Chapter 10

Approximation Methods for Stationary States

In more complicated situations, an exact solution of the quantum mechanical problem may not be possible. Under such circumstances one has to rely on approximative methods. For the calculation of stationary states and energy eigenvalues, these methods are perturbation theory, variational methods and the WKB-approximation. Perturbation theory can be applied when the problem to be solved deviates only slightly from an exactly solvable problem. Variational methods are useful for the calculation of ground state energies, if one has some qualitative idea about the form of the wave function, and the WKB method is suited for the almost classical limit.

10.1 Time-Independent Perturbation Theory (Rayleigh-Schrödinger)

The assumption is that the Hamiltonian H of a system can be written as

$$H = H_0 + H'. (10.1)$$

Here H_0 is called the **unperturbed** Hamiltonian, which can be treated exactly, and H' denotes the "small" perturbation. What "small" means in the context of operators has to be seen. In order to characterize an expression, we introduce a parameter λ and write

$$H = H_0 + \lambda H' \tag{10.2}$$

and set as goal to represent the energy eigenvalues and eigenstates of H as power series in λ . For solving

$$H \mid E \rangle = (H_0 + \lambda H') \mid E \rangle = E \mid E \rangle \tag{10.3}$$

we start with the ansatz

$$E = E^{(0)} + \lambda E^{(1)} + \dots = \sum_{\nu=0}^{\infty} \lambda^{\nu} E^{(\nu)}$$

$$|E\rangle = |E\rangle^{(0)} + \lambda |E\rangle^{(1)} + \dots = \sum_{\nu=0}^{\infty} \lambda^{\nu} |E\rangle^{(\nu)}.$$
(10.4)

We rewrite (10.3) as $H_0 \mid E \rangle = (E - \lambda H') \mid E \rangle$ and subtract $E^{(0)}$ from both sides

$$(H_0 - E^{(0)} | E) = (E - E^{(0)}) | E) - \lambda H' | E \rangle.$$
 (10.5)

¿From (10.4) follows

$$E - E^{(0)} = \sum_{\nu=1}^{\infty} \lambda^{\nu} E^{(\nu)} = \lambda \sum_{\nu=0}^{\infty} \lambda^{\nu} E^{(\nu+1)}.$$
 (10.6)

Inserting (10.4) and (10.6) into (10.5) gives

$$(H_0 - E^{(0)}) = \sum_{\nu=0}^{\infty} \lambda^{\nu} |E\rangle^{(\nu)} = \lambda \left[\sum_{\nu=0}^{\infty} \lambda^{\nu} E^{(\nu+1)} - H' \right] \sum_{\nu=0}^{\infty} \lambda^{\nu} |E\rangle^{(\nu)} . \tag{10.7}$$

Terms of order 0 in λ occur only on the left-hand side of (10.7) and in 0^{th} order follows with

$$\mid E\rangle \approx \mid E\rangle^{(0)} \tag{10.8}$$

$$(H_0 - E^{(0)}) \mid E\rangle^{(0)} = 0,$$
 (10.9)

which is just the eigenvalue equation for the unperturbed Hamiltonian H_0 . The first order in the perturbation expansion is obtained by equating the coefficients of λ^1 :

$$(H_0 - E^{(0)}) \mid E\rangle^{(1)} = (E^{(1)} - H') \mid E\rangle^{(0)} =: \mid \phi\rangle.$$
 (10.10)

We now consider consequences of (10.9) and (10.10).

10.1.1 Perturbation of a Non-Degenerate Eigenvalue

According to (10.9), the 0^{th} order approximation $|E\rangle^{(0)}$ is eigenstate of H_0 . One has to pick a specific eigenvalue of H_0 , from which the exact eigenvalues are supposed to be obtained, i.e., we pick ε_n (n fixed) as eigenvalues of H_0 , and ε_n is assumed to be non-generate, so that the eigenstate $|\varepsilon_n\rangle$ of

$$H_0 \mid \varepsilon_n \rangle = \varepsilon_n \mid \varepsilon_n \rangle \tag{10.11}$$

is uniquely determined up to a phase factor. With

$$E^{(0)} = \varepsilon_n \tag{10.12}$$

one obtaines from (10.9)

$$|E\rangle^{(0)} = e^{i\alpha} |\varepsilon_n\rangle. \tag{10.13}$$

At present we set the phase factor to 1, i.e., $\alpha = 0$ and may later change it to make the calculations easier. Multiplication of (10.10) with $\langle \varepsilon_m |$ gives

$$\langle \varepsilon_m \mid (H_0 - E^{(0)}) \mid E \rangle^{(1)} = \langle \varepsilon_m \mid \phi \rangle. \tag{10.14}$$

Since H_0 is hermitian, we obtain with (10.12)

$$(\varepsilon_m - \varepsilon_n) \langle \varepsilon_m \mid E \rangle^{(1)} = \langle \varepsilon_m \mid \phi \rangle . \tag{10.15}$$

From this follows that the vector $|\phi\rangle$ has to be perpendicular to $|\varepsilon_n\rangle$,

$$\langle \varepsilon_n \mid \phi \rangle = 0 . \tag{10.16}$$

Inserting the definition of $|\phi\rangle$, (10.10) gives

$$E^{(1)} = \langle \varepsilon_n \mid H' \mid \varepsilon_n \rangle . \tag{10.17}$$

From (10.4) follows that

$$E^{(0)} + \lambda E^{(1)}$$

is the first approximation of the eigenvalue E_n , which develops from the unperturbed eigenvalue ε_n through the perturbation H'. Thus we can write

$$E_n = E^{(0)} + \lambda E^{(1)} + O(\lambda^2) \tag{10.18}$$

and using (10.12) and (10.17) write

$$E_n = \langle \varepsilon_n \mid H \mid \varepsilon_n \rangle + O(\lambda^2) . \tag{10.19}$$

In words: The first approximation to the energy eigenvalue E_n is given by the expectation value of H in the unperturbed eigenstates $|\varepsilon_n\rangle$. To calculate the vector $|E\rangle^{(1)}$, we start from (10.15), which gives for $n \neq m$

$$\langle \varepsilon_m \mid E \rangle^{(1)} = \frac{1}{\varepsilon_m - \varepsilon_n} \langle \varepsilon_m \mid \phi \rangle.$$
 (10.20)

With (10.10) and (10.13) follows

$$\langle \varepsilon_m \mid E \rangle^{(1)} = \frac{1}{\varepsilon_n - \varepsilon_m} \langle \epsilon_m \mid H' \mid \varepsilon_n \rangle.$$
 (10.21)

This result is valid for all eigenvectors $|\varepsilon_m\rangle \neq |\varepsilon_n\rangle$, whether they belong to the discrete or continuous spectrum to H_0 . Since H_0 is hermitian, the vectors $|\varepsilon_m\rangle$ form a complete set, and it follows that

$$|E\rangle^{(1)} = |\varepsilon_n\rangle\langle\varepsilon_n | E\rangle^{(1)} + \sum_{m \neq n} \frac{1}{\varepsilon_n - \varepsilon_m} |\varepsilon_m\rangle\langle\varepsilon_m | H' | \varepsilon_n\rangle.$$
 (10.22)

Here the sum contains the integral over the continuous spectrum of H_0 , if this exists. As one can see from the denominator in (10.20), the further away the eigenvalues are from ε_n , the lesser their contribution becomes (unless the matrix elements $\langle \varepsilon_m \mid H' \mid \varepsilon_n \rangle$ increase proportional to $|\varepsilon_m - \varepsilon_n|$).

The first term on the right-hand side of (10.22) is still undetermined. Its value is given through the normalization $\langle E \mid E \rangle = 1$. From

$$|E\rangle = |\varepsilon_n\rangle + \lambda |E\rangle^{(1)} + O(\lambda^2)$$

follows

$$\langle E \mid E \rangle = 1 + \lambda \left[\langle \varepsilon_n \mid E \rangle^{(1)} + {}^{(1)} \langle E \mid \varepsilon_n \rangle \right] + O(\lambda^2) .$$
 (10.23)

Because of the normalization condition, the term proportional to λ must be zero, thus $\langle \varepsilon_n \mid E \rangle^{(1)}$ must be purely imaginary:

$$\langle \varepsilon_n \mid E \rangle^{(1)} = i\alpha \quad \text{with } \alpha \in \mathbf{R}$$
 (10.24)

and

$$\langle \varepsilon_n \mid E \rangle = 1 + i\alpha\lambda + O(\lambda^2) .$$
 (10.25)

The last equation is just the Taylor expansion of $e^{i\alpha\lambda}$, so that one can write

$$\langle \varepsilon_n \mid E \rangle = e^{i\alpha\lambda}$$
.

The phase can be eliminated through redefining the state $|E\rangle$:

$$|E\rangle \longrightarrow e^{-i\lambda\alpha} |E\rangle = (1 - i\alpha\lambda)(|\varepsilon_n\rangle + \lambda |E\rangle^{(1)}) + O(\lambda^2)$$

= $|\varepsilon_n\rangle + \lambda (|E\rangle^{(1)} - i\alpha |\varepsilon_n\rangle) + O(\lambda^2)$.

Using (10.24) this relation becomes

$$|E\rangle \longrightarrow |\varepsilon_n\rangle + \lambda \left(|E\rangle^{(1)} - |\varepsilon_n\rangle\langle\varepsilon_n|E\rangle^{(1)}\right) + O(\lambda^2)$$
.

This redefinition of $|E\rangle$ eliminates the first unknown term of the right-hand side of (10.22), and we obtain as result for the first approximation of the eigenstate

$$|E\rangle^{(1)} = \sum_{m \neq n} \frac{1}{\varepsilon_n - \varepsilon_m} |\varepsilon_m\rangle\langle\varepsilon_m|H'|\varepsilon_n\rangle.$$
 (10.26)

Thus, for the energy eigenstate we obtain from (10.4) in first-order approximation

$$|E_n\rangle = |\varepsilon_n\rangle + \sum_{m\neq n} \frac{1}{\varepsilon_n - \varepsilon_m} |\varepsilon_m\rangle\langle\varepsilon_m|\lambda H'|\varepsilon_n\rangle + O(\lambda^2).$$
 (10.27)

This expression can be reformulated in such a way which allows a more easy access to higher order approximations. We introduce the projection operator

$$Q_n := 1 - |\varepsilon_n\rangle\langle\varepsilon_n| = \sum_{m \neq n} |\varepsilon_m\rangle\langle\varepsilon_m|, \qquad (10.28)$$

i.e., Q_n projects on the part of the Hilbert space which is orthogonal to $|\varepsilon_n\rangle$. Since Q_n and H_0 commute, we can write

$$\sum_{m \neq n} \frac{1}{\varepsilon_n - \varepsilon_m} | \varepsilon_m \rangle \langle \varepsilon_m | = \frac{1}{\varepsilon_n - H_0} \sum_{m \neq n} | \varepsilon_m \rangle \langle \varepsilon_m |$$

$$= \frac{Q_n}{\varepsilon_n - H_0}$$
(10.29)

and express (10.27) as

$$|E_n\rangle = \left(1 + \frac{Q_n}{\varepsilon_n - H_0} \lambda H'\right) |\varepsilon_n\rangle + O(\lambda^2)$$
 (10.30)

and (10.26) as

$$|E\rangle^{(1)} = \frac{Q_n}{\varepsilon_n - H_0} H' |\varepsilon_n\rangle. \qquad (10.31)$$

We are now equipped to consider the second-order approximation of the energy eigenvalue E_n . Comparing the terms proportional to λ^2 in (10.7) gives

$$(H_0 - E^{(0)}) \mid E\rangle^{(2)} = E^{(2)} \mid E\rangle^{(0)} + (E^{(1)} - H') \mid E\rangle^{(1)}.$$
 (10.32)

Multiplying from the left with $|\varepsilon_m\rangle$ and using the same arguments that led to (10.16) give that the left-hand side of (10.32) had to be zero. According to (10.13) $|E\rangle^{(0)} \sim |\varepsilon_n\rangle$, then

$$E^{(2)} = \langle \varepsilon_n \mid (H' - E^{(1)}) \mid E \rangle^{(1)}. \tag{10.33}$$

¿From (10.26) follows that $|E\rangle^{(1)}$ is orthogonal to $|\varepsilon_n\rangle$, thus

$$E^{(2)} = \langle \varepsilon_{n} | H' | E \rangle^{(1)}$$

$$= \sum_{m \neq n} \langle \varepsilon_{n} | H' | \varepsilon_{m} \rangle \frac{1}{\varepsilon_{n} - \varepsilon_{m}} \langle \varepsilon_{m} | H' | \varepsilon_{n} \rangle$$

$$= \langle \varepsilon_{n} | H' \frac{Q_{n}}{\varepsilon_{n} - H_{0}} H' | \varepsilon_{n} \rangle.$$
(10.34)

For the last relation, the representation given in (10.31) was used. This result can be summarized as follows:

• The second-order approximation to the energy eigenvalue can be calculated via a two-step process: Starting from $|\varepsilon_n\rangle$, there is a transition to $|\varepsilon_m\rangle$ via H', then an energy denominator $\frac{1}{\varepsilon_n - \epsilon_m}$ is multiplied and finally H' drops back to $|\varepsilon_n\rangle$.

Fig. 10.1 shows this result graphically:

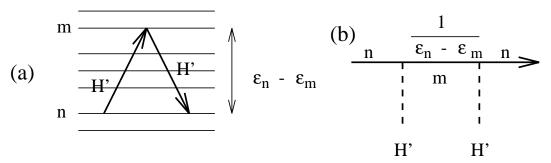


Fig. 10.1 Graphical representation of the second order of the Schrödinger perturbation expansion.

Fig. 10.1.a illustrates the energy difference as function of the distance of the levels, Fig. 10.1.b is a first step in the direction of a Feynman diagram.

Combining (10.26) and (10.34) gives for the energy eigenvalue E_n

$$E_n = \langle \varepsilon_n \mid \left[H_0 + \lambda H' + \lambda H' \frac{Q_n}{\varepsilon_n - H_0} \lambda H' \right] \mid \varepsilon_n \rangle + O(\lambda^3) . \tag{10.35}$$

The results given in (10.30) for the energy eigenstate and in (10.35) for the energy eigenvalue can be considered as the first terms in a power series expansion in λ . Without proof, a guess for its structure is

$$|E_n\rangle = \sum_{\nu=0}^{\infty} \left(\frac{Q_n}{\varepsilon_n - H_0} \lambda H'\right)^{\nu} |\varepsilon_n\rangle$$
 (10.36)

and

$$E_n = \langle \varepsilon_n \mid \left[H_0 + \lambda H' \sum_{\nu=0}^{\infty} \left(\frac{Q_n}{\varepsilon_n - H_0} \lambda H' \right)^{\nu} \right] \mid \varepsilon_n \rangle . \tag{10.37}$$

In both series, powers of the operator

$$\frac{Q_n}{\varepsilon_n - H_0} \lambda H' \tag{10.38}$$

and the corresponding matrix elements

$$\frac{\langle \varepsilon_m \mid \lambda H' \mid \varepsilon_n \rangle}{\varepsilon_n - \varepsilon_m} \tag{10.39}$$

do appear. With the help of (10.38) and (10.39), we are able to determine under which circumstances a perturbation can be considered small. In order for the power series (10.36) and (10.37) to be convergent, the matrix elements must be smaller than 1 for all $m \neq n$. The first few terms in the series will be sufficient if

$$|\langle \varepsilon_m \mid \lambda H' \mid \varepsilon_n \rangle| << |\varepsilon_m - \varepsilon_n|$$
 (10.40)

for all m and n, i.e., the off-diagonal elements of H' have to be much smaller than the energy differences if the perturbation expansion is supposed to converge

10.1.2 Simple Example

Consider the Hamiltonian

$$H = \frac{P^2}{2m} - (Z+1) \frac{e^2}{|\vec{X}|} = \frac{P^2}{2m} - \frac{Ze^2}{|\vec{X}|} - \frac{e^2}{|\vec{X}|}$$
(10.41)

with

$$H_{0} = \frac{P^{2}}{2m} - \frac{Ze^{2}}{|\vec{X}|}$$

$$H' = -\frac{e^{2}}{|\vec{X}|}.$$
(10.42)

The problem (10.41) can be solved exactly, and the solution for the energy eigenvalues is given by

$$E_{n,\ell} = -\frac{1}{2n^2} \alpha^2 mc^2 (Z+1)^2 . {(10.43)}$$

It is illustrative to consider the perturbative treatment as indicated in (10.42). For the first approximation, one obtains

$$E_{n,\ell}^{(1)} = \langle E_{n,ell} \mid -\frac{e^2}{\mid \vec{X} \mid} \mid E_{n,\ell} \rangle = -\frac{1}{n^2} Z \alpha^2 m^2 c^2$$
 (10.44)

by calculating explicitly the matrix elements of $\frac{1}{|\vec{X}|}$. Thus one obtains for the first two terms in the perturbation expansion for the energy eigenvalue

$$E_{n,\ell}^{(0)} + E_{n,\ell}^{(1)} = -\frac{1}{2n^2} (Z\alpha)^2 mc^2 - \frac{1}{n^2} Z\alpha^2 mc^2$$

$$= -\frac{1}{2n^2} \alpha^2 mc^2 (Z+2)Z.$$
(10.45)

This result disagrees with the exact result (10.43), and the relative deviation is given by

$$\frac{\Delta E_{n,\ell}}{E_{n,\ell}} = \frac{Z(Z+2) - (Z+1)^2}{(Z+1)^2} = \frac{-1}{(Z+1^2)}, \qquad (10.46)$$

which shows that the perturbative treatment gets better the higher Z is.

10.1.3 Perturbation of Degenerate Eigenvalues

In practice application, it is often the case that the unperturbed Hamiltonian H_0 has a symmetry, which leads to a degeneracy of the corresponding energy eigenvalues. If the perturbation H' does not have this symmetry, then applying the perturbation removes the

original degeneracy. In case of degenerate eigenvalues (10.9) and (10.10) remains valid. However, from (10.9) only follows that

$$|E\rangle^{(0)} = \sum_{\alpha} |\varepsilon_{n,\alpha}\rangle a_{\alpha} \qquad (10.47)$$

with coefficients

$$a_{\alpha} = \langle \varepsilon_{n,\alpha} \mid E \rangle^{(0)} \quad \alpha = 1, 2, 3, \cdots$$
 (10.48)

which still have to be determined. As in the non-degenerate case from (10.10) follows

$$\langle \varepsilon_{n,\alpha} \mid \phi \rangle = 0 \tag{10.49}$$

for all α . This leads to a system of equations

$$\sum_{\beta} \langle \varepsilon_{n,\alpha} \mid (E^{(1)} - H') \mid \varepsilon_{n,\beta} \rangle \langle \varepsilon_{n,\beta} \mid E \rangle^{0} = 0.$$
 (10.50)

Using (10.47), one obtains

$$\sum_{\beta} H'_{\alpha\beta} a_{\beta} = E^{(1)} a_{\alpha} \tag{10.51}$$

where

$$H'_{\alpha\beta} = \langle \varepsilon_{n,\alpha} \mid H' \mid \varepsilon_{n,\beta} \rangle . \tag{10.52}$$

The matrix $(H'_{\alpha\beta})$, which is either finite or infinite depending on the degeneracy, is given by the operator H' restricted to the space $\mathbf{R}_{\varepsilon_n}$ to ε_n . The coefficients a_{α} determine a vector from $\mathbf{R}_{\varepsilon_n}$, and (10.51) states that this vector has to be eigenvector to $(H'_{\alpha\beta})$. Thus, to determine the energy eigenvalues $E_{n,\alpha}$ in first-order perturbation theory, one has to solve the eigenvalue problem for $H = H_0 + \lambda H'$ in the subspace $\mathbf{R}_{\varepsilon_n}$. If the degeneracy is finite, (10.51) has a non-trivial solution if

$$det(H'_{\alpha\beta} - \delta_{\alpha\beta}E^{(1)}) = 0. (10.53)$$

This is a linear equation of degree $d_n = \dim \mathbf{R}_{\varepsilon_n}$ for the eigenvalue $E^{(1)}$ and has in general d_n different solutions $E_{n,1}^{(1)}, \dots, E_{n,d_n}^{(1)}$. If there are d_n different solutions, the degeneracy is completely removed. However, the degeneracy does not need to be totally removed; part of it can remain. Especially, all $E_{n,\alpha}^{(1)}$ will coincide, if H' had the same symmetry as H_0 . In selected cases, one may be able to find a solution of (10.51) by guessing, i.e., by finding a basis of $\mathbf{R}_{\varepsilon_n}$ in which H' is diagonal, i.e., $H'_{\alpha\beta} = 0$ for $\alpha \neq \beta$. In this special case, the solutions of (10.52) are given by

$$E_{n,\alpha}^{(1)} = H_{\alpha\alpha}' = \langle \varepsilon_{n,\alpha} \mid H' \mid \varepsilon_{n,\alpha} \rangle , \qquad (10.54)$$

which is a generalization of (10.17). In case the degeneracy of the eigenvalues has been removed by the perturbation H', all higher approximations can only lead to shifts in the energy levels $E_{n,\alpha}^{(1)}$. Without proof, the result for the energy eigenvalues $E_{n,\alpha}$ up to second order in λ can be obtained by diagonalizing the following effective Hamiltonian:

$$H_{\alpha\beta}^{eff} = \langle \varepsilon_{n,\alpha} \mid \left(H_0 + \lambda H' + \lambda H' \frac{Q_n}{\varepsilon_n - H_0} \lambda H' \right) \mid \varepsilon_{n,\beta} \rangle . \tag{10.55}$$

Here Q_n contains the sum over all eigenvectors $|\varepsilon_m\rangle \neq |\varepsilon_n\rangle$ of H_0 , which makes the calculation of $H_{\alpha\beta}^{eff}$ quite difficult.

10.2 Brillouin-Wigner Perturbation Theory

The time-independent perturbation theory, according to Rayleigh-Schrödinger, contains as energy denominators the energy eigenvalues ε_n of the unperturbed Hamiltonian H_0 . In contrast, the Brillouin-Wigner perturbation series (for stationary states) contains the exact energy eigenvalues in the energy denominators. We start again from the time-independent Schrödinger equation (10.3) and choose a specific energy state $|E_n\rangle$

$$H \mid E_n \rangle = E_n \mid E_n \rangle = (H_0 + \lambda H') \mid E_n \rangle \tag{10.56}$$

and choose the normalization $\langle \varepsilon_n \mid E_n \rangle = 1$, where $\mid \varepsilon_n \rangle$ is defined (10.12), (10.9). We write (10.56) in the form

$$(E_n - H_0) \mid E_n \rangle = \lambda H' \mid E_n \rangle \tag{10.57}$$

and multiply from the left with $|\varepsilon_n\rangle$ in order to obtain the recursion relation for the energy eigenvalue:

$$\langle \varepsilon_n \mid E_n - H_0 \mid E_n \rangle = \lambda \langle \varepsilon_n \mid H' \mid E_n \rangle , \qquad (10.58)$$

from which follows

$$E_{n} = E_{n}^{(0)} + \lambda \langle \varepsilon_{n} \mid H' \mid E_{n} \rangle$$

$$= \varepsilon_{n} + \lambda \langle \varepsilon \mid H' \mid E_{n} \rangle .$$
(10.59)

In order to obtain the energy eigenstate $|E_n\rangle$, we multiply (10.57) from the left with $|\varepsilon_m\rangle$ and obtain

$$\langle \varepsilon_m \mid E_n - H_0 \mid E_n \rangle = \lambda \langle \varepsilon_m \mid H' \mid E_n \rangle, \qquad (10.60)$$

from which follows

$$(E_n - E_m^{(0)})\langle \varepsilon_m \mid E_n \rangle = \lambda \langle \varepsilon_m \mid H' \mid E_n \rangle \tag{10.61}$$

or

$$\langle \varepsilon_m \mid E_n \rangle = \frac{1}{E_n - \varepsilon_m} \lambda \langle \varepsilon_m \mid H' \mid E_n \rangle.$$
 (10.62)

Furthermore, we expand the full state $|E_n\rangle$ into unperturbed states

$$|E_{n}\rangle = \sum_{n=0}^{\infty} |\varepsilon_{n}\rangle\langle\varepsilon_{n}|E_{n}\rangle$$

$$= |\varepsilon_{n}\rangle + \sum_{m\neq n} |\varepsilon_{m}\rangle\langle\varepsilon_{m}|E_{n}\rangle. \qquad (10.63)$$

Inserting of (10.62) into (10.63) yields

$$|E_n\rangle = |\varepsilon_n\rangle + \sum_{m\neq n} |\varepsilon_m\rangle \frac{1}{E_n - \varepsilon_m} \lambda \langle \varepsilon_m | H' | E_n \rangle.$$
 (10.64)

Introducing the operator Q_n from (10.28) gives

$$|E_n\rangle = |\varepsilon_n\rangle + \frac{Q_n}{E_n - H_0} \lambda H' |E_n\rangle.$$
 (10.65)

Eqs. (10.64) or (10.65) for the state $|E_n\rangle$, where $|E_n\rangle$ appears on the left as well as on the right-hand side, can be solved by iteration, i.e., inserting $|E_n\rangle$ always into the right side.

$$|E_{n}\rangle = |\varepsilon_{n}\rangle + \lambda \sum_{m \neq n} |\varepsilon_{m}\rangle \frac{1}{E_{n} - \varepsilon_{m}} \langle \varepsilon_{m} | H' | \varepsilon_{n}\rangle$$

$$+ \lambda^{2} \sum_{\substack{m \neq n \\ j \neq n}} |\varepsilon_{j}\rangle \frac{1}{E_{n} - \varepsilon_{j}} \langle \varepsilon_{j} | H' | \varepsilon_{m}\rangle \frac{1}{E_{n} - \varepsilon_{m}} \langle \varepsilon_{m} | H' | \varepsilon_{n}\rangle$$

$$+ \cdots \qquad (10.66)$$

Here the energy denominators contain the exact energy E_n . If E_n is known, e.g., through a variational calculation, the Brillouin-Wigner series is a faster converging series than the Rayleigh-Schrödinger series. Inserting (10.65) into (10.59), one obtains for the energy eigenvalue

$$E_n = \varepsilon_n + \lambda \langle \varepsilon_n \mid H' \left\{ \mid \varepsilon_n \rangle + \frac{Q_n}{E_n - H_0} \lambda H' \mid E_n \rangle \right\} , \qquad (10.67)$$

or in closed form

$$E_n = \varepsilon_n + \langle \varepsilon_n \mid \lambda H' \sum_{\nu=0}^{\infty} \left(\frac{Q_n}{E_n - H_0} \lambda H' \right)^{\nu} \mid \varepsilon_n \rangle$$
 (10.68)

which constitutes the Brillouin-Wigner series for the energy eigenvalue E_n .

10.3 Variational Principle

Define an energy functional as

$$E[\psi] := \frac{\langle \psi \mid H \mid \psi \rangle}{\langle \psi \mid \psi \rangle} . \tag{10.69}$$

Then the following **theorem** holds:

• Each state in which $E[\psi]$ is stationary is eigenstate of H, and vice versa. The stationary value of $E[\psi]$ is the corresponding eigenvalue of H.

A variation of $|\psi\rangle$ means

$$|\psi\rangle \longrightarrow |\psi\rangle + |\delta\psi\rangle.$$
 (10.70)

Then we have for a variation of $E[\psi]$:

$$\begin{split} \delta E[\psi] &= \delta \frac{\langle \psi \mid H \mid \psi \rangle}{\langle \psi \mid \psi \rangle} \\ &= \frac{\delta \langle \psi \mid H \mid \psi \rangle}{\langle \psi \mid \psi \rangle} - \frac{\langle \psi \mid H \mid \psi \rangle}{\langle \psi \mid \psi \rangle^2} \delta \langle \psi \mid \psi \rangle \\ &= \frac{\langle \delta \psi \mid H \mid \psi \rangle}{\langle \psi \mid \psi \rangle} + \frac{\langle \psi \mid H \mid \delta \psi \rangle}{\langle \psi \mid \psi \rangle} - E[\psi] \frac{\langle \delta \psi \mid \psi \rangle}{\langle \psi \mid \psi \rangle} - E[\psi] \frac{\langle \psi \mid \delta \psi \rangle}{\langle \psi \mid \psi \rangle} \end{split}$$

$$= \frac{\langle \delta \psi \mid H \mid \psi \rangle}{\langle \psi \mid \psi \rangle} - E[\psi] \frac{\langle \delta \psi \mid \psi \rangle}{\langle \psi \mid \psi \rangle} + \frac{\langle \psi \mid H \mid \delta \psi \rangle}{\langle \psi \mid \psi \rangle} - E[\psi] \frac{\langle \psi \mid \delta \psi \rangle}{\langle \psi \mid \psi \rangle}$$

$$= \frac{\langle \delta \psi \mid H - E[\psi] \mid \psi \rangle}{\langle \psi \mid \psi \rangle} + \frac{\langle \psi \mid H - E[\psi] \mid \delta \psi \rangle}{\langle \psi \mid \psi \rangle} = 0.$$
(10.71)

Choosing $|\delta\psi'\rangle := i |\delta\psi\rangle$ and $\langle\delta\psi'| := -i\langle\delta\psi|$, we obtain

$$\delta E[\psi] = -\frac{\langle \delta \psi \mid H - E[\psi] \mid \psi \rangle}{\langle \psi \mid \psi \rangle} + \frac{\langle \psi \mid H - E[\psi] \mid \delta \psi \rangle}{\langle \psi \mid \psi \rangle} = 0. \quad (10.72)$$

Adding and subtracting the two conditions (10.71) and (10.72) gives

$$\langle \delta \psi \mid H - E[\psi] \mid \psi \rangle = 0$$

$$\langle \psi \mid H - E[\psi] \mid \delta \psi \rangle = 0.$$
 (10.73)

For arbitrary variations, $|\delta\psi\rangle$ follows the condition for being stationary

$$(H - E[\psi]) \mid \psi \rangle = 0 , \qquad (10.74)$$

and thus that $|\psi\rangle$ is eigenstate of H with eigenvalue $E[\psi]$. The second condition $\langle \psi | (H - E[\psi]) = 0$ gives the same result, since $H = H^{\dagger}$ and $E[\psi]$ real. To show the other direction, we assume that $|\psi\rangle$ is eigenstate of H with eigenvalue E. Then

$$E[\psi] = \frac{\langle \psi \mid H \mid \psi \rangle}{\langle \psi \mid \psi \rangle} = E , \qquad (10.75)$$

i.e., for $|\psi\rangle$, $E[\psi]$ is stationary.

Theorem:

• The energy functional is an upper bound for the ground state energy E_0 :

$$E[\psi] \geq E_0 . \tag{10.76}$$

Proof:

Consider

$$E[\psi] - E_0 = \frac{\langle \psi \mid H - E_0 \mid \psi \rangle}{\langle \psi \mid \psi \rangle}. \tag{10.77}$$

Considering the spectral decomposition of H

$$H = \sum_{n=0}^{\infty} E_n \mid \psi_n \rangle \langle \psi_n \mid$$
 (10.78)

and inserting this into (10.77) gives

$$E[\psi] - E_0 = \frac{1}{\langle \psi \mid \psi \rangle} \sum_{n=0}^{\infty} |\langle \psi \mid \psi_n \rangle|^2 (E_n - E_0)$$

$$= \frac{1}{\langle \psi \mid \psi \rangle} \sum_{n=1}^{\infty} |\langle \psi \mid \psi_n \rangle|^2 (E_n - E_0) \ge 0.$$
 (10.79)

The variational principle, according to Ritz, consists of choosing a trial wave function $|\psi(\mu)\rangle$ as function of one or more parameters μ and then a determination of the minimum of

$$E(\mu) := \frac{\langle \psi(\mu) \mid H \mid \psi(\mu) \rangle}{\langle \psi(\mu) \mid \psi(\mu) \rangle}. \tag{10.80}$$

The minimum of $E(\mu)$ is then the upper bound for the ground state energy. A relatively simple case is a linear dependence of the trial wave function on parameters:

$$|\psi(\mu)\rangle := \sum_{\mu=1}^{N} c_{\mu} |\varphi_{\mu}\rangle,$$
 (10.81)

where $\{\varphi_{\mu}\}$ are known functions and c_{μ} the parameters to be determined. Setting $\delta E[\psi] = 0$ means

$$\langle \delta \psi \mid H - E[\psi] \mid \psi \rangle \ = \ 0 \ ,$$

where

$$|\delta\psi\rangle = \sum_{\mu} \delta c_{\mu} |\varphi_{\mu}\rangle$$

with δc_{μ} arbitrary. This leads to

$$\langle \varphi_{\mu} \mid H - E[\psi] \mid \sum_{\nu} c_{\nu} \mid \varphi_{\nu} \rangle = 0 , \qquad (10.82)$$

or equivalently

$$\sum_{\nu} \langle \varphi_{\mu} \mid H \mid \varphi_{\nu} \rangle \ c_{\nu} = E[\psi] \ c_{\mu} \ . \tag{10.83}$$

This is an eigenvalue problem of H in the space of states $\{\varphi_{\mu}\}$. The lowest eigenvalue is the upper bound for the ground state energy. If the quantum numbers of $\{\varphi_{\nu}\}$ correspond to

excited states, then the lowest eigenvalue is the upper bound of the corresponding excited state of H.

Remarks: Since one has to choose a trial wave function, the variational principle always gives better results for the energy than for the wave function. Once the energy is obtained, one can, e.g., use the Brillouin-Wigner perturbation series to improve on the wave function.

10.4 Applications

10.4.1 The He-Atom

In Section 9.5 we define the Hamiltonian for the He atom as (9.67):

$$H = \left(\frac{\vec{P}_{1}^{2}}{2m_{e}} - \frac{2e^{2}}{|\vec{r}_{1}|}\right) + \left(\frac{\vec{P}_{2}^{2}}{2m_{e}} - \frac{2e^{2}}{|\vec{r}_{2}|}\right) + \frac{e^{2}}{|\vec{r}_{2} - \vec{r}_{1}|}$$

$$= H_{0}(1) + H_{2}(2) + V_{12}. \tag{10.84}$$

In Section 9.5 we concentrated on the energy spectrum as obtained from the Hamiltonian $\hat{H} = H_0^{(1)} + H_0^{(2)}$ and considered the consequences of the electrons being identical particles. The energy eigenvalues of \hat{H} are given by (9.69)

$$E^{(0)} = \varepsilon_n + \varepsilon_{n'} . ag{10.85}$$

If both electrons are in the lowest state (singlet), the wave function is given by

$$\psi^{(0)}(1,2) = \varphi_{100}(\vec{r_1}) \varphi_{100}(\vec{r_2}) \chi_{00}(1,2) \tag{10.86}$$

where

$$\varphi_{100}(r) = \sqrt{\frac{\beta^3}{\pi}} e^{-\beta r} , \quad \beta = \frac{1}{\hbar^2} Z e^2 m .$$
(10.87)

The explicit value of the lowest energy (in 0^{th} order) is

$$E_{100} = -\left(\frac{me^4}{2\hbar^2}\right) = -4 \cdot 13.6 \ eV = -54 \ eV$$
 (10.88)

and thus

$$E^{(0)} = -108 \ eV \ . \tag{10.89}$$

Next we consider the corrections to $E^{(0)}$ due to the electrostatic interaction $e^2/|\vec{r}_2 - \vec{r}_1|$ in a perturbation expansion. With the general definition of the eigenfunctions of \hat{H}_0 as given in (9.77), we obtain for the first-order correction to the energy

$$E_{n^{2S+1}L_J} = \langle^{2S+1}\psi_{n,JM} \mid H \mid^{2S+1}\psi_{n,JM}\rangle.$$
 (10.90)

Since the perturbation V_{12} is spin-independent, this leads to

$$E_{n^{1}L_{J}} = \varepsilon_{1S} + \varepsilon_{n\ell} + \langle \phi_{1S,n\ell m}^{S} | V_{12} | \phi_{1S,n\ell m}^{S} \rangle$$

$$E_{n^{3}L_{J}} = \varepsilon_{1S} + \varepsilon_{n\ell} + \langle \phi_{1S,n\ell M}^{A} | V_{12} | \phi_{1S,n\ell m}^{A} \rangle.$$
(10.91)

Introducing the explicit form (9.76) for the spatial part of the wave function, one obtains for the correction term in S-states:

$$\Delta E_{n \, {}^{1}S_{0}} := \langle \phi_{1S,nS0}^{S} \mid V_{12} \mid \phi_{1S,nS0}^{S} \rangle = A + B$$

$$\Delta E_{n \, {}^{3}S_{1}} := \langle \phi_{1S,nS0}^{A} \mid V_{12} \mid \phi_{1S,nS0}^{A} \rangle = A - B$$
(10.92)

where A is the Coulomb interaction energy

$$A := e^{2} \int d^{3}r_{1} d^{3}r_{2} \frac{\rho_{1S}(\vec{r}_{1})\rho_{nS}(\vec{r}_{2})}{|\vec{r}_{1} - \vec{r}_{2}|}$$

$$(10.93)$$

with the density function

$$\rho_{nS}(\vec{r}) := |\phi_{nS}(\vec{r})|^2 \tag{10.94}$$

and B is the exchange interaction energy

$$B := e^2 \int d^3r_1 d^3r_2 \frac{\phi_{1S}^*(\vec{r}_1) \phi_{nS}^*(\vec{r}_2) \phi_{nS}(\vec{r}_1) \phi_{1S}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}.$$
 (10.95)

Since all integrals are positive, the ${}^{1}S_{0}$ levels are shifted higher than the ${}^{3}S_{0}$ levels with respect to $E^{(0)}$, so that $E_{n^{1}S_{0}} > E_{n^{3}S_{1}}$. Let us explicitly calculate the correction in first order to the singlet ground state energy using the wave function $\psi^{(0)}(1,2)$ of (10.86) as ground state wave function.

$$\Delta E_{1^{1}S_{0}} = \int d^{3}r_{1} d^{2}\vec{r}_{2} |\psi^{(0)}|^{2} \frac{e^{2}}{|\vec{r}_{1} - \vec{r}_{2}|}$$

$$= \frac{\beta^{6}e^{2}}{\pi^{2}} \int d^{3}r_{1} \int d^{3}r_{2} e^{-\beta(r_{1} + r_{2})} \frac{1}{|\vec{r}_{1} - \vec{r}_{2}|}.$$
(10.96)

Using

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \frac{1}{r_>} \sum_{\ell=0}^{\infty} \left(\frac{r_<}{r_>}\right)^{\ell} \frac{4\pi}{2\ell + 1} \sum_{m=-\ell}^{\ell} Y_{\ell m}(\hat{r}_1) Y_{\ell m}^*(\hat{r}_2)$$
 (10.97)

in (10.96), one obtains

$$\Delta E_{1^{1}S_{0}} = \frac{\beta^{6}e^{2}}{\pi^{2}} (4\pi)^{2} \int_{0}^{\infty} dr_{1}r_{1}^{2} \int_{0}^{\infty} dr_{2}r_{2}^{2} \frac{1}{r} e^{-2\beta(r_{1}+r_{2})}$$

$$= \frac{\beta^{6}e^{2}}{\pi^{2}} (4\pi)^{2} \left[\int_{0}^{\infty} dr_{1}r_{1}^{2} e^{-2\beta r_{1}} \frac{1}{r_{1}} \int_{0}^{r_{1}} dr_{2}r_{2}^{2} e^{-2\beta r_{2}} \right]$$

$$+ \int_{0}^{\infty} dr_{1}r_{1}^{2} e^{-2\beta r_{1}} \int_{r_{1}}^{\infty} dr_{2}r_{2}^{2} \frac{1}{r_{2}} e^{-2\beta r_{2}} \right]$$

$$= \frac{5}{8} e^{2}\beta = 34 \ eV \ . \tag{10.98}$$

Together with (10.89), the energy $E_{1^1S_0}$ is given in first-order perturbation theory

$$E_{1^1S_0} = -108eV + 34eV = -74eV. (10.99)$$

This result has to be compared with the experimental value $E^{exp} = -79eV$. The fact that the correction ΔE is not small compared to $E^{(0)}$ means that the ansatz for the ground state wave function was not very good.

Historically the correct prediction of the ground state energy of the He atom was a crucial proof for the correctness of quantum mechanics and QED (here agreement between theory and experiment within six or more significant figures).

10.4.2 Zeeman Effect

Historical facts: 1896 Pieter Zeeman discovered that the spectral lines of atoms split up, when the atoms are brought into a strong magnetic field. 1897 H.A. Lorentz explained this effect in the framework of classical physics as effect of the Lorentz force on the emitting electron.

Quantum mechanically, the Lorentz force enters the Hamiltonian via the vector potential \vec{A} :

$$H = \frac{1}{2m_e} \left(\vec{P} - \frac{e}{c} \vec{A} \right)^2 + V , \qquad (10.100)$$

where m_e is the electron mass. Using the gauge $div \vec{A} = 0$, one obtains from (10.100)

$$H = \frac{P^2}{2m_e} + V - \frac{e}{m_e c} \vec{A} \cdot \vec{P} + \frac{e^2}{2m_e c^2} \vec{A}^2 . \tag{10.101}$$

Due to the gauge $div \vec{A} = 0$, \vec{P} and \vec{A} commute (for a vector operator \vec{A} : $[\vec{P}, \vec{A}] = \frac{\hbar}{i} div \vec{A}$),

thus the canonical binomial formula can be used. For a constant magnetic field \vec{B} , we have

$$\vec{A}(\vec{r}) = \frac{1}{2} \ (\vec{B} \times \vec{r})$$
, and $\vec{B} = \vec{\nabla} \times \vec{A}$, and

$$H' = \frac{e}{2m_e c} (\vec{B} \times \vec{r}) \cdot \vec{P} = -\frac{e}{2m_e c} (\vec{r} \times \vec{P}) \cdot \vec{B} = -\frac{e\hbar}{2m_e c} \vec{L} \cdot \vec{B} . \quad (10.102)$$

This operator describes the interaction of the magnetic moment

$$\vec{\mu} = \frac{e\hbar}{2m_e c} \vec{L} = -\mu_B \vec{L} \tag{10.103}$$

with the magnetic field \vec{B} . The factor

$$\mu_B = \frac{|e|}{2m_e} \frac{\hbar}{c} = \frac{1}{2} \text{ charge } \times \text{ Compton wave length}$$
 (10.104)

is called Bohr magneton, with $\mu_B = 5.66 \cdot 10^{-5} \frac{eV}{T}$. The term quadratic in \vec{A} ,

 $H^{11} = \frac{e^2}{2m_ec^2}\vec{A}^2$ is neglected due to the small coupling constant if the perturbation H' is present. For the spin, one has an analogous term (with factor 2). Thus the Hamiltonian describing an one-electron atom in a magnetic field \vec{B} (\vec{B} assumed to be in z-direction) is given by

$$H = H_0 + H'$$

$$H_0 = \frac{P^2}{2m_e} + V(r) + W(r) \vec{L} \cdot \vec{S}$$

$$H' = \frac{|e|\hbar}{2m_e c} B(L_3 + 2S_3) = \frac{|e|\hbar}{2m_e c} B(J_3 + S_3) = \mu B(J_3 + S_3) .$$
(10.105)

The eigenstates of H_0 (unperturbed states) are characterized by $\mid n\ell \ \frac{1}{2} \ jm_j \rangle$ with $-j \le m_j \le j$. The energy $E_{\ell j}^n$ has a (2j+1)-fold degeneracy, e.g., the states $p_{1/2}, s_{1/2}$ are two-fold degenerate, $p_{3/2}$ is four-fold degenerate. If the magnetic field is weak, H' can

be treated perturbatively. Here we have to consider perturbation theory for degenerate states. We define the state for fixed j as

$$|j\rangle \equiv \sum_{mj} C_{mj} |n\ell| \frac{1}{2} jm_j \rangle \qquad (10.106)$$

and omit the quantum number n in the following to simplify the notation. We need to consider

$$|\langle \ell \frac{1}{2} j m_j | H' | \ell \frac{1}{2} j m'_j \rangle - E_j^{(1)} \delta_{m_j m'_j} | = 0$$
 (10.107)

according to (10.52). The matrix elements of H' are given as

$$\langle \ell \, \frac{1}{2} \, j m_j \mid H' \mid \ell \, \frac{1}{2} \, j m'_j \rangle = \mu B \, \langle \ell \, \frac{1}{2} \, j m_j \mid J_3 + S_3 \mid \ell \, \frac{1}{2} \, j m'_j \rangle$$

$$= \mu B(m_j \, \delta_{m_j m'_j} + \langle \ell \, \frac{1}{2} \, j m_j \mid S_3 \mid \ell \, \frac{1}{2} \, j m'_j \rangle \, . (10.108)$$

Here $S_3 \equiv T_0^{(1)}$, i.e., a tensor operator of rank 1 with magnetic quantum number q = 0. Applying the Wigner-Eckart Theorem gives

$$\langle \ell \frac{1}{2} j m_j \mid S_3 \mid \ell \frac{1}{2} j m'_j \rangle = \langle \ell \frac{1}{2} j \parallel S_3 \parallel \ell \frac{1}{2} j \rangle C(jj0; m_j m'_j 0)$$
 (10.109)

from which follows that $m'_j = m_j$. Inserting (10.109) into (10.108) gives for the splitting of the levels due to the perturbation H'

$$\langle \ell \frac{1}{2} j m_j | H' | \ell \frac{1}{2} j m'_j \rangle = \mu B \delta m_j m'_j \left(m_j \pm \frac{m_j}{2\ell + 1} \right)$$

$$= \delta_{m_j m'_m} \mu B m_j \left(1 \pm \frac{1}{2\ell + 1} \right)$$
(10.110)

for $j = \ell \pm \frac{1}{2}$. For a weak magnetic field, the splitting of the levels is linear and for specific states, the splitting is smaller than the energy difference between the unperturbed levels.

For the case of a **strong magnetic field**, the perturbative term H' has the same order of magnitude as the spin-orbit force. Thus, one can no longer treat H' as perturbation within the subspace of degenerate energy levels for each j. One has to diagonalize the Hamiltonian in a larger space. An obvious solution is to consider the superposition of unperturbed states whose energies are close:

$$|\psi\rangle = \sum_{jm_j} C_{jm_j} |\ell| \frac{1}{2} jm_j\rangle. \qquad (10.111)$$

As example, the states $p_{3/2}$ and $p_{1/2}$ can build the state $|\psi\rangle$ of (10.111). Then one has instead of (10.107)

$$\sum_{j'm'_{j}} \langle jm_{j} | H - E | j'm'j \rangle C_{j'm'_{j}} = 0 , \qquad (10.112)$$

where the indices $(\ell \frac{1}{2})$ were dropped to simplify the notation. The matrix elements of H are given by

$$\langle jm_j \mid H \mid j'm'_j \rangle = E_j^{(0)} \delta_{jj'} \delta_{m_jm'_j} + \mu B m_j \delta_{jj'} \delta_{m_jm'_j} + \mu B \langle jm_j \mid S_3 \mid j'm'_j \rangle (10.113)$$

Since S_3 corresponds to a tensor operator $T_0^{(1)}$, applying the Wigner-Eckart theorem gives (k=1, q=0)

$$\langle jm_j \mid S_3 \mid j'm_j' \rangle = C(j'1j; m_j'0m_j) \langle j \parallel S_3 \parallel j \rangle.$$
 (10.114)

From the CG-coefficient follows that

$$m_{j} = m'_{j}$$

 $j = j'$
 $j = j' \pm 1$. (10.115)

We need to calculate the matrix elements of S_3 , and start from

$$|\ell \frac{1}{2} j m_j \rangle = \sum_{m_s m_s} C(\ell \frac{1}{2} j, m_\ell m_s m_j) |\ell m_\ell \rangle |\frac{1}{2} m_s \rangle.$$
 (10.116)

Then

$$\langle \ell \frac{1}{2} j m_{j} | S_{3} | \ell \frac{1}{2} j m_{j} \rangle = \sum_{m_{\ell} m_{s}} \sum_{m'_{\ell} m'_{s}} C(\ell \frac{1}{2} j; m_{\ell} m_{s} m_{j}) C(\ell \frac{1}{2} j; m'_{\ell} m'_{s} m_{j})$$

$$\times \langle \ell m_{\ell} | \ell m'_{\ell} \rangle \langle \frac{1}{2} m_{s} | S_{3} | \frac{1}{2} m'_{s} \rangle$$

$$= \sum_{m_{\ell} m_{s}} C(\ell \frac{1}{2} j; m_{\ell} m_{s} m_{j})^{2} m_{s}$$
(10.117)

	$m_\ell = m_j - \frac{1}{2}$	$m_{\ell} = m_j + \frac{1}{2}$
$j = \ell \pm \frac{1}{2}$	$\sqrt{\frac{\ell\!+\!m_j\!+\!\frac{1}{2}}{2\ell\!+\!1}}$	$\sqrt{\frac{\ell\!-\!m_j\!+\!\frac{1}{2}}{2\ell\!+\!1}}$
$j = \ell - \frac{1}{2}$	$-\sqrt{\frac{\ell\!-\!m_j\!+\!\frac{1}{2}}{2\ell\!+\!1}}$	$\sqrt{\frac{\ell\!+\!m_j\!+\!\frac{1}{2}}{2\ell\!+\!1}}$

Table for $C(\ell \frac{1}{2} j; m_{\ell} m_s m_j)$ for $\ell > 0$.

Thus (10.117) gives for

$$j = \ell + \frac{1}{2} : \langle \cdots \rangle = \frac{1}{2} \left(\frac{\ell + m_j + \frac{1}{2}}{2\ell + 1} - \frac{\ell - m_j + \frac{1}{2}}{2\ell + 1} \right) = \frac{m_j}{2\ell + 1}$$

$$j = \ell - \frac{1}{2} : \langle \cdots \rangle = \frac{1}{2} \left(\frac{\ell - m_j + \frac{1}{2}}{2\ell + 1} - \frac{\ell + m_j + \frac{1}{2}}{2\ell + 1} \right) = \frac{-m_j}{2\ell + 1} .$$
(10.118)

The result of (10.118) was explicitly used in (10.110).

Let us consider as explicit example the states $p_{3/2}$ and $p_{1/2}$. The states are given as

$$|\ell = 1, j = \frac{1}{2}, m_{j} = -\frac{1}{2}\rangle = -\sqrt{\frac{1}{3}} |\ell = 1, m_{\ell} = 0\rangle |\frac{1}{2}m_{s} = \frac{1}{2}\rangle + \sqrt{\frac{2}{3}} |\ell = 1, m_{\ell} = 1\rangle |\frac{1}{2}m_{s} = \frac{1}{2}\rangle |\ell = 1, j = \frac{3}{2}, m_{j} = \frac{1}{2}\rangle = \sqrt{\frac{2}{3}} |\ell = 1, m_{\ell} = 0\rangle |\frac{1}{2}m_{s} = \frac{1}{2}\rangle + \sqrt{\frac{1}{3}} |\ell = 1, m_{\ell} = 1\rangle |\frac{1}{2}m_{s} = \frac{1}{2}\rangle . (10.119)$$

Using the CG-coefficients from the table, one obtains

$$\langle \ell \frac{1}{2} j = \ell - \frac{1}{2} m_j \mid S_3 \mid \ell \frac{1}{2} j = \ell + \frac{1}{2} m_j \rangle = -\frac{1}{2\ell + 1} \sqrt{(\ell + \frac{1}{2})^2 - m_j^2}$$

$$= \langle \ell \frac{1}{2} j = \ell + \frac{1}{2} m_j \mid S_3 \mid \ell \frac{1}{2} j = \ell - \frac{1}{2} m_j \rangle . \quad (10.120)$$

The matrix element of H is then given by

$$\langle jm_j \mid H \mid j'm'_j \rangle = \delta_{m_jm'_j} (E_{jm_j} \delta_{jj'} + E_{jm_j,j'j_m})$$
 (10.121)

with

$$E_{jm_{j}} = E_{j}^{(0)} + \mu B m_{j}$$

$$E_{jm_{j},j'm_{j}} = \mu B \langle jm_{j} | S_{3} | j'm_{j} \rangle . \qquad (10.122)$$

Thus the eigenvalue problem (10.112) is characterized by the different m_j 's:

$$(E_{jm_j} - E) C_{jm_j} + \sum_{j'} E_{jm_j,j'm_j} C_{j'm_j} = 0.$$
 (10.123)

For the example $p_{3/2}$ and $p_{1/2}$, there are two different values of m_j :

- $m_j = \pm \frac{3}{2}$, $j = \frac{3}{2}$ $(j = \frac{1}{2} \text{ does not contribute})$
- $m_j = \pm \frac{1}{2}$; $j = \frac{3}{2}$ and $j = \frac{1}{2}$ contribute.

This gives a system of two linear coupled equations to determine E. The determinant of this system is given by

$$\begin{vmatrix} E_{\frac{1}{2}m_j} + E_{\frac{1}{2}m_j, \frac{1}{2}m_j} - E & E_{\frac{1}{2}m_j, \frac{3}{2}m_j} \\ E_{\frac{3}{2}m_j, \frac{1}{2}m_j} & E_{\frac{3}{2}m_j} + E_{\frac{3}{2}m_j, \frac{3}{2}m_j} - E \end{vmatrix} = \begin{vmatrix} E_{11} & E_{12} \\ E_{21} & E_{22} \end{vmatrix} = 0 . \quad (10.124)$$

This gives a quadratic equation for E:

$$E = \frac{1}{2} \left(E_{11} + E_{22} \pm \sqrt{(E_{11} - E_{22})^2 + 4E_{12}^2} \right) , \qquad (10.125)$$

where $E_{12} = E_{21}$ has been taken into consideration.

For a weak magnetic field $|E_{12}| << |E_{11} - E_{22}|$, i.e., die off-diagonal elements are small compared to the diagonal ones. Thus, in the case of a weak field:

$$E = \left\{ \begin{array}{l} E_{11} \\ E_{22} \end{array} \right.$$

as seen before. For a very **strong magnetic field**, H' dominates over the spin-orbit interaction. Then

$$E_{11} - E_{22} = E_{\frac{1}{2}}^{(0)} + \mu B \, m_j + E_{\frac{1}{2}m_j, \frac{1}{2}m_j} - E_{\frac{3}{2}}^0 - \mu B \, m_j - E_{\frac{3}{2}m_j, \frac{3}{2}m_j}$$

$$= E_{\frac{1}{2}}^{(0)} - E_{\frac{3}{2}}^{(0)} + E_{\frac{1}{2}m_j, \frac{1}{2}m_j} - E_{\frac{3}{2}m_j, \frac{3}{2}m_j}$$

$$\approx E_{\frac{1}{2}m_j, \frac{1}{2}m_j} - E_{\frac{3}{2}m_j, \frac{3}{2}m_j}$$

$$= -\frac{2\mu B \, m_j}{2\ell + 1}$$

$$(10.126)$$

Thus we have

$$\sqrt{(E_{11} - E_{22})^2 + 4E_{12}^2} \approx \sqrt{\left(\frac{2\mu B}{2\ell + 1}\right)^2 m_j^2 + \left(\frac{2\mu B}{2\ell + 1}\right)^2 \left(\left(\ell + \frac{1}{2}\right)^2 - m_j^2\right)} \\
= \mu B. \tag{10.127}$$

Therefore, in this limit and for $|m_j| = \frac{1}{2}$:

$$E = \frac{1}{2} \left(E_{\frac{1}{2}}^{(0)} + \mu B \, m_j - \frac{\mu B}{2\ell + 1} \, m_j + E_{\frac{3}{2}}^{(0)} \, \mu B \, m_j + \frac{\mu B}{2\ell + 1} \, m_j \pm \mu B \right)$$

$$= \frac{1}{2} \left(E_{\frac{1}{2}}^{(0)} + E_{\frac{3}{2}}^{(0)} \right) + \mu B \left(m_j \pm \frac{1}{2} \right). \tag{10.128}$$

The term proportional to B is the expectation value of $H' = \mu B(L_3 + 2S_3)$ with respect to the states $|\ell m_{\ell}\rangle \frac{1}{2} m_s\rangle$; namely $\mu B(m_{\ell} + 2m_s)$. Those states are eigenstates to H_0 if one neglects the spin-orbit interaction. The first term is the energy $E_{\ell=1}^{(0)}$. The energy shifts $\mu B(m_j \pm \frac{1}{2})$ can be classified according to

$$|\ell m_{\ell}\rangle \mid \frac{1}{2} m_{s}\rangle$$

$$m_{j} = 1/2 : |10\rangle \mid \frac{1}{2} \frac{1}{2}\rangle$$

$$|11\rangle \mid \frac{1}{2} - \frac{1}{2}\rangle$$

$$m_{j} = -\frac{1}{2} : |1-1\rangle \mid \frac{1}{2} \frac{1}{2}\rangle$$

$$|10\rangle \mid \frac{1}{2} - \frac{1}{2}\rangle. \tag{10.129}$$

Explicitly for $m_j = \frac{1}{2}$ we find for the energies:

$$E_{\frac{1}{2}\frac{1}{2}} = E_{\frac{1}{2}}^{(0)} + \mu B \frac{1}{2}$$

$$E_{\frac{1}{2}\frac{1}{2},\frac{1}{2}\frac{1}{2}} = -\frac{1}{6} \mu B$$

$$E_{\frac{3}{2}\frac{1}{2}} = E_{\frac{3}{2}}^{(0)} + \mu B \frac{1}{2}$$

$$E_{\frac{3}{2}\frac{1}{2},\frac{3}{2}\frac{1}{2}} = \frac{1}{6} \mu B$$

$$E_{\frac{1}{2}\frac{1}{2},\frac{3}{2}\frac{1}{2}} = -\frac{\sqrt{2}}{3} \mu B$$

$$(10.130)$$

Thus for a strong field B, one has

$$E = \frac{1}{2} \left(E_{\frac{1}{2}}^{(0)} + E_{\frac{3}{2}}^{(0)} \right) + \begin{cases} \mu B \\ 0 \end{cases} . \tag{10.131}$$

One still has to solve the homogeneous equations for the coefficients $C_j m_j$ in (10.123). In the limit of a strong field B, one obtains:

$$C_{\frac{3}{2}\frac{1}{2}} = \frac{\frac{1}{2} \left(E_{\frac{3}{2}}^{(0)} - E_{\frac{1}{2}}^{(0)} \right) + \mu B \left(-\frac{2}{3} \right)}{-\mu B \sqrt{2}/3} C_{\frac{1}{2}\frac{1}{2}}$$

$$\longrightarrow \left(-\sqrt{2} \right) C_{\frac{1}{2}\frac{1}{2}}.$$

$$(10.132)$$

Thus we finally obtain for the state $|\psi\rangle$ of (10.111)

$$|\psi\rangle_{m_{j}=\frac{1}{2}} = \begin{cases} C_{\frac{1}{2}\frac{1}{2}} (|\ell=1, j=\frac{1}{2}, m_{j}=\frac{1}{2}) - \sqrt{2} |\ell=1, j=\frac{3}{2}, m_{j}=\frac{1}{2}) \\ C_{\frac{1}{2}\frac{1}{2}} (|\ell=1, j=\frac{1}{2}, m_{j}=\frac{1}{2}) + \frac{1}{\sqrt{2}} |\ell=1, j=\frac{3}{2}, m_{j}=\frac{1}{2}) \end{cases}$$

$$\approx \begin{cases} |\ell=1, m_{\ell}=0\rangle | \frac{1}{2} m_{s}=\frac{1}{2} \\ |\ell=1, m_{\ell}=0\rangle | \frac{1}{2} m_{s}=-\frac{1}{2} \end{cases} . \tag{10.133}$$

¿From (10.133) we see that in the presence of a strong magnetic field B the energy levels are no longer organized according to the total angular momentum J, i.e., according to (10.110), and levels of different J_3 can cross. This effect is called **Paschen-Back-Effect**.

10.4.3 The H_2 Molecule

The application of quantum mechanics to problems in molecular physics span a wide range, especially in quantum chemistry. Here only a very simple application is being discussed, the H_2 molecule. The Schrödinger equation is given as

$$\left(-\frac{\hbar^2}{2m} \sum_{i=1}^2 \nabla_{r_i}^2 - \frac{\hbar^2}{2M} \sum_{j=1}^2 \nabla_{R_j}^2 + V\right) \psi = E\psi ,$$
(10.134)

where the first term refers to the kinetic energy of the electrons and the second to the kinetic energy of the protons. In principle, the H_2 molecule would be a four-body problem. However, since both nuclei are much heavier than the electrons, the protonic motion can be neglected in a first approximation, and the motion of the electrons in the field of the spatially fixed protons is considered (**Born-Oppenheimer approximation**).

In this approximation, we make the ansatz $\psi(\vec{r}_i, \vec{R}_j) = u_{\vec{R}_j}(\vec{r}_i) \ v(\vec{R}_j)$ for the total wave function. Neglecting the kinetic energy of the nucleons, the Schrödinger equation reads

$$\left(-\frac{\hbar^2}{2m} \sum_{i} \nabla_{r_i}^2 + V(\vec{r}_i, \vec{R}_j)\right) u_{\vec{R}_j}(\vec{r}_i) \equiv W(\vec{R}_j) u_{\vec{R}_j}(\vec{r}_i) . \tag{10.135}$$

The positions \vec{R}_j of the fixed nucleus are parameters for the "electronic" Schrödinger equation (10.135); the eigenvalues $W(\vec{R}_j)$ constitute the electron energies. Inserting this purely electronic solution back into the full problem gives

$$\left(\frac{-\hbar^{2}}{2M}\sum_{j}\nabla_{R_{j}}^{2} - \frac{\hbar^{2}}{2m}\sum_{i}\nabla_{r_{i}}^{2} + V(\vec{r}_{i}, \vec{R}_{j})\right)u_{\vec{R}_{j}}(\vec{r}_{i})v(\vec{R}_{j})$$

$$= \left(\frac{-\hbar^{2}}{2M}\sum_{j}\nabla_{R_{j}}^{2} + W(\vec{R}_{j})\right)u_{\vec{R}_{j}}(\vec{r}_{i})v(\vec{R}_{j})$$

$$= E u_{\vec{R}_{j}}(\vec{r}_{i})v(\vec{R}_{j}).$$
(10.136)

The term for the kinetic energy for the protons gives

$$\nabla^{2}_{\vec{R}_{j}} u_{\vec{R}_{j}}(\vec{r}_{i}) v(\vec{R}_{j}) = u_{\vec{R}_{j}}(\vec{r}_{i}) \nabla^{2}_{\vec{R}_{j}} v(\vec{R}_{j}) + v(\vec{R}_{j}) \nabla^{2}_{R_{j}} u_{\vec{R}_{j}}(\vec{r}_{i}) + 2\vec{\nabla}_{R_{j}} v(\vec{R}_{j}) \cdot \vec{\nabla}_{R_{j}} u_{R_{j}}(\vec{r}_{i}) .$$

$$(10.137)$$

If we neglect the parameter dependence of the electronic wave function $u_{R_j}(\vec{r_i})$, then only the first term on the right-hand side of (10.137) survives. Inserting this result in (10.136) allows to decouple the electronic motion from the nuclear motion, i.e., we obtain for $v(\vec{R_i})$

$$\left(\frac{-\hbar^2}{2\vec{M}} \sum_{j} \nabla_{R_j}^2 + W(\vec{R}_j)\right) v(\vec{R}_j) = E v(\vec{R}_j) , \qquad (10.138)$$

when the electron energy $W(\vec{R}_i)$ is potential energy with respect to the nuclear motion.

We now consider the Schrödinger equation for the electrons, neglecting all but electrostatic interactions. The choice of coordinates is given in Fig. 10.2.

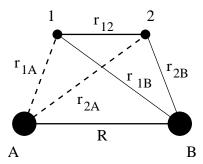


Fig. 10.2 Radial distances appropriate to the H_2 molecule.

The Schrödinger equation for the electrons is given by

$$hu \equiv \left\{ \frac{-\hbar^2}{2m} \left(\nabla_{r_i}^2 + \nabla_{r_2}^2 \right) + e^2 \left[\frac{1}{R} + \frac{1}{r_{12}} - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2B}} - \frac{1}{r_{2A}} \right] \right\} u(\vec{r}_1, \vec{r}_2)$$

$$= W(R) u(\vec{r}_1, \vec{r}_2) . \tag{10.139}$$

To reiterate, in the Born-Oppenheimer approximation, the Schrödinger equation for the electrons can be completely decoupled from the nucleonic part of the problem. If one lets $R \to \infty$ in (10.139), one obtains two degenerate solutions

$$u_1(\vec{r}_1, \vec{r}_2) = u_A(\vec{r}_1) u_B(\vec{r}_2) u_2(\vec{r}_1, \vec{r}_2) = u_A(\vec{r}_2) u_B(\vec{r}_1) ,$$
 (10.140)

where u_A, u_B are eigenstates of hydrogen.

Next one has to consider the spin states of the two electrons and consider eigenfunctions to the total spin $\vec{S} = \vec{s}_1 + \vec{s}_2$. Combining a symmetric spin wave function with an antisymmetric spatial wave function and vice versa gives

$$u_{s=0}(1,2) = [u_1(\vec{r}_1, \vec{r}_2) + u_2(\vec{r}_2, \vec{r}_1)] \chi_{s=0}(1,2)$$

$$u_{s=1}(1,2) = [u_1(\vec{r}_1, \vec{r}_2) - u_2(\vec{r}_2, \vec{r}_1)] \chi_{s=1}(1,2) .$$
(10.141)

These states (10.141) built from the asymptotic wave functions can be taken as the starting point for a variational determination of the energy W(R). A variational calculation gives

$$W(r) \leq \frac{\langle u \mid h \mid u \rangle}{\langle u \mid u \rangle} , \qquad (10.142)$$

where the right-hand side is an upper bound for the electron energy. For the norm, we obtain:

$$\langle u \mid u \rangle = \langle u_1 \pm u_2 \mid u_1 \pm u_2 \rangle$$

$$= 1 \pm \langle u_1 \mid u_2 \rangle \pm \langle u_2 \mid u_1 \rangle + 1$$

$$= 2 \pm 2\langle u_1 \mid u_2 \rangle.$$
(10.143)

The overlap $\langle u_1 \mid u_2 \rangle$ only vanishes for $R \to \infty$.

$$\langle u \mid h \mid u \rangle = \langle u_1 \pm u_2 \mid h \mid u_1 \pm u_2 \rangle$$

$$= \langle u_1 \mid h \mid u_2 \rangle \pm \langle u_1 \mid h \mid u_2 \rangle \pm \langle u_2 \mid h \mid u_1 \rangle + \langle u_2 \mid h \mid u_2 \rangle.$$
(10.144)

Since h is symmetric in (1) and (2): $\langle u_1 \mid h \mid u_1 \rangle = \langle u_2 \mid h \mid u_2 \rangle$ and since h hermitian: $\langle u_1 \mid h \mid u_2 \rangle = \langle u_2 \mid h \mid u_1 \rangle$. Thus one obtaines for (10.142)

$$W(R) \leq \frac{\langle u_1 \mid h \mid u_1 \rangle \pm \langle u_1 \mid h \mid u_2 \rangle}{1 \pm \langle u_1 \mid u_2 \rangle}. \tag{10.145}$$

For the eigenstates of hydrogen, the integrals can be calculated analytically, and one obtained qualitatively the following behavior for W(R):

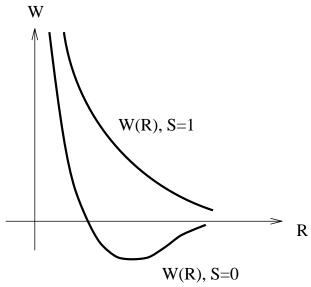


Fig. 10.3 Qualitative behavior of the energy W(R).

 $W_{S=1}$ and $W_{S=0}$ differ by the so-called exchange integral $\langle u_1 \mid h \mid u_2 \rangle$, which originates from the antisymmetrization of the states. This is a purely quantum mechanical effect and does not have a classical analogon. The lowering of the energy for the S=0 state gives the molecular binding. The probability

$$|u_{S=0}(\vec{r_1}, \vec{r_2})|^2 = |u_1(\vec{r_1}, \vec{r_2}) + u_2(\vec{r_2}, \vec{r_1})|^2$$
 (10.146)

is large if both electrons are located between the protons, there $u_1 = u_2$. The H_2 molecule exists only for S = 0, not for S = 1.

We can now incorporate the motion of the two protons into the solution for $\vec{S} = 0$. Starting from (10.138) and introducing relative coordinates, we obtain

$$\left(\frac{-\hbar^2}{2\bar{M}} \nabla_R^2 + W(R)\right) v(\vec{R}) = E v(\vec{R}) , \qquad (10.147)$$

where $\bar{M} = M/2$ is the reduced proton mass. Writing

$$v(\vec{R}) = \frac{1}{R} \xi(R) \mathcal{Y}_{LM_L}(\hat{R}) \; ; \; L = 0, 1, 2, \cdots$$
 (10.148)

the radial equation reads

$$\left\{ \frac{-\hbar^2}{2\bar{M}} \frac{d^2}{dR^2} + \frac{\hbar^2 L(L+1)}{2\bar{M}R^2} + W(R) \right\} \xi(R) = E \xi(R)
\left\{ \frac{-\hbar^2}{2\bar{M}} \frac{d^2}{dR^2} + \tilde{W}(R) \right\} \xi(R) = E \xi(R) .$$
(10.149)

Here $\tilde{W}(R)$ is an effective potential containing the angular momentum barrier. In order to further calculate the problem in an approximate fashion, one expands $\tilde{W}(R)$ around the minimum:

$$\tilde{W}'(R) = W'(R) - \frac{\hbar^2 L(L+1)}{\bar{M}R^3} = 0,$$
 (10.150)

which gives a value R_0 for the equilibrium distance between the two protons. Then one expands $\tilde{W}(R)$ around R_0 :

$$\tilde{W}(R) = \tilde{W}(R_0) + \frac{(R - R_0)^2}{2!} \tilde{W}''(R_0) + \cdots
\approx W(R_0) + \frac{\hbar^2}{2\bar{M}} \frac{L(L+1)}{R_0^2} + \frac{(R - R_0)^2}{2} K_0 ,$$
(10.151)

where the last term corresponds to a harmonic oscillator potential. In this approximation, the total energy E of the molecule is given by

$$E = W(R_0) + \frac{\hbar^2}{2\bar{M}_0} \frac{L(L+1)}{R_0^2} + \hbar \sqrt{\frac{K_0}{\bar{M}}} (n + \frac{1}{2}) + \cdots$$
 (10.152)

and consists of

- the electron energy $W(R_0)$ at the equilibrium point R_0
- the vibrational energy $\hbar\omega$ $(n+\frac{1}{2})$
- the rotational energy $\frac{\hbar^2 L(L+1)}{2\bar{M}R_0^2}$, here $\bar{M}R_0^2$: moment of inertia.

If one wants to be more precise, one has to consider that a rotation stretches the molecule, and thus R_0 increases with L and thus K_0 changes. Thus rotation and vibration influence each other. Considering the symmetry of the proton wave function (10.148), we obtain when interchanging (1) and (2):

$$\vec{R} \longrightarrow -\vec{R} \text{ or}$$
 $\hat{R} \longrightarrow -\hat{R}$
 $\theta, \varphi \longrightarrow \pi - \theta, \ \varphi + \pi$
 $\mathcal{Y}_{LM_L}(-\hat{R}) \longrightarrow (-1)^L \ \mathcal{Y}_{LM_L}(\hat{R}) \ .$

$$(10.153)$$

From this follows that if the protons are in a S = 0 state, L has to be even; if the protons are in a S = 1 state, L has to be odd. There exists two types of rotational bands:

- S = 1 states have three magnetic states
- S = 0 states have one magnetic state.

This has consequences for the specific heat of hydrogen gas (see thermodynamics and statistics).

10.5 Time-Dependent Perturbation Theory

Let the perturbation be given by the time-dependent potential V(t). Thus, the Hamiltonian will be time dependent

$$H \equiv H(t) = H_0 + V(t) \tag{10.154}$$

and one needs to find solutions to H(t) given as

$$i\hbar \frac{\partial \psi(t)}{\partial t} = H\psi(t) \ .$$
 (10.155)

Since H_0 is time independent, the solutions are stationary,

$$H_0 \varphi_n = E_n \varphi_n \ . \tag{10.156}$$

In the interaction picture, the time dependence of a wave function is given as

$$\psi(t) \equiv e^{iH_0t/\hbar} \ \psi_I(t) \tag{10.157}$$

and thus (10.155) gives

$$i\hbar \frac{d\psi_I(t)}{dt} = e^{iH_0t/\hbar} V(t) e^{-iH_0t/\hbar} \psi_I(t) .$$
 (10.158)

The solution φ_n to H_0 form a complete set of eigenvectors, and $\psi_I(t)$ can be expanded in that basis:

$$\psi_I(t) = \sum_{N} C_n(t) \varphi_n , \qquad (10.159)$$

where the time dependence is now contained in the coefficients $C_n(t)$. Inserting (10.159) into (10.158) and projecting on φ_n leads to an equation for the coefficients

$$i\hbar \frac{dC_n(t)}{dt} = e^{iE_n t/\hbar} \sum_m \langle \varphi_n | V(t) | \varphi_m \rangle e^{iE_m t/\hbar} C_m(t) ,$$
 (10.160)

which becomes in integral form

$$C_n(t) = C_n(t_0) + \frac{1}{i\hbar} \int_{t_0}^t dt' \sum_m e^{i(E_n - E_m)t'/\hbar} \langle \varphi_n | V(t) | \varphi_m \rangle C_m(t')$$
 (10.161)

with the boundary condition

$$C_n(t_0) = \delta_{nr} \ . \tag{10.162}$$

Here the choice is made such that at $t = t_0$ only the start r is occupied. It is also reasonable to assume that the perturbation V(t) is switched on at $t = t_0$.

The lowest order perturbation theory one obtains

$$C_n(t) = \delta_{nr} + \frac{1}{i\hbar} \int_{t_0}^{t'} dt' \ e^{i(E_n - E_r)t'/\hbar} < \varphi_n |V(t)| \varphi_r > .$$
 (10.163)

The transition probability at a time t to a state n is then

$$|\langle \varphi_n | \psi(t) \rangle|^2 = |e^{-iE_n t/\hbar} C_n(t)|^2 = |C_n(t)|^2$$
 (10.164)

Let

$$V(t) Oe^{i\omega_t} + O^{\dagger} e^{-\omega t} \tag{10.165}$$

and

$$\omega_{nr} \equiv (E_n - E_r)/\hbar \ . \tag{10.166}$$

Thus the integral in (10.163) becomes

$$\int_{t_0}^{t'} dt' \ e^{i(\omega_{nr} \pm \omega)t'} = e^{i(\omega_{nr} \pm \omega)\left(\frac{t+t_0}{2}\right)} \ \frac{2\sin\left(\omega_{nr} \pm \omega\right)\left(\frac{t-t_0}{2}\right)}{(\omega_{nr} \pm \omega)} \ . \tag{10.167}$$

Thus, for $n \neq r$

$$|C_{n}(t)|^{2} = \frac{4}{\hbar^{2}} |e^{i(\omega_{nr}+\omega)\left(\frac{t+t_{0}}{2}\right)} \frac{\sin(\omega_{nr}+\omega)\left(\frac{t-t_{0}}{2}\right)}{\omega_{nr}+\omega} < \varphi_{n}|O|\varphi_{r} >$$

$$+ e^{i(\omega_{nr}-\omega)\left(\frac{t+t_{0}}{2}\right)} \frac{\sin(\omega_{nr}-\omega)\left(\frac{t-t_{0}}{2}\right)}{(\omega_{nr}-\omega)} < \varphi_{n}|O^{+}|\varphi_{r} > |^{2}$$

$$= \frac{4}{\hbar^{2}} \left\{ \frac{\sin^{2}(\omega_{nr}+\omega)\left(\frac{t-t_{0}}{2}\right)}{(\omega_{nr}-\omega)^{2}} |<\varphi_{n}|O|\varphi_{r} > |^{2} \right.$$

$$+ \frac{\sin^{2}(\omega_{nr}-\omega)\left(\frac{t-t_{0}}{2}\right)}{(\omega_{nr}-\omega)^{2}} |<\varphi_{n}|O^{\dagger}|\varphi_{r} > |^{2}$$

$$+ 2Re\left(e^{i\omega(t+t_{0})} \frac{\sin(\omega_{nr}+\omega)\left(\frac{t-t_{0}}{2}\right)}{\omega_{nr}+\omega} \frac{\sin(\omega_{nr}-\omega)\left(\frac{t-t_{0}}{2}\right)}{\omega_{nr}-\omega} < \varphi_{n}|O|\varphi_{r} > < \varphi_{n}|O^{\dagger}|\varphi_{r} > \right) \right\}$$

$$(10.168)$$

This expression shows that the transition probability oscillates over time! Consider $T \equiv \frac{(t-t_0)}{2} \to \infty$. Then one needs to consider expressions like $\sin^2 \Omega T/\Omega^2$.

For the norm, one obtains

$$\int_{-\infty}^{\infty} d\Omega \frac{\sin^2 \Omega T}{\Omega^2} = \frac{1}{T} \int_{-\infty}^{\infty} dx \frac{\sin^2 x}{x^2} T^2$$
$$= T \int_{-\infty}^{\infty} dx \frac{\sin^2 x}{x^2} = \pi T$$
(10.169)

and thus

$$\lim_{T \to \infty} \frac{\sin^2 \Omega T}{\Omega^2} = \lim_{T \to \infty} \pi T \,\delta(\Omega) \,. \tag{10.170}$$

Thus for $t \to \infty$, one obtains

$$|C_{n}(t)|^{2} \rightarrow (t - t_{0}) \frac{2\pi}{\hbar^{2}} | \langle \varphi_{n} | O | \varphi_{r} \rangle |^{2} \delta(\omega_{nr} + \omega)$$

$$+ (t - t_{0}) \frac{2\pi}{\hbar^{2}} | \langle \varphi_{n} | O^{\dagger} | \varphi_{r} \rangle |^{2} \delta(\omega_{nr} - \omega)$$

$$+ \text{ oscillating interference terms}. \qquad (10.171)$$

The δ -functions lead to the conditions

$$\omega_{nr} + \omega = \frac{1}{\hbar} \left(E_n - E_r \right) + \omega = 0 \tag{10.172}$$

or

$$E_r = E_n + \hbar\omega . ag{10.173}$$

This describes the energy loss $\hbar\omega$ to the external field V(t) under de-excitation $E_r\to E_n$.

From the second δ -function, one obtains

$$\omega_{nr} - \omega = \frac{1}{\hbar} \left(E_n - E_r \right) - \omega = 0 \tag{10.174}$$

or

$$E_n = E_r + \hbar\omega , \qquad (10.175)$$

which describes the energy gain $\hbar\omega$ from the external field V(t) under excitation $E_r\to E_n$.

The transition probability for large times grows linearly in t for the energy gain or loss.

The transition probabilities per unit time are given for the energy loss as

$$\omega_{nr} = \frac{2\pi}{\hbar} |\langle \varphi_n | O | \varphi_r \rangle|^2 \delta(E_n - E_r - \hbar \omega)$$
 (10.176)

and for the energy gain as

$$\omega_{nr} = \frac{2\pi}{\hbar} |\langle \varphi_n | O^{\dagger} \varphi_r |^2 \delta(E_n - E_r - \hbar \omega) . \qquad (10.177)$$

These expressions only make sense when one integrates over the δ -functions. This means either V(t) is a superposition of different ω , or the states are in the continuum. The oscillating terms do not contribute to those integrations.

As special case, let V be time independent, i.e., $\omega = 0$. Then

$$\omega_{rn} = \frac{2\pi}{\hbar} |\langle \varphi_n | V | \varphi_r \rangle|^2 \delta(E_r - E_n) . \tag{10.178}$$

This expression for ω_{rn} is "Fermi's Golden Rule" for the transition probability per unit time. Notice that this expression is only in lowest order in V.

10.5.1 Atomic Transitions

Atomic transitions are the absorption and emission of electromagnetic radiation by atoms (molecules).

Consider the interaction for one electron in an electromagentic field:

$$V(t) = -\frac{e}{mc} \vec{A}(t) \cdot \vec{p} - \frac{e\hbar}{2mc} \vec{\sigma} \cdot \vec{B}(t) . \qquad (10.179)$$

(Here we work in Coulomb Gauge, i.e., $div \vec{A} = 0$).

The free radion is described by

$$\vec{A}(\vec{x},t) = \vec{A}_0 \cos(\vec{k} \cdot \vec{x} - \omega t)$$

$$\omega = k \cdot c$$

$$\vec{B} = \vec{\nabla} \times \vec{A}$$

$$E = -\frac{1}{c} \vec{A}.$$
(10.180)

Because of $\operatorname{div}\,A=0\,:\,\vec{A}_0\bot\vec{k},$ i.e., one has transverse polarization

$$\vec{B} = \vec{\nabla} \times \vec{A} = -(\vec{k} \times \vec{A}_0) \sin(\vec{k} \cdot \vec{x} - \omega t)$$

$$\vec{E} = -\frac{\omega}{c} \vec{A}_0 \sin(\vec{k} \cdot \vec{x} - \omega t) = -k \vec{A}_0 \sin(\vec{k} \cdot \vec{x} - \omega t) . \qquad (10.181)$$

Then

$$V(t) = -\frac{e}{mc}\cos\left(\vec{k}\cdot\vec{x} - \omega t\right)\vec{A}_{0}\cdot\vec{p} + \frac{e\hbar}{2mc}\vec{\sigma}\cdot\left(\vec{k}\times\vec{A}_{0}\right)\sin\left(\vec{k}\cdot\vec{x} - \omega t\right)$$

$$= -\frac{e}{2mc}e^{-i\vec{k}\cdot\vec{x}}\vec{A}_{0}\cdot\left(\vec{p} + \frac{\hbar}{2i}\vec{\sigma}\times\vec{K}\right)e^{i\omega t} - \frac{e}{2mc}e^{i\vec{k}\times\vec{x}}\vec{A}_{0}\cdot\left(\vec{p} - \frac{\hbar}{2i}\vec{\sigma}\times\vec{K}\right)e^{-i\omega t}$$

$$\equiv Oe^{i\omega t} + O^{\dagger}e^{-i\omega t}$$

$$(10.182)$$

Thus, the absorption rate for electromagnetic radiation is given by

$$\omega_{nr} = \frac{2\pi}{\hbar} \frac{e^2}{4m^2c^2} | \langle \varphi_n | e^{i\vec{k}\cdot\vec{x}} | \vec{A}_0 \cdot \left(\vec{p} + \frac{\hbar i}{2} | \vec{\sigma} \times \vec{k} \right) | \varphi_r \rangle |^2 \delta(E_n - E_r - \hbar \omega) . (10.183)$$

The induced emission rate is exactly the same since

$$| \langle \varphi_n | O^{\dagger} | \varphi_r \rangle |^2 = | \langle \varphi_r | O | \varphi_n \rangle^2 .$$
 (10.184)

Consider the **Dipole approximation**.

Transition matrix element:

$$M_{nr} \equiv e < \varphi_n | e^{i\vec{k}\cdot\vec{x}} \hat{A}_0 \cdot \left(\vec{p} + \frac{\hbar i}{2} \vec{\sigma} \times \vec{k} \right) | \varphi_r > . \tag{10.185}$$

Consider $\hat{A}_0 \cdot \vec{k} = 0$, e.g., $\hat{A}_0 \equiv \hat{k}$ and $\hat{k} \equiv \hat{z}$. Then

$$M_{nr} = e \langle \varphi_n | e^{ikz} \left(p + \frac{\hbar i}{2} \sigma_y k \right) | \varphi_r \rangle . \tag{10.186}$$

The typical site of an atom is about $R \sim 10^{-8} = cm \ 1 \dot{A}$. The wavelength of the emitted or absorbed light is $\lambda \sim 10^{-5} \ cm$. Thus, $\lambda >> R$ and we consider the so-called long wavelength approximation

$$\lambda = \frac{2\pi}{k} \to kR = 2\pi \frac{R}{\lambda} \sim 10^{-3} .$$

Then $e^{ikz} \to \mathbf{1}$.

The spin matrix element is small with respect to the monetum matrix element (rough estimate):

$$\left| \frac{\langle \varphi_n | \frac{\hbar}{2} x \sigma | \varphi_r \rangle}{\langle \varphi_n | p_x | \varphi_r \rangle} \right| \approx \frac{\hbar K}{\hbar R} = \frac{2\pi R}{\lambda} << 1.$$
 (10.187)

In the case that the momentum matrix element vanishes, the spin matrix element is, of course, important, together with terms in the expansion of the exponential function.

Consider the momentum matrix element

$$M \equiv e < \varphi_n | p_x | \varphi_r > \tag{10.188}$$

with

$$p_x = \frac{im}{\hbar} [H_0, x] .$$

Then

$$M = \frac{ime}{\hbar} < \varphi_n | [H_0, x] | \varphi_r >$$

$$= \frac{ime}{\hbar} (E_n - E_r) < \varphi_n | X | \varphi_r >$$

$$= im \omega_{nr} < \varphi_n | e \cdot x | \varphi_r > , \qquad (10.189)$$

where $e \cdot x$ is the electric dipole operator. As a fact, dipole transitions are the most common transitions in atoms.

10.5.2 Selection Rules

Selection rules are conditions with respect to quantum numbers of operators as well as states, which force certain matrix elements to vanish.

Consider dipole transitions between eigenfunctions of hydrogen, $|\varphi\rangle \equiv |n\ell jm\rangle$. The dipole operator \vec{X} is a vector operator, i.e., a tensor operator of rank 1.

$$T_{1}^{1} \equiv x_{1} = -\frac{1}{\sqrt{2}} (x + iy)$$

$$T_{0}^{1} \equiv x_{0} = Z$$

$$T_{-1}^{1} = x_{-1} = \frac{1}{\sqrt{2}} (x - iy)$$
(10.190)

As tensor operator \vec{x} fulfills all relations for tensor operators, and thus the matrix elements are of the type

$$< n\ell j m |x_{\mu}| n'\ell' j' m' > = C(1j'j; \mu m'm) < n\ell j |x| n'l'j')$$
 (10.191)

Considering the Glebsch-Gordan coefficient, one obtains

$$\Delta j = 0_1 \pm 1 \quad (j' = j; j' = j \pm 1)$$

 $\Delta m = 0_1 \pm 1 \quad (m = m' + \mu)$.

Considering the parity of the states gives:

$$P|n\ell jm\rangle = (-1)^l |n\ell jm\rangle$$

$$Px_{\mu} = -x_{\mu}P. \qquad (10.192)$$

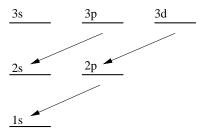
Thus

$$< n\ell j m |x_{\mu}| n' \ell' j' m' > = < n\ell j m |P^{2} x_{\mu}| n' \ell' j' m' >$$

$$= - < n\ell j m |P x_{\mu} P| n' \ell' j' m' >$$

$$= (-1)^{\ell + \ell' + 1} < n\ell j m |x_{\mu}| n' \ell' j' m' > .$$

From which follows that $(-1)^{\ell'+\ell+1} = 1$ for the transition. Due to the odd parity of the dipole operator, transitions can only occur between states with different parity, $\Delta \ell = \pm 1$.



The direct transition 3d - 1s is suppressed.

10.6 Time Dependence of Quantum Mechanical Systems

Time evolution operator (unitary)

$$U(t) = e^{\frac{i}{\hbar} Ht} . \tag{10.193}$$

Consider a system which has no external forces, and which is prepared in a state $|\psi\rangle$. We are interested in the time dependence of the expectation values of observables,

$$< A > (t) \equiv <\psi |A|\psi > (t)$$
 (10.194)

In principle, the operators and the state vectors may be time dependent. i.e., $|\psi(t)\rangle$ and A(t). Thus, the expectation value could be

$$\langle A \rangle(t) \equiv \langle \psi(t)|A(t)|\psi(t) \rangle$$
.

Consider the two extremes, namely in one case, the time dependence is completely determined by the time dependence of the state vectors (Schrödinger picture), and in the other case, the time dependence in only contained in the operators (Heisenberg picture).

10.6.1 Heisenberg and Schrödinger Picture

The assumptions for the **Schrödinger picture** are that the time dependence is carried by the state vectors, and the operators are time independent:

$$< A > (t) = <\psi_s(t)|A_s|\psi(s)(t)>$$
 (10.195)

where A_s is time independent. The time evolution of $|\psi_s(t)|$ is given by

$$|\psi_s(t)\rangle \equiv u(t)|\psi_s(O)\rangle . \tag{10.196}$$

Obviously, the operators of the Schrödinger picture fulfill

$$\frac{d}{dt} A_s = 0 .$$

Time translation leads to the Operator Schrödinger equation

$$i\hbar \frac{d}{dr} U(t) = HU(t) . (10.197)$$

Applying this on $|\psi_s(O)\rangle$ gives the Schrödinger equation

$$i\hbar \frac{d}{dt} |\psi_s(t)\rangle = H|\psi_s(t)\rangle$$
 (10.198)

which is closely related to the differential equation used in the wave mechanics, but is more general since

- ullet the Hamiltonian H is not yet specified.
- It is valid for general Hilbert space vectors.

Reformulating (10.195) leads to

$$< A > (t) = < \psi_s(t)|A_s|\psi(s)(t) >$$

= $< \psi_s(O)|U^{-1}(t)|A_s|U(t)|\psi_s(0) > .$

Define a time-dependent operator

$$A_H(t) := U^{-1}(t) A_s U(t)$$
 (10.199)

and a time-independent state vector

$$|\psi_H\rangle := |\psi_s(0)\rangle$$
 (10.200)

Then the expectation value becomes

$$< A > (t) = < \psi_H |A_H(t)| \psi_H > ,$$

which describes the time dependence of the expectation value of A with time-dependent state vectors and time-dependent operators. This defines the **Heisenberg picture**.

More precisely, in the Heisenberg picture one starts with states and operators that coincide at t=0 with the quantities $|\psi_s(0)| >$ and A_s of the Schrödinger picture and defines for arbitrary times t

$$|\psi_H\rangle = |\psi_s(0)\rangle$$

 $A_H(t) = U^{-1}(t) A_s U(t)$. (10.201)

Because of U(t = 0), 1 the operators and states coincide at t = 0 in both pictures. For the Heisenberg picture, one requires

$$\frac{d}{dt} |\psi_H> = 0$$
.

Consider the operators

$$A_H(t) = U^{-1}(t) \ A_s u(t) = U^{\dagger}(t) \ A_H U(t)$$

and

$$i\hbar \frac{d}{dt} U(t) = HU(t)$$

and

$$-i\hbar \frac{d}{dt} U^{\dagger}(t) = U^{\dagger}(t)H$$
, where $H = H^{\dagger}$.

Then

$$i\hbar \frac{d}{dt} A_H(t) = i\hbar \left(\frac{d}{dt} U^{\dagger}(t)\right) A_s U(t) + i\hbar U^{\dagger}(t) A_s \left(\frac{d}{dt} u(t)\right)$$

$$= -U^{\dagger}(t) H A_s U(t) + u^{\dagger}(t) A_s H U(t)$$

$$= -H U^{\dagger} = A_s U + U^{\dagger} A_s U H$$

$$= -H A_H(t) + A_H(t) H = [A_H(t), i]$$

where [U, H] = 0 was used.

Thus, for the operators of the Heisenberg picture follows the equation of motion

$$\frac{d}{dt} A_H(t) = \frac{i}{\hbar} [H, A_H(t)] \tag{10.202}$$

which fulfills the same role as the Schrödinger equation (10.198).

10.6.2 Time Evolution of One-Body Systems

Consider a Hamiltonian of the form

$$H(\vec{P}, \vec{Q}) = \frac{1}{2m} \vec{P}^2 + V(\vec{Q})$$
.

In the Schrödinger picture, the operators \vec{P}_s and \vec{Q}_S are constant, and thus the Hamiltonian is constant with respect to time. The operators \vec{P}_s and \vec{Q}_s obey the canonical commutation

$$[\vec{P}_s, \vec{Q}_s] = \frac{\hbar}{i} \mathbf{1}$$
 .

The entire time dependence is carried by the state vectors as

$$|\psi_s(t)>=e^{-\frac{\hbar}{i}H(\vec{P_s},\vec{Q_s})t}|\psi_s(O)>$$
.

The evaluation of the operator exponential function is non-trivial, even for the free motion

$$|\psi_s(t)\rangle = e^{-\frac{\hbar}{t} \frac{\vec{P}_s^2}{2m} t} |\psi_s(O)\rangle$$
 (10.203)

In the Heisenberg picture, the state vectors are time independent, $|\psi_H\rangle$, but the operators $\vec{P}_H(t)$ and $\vec{Q}_H(t)$ are time dependent. Thus, the Hamiltonian

$$H - \frac{1}{2m} \vec{P}_H^2(t) + v (Q_H(t))$$

is time dependent. Though the operator P_H and Q_H depend in a non-trivial way out, they must fulfill a commutation relation for all times t

$$[P_H(t), Q_H(t)] = \frac{\hbar}{i} \mathbf{1} .$$

They all fulfill equations of motion

$$\frac{d}{dt} P_H(t) = \frac{i}{\hbar} [H(P_H, Q_H), P_H(t)]$$

$$\frac{d}{dt} Q_H(t) = \frac{i}{\hbar} [H, Q_H(t)].$$

As shown in Chapter 5, the commutator of an operator with H can be identified with the derivative of H with respect to the conjugate of this operator. Thus,

$$\frac{d}{dt} Q_H(t) = \frac{\partial H}{\partial P_H}
\frac{d}{dt} P_H(t) = -\frac{\partial H}{\partial Q_H}.$$
(10.204)

These equations are formally identical with the canonical Hamiltonian differential equations of classical mechanics, however, the contain operators instead of functions. These operator valued equations can be turned into equations with c-numbers, if one considers expectations values with the time-dependent Heisenberg state vectors

$$\frac{d}{dt} < \psi_H | Q_H(t) | \psi_H \rangle = \langle \psi_H | \frac{\partial H}{\partial P_H} | \psi_H \rangle
\frac{d}{dt} < \psi_H | P_H(t) | \psi_H \rangle = -\langle \psi_H | \frac{\partial H}{\partial Q_H} | \psi_H \rangle .$$
(10.205)

These equations (10.205) are the essence of the **Ehrenfest Theorem** which states that the expectation values of space and momentum fulfill the canonical differential equations of classical mechanics.

Reminder:

$$< \frac{\partial}{\partial P_H} H > \neq \frac{\partial}{\partial < P_H >} < H >$$
.

10.6.3 One-Dimensional Particle Motion

Consider the free Hamiltonian

$$H_0 = \frac{P^2}{2m} .$$

In the Heisenberg picture, one obtains for the monentum

$$\frac{d}{dt} P_H(t) = \frac{i}{\hbar} [H_0, P_H(t)] = 0 ,$$

thus

$$P_H(t) = P_H(O) = P . (10.206)$$

As in classical mechanics, the momentum is conserved

$$\frac{d}{dt} Q_H(t) = \frac{i}{\hbar} [H_0, Q_H(t)] = \frac{\partial H}{\partial P_H} = \frac{P}{m}.$$

Thus, the operator differential equation for Q_H has the solution (as in classical mechanics)

$$Q_H(t) = Q_H(O) + \frac{P}{m} t . (10.207)$$

For the commutators, one gets

$$[P, Q_H(t)] = [P, Q_H(O)] = \frac{\hbar}{i} \mathbf{1}$$
 (10.208)

$$[Q_H(t), Q_H(O)] = \left[\frac{P}{m} \ t, Q_H(O)\right] = \frac{\hbar}{m_i} \ t \ \mathbf{1}$$
 (10.209)

Thus, the operator Q_H for different times do **not** commute. The value of the commutator increases linearly with t!

Calculate the Free Motion in the Heisenberg Picture

Since the operator $Q_H(t)$ depends on t, the eigenvectors will also be time dependent. Let $|x,t\rangle$ be eigenvector of $Q_H(t)$.

Then

$$Q_H(t) | x, t >= x | x, t > .$$

Here t considered as parameter of the state $|x, t\rangle$. Applying (10.207) leads to

$$\left(Q_H(O) + \frac{P}{m}t\right) |x,t> = x |x,t>$$
 (10.210)

Up to now, the properties of $P_H(t)$ have not yet been used. Remember that for each t the Heisenberg picture implies that there is a specific coordinate representation for each t. One has to fix one choice, and it is logical to fix values at t = 0.

Then, the eigenvalues are

$$|x'>:=|x,t=0>$$

with

$$Q_H(O)|x'> := |x, t=0>$$
.

With respect to this basis at t = 0, one obtains from (10.210)

$$\left(x' + \frac{t}{m} \frac{\hbar}{i} \frac{d}{dx'}\right) < x'|x, t > = x < x'|x, t > . \tag{10.211}$$

Thus, we obtain a wave function

$$\psi_{x,t}(x') := \langle x' | x, t \rangle$$

which is a function of x' and depends parameterically on x and t. Since P is time independent, it can be applied to all coordinate representations and acts as differential operator

$$P \psi_{x,t}(x') = \frac{\hbar}{i} \frac{d}{dx'} \psi_{x,t}(x') ,$$

and thus (10.211) turns into an ordinary differential equation of first order

$$\frac{d}{dx'} \psi_{x,t}(x') = \frac{i \ m(x - x')}{\hbar t} \ \psi_{x,t} \ (x')$$

which has the solution

$$\psi_{x,t}(x') = A e^{-i\frac{m}{2\hbar t}(x-x')^2}$$
(10.212)

where the constant A can be fixed by considering t = 0.

$$\psi_{x,t=0}(x') = \langle x'|x, t=0 \rangle = \langle x'|x \rangle = \delta(x-x')$$
.

In fact, (10.212) is singular for t = 0. Instead of determining the limit $t \to 0$, one can start from (10.211), which becomes for t = 0

$$(x'-x) \ \psi_{x,t=0}(x')=0$$

with the general solution $\psi_{x,t=0}(x') = a\delta(x-x')$. The constant a must be fixed as a=1 because of the normalization.

Consider (10.212) for the limit $t \to 0$:

$$\lim_{t \to 0} A \int dx e^{-i \frac{m}{2\hbar t} (x - x')^2} = 1$$

with $y = \sqrt{\frac{m}{2\hbar t}} (x - x')$ follows

$$\int_{-\infty}^{\infty} dx \ e^{-i \frac{m}{2\hbar t} - (x - x')^2} \ = \ 2 \ \frac{2\hbar t}{m} \ \int_{0}^{\infty} \ dy \ e^{-iy^2} = 2 \ \frac{2\hbar t}{m} \ \cdot \ \frac{1}{2} \ \sqrt{\frac{\pi}{i}} \ ,$$

and thus $A = \sqrt{\frac{mi}{2\pi\hbar t}}$. With this, the time-dependent wave function becomes

$$\psi_{x,t}(x') \equiv \langle x', O | x, t \rangle = \sqrt{\frac{mi}{2\pi\hbar t}} e^{-i\frac{m}{2\hbar t}(x-x')^2}$$
 (10.213)

Generalizing from t = 0 to an arbitrary t' gives

$$\langle x', t' | x, t \rangle = \sqrt{\frac{mi}{2\pi\hbar(t - t')}} e^{-i\frac{m}{2\hbar(t, t')}(x - x')^2}.$$
 (10.214)

Free Motion in the Schrödinger Picture

In the Schrödinger picture $|x,t>_s$ is the state, which is obtained from the time evolution

$$|x,t>_{s}=e^{-\frac{i}{\hbar}H_{0}t}|x,t=0>=e^{-\frac{i}{\hbar}H_{0}t}|x>$$
 (10.215)

of the eigenstates |x> of the operator $Q_s=Q_H(O)$. The state $|x,t>_s$ obeys the Schrödinger equation

$$i\hbar \frac{d}{dt} |x,t>_s = H_0|x,t>_s$$
.

In the coordinate representation follows

$$i\hbar \frac{\partial}{\partial t} \langle x'|x,t\rangle_s = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \langle x'|x,t\rangle_s$$

where x' and t are the variables, and x a fixed parameter. Define a wave function $\psi_x(x',t) := \langle x'|x,t\rangle_s$, for which the full Schrödinger equation takes the form

$$i\hbar \frac{\partial \psi_x(x',t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x'} \psi_x(x',t)$$

with the initial conditions

$$\psi_x(x', t = 0) = \langle x' | x \rangle = \delta(x' - x)$$
.

The solution is related to the **Green's function** of the Schrödinger operator

$$i\hbar \frac{\partial}{\partial t} + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$
,

which is determined by the differential equation

$$\left(i\hbar \frac{\partial}{\partial t} + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}\right) D(x - x', t - t') = \delta(x - x') \delta(t - t')$$

and the retardation condition

$$D(x - x', t - t') = 0$$
 for $t < t'/$.

Differentiation of (10.214) shows that $\psi_x(x',t)$ fulfills the Schrödinger equation.

One can also directly construct $\psi_x(x',t)$ by obtaining from (10.215) and consider $\psi_x(x',t)$ as matrix element

$$\psi_x(x',t) = \langle x'|e^{-\frac{i}{\hbar}\frac{p^2}{2m}t}|x\rangle$$

and directly evaluates the matrix element.

10.6.4 The Interaction Picture

Consider the Hamiltonian $H = H_0 + H'$, where H_0 is the Hamiltonian for an imperturbed system. The solutions of the H_0 can be calculated exactly. H' is considered as perturbation.

An example is the Hamiltonian for an electron, $H = \frac{1}{2m} \left(P - \frac{e}{c} A \right)^2 + e\phi$.

In such a case, it is useful to make the ansatz that the operators <u>and</u> the states time dependent. In addition to the operator $u(t, t = 0) \equiv u(+)$, one introduces the operator

$$u_0(t) = e^{-\frac{i}{\hbar} H_0 t} \tag{10.216}$$

and defines the Interaction picture or Schrödinger picture as

$$A_I(t) := U_0^{-1}(t) A_S U_0(t) |\psi_I(t)\rangle := U_0^{-1}(t) U(t) |\psi_x(O)\rangle .$$
 (10.217)

For t = 0 follows

$$A_I(O) = A_S = A_H(O) = A$$

 $|\psi_I(O)\rangle = |\psi_s(O)\rangle = |\psi_H\rangle$.

Similar to the Heisenberg picture, the Interaction picture is evolving from the Schrödinger picture through a unitary transformation, where $u_0^{-1}(t)$. The difference is that the time dependence introduced by H' is now transferred on the states, which are constant in the Heisenberg picture. The time dependence is given according to (10.217) through the unitary operator

$$\omega(t) = U_0^{-1}(t) \ U(t) \ . \tag{10.218}$$

If H is time independent, then

$$\omega(t) \ U_0^{-1}(t) \ U(t) = e^{-\ \frac{i}{\hbar} \ H_0 t} \ e^{-\ \frac{i}{\hbar} \ H t} \ .$$

Derivation of a different equation for $\omega(t)$:

$$i\hbar \frac{d}{dt} \omega(t) = i\hbar \left(\frac{d}{dt} U_0(t)\right) U + i\hbar U_0^{\dagger} \frac{d}{dt} U \equiv -U_0^{\dagger} H u + U_0^{\dagger} H U$$
$$= U_0^{-1} (H - H_0) U$$

Introduce the operator

$$H_I(t) := U_0^{-1}(t) H'U_0(t)$$
 (10.219)

so that

$$i\hbar \frac{d\omega(t)}{dt} = H_I(t)\omega(t)$$

$$\omega(0) = \mathbf{1}$$

$$|\psi_I(t)\rangle = \omega(t) |\psi_s(0)\rangle. \qquad (10.220)$$

 $H_I(t)$ is called "interaction operator" and essentially carries the time dependence

$$H(t) = H_0 + H'(t) .$$

All previous derivations stay valid since the differential equation $i\hbar \frac{d}{dt} U(t, t_0) = H(t) U(t, t_0)$ was only used for U(t) = U(t, 0). It is important to realize that $H_I(t)$ for different times does not commute

$$[H_I(t), H_I(t')] \neq 0 \quad \text{for } t \neq t' .$$
 (10.221)

Consider the one-dimensional motion

$$Q_I(t) = e^{-\frac{i}{\hbar} H_0 t} Q(O) e^{-\frac{i}{\hbar} H_0 t} = Q(O) + \frac{p}{m} t ,$$

$$H_I(t) = H'(Q_I(t)) = H'(Q(O) + \frac{P}{m} t) ,$$

and

$$[Q_I(t), Q_I(t')] - \frac{\hbar}{im} (t - t')$$
.

10.6.5 Dirac-Dyson Time-Dependent Perturbation Theory

In general, the differential equation for the operator $\omega(t)$,

$$i\hbar \frac{d}{dt} \omega(t) = H_I(t) \omega(t)$$
 (10.222)

or in integral (solved) form

$$\omega(t) = \mathbf{1} - \frac{i}{\hbar} \int_0^t d\tau \ H_I(\tau) \ \omega(\tau) \ . \tag{10.223}$$

The boundary condition $\omega(0) = 1$ is incorporated in (10.223). The advantage of this formulation is that one can impose an iterative procedure for determining $\omega(t)$.

- On the right-hand side, stet $\omega(\tau) = 0$, then $\omega(t) \approx \omega(t) = 1$.
- One puts $\omega(\tau) = 0$, and thus $\omega(t) \approx \omega_0(t) = 1$.

Inserting $\omega(\tau_1) = \mathbf{1}$ one obtains

$$\omega(t) \approx \mathbf{1} - \frac{i}{\hbar} \int_0^t dt \ H_I(\tau_1) \ d\tau$$
$$= \omega_1 + \omega_2(t) \ .$$

The result is reinserted into (10.223), and one obtains as second-order approximation

$$\omega(t) \approx -\frac{1}{\hbar} \int_0^t H_I(\tau_1) \left\{ \mathbf{1} - \frac{i}{\hbar} \int_0^{\tau_1} H_I(\tau_2) d\tau_2 \right\} d\tau_1
= \mathbf{1} - \frac{i}{\hbar} \int_0^t H_I(\tau_1) + \left(\frac{-1}{\hbar} \right)^2 \int_0^t d\tau_1 \int_0^{t_2} H_I(\tau_1) H_I(\tau_2) d\tau_1 d\tau_2
:= \omega_0 + \omega_1(t) + \omega_2(t) .$$

This procedure can be continued for arbitrary, and one obtains an infinite series:

$$\omega(t) = \sum_{k=0}^{\infty} \omega_H(t) \tag{10.224}$$

with the terms

$$\omega_{0} = \mathbf{1}
\omega_{1}(t) = -\frac{i}{\hbar} \int_{0}^{t} H_{I}(\tau_{1}) d\tau_{1}
\omega_{2}(t) = \left(-\frac{i}{\hbar}\right)^{2} \int_{0}^{t} \int_{0}^{t_{1}} H_{I}(\tau_{1}) H_{i}(\tau_{2}) d\tau_{1} d\tau_{2}
\vdots
\omega_{n}(t) = \left(\frac{-1}{\hbar}\right)^{n} \int_{0}^{t} \int_{0}^{\tau_{1}} \cdots \int_{0}^{\tau_{n-1}} H_{I}(t_{1}) H_{I}(\tau_{2}) \cdots H_{I}(\tau_{n}) d\tau_{n} \cdots d\tau_{2} dt (\mathfrak{A}) 0.225)$$

Assuming that the series converges and that the differentation is allowed, (10.225) is an explicit construction of solutions to (10.222):

$$i\hbar \frac{d}{dt} \omega_n(t) = \left(\frac{-i}{\hbar}\right)^{n-1} H_I(t) \int_0^t \int_0^{\tau_{n-1}} H_I(\tau_2) H_I(\tau_3) \cdots H_I(\tau_n) d\tau_n \cdots d\tau_{n-1}$$

= $H_I(t) \omega_{n-1}(t)$.

Thus

$$i\hbar \frac{d}{dt} \omega(t) = \sum_{n=1}^{\infty} H_I(t) \omega_{n-1}(t) = H_I(t) \sum_{n=1}^{\infty} \omega_n(t)$$
$$= H_I(t) \omega(t) .$$

The initial conditions are fulfilled since

$$\omega_n(0) = 0$$
 for $n = 1, 2, \cdots$.

Define a time-ordered product

$$T(H_I(\tau_1) \ H_I(\tau_2)) \equiv \begin{cases} H_I(\tau_1) \ H_I(\tau_2) & \text{for } \tau_1 \ge \tau_2 \\ H_I(\tau_2) \ H_I(\tau_1) & \text{for } \tau_2 \ge \tau_1 \end{cases}$$
 (10.226)

The operator with the largest time sits to the left.

From this follows

$$\int_{0}^{t} \int_{0}^{t} T(H_{I}(\tau_{1}) H_{I}(\tau_{2})) d\tau_{1} d\tau_{2}$$

$$= \int_{0}^{t} \int_{0}^{\tau_{2}} T(H_{I}(\tau_{1}) H_{I}(\tau_{2})) d\tau_{1} d\tau_{2} + \int_{0}^{t} \int_{\tau_{1}}^{1} T(H_{I}(\tau_{1}) H_{I}(\tau_{2})) d\tau_{1} d\tau_{2}$$

$$= \int_{0}^{t} \int_{0}^{\tau_{1}} H_{I}(\tau_{1}) H_{I}(\tau_{2}) d\tau_{1} d\tau_{2} + \int_{0}^{t} \int_{\tau_{1}}^{t} H_{I}(\tau_{2}) H_{I}(\tau_{1}) d\tau_{1} d\tau_{2} . \quad (10.227)$$

The second term can be further modified.

For arbitrary functions one has

$$\int_0^t \int_{\tau_1}^t T(\tau_1, \tau_2) \ d\tau_2 \ d\tau_1 = \int_0^t \int_0^{\tau_2} T(\tau_1, \tau_2) \ d\tau_1 \ d\tau_2 \ .$$

On both sides of the equation, one integrates over the same region. Applied in the current situation, this means

$$\int_{0}^{t} \int_{t_{1}}^{t} H_{I}(\tau_{2}) H_{I}(\tau_{1}) d\tau_{1} d\tau_{2} = \int_{0}^{t} \int_{0}^{\tau_{2}} H_{I}(\tau_{2}) H_{I}(\tau_{1}) d\tau_{1} d\tau_{2}
= \int_{0}^{t} \int_{0}^{\tau_{1}} H_{I}(\tau_{1}) H_{I}(t_{2}) d\tau_{2} d\tau_{1}.$$

Thus, one see that the two integral in (10.227) are identical. One can obtain this result immediately if one notices that

$$T(H_I(\tau_1)H_I(\tau_2)) = T(H_I(\tau_2) H_I(\tau_1))$$
,

i.e., that the integrand of (10.227) is symmetric with respect to the diagonal $\tau_1 = \tau_2$.

Thus we get for $\omega_2(t)$:

$$\omega_2(t) = \frac{1}{2!} \left(\frac{-i}{\hbar}\right)^2 \int_0^t \int_0^t T(H_I(\tau_1) H_I(\tau_2)) d\tau_1 d\tau_2$$
 (10.228)

and

$$\omega_n(t) = \frac{1}{h!} \left(\frac{-1}{\hbar} \right)^n \int_0^t \cdots \int_0^t T(H_I(\tau_1) \ H_I(\tau_2) \cdots H_I(\tau_n)) \ d\tau_n \cdots d\tau_2 \ d\tau_3 \ . (10.229)$$

Thus the expansion

$$\omega(t) = \sum_{n=0}^{\infty} \omega_n(t)$$

proved to be correct.

This series can be written as

$$\omega(t) = T\left(e^{\frac{i}{\hbar}} \int_0^t H_I(\tau) d\tau_2\right)$$

$$:= \sum_{n=0}^{\infty} \frac{1}{h!} \left(\frac{-1}{\hbar}\right)^n \int_0^t \cdots \int_0^t T(H_I(\tau_1) H_2(\tau_2) \cdots H_I(\tau_n) d\tau_n \cdots d\tau_2 d\tau_2.$$

This expression is also known as **Dyson's formula**.