta) - 1\right]\hbar/4$, we have

$$\left\langle \varepsilon_1, \varepsilon_2 \left| \hat{W} \right| \varepsilon_1, \varepsilon_2 \right\rangle = \varepsilon_1 \varepsilon_2 \hbar\Omega, \tag{5.56}$$

and the perturbed energy levels become

$$\begin{aligned}
E^1_{-,-} &= -\frac{\hbar}{2}(\omega_1 + \omega_2) + \hbar\Omega && (5.57)\\
E^1_{-,+} &= -\frac{\hbar}{2}(\omega_1 - \omega_2) - \hbar\Omega && (5.58)\\
E^1_{+,-} &= \frac{\hbar}{2}(\omega_1 - \omega_2) - \hbar\Omega && (5.59)\\
E^1_{+,+} &= \frac{\hbar}{2}(\omega_1 + \omega_2) + \hbar\Omega. && (5.60)
\end{aligned}$$

From equation (5.34) we determined the perturbed ket associated with the $E^0_{-,-}$ energy level to be

$$\begin{aligned}
|\psi_{-,-}\rangle &= |-,-\rangle + \xi(r)\left[\frac{\left\langle -,+\left|\hat{T}_1\right|-,-\right\rangle}{E^0_{-,-} - E^0_{-,+}}|-,+\rangle + \right.\\
&\quad \left. + \frac{\left\langle +,-\left|\hat{T}_1\right|-,-\right\rangle}{E^0_{-,-} - E^0_{+,-}}|+,-\rangle + \frac{\left\langle +,+\left|\hat{T}_2\right|-,-\right\rangle}{E^0_{-,-} - E^0_{+,+}}|+,+\rangle\right]\\
&= |-,-\rangle - \xi(r)\left\{\frac{3}{4}\hbar\sin(\theta)\cos(\theta)\left[\frac{e^{-i\phi}|-,+\rangle}{2(\omega_2 - 2\Omega)} + \frac{e^{i\phi}|+,-\rangle}{2(\omega_1 - 2\Omega)}\right]\right.\\
&\quad \left. + \frac{3\hbar\sin^2(\theta)\, e^{-i2\phi}}{4(\omega_1 + \omega_2)}|+,+\rangle\right\}. && (5.61)
\end{aligned}$$

Similar perturbed states could be calculated for the three other combinations of $|\varepsilon_1, \varepsilon_2\rangle$. It is apparent that the four perturbed states are not orthogonal to one another.

c) When the two particles have the same gyromagnetic moment (but are assumed distinguishable) $\gamma = \gamma_1 = \gamma_2$ and $\omega = \omega_1 = \omega_2$, and we have

$$\begin{aligned}
E^0_{-,-} &= -\hbar\omega && (5.62)\\
E^0_{-,+} &= E^0_{+,-}\\
&= 0 && (5.63)\\
E^0_{+,+} &= \hbar\omega. && (5.64)
\end{aligned}$$

For the non-degenerate levels we have

$$\begin{aligned}\left\langle -,- \middle| \hat{W} \middle| -,- \right\rangle &= \left\langle +,+ \middle| \hat{W} \middle| +,+ \right\rangle \\ &= \hbar\Omega, \end{aligned} \tag{5.65}$$

as before. For the degenerate levels, according to the material covered in Section 5.1.2 we need to diagonalize the matrix associated to $\hat{W}$ in this two-dimensional subspace. We therefore calculate the different matrix elements

$$\begin{aligned}\left\langle +,- \middle| \hat{W} \middle| +,- \right\rangle &= \left\langle -,+ \middle| \hat{W} \middle| -,+ \right\rangle \\ &= \left\langle +,- \middle| \hat{T}_0 \middle| +,- \right\rangle \\ &= -\hbar\Omega \end{aligned} \tag{5.66}$$

$$\begin{aligned}\left\langle +,- \middle| \hat{W} \middle| -,+ \right\rangle &= \left\langle -,+ \middle| \hat{W} \middle| +,- \right\rangle \\ &= \left\langle +,- \middle| \hat{T}_0' \middle| -,+ \right\rangle \\ &= -\hbar\Omega, \end{aligned} \tag{5.67}$$

and we need to diagonalize the following matrix

$$\hat{W}_{+,-} = -\hbar\Omega \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}. \tag{5.68}$$

It is straightforward to determine that the eigenvalues of this matrix are 0 and $-2\hbar\Omega$, with for eigenvectors

$$|\psi_A\rangle = \frac{1}{\sqrt{2}}\left(|+,-\rangle - |-,+\rangle\right) \tag{5.69}$$

$$|\psi_S\rangle = \frac{1}{\sqrt{2}}\left(|+,-\rangle + |-,+\rangle\right), \tag{5.70}$$

respectively. Finally, the perturbed energy levels are

$$E^1_{-,-} = -\hbar\left(\omega - \Omega\right) \tag{5.71}$$

$$E^1_S = -2\hbar\Omega \tag{5.72}$$

$$E^1_A = 0 \tag{5.73}$$

$$E^1_{+,+} = \hbar\left(\omega + \Omega\right), \tag{5.74}$$

the degeneracy is thus lifted.

5.2 Time-dependent Perturbations Theory

We now consider the more general case when, although the unperturbed Hamiltonian $\hat{H}_0$ is not, the perturbation $\hat{W}'(t) = \lambda\hat{W}(t)$ is time-dependent. As before, we denote the eigenvalues and eigenvectors of $\hat{H}_0$ with E_n^0 and $|u_n\rangle$, respectively. These kets are stationary states and their set $\{|u_n\rangle\}$ forms a basis.

Our goal is to solve the Schrödinger equation

$$i\hbar\frac{d}{dt}|\psi(t)\rangle = \left[\hat{H}_0 + \lambda\hat{W}(t)\right]|\psi(t)\rangle \tag{5.75}$$

using the eigenvectors of $\hat{H}_0$ for an expansion of the state vector

$$|\psi(t)\rangle = \sum_n c_n(t)\, e^{-iE_n^0 t/\hbar}|u_n\rangle . \tag{5.76}$$

This equation is slightly different to the formal expansion introduced in Chapter 1 (see equation (1.58)) where the coefficients c_n are time-independent. Its form is justified by the fact that when $\lambda = 0$ the coefficients $c_n(t)$ lose their time dependency and becomes constant, while when $\lambda \ll 1$ we would expect them to be slowly varying with time.

Inserting equation (5.76) into the Schrödinger equation and projecting on $|u_k\rangle$, we have

$$i\hbar\frac{d}{dt}c_k(t)\, e^{-iE_k^0 t/\hbar} + E_k^0 c_k(t)\, e^{-iE_k^0 t/\hbar} = E_k^0 c_k(t)\, e^{-iE_k^0 t/\hbar} + \lambda\sum_n W_{kn}(t)\, c_n(t)\, e^{-iE_n^0 t/\hbar} \tag{5.77}$$

with $W_{kn} = \left\langle u_k \middle| \hat{W} \middle| u_n \right\rangle$. Multiplying on both sides by $e^{iE_k^0 t/\hbar}$ we get

$$i\hbar\frac{d}{dt}c_k(t) = \lambda\sum_n W_{kn}(t)\, c_n(t)\, e^{i\omega_{kn}t/\hbar} \tag{5.78}$$

where we introduced the Bohr frequency $\omega_{kn} = \left(E_k^0 - E_n^0\right)/\hbar$. This is the system of differential equations we need to solve. We propose to achieve this using the following power series in λ

$$c_k(t) = \sum_{j=0}^{\infty}\lambda^j c_k^{(j)}(t), \tag{5.79}$$

which we insert in equation (5.78)

$$i\hbar\sum_{j=0}^{\infty}\lambda^j\frac{d}{dt}c_k^{(j)}(t) \quad = \quad \sum_{j=0}^{\infty}\lambda^{j+1}\sum_n W_{kn}(t)\, e^{i\omega_{kn}t}c_n^{(j)}(t). \tag{5.80}$$

We can now match orders on both sides of equation (5.80) and get, for the zeroth order

$$i\hbar\frac{d}{dt}c_k^{(0)}(t) = 0, \tag{5.81}$$

for the first order

$$i\hbar\frac{d}{dt}c_k^{(1)}(t)=\sum_n W_{kn}(t)\,e^{i\omega_{kn}t}c_n^{(0)}(t)\,, \tag{5.82}$$

and to an arbitrary other p

$$i\hbar\frac{d}{dt}c_k^{(p)}(t)=\sum_n W_{kn}(t)\,e^{i\omega_{kn}t}c_n^{(p-1)}(t)\,. \tag{5.83}$$

The solution of order 0 corresponds to the case when $\lambda=0$, i.e., for the unperturbed time-independent system. That is, the coefficient $c_k^{(0)}$ correspond to the constant values c_k for the initial state of the system $|\psi(0)\rangle=\sum_k c_k|u_k\rangle$, before the perturbation was turned on (i.e., at $t=0$). This state and its associated coefficients are known a priori. An iterative procedure can then be adopted, where the $c_n^{(0)}$ are inserted in equation (5.82) to obtain $c_k^{(1)}$ and so to successive orders.

5.2.1 First Order Solution - Transition Probability

We assume that the system is initially in a non-degenerate state $|u_i\rangle$ and then subjected to the perturbation for $t>0$. The 0 order solution is thus

$$c_n^{(0)}(t)=\delta_{ni}. \tag{5.84}$$

Insertion in equation (5.82) for the first order solution yields

$$c_k^{(1)}(t)=\frac{1}{i\hbar}\int_0^t W_{ki}(t)\,e^{i\omega_{ki}t'}dt' \tag{5.85}$$

and

$$|\psi(t)\rangle\simeq\left[c_i^{(0)}(t)+c_i^{(1)}(t)\right]e^{-iE_i^0t/\hbar}|u_i\rangle+\sum_{n\neq i}c_n^{(1)}(t)\,e^{-iE_n^0t/\hbar}|u_n\rangle\,. \tag{5.86}$$

We can inquire on the probability of finding the system in a state $|u_k\rangle$, with $k\neq i$, at time t. This corresponds to a transition from the initial $|u_i\rangle$ to the final $|u_k\rangle$ states, which, of course, is calculated through the probability amplitude

$$\begin{aligned}S_{ik}(t) &= \lambda\langle u_k\,|\,\psi(t)\rangle\\ &= \frac{1}{i\hbar}\int_{-\infty}^t W'_{ki}(t')\,e^{i\omega_{ki}t'}dt',\end{aligned} \tag{5.87}$$

while the corresponding probability is

$$\begin{aligned}\mathcal{P}_{ik}(t) &= |S_{ik}|^2\\ &= \frac{1}{\hbar^2}\left|\int_{-\infty}^t W'_{ki}(t')\,e^{i\omega_{ki}t'}dt'\right|^2.\end{aligned} \tag{5.88}$$

Exercise 5.2. We consider the case of a sinusoidal perturbation

$$\hat{W}'(t) = \hat{W}' \cos(\omega t) \tag{5.89}$$

applied for $t > 0$. Calculate the probability of transition $\mathcal{P}_{ki}(t)$ to the first order in precision.

Solution.

The probability amplitude can be determined with

$$\begin{aligned} S_{ik}(t) &= \frac{W'_{ki}}{i\hbar} \int_0^t \cos(\omega t)\, e^{i\omega_{ki} t'} dt' \\ &= \frac{W'_{ki}}{2i\hbar} \int_0^t \left[e^{i(\omega_{ki}-\omega)t'} + e^{i(\omega_{ki}+\omega)t'} \right] dt' \\ &= \frac{W'_{ki}}{2\hbar} \left[\frac{1 - e^{i(\omega_{ki}-\omega)t}}{\omega_{ki}-\omega} + \frac{1 - e^{i(\omega_{ki}+\omega)t}}{\omega_{ki}+\omega} \right] \end{aligned} \tag{5.90}$$

When $\omega_{ki} > 0$ a significant amplitude (and probability of transition) will occur when $|\omega_{ki} - \omega| \ll \omega$, in which case the second term on the right-hand side of equation (5.90) dominates over the third. These terms are respectively called ***quasi-resonant*** and ***anti-resonant***. We therefore calculate the probability of transition using the so-called ***rotating-wave approximation***, i.e., by neglecting the anti-resonant term

$$\begin{aligned} S_{ik}(t) &\simeq \frac{W'_{ki}}{2\hbar} \left[\frac{1 - e^{i(\omega_{ki}-\omega)t}}{\omega_{ki}-\omega} \right] \\ &\simeq -\frac{itW'_{ki}}{2\hbar} e^{i(\omega_{ki}-\omega)t/2} \operatorname{sinc}\left[(\omega_{ki}-\omega)\frac{t}{2} \right], \end{aligned} \tag{5.91}$$

where $\operatorname{sinc}(x) = \sin(x)/x$, and

$$\mathcal{P}_{ik}(t) = \frac{t^2 |W'_{ki}|^2}{4\hbar^2} \operatorname{sinc}^2\left[(\omega_{ki}-\omega)\frac{t}{2} \right]. \tag{5.92}$$

This function is strongly peaked around $\omega = \omega_{ki}$ and goes to 0 at $|\omega_{ki} - \omega| = 2\pi/t$. It follows that the state $|u_k\rangle$ can only be significantly populated after an interaction time t if

$$\omega_{ki} - \frac{\pi}{t} < \omega < \omega_{ki} + \frac{\pi}{t}. \tag{5.93}$$

Since $E_k^0 > E_i^0$, it follows that the transition must result from the absorption of a quantum of energy $\hbar\omega \simeq \hbar\omega_{ki}$.

In cases when $\omega_{ki} < 0$, the roles are inverted in equation (5.90) and the term containing $\omega_{ki} + \omega$ is kept while the one containing $\omega_{ki} - \omega$ is neglected. The transition process then stems from the emission of quantum of energy $\hbar\omega \simeq \hbar\omega_{ik}$.

5.2.2 Second Order Solution

It is often the case where the first order calculations presented in the previous section do not bring any correction due to the fact the perturbation does not couple the initial and final states, i.e., $W_{ik} = \left\langle u_i \middle| \hat{W} \middle| u_k \right\rangle = 0$ for $i \neq k$. We must then resort to second order calculations since these two states may also couple to a third state $|u_j\rangle$, such that $W_{ij}W_{jk} = \left\langle u_i \middle| \hat{W} \middle| u_j \right\rangle \left\langle u_j \middle| \hat{W} \middle| u_k \right\rangle \neq 0$. The second order term would then dominate the perturbation for such processes.

More precisely, when dealing with a system prepared such that

$$c_k^{(0)}(t) = \delta_{ki}, \tag{5.94}$$

we find by inserting equation (5.85) into equation (5.83) for $p = 2$ (i.e., the second order equation) that

$$\begin{aligned} i\hbar \frac{d}{dt} c_k^{(2)}(t) &= \sum_j W_{kj}(t)\, e^{i\omega_{kj}t} c_j^{(1)}(t) \\ &= \sum_j W_{kj}(t)\, e^{i\omega_{kj}t} \left[\frac{1}{i\hbar} \int_{-\infty}^{t} W_{ji}(t')\, e^{i\omega_{ji}t'} dt' \right]. \end{aligned} \tag{5.95}$$

The transition amplitude then becomes after an interval of interaction t

$$\begin{aligned} S_{ik}(t) &= \lambda^2 c_k^{(2)} \\ &= -\frac{1}{\hbar^2} \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \sum_{j \neq i,k} W'_{kj}(t')\, W'_{ji}(t'')\, e^{i\omega_{kj}t'} e^{i\omega_{ji}t''}, \end{aligned} \tag{5.96}$$

where we note that the summation is on states $j \neq i$ and k since we assumed that $W_{ik} = 0$.

We will now concentrate on the special case where

$$\hat{W}'(t) = \hat{W}' H(t), \tag{5.97}$$

where $H(t)$ is some function akin to the ***Heaviside unit-step distribution***. That is, we make the approximation that the perturbation is "switched on" approximately at time $t = 0$ and that the interval needed to go from 0 to 1 is much smaller than the duration of the interaction. However, we also require that the switch on time is much larger than the characteristic evolution times of the system (i.e., much larger than ω_{kj}^{-1}). For example, we can set

$$H(t) = \begin{cases} 1, & \text{for } t > \varepsilon/2 \\ t/\varepsilon, & \text{for } |t| \leq \varepsilon/2 \\ 0, & \text{for } t < -\varepsilon/2, \end{cases} \tag{5.98}$$

with $\varepsilon \gg \omega_{kj}^{-1}$. Under these conditions we can calculate

$$\begin{aligned}
\int_{-\infty}^{t'} dt'' e^{i\omega_{ji}t''} H\left(t''\right) &= \frac{1}{i\omega_{ji}} e^{i\omega_{ji}t''} H\left(t''\right)\Big|_{-\infty}^{t'} - \frac{1}{i\omega_{ji}} \int_{-\infty}^{t'} dt'' e^{i\omega_{ji}t''} \frac{d}{dt''} H\left(t''\right) \\
&= \frac{1}{i\omega_{ji}} e^{i\omega_{ji}t'} - \frac{1}{i\omega_{ji}\varepsilon} \int_{-\varepsilon/2}^{\varepsilon/2} dt'' e^{i\omega_{ji}t''} \\
&= \frac{1}{i\omega_{ji}} e^{i\omega_{ji}t'} - \frac{2}{i\omega_{ji}\varepsilon} \frac{\sin\left(\omega_{ji}\varepsilon/2\right)}{\omega_{ji}} \\
&\simeq \frac{1}{i\omega_{ji}} e^{i\omega_{ji}t'} \qquad (5.99)
\end{aligned}$$

and

$$\begin{aligned}
S_{ik}\left(t\right) &= -\frac{1}{\hbar^2} \sum_{j\neq i,k} W'_{kj} W'_{ji} \int_{-\infty}^{t} dt' e^{i\omega_{kj}t'} H\left(t'\right) \int_{-\infty}^{t'} dt'' e^{i\omega_{ji}t''} H\left(t''\right) \\
&\simeq -\frac{1}{\hbar^2} \sum_{j\neq i,k} W'_{kj} W'_{ji} \int_{-\infty}^{t} dt' e^{i\omega_{kj}t'} H\left(t'\right) \int_{0}^{t'} dt'' e^{i\omega_{ji}t''} \\
&\simeq -\frac{1}{\hbar^2} \sum_{j\neq i,k} W'_{kj} W'_{ji} \frac{1}{i\omega_{ji}} \int_{-\infty}^{t} dt' e^{i\left(\omega_{kj}+\omega_{ji}\right)t'} H\left(t'\right) \\
&\simeq -\frac{1}{\hbar^2} \sum_{j\neq i,k} W'_{kj} W'_{ji} \frac{1}{i\omega_{ji}} \int_{0}^{t} dt' e^{i\omega_{ki}t'} \\
&\simeq \frac{it}{\hbar} \sum_{j\neq i,k} \frac{W'_{kj} W'_{ji}}{E_j^0 - E_i^0} e^{i\omega_{ki}t/2} \mathrm{sinc}\left(\frac{1}{2}\omega_{ki}t\right), \qquad (5.100)
\end{aligned}$$

where used $\omega_{kj} + \omega_{ji} = \omega_{ki}$ and $\int_0^t dt' e^{i\omega t'} = te^{i\omega t/2}\mathrm{sinc}\left(\frac{1}{2}\omega t\right)$. The probability of transition from $|u_i\rangle$ to $|u_k\rangle$ is thus

$$\mathcal{P}_{ik}\left(t\right) \simeq \frac{t^2}{\hbar^2} \left| \sum_{j\neq i,k} \frac{W'_{kj} W'_{ji}}{E_j^0 - E_i^0} \right|^2 \mathrm{sinc}^2\left(\frac{1}{2}\omega_{ki}t\right). \qquad (5.101)$$

We note that for $t \ll 2\pi/\omega_{ki}$ we find that the transition probability is proportional to t^2

$$\mathcal{P}_{ik}\left(t\right) \simeq \frac{t^2}{\hbar^2} \left| \sum_{j\neq i,k} \frac{W'_{kj} W'_{ji}}{E_j^0 - E_i^0} \right|^2. \qquad (5.102)$$

5.3 Coupling of a Discrete State to a Continuum and Fermi's Golden Rule

We consider the transition between an initial discrete and non-degenerate state $|u_i\rangle$ of energy $E_i^0 = 0$ to a quasi-continuum of orthogonal states $\{|u_k\rangle\}$ of energies $E_k = k\epsilon$, with k an integer and ϵ very small. We also assume that the perturbation $\hat{W}'$ can couple the initial state to any continuum state with a single (real) matrix element w, but cannot couple two continuum states. That is,

$$\left\langle u_k \middle| \hat{W}' \middle| u_i \right\rangle = w \tag{5.103}$$

$$\left\langle u_k \middle| \hat{W}' \middle| u_{k'} \right\rangle = 0, \tag{5.104}$$

with $|u_k\rangle$ and $|u_{k'}\rangle$ two continuum states, and we also assume that

$$\left\langle u_i \middle| \hat{W}' \middle| u_i \right\rangle = 0. \tag{5.105}$$

5.3.1 Short-time Behaviour: Transition Rate to the Continuum

We start by calculating the probability that the system remains in the initial state after a time t, which can be written as

$$\mathcal{P}_i(t) = 1 - \sum_{k=-\infty}^{\infty} \mathcal{P}_{ik}(t). \tag{5.106}$$

The probability of transition $\mathcal{P}_{ik}(t)$ can be calculated to the first order from equation (5.88) to be

$$\mathcal{P}_{ik}(t) = t^2 \frac{w^2}{\hbar^2} \mathrm{sinc}^2\left(\frac{k\epsilon}{2\hbar} t\right). \tag{5.107}$$

In cases where $t \ll 2\pi\hbar/\epsilon$ we can replace the summation in equation (5.106) by an integral

$$\begin{aligned} \mathcal{P}_i(t) &= 1 - t^2 \frac{w^2}{\hbar^2} \int_{-\infty}^{\infty} \mathrm{sinc}^2\left(\frac{Et}{2\hbar}\right) \frac{dE}{\epsilon} \\ &= 1 - t^2 \frac{w^2}{\hbar^2} \frac{2\hbar}{t\epsilon} \int_{-\infty}^{\infty} \mathrm{sinc}^2(x)\, dx \\ &= 1 - t \frac{2\pi w^2}{\hbar\epsilon}, \end{aligned} \tag{5.108}$$

since $\int_{-\infty}^{+\infty} \mathrm{sinc}^2(x)\, dx = \pi$. We therefore find that the ***transition rate*** Γ (to any continuum state) is independent of the period of interaction

$$\begin{aligned} \Gamma &= \frac{1}{t}\left[1 - \mathcal{P}_i(t)\right] \\ &= \frac{2\pi w^2}{\hbar\epsilon}. \end{aligned} \tag{5.109}$$

This result is different to the linear dependence in time found for the transition rate between two discrete state (see equation (5.107) for the first order when we set $k\epsilon = \omega_{ki}$, or equation (5.102) for the second order calculations).

5.3.2 Long-time Behaviour: Exponential Decay

Equation (5.109) only applies when $t \ll 2\pi w^2/(\hbar\epsilon)$. For longer timescales we must adapt our formalism to this problem. First, we expand the state of the system with

$$|\psi(t)\rangle = c_i(t)|u_i\rangle + \sum_{k'=-\infty}^{\infty} c_{k'}(t)\, e^{-ik'\epsilon t/\hbar}|u_{k'}\rangle, \tag{5.110}$$

which upon insertion in the Schrödinger equation yields

$$\begin{aligned} i\hbar\frac{d}{dt}c_i(t)|u_i\rangle + i\hbar\sum_{k'=-\infty}^{\infty}\frac{d}{dt}c_{k'}(t)\, e^{-ik'\epsilon t/\hbar}|u_{k'}\rangle &= c_i(t)\hat{W}'|u_i\rangle \\ &\quad + \sum_{k'=-\infty}^{\infty} c_{k'}(t)\, e^{-ik'\epsilon t/\hbar}\hat{W}'|u_{k'}\rangle. \end{aligned} \tag{5.111}$$

First projecting this equation on $\langle u_i|$, and then on $\langle u_k|$ while multiplying by $e^{ik\epsilon t/\hbar}$ gives

$$i\hbar\frac{d}{dt}c_i(t) = w\sum_{k=-\infty}^{\infty} c_k(t)\, e^{-ik\epsilon t/\hbar} \tag{5.112}$$

$$i\hbar\frac{d}{dt}c_k(t) = wc_i(t)\, e^{ik\epsilon t/\hbar}. \tag{5.113}$$

The last of these equations is readily inverted to find

$$c_k(t) = \frac{w}{i\hbar}\int_0^t c_i(t')\, e^{ik\epsilon t'/\hbar}dt', \tag{5.114}$$

which upon insertion in equation (5.112) yields

$$\begin{aligned} \frac{d}{dt}c_i(t) &= -\frac{w^2}{\hbar^2}\sum_{k=-\infty}^{\infty} e^{-ik\epsilon t/\hbar}\int_0^t c_i(t')\, e^{ik\epsilon t'/\hbar}dt' \\ &= -\frac{\Gamma\epsilon}{2\pi\hbar}\int_0^t dt' c_i(t')\left[\sum_{k=-\infty}^{\infty} e^{ik\epsilon(t'-t)/\hbar}\right], \end{aligned} \tag{5.115}$$

where equation (5.109) was used. If we once again assume that $t \ll 2\pi\hbar/\epsilon$, then the summation within brackets can be replaced by an integral

$$
\begin{aligned}
\sum_{k=-\infty}^{\infty} e^{ik\epsilon(t'-t)/\hbar} &= \frac{1}{\epsilon}\int_{-\infty}^{\infty} e^{iE(t'-t)/\hbar} dE \\
&= \frac{2\pi\hbar}{\epsilon}\delta\left(t'-t\right).
\end{aligned}
\tag{5.116}
$$

It follows that equation (5.115) is transformed to

$$
\begin{aligned}
\frac{d}{dt}c_i(t) &= -\Gamma\int_0^t c_i\left(t'\right)\delta\left(t'-t\right)dt' \\
&= -\Gamma\int_{-\infty}^t c_i\left(t'\right)\delta\left(t'-t\right)dt' \\
&= -\Gamma c_i(t)\int_{-\infty}^0 \delta(\lambda)\,d\lambda \\
&= -\Gamma c_i(t)\left[\frac{1}{2}\int_{-\infty}^{\infty}\delta(\lambda)\,d\lambda\right] \\
&= -\frac{1}{2}\Gamma c_i(t),
\end{aligned}
\tag{5.117}
$$

which implies that

$$
c_i(t) = e^{-\Gamma t/2} \tag{5.118}
$$

since $c_i(0) = 1$. The probability of finding the system in the initial state $|u_i\rangle$ therefore decays exponentially with time

$$
\mathcal{P}_{ik}(t) = e^{-\Gamma t} \tag{5.119}
$$

and tends to equation (5.108) when $\Gamma t \ll 1$. The form of equation (5.119) is the reason why Γ^{-1} is commonly referred to as the ***lifetime of the state*** $|u_i\rangle$.

It is interesting to insert equation (5.119) into equation (5.114) to get

$$
\begin{aligned}
c_k(t) &= \frac{w}{i\hbar}\int_0^t c_i\left(t'\right)e^{ik\epsilon t'/\hbar}dt' \\
&= \frac{w}{i\hbar}\int_0^t e^{i(k\epsilon+i\hbar\Gamma/2)t'/\hbar}dt' \\
&= w\frac{1-e^{i(k\epsilon+i\hbar\Gamma/2)t/\hbar}}{k\epsilon+i\hbar\Gamma/2},
\end{aligned}
\tag{5.120}
$$

and for the probability of finding the system in the continuum state $|u_k\rangle$ as $t\to+\infty$

$$
\mathcal{P}_k = \frac{w^2}{(k\epsilon)^2+\hbar^2\Gamma^2/4}. \tag{5.121}
$$

Furthermore, the probability of finding the system in a state of energy contained between E and $E + dE$ is given by

$$\mathcal{P}(E) = \mathcal{P}_k \frac{dE}{\epsilon} \tag{5.122}$$

since dE/ϵ is the number of states in that energy interval. It follows from equation (5.109) that

$$\frac{d}{dE}\mathcal{P}(E) = \frac{\hbar\Gamma}{2\pi}\frac{1}{E^2 + \hbar^2\Gamma^2/4}. \tag{5.123}$$

This is the so-called ***Lorentzian profile*** for the final distribution of energy in the quasi-continuum of states.

5.3.3 Fermi's Golden Rule

We have so far used the idealizations that the energy levels in the quasi-continuum were separated by a constant level ϵ and that the matrix element $\left\langle u_i \middle| \hat{W}' \middle| u_k \right\rangle = w$, with w a constant (we still have $|u_i\rangle$ for the initial discrete state and $|u_k\rangle$ a continuum state). We now abandoned these approximations. Rather, we now allow the density of state $\rho(E)$ between E and $E + dE$ to be a function of the energy, i.e.,

$$\rho(E) = \frac{dN(E)}{dE} \tag{5.124}$$

with $N(E)$ is the number of states in that energy range. We also no more consider the range of energies available to the continuum to be infinite, as was previously the case.

When dealing with a non-degenerate continuum we can generalize equations (5.106) and (5.107) for first order calculations when $t \ll 2\pi\hbar/d(E)$ to

$$\mathcal{P}_i(t) = 1 - \sum_k t^2 \frac{|W'_{ki}|^2}{\hbar^2}\mathrm{sinc}^2\left(\frac{1}{2}\omega_{ki}t\right). \tag{5.125}$$

If W'_{ki} and $\rho(E_k)$ are slowly varying in comparison to $\mathrm{sinc}(\omega_{ki}t/2)$, we can then replace the summation by an integral with $\sum_k \to \int \rho(E_k)\, dE_k$ and

$$\begin{aligned}
\mathcal{P}_i(t) &= 1 - \frac{t^2}{\hbar^2}\int dE_k \rho(E_k)\left|W'_{ki}\right|^2 \mathrm{sinc}^2\left(\frac{1}{2}\omega_{ki}t\right) \\
&= 1 - \frac{t^2}{\hbar^2}\rho(E_i)\left|W'_{ki}\right|^2 \int dE_k \mathrm{sinc}^2\left(\frac{1}{2}\omega_{ki}t\right) \\
&= 1 - \frac{2t}{\hbar}\rho(E_i)\left|W'_{ki}\right|^2 \int \mathrm{sinc}^2(x)\, dx \\
&= 1 - \frac{2\pi t}{\hbar}\rho(E_i)\left|W'_{ki}\right|^2 \\
&= 1 - \Gamma t,
\end{aligned} \tag{5.126}$$

where we used $\int \mathrm{sinc}^2(x)\,dx = \pi$ and redefined the transition rate to

$$\Gamma = \frac{2\pi}{\hbar}\left|W'_{ki}\right|^2 \rho\left(E_k = E_i\right). \tag{5.127}$$

Equation (5.127) is referred to as ***Fermi's Golden Rule***.

For a degenerate continuum other quantum numbers, beyond the energy E_k, will be needed to specify a given state. If we denote these parameters by β, then the continuum states can be labelled with $|E_k, \beta\rangle$. The presence of the degeneracy brings another integral (or summation) in the first line of equation (5.126), such that we can write

$$\begin{aligned}\mathcal{P}_i(t) &= 1 - t\int d\beta\frac{d\Gamma}{d\beta}\\ &= 1 - \Gamma t,\end{aligned} \tag{5.128}$$

with

$$\frac{d\Gamma}{d\beta} = \frac{2\pi}{\hbar}\left|\left\langle E_k,\beta\left|\hat{W}'\right|u_i\right\rangle\right|^2 \rho\left(E_k = E_i,\beta\right). \tag{5.129}$$

Exercise 5.3. Generalize Fermi's Golden Rule for a non-degenerate continuum to the case of a sinusoidal perturbation

$$\hat{W}'(t) = \hat{W}'\cos(\omega t) \tag{5.130}$$

applied for $t > 0$.

Solution.

We start with the first order calculations that yielded equation (5.90)

$$\begin{aligned}S_{ik}(t) &= \frac{W'_{ki}}{i\hbar}\int_0^t \cos(\omega t)\,e^{i\omega_{ki}t'}dt'\\ &= \frac{W'_{ki}}{2i\hbar}\int_0^t\left[e^{i(\omega_{ki}-\omega)t'} + e^{i(\omega_{ki}+\omega)t'}\right]dt'\\ &= \frac{W'_{ki}}{2\hbar}\left[\frac{1-e^{i(\omega_{ki}-\omega)t}}{\omega_{ki}-\omega} + \frac{1-e^{i(\omega_{ki}+\omega)t}}{\omega_{ki}+\omega}\right]\\ &= -\frac{itW'_{ki}}{2\hbar}\left\{e^{i(\omega_{ki}-\omega)t/2}\mathrm{sinc}\left[(\omega_{ki}-\omega)\frac{t}{2}\right]\right.\\ &\qquad\left.+e^{i(\omega_{ki}+\omega)t/2}\mathrm{sinc}\left[(\omega_{ki}+\omega)\frac{t}{2}\right]\right\}.\end{aligned} \tag{5.131}$$

If we again assume that the widths of the $\mathrm{sinc}\left[(\omega_{ki}\pm\omega)t/2\right]$ functions are much narrower than their separation ($\sim 2\omega$), then we can approximate the product

$$\mathrm{sinc}\left[(\omega_{ki}+\omega)t/2\right]\mathrm{sinc}\left[(\omega_{ki}-\omega)t/2\right] \approx 0 \tag{5.132}$$

and

$$\mathcal{P}_{ik}(t) = \frac{t^2 \left|W'_{ki}\right|^2}{4\hbar^2} \left\{ \mathrm{sinc}^2 \left[(\omega_{ki} - \omega) \frac{t}{2} \right] + \mathrm{sinc}^2 \left[(\omega_{ki} + \omega) \frac{t}{2} \right] \right\}. \tag{5.133}$$

Referring to equation (5.126) we have

$$\begin{aligned} \mathcal{P}_i(t) &= 1 - \frac{t^2}{4\hbar^2} \int dE_k \rho(E_k) \left|W'_{ki}\right|^2 \left\{ \mathrm{sinc}^2 \left[(\omega_{ki} - \omega) \frac{t}{2} \right] + \mathrm{sinc}^2 \left[(\omega_{ki} + \omega) \frac{t}{2} \right] \right\} \\ &= 1 - \frac{\pi t}{2\hbar} \left\{ \left|W'_{ki}\right|^2 \rho(E_i - \hbar\omega) + \left|W'_{ki}\right|^2 \rho(E_i + \hbar\omega) \right\} \\ &= 1 - \Gamma t, \end{aligned} \tag{5.134}$$

with

$$\Gamma = \frac{\pi}{2\hbar} \left\{ \left|W'_{ki}\right|^2 \rho(E_k = E_i - \hbar\omega) + \left|W'_{k'i}\right|^2 \rho(E_{k'} = E_i + \hbar\omega) \right\}. \tag{5.135}$$