Chapter 9
Stationary Perturbations in Quantum Mechanics

We denote a quantum system with a time-independent Hamiltonian H_0 as *solvable* (or sometimes also as *exactly solvable*) if we can calculate the energy eigenvalues and eigenstates of H_0 analytically. The harmonic oscillator and the hydrogen atom provide two examples of solvable quantum systems. Exactly solvable systems provide very useful models for quantum behavior in physical systems. The harmonic oscillator describes systems near a stable equilibrium, while the Hamiltonian with a Coulomb potential is an important model system for atomic physics and for every quantum system which is dominated by Coulomb interactions. However, in many cases the Schrödinger equation will not be solvable, and we have to go beyond solvable model systems to calculate quantitative properties. In these cases we have to resort to the calculation of approximate solutions. The methods developed in the present chapter are applicable to perturbations of discrete energy levels by time-independent perturbations V of the Hamiltonian, $H_0 \to H = H_0 + V$.

9.1 Time-independent perturbation theory without degeneracies

We consider a perturbation of a solvable time-independent Hamiltonian H_0 by a time-independent term V, and for bookkeeping purposes we extract a coupling constant λ from the perturbation,

$$H = H_0 + V \to H = H_0 + \lambda V.$$

After the relevant expressions for shifts of states and energy levels have been calculated to the desired order in λ, we usually subsume λ again in V, such that e.g. $\lambda\langle\phi^{(0)}|V|\psi^{(0)}\rangle \to \langle\phi^{(0)}|V|\psi^{(0)}\rangle$.

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We know the unperturbed energy levels and eigenstates of the solvable Hamiltonian H_0,

$$H_0|\psi_j^{(0)}\rangle = E_j^{(0)}|\psi_j^{(0)}\rangle.$$

In the present section we assume that the energy levels $E_j^{(0)}$ are not degenerate, and we want to calculate in particular approximations for the energy level E_i which arises from the unperturbed energy level $E_i^{(0)}$ due to the presence of the perturbation V. We will see below that consistency of the formalism requires that the differences $|E_i^{(0)} - E_j^{(0)}|$ for $j \neq i$ must have a positive minimal value, i.e. the unperturbed energy level $E_i^{(0)}$ for which we want to calculate corrections has to be discrete[1].

Orthogonality of eigenstates for different energy eigenvalues implies

$$\langle\psi_i^{(0)}|\psi_j^{(0)}\rangle = \delta_{ij}.$$

In the most common form of time-independent perturbation theory we try to find an approximate solution to the equation

$$H|\psi_i\rangle = E_i|\psi_i\rangle$$

in terms of power series expansions in the coupling constant λ,

$$|\psi_i\rangle = \sum_{n\geq 0}\lambda^n|\psi_i^{(n)}\rangle, \quad \langle\psi_i^{(0)}|\psi_i^{(n\geq 1)}\rangle = 0, \quad E_i = \sum_{n\geq 0}\lambda^n E_i^{(n)}. \tag{9.1}$$

Depending on the properties of V, these series may converge for small values of $|\lambda|$, or they may only hold as asymptotic expansions for $|\lambda| \to 0$. The book by Kato [21] provides results and resources on convergence and applicability properties of the perturbation series. Here we will focus on the commonly used first and second order expressions for wave functions and energy levels.

We can require

$$\langle\psi_i^{(0)}|\psi_i^{(n)}\rangle = \delta_{n,0} \tag{9.2}$$

because the recursion equation (9.3) below, which is derived without the assumption (9.2), does not determine these particular coefficients. One way to understand this is to observe that we can decompose $|\psi_i^{(n\geq 1)}\rangle$ into terms parallel and orthogonal to $|\psi_i^{(0)}\rangle$,

$$|\psi_i^{(n\geq 1)}\rangle = |\psi_i^{(0)}\rangle\langle\psi_i^{(0)}|\psi_i^{(n\geq 1)}\rangle + |\psi_i^{(n\geq 1)}\rangle - |\psi_i^{(0)}\rangle\langle\psi_i^{(0)}|\psi_i^{(n\geq 1)}\rangle.$$

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[1] This condition is not affected by a possible degeneracy of $E_i^{(0)}$, as will be shown in Section 9.2.

Inclusion of the parallel part $|\psi_i^{(0)}\rangle\langle\psi_i^{(0)}|\psi_i^{(n\geq 1)}\rangle$ in the zeroth order term, followed by a rescaling by

$$\left(1+\langle\psi_i^{(0)}|\psi_i^{(n\geq 1)}\rangle\right)^{-1} = 1-\langle\psi_i^{(0)}|\psi_i^{(n\geq 1)}\rangle + \mathcal{O}(\lambda^{2n})$$

to restore a coefficient 1 in the zeroth order term, affects only terms of order λ^{n+1} or higher in the perturbation series. This implies that if we have solved the Schrödinger equation to order λ^{n-1} with the constraint

$$\langle\psi_i^{(0)}|\psi_i^{(m)}\rangle = \delta_{m,0}, \quad 0\leq m\leq n-1,$$

then ensuring that constraint also to order λ^n preserves the constraint for the lower order terms. Therefore we can fulfill the constraint (9.2) to any desired order in which we wish to calculate the perturbation series.

Substitution of the perturbative expansions into the Schrödinger equation $H|\psi_i\rangle = E_i|\psi_i\rangle$ yields

$$\begin{aligned}\sum_{n\geq 0}\lambda^n H_0|\psi_i^{(n)}\rangle + \sum_{n\geq 0}\lambda^{n+1}V|\psi_i^{(n)}\rangle &= \sum_{m,n\geq 0}\lambda^{m+n}E_i^{(m)}|\psi_i^{(n)}\rangle \\ &= \sum_{n\geq 0}\sum_{m=0}^{n}\lambda^n E_i^{(m)}|\psi_i^{(n-m)}\rangle.\end{aligned}$$

This equation is automatically fulfilled at zeroth order. Isolation of terms of order λ^{n+1} for $n\geq 0$ yields

$$H_0|\psi_i^{(n+1)}\rangle + V|\psi_i^{(n)}\rangle = \sum_{m=0}^{n+1}E_i^{(m)}|\psi_i^{(n-m+1)}\rangle,$$

and projection of this equation onto $|\psi_j^{(0)}\rangle$ yields

$$\begin{aligned}E_j^{(0)}\langle\psi_j^{(0)}|\psi_i^{(n+1)}\rangle + \langle\psi_j^{(0)}|V|\psi_i^{(n)}\rangle = &\sum_{m=0}^{n}E_i^{(m)}\langle\psi_j^{(0)}|\psi_i^{(n-m+1)}\rangle \\ &+E_i^{(n+1)}\delta_{ij}.\end{aligned} \tag{9.3}$$

We can first calculate the first order corrections for energy levels and wave functions from this equation, and then solve it recursively to any desired order.

First order corrections to the energy levels and eigenstates

The first order corrections are found from equation (9.3) for $n = 0$. Substitution of $j = i$ implies for the first order shifts of the energy levels the result

$$E_i^{(1)} = \langle\psi_i^{(0)}|V|\psi_i^{(0)}\rangle, \tag{9.4}$$

and $j \neq i$ yields with $E_i^{(0)} \neq E_j^{(0)}$ the first order shifts of the energy eigenstates

$$\langle\psi_j^{(0)}|\psi_i^{(1)}\rangle = \frac{\langle\psi_j^{(0)}|V|\psi_i^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}}. \tag{9.5}$$

Recursive solution of equation (9.3) for n ≥ 1

We first observe that $j = i$ in equation (9.3) implies with the condition (9.2)

$$E_i^{(n+1)} = \langle\psi_i^{(0)}|V|\psi_i^{(n)}\rangle - \sum_{m=1}^{n} E_i^{(m)}\langle\psi_i^{(0)}|\psi_i^{(n-m+1)}\rangle = \langle\psi_i^{(0)}|V|\psi_i^{(n)}\rangle, \tag{9.6}$$

and $i \neq j$ yields

$$\begin{aligned}\left(E_i^{(0)} - E_j^{(0)}\right)\langle\psi_j^{(0)}|\psi_i^{(n+1)}\rangle &= \langle\psi_j^{(0)}|V|\psi_i^{(n)}\rangle \\ &\quad - \sum_{m=1}^{n} E_i^{(m)}\langle\psi_j^{(0)}|\psi_i^{(n-m+1)}\rangle.\end{aligned} \tag{9.7}$$

The right hand side of both equations depends only on lower order shifts of energy levels and eigenstates. Therefore these equations can be used for the recursive solution of equation (9.3) to arbitrary order.

Second order corrections to the energy levels and eigenstates

Substitution of $n = 1$ into equation (9.6) yields with (9.5) and

$$\sum\!\!\!\!\!\!\int_k |\psi_k^{(0)}\rangle\langle\psi_k^{(0)}| = 1$$

the second order shift

$$E_i^{(2)} = \sum\!\!\!\!\!\!\int_{k\neq i} \frac{\langle\psi_i^{(0)}|V|\psi_k^{(0)}\rangle\langle\psi_k^{(0)}|V|\psi_i^{(0)}\rangle}{E_i^{(0)} - E_k^{(0)}} = \sum\!\!\!\!\!\!\int_{k\neq i} \frac{|\langle\psi_i^{(0)}|V|\psi_k^{(0)}\rangle|^2}{E_i^{(0)} - E_k^{(0)}}. \tag{9.8}$$

States in the continuous part of the spectrum of H_0 will also contribute to the shifts in energy levels and eigenstates. It is only required that the energy level $E_i^{(0)}$, for which we want to calculate the corrections, is discrete and does not overlap with any continuous energy levels.

Note that equation (9.8) implies that the second order correction to the ground state energy is always negative.

For the eigenstates, equation (9.7) yields with the first order results (9.4, 9.5) the equation (recall $i \neq j$ in (9.7))

$$\langle\psi_j^{(0)}|\psi_i^{(2)}\rangle = \sum_{k\neq i} \frac{\langle\psi_j^{(0)}|V|\psi_k^{(0)}\rangle\langle\psi_k^{(0)}|V|\psi_i^{(0)}\rangle}{\left(E_i^{(0)} - E_j^{(0)}\right)\left(E_i^{(0)} - E_k^{(0)}\right)} - \frac{\langle\psi_i^{(0)}|V|\psi_i^{(0)}\rangle\langle\psi_j^{(0)}|V|\psi_i^{(0)}\rangle}{\left(E_i^{(0)} - E_j^{(0)}\right)^2}. \tag{9.9}$$

Now we can explain why it is important that our original unperturbed energy level $E_i^{(0)}$ is discrete. To ensure that the n-th order corrections to the energy levels and eigenstates in equations (9.1) are really of order λ^n (or smaller than all previous terms), the matrix elements $|\langle\psi_j^{(0)}|V|\psi_k^{(0)}\rangle|$ of the perturbation operator should be at most of the same order of magnitude as the energy differences $|E_i^{(0)} - E_j^{(0)}|$ between the unperturbed level $E_i^{(0)}$ and the other unperturbed energy levels in the system. This implies in particular that the minimal absolute energy difference between $E_i^{(0)}$ and the other unperturbed energy levels must not vanish, i.e. $E_i^{(0)}$ must be a discrete energy level.

Equations (9.4) and (9.8) (and their counterparts (9.16) and (9.24) in degenerate perturbation theory below) used to be the most frequently employed equations of time-independent perturbation theory, because historically many experiments were concerned with spectroscopic determinations of energy levels. However, measurements e.g. of local electron densities or observations of wave functions (e.g. in scanning tunneling microscopes or through X-ray scattering using synchrotrons) are very common nowadays, and therefore the corrections to the states are also directly relevant for the interpretation of experimental data.

Summary of non-degenerate perturbation theory in second order

If we include λ with V, the states and energy levels in second order are

$$\begin{aligned}|\psi_i\rangle &= |\psi_i^{(0)}\rangle + |\psi_i^{(1)}\rangle + |\psi_i^{(2)}\rangle = |\psi_i^{(0)}\rangle \\ &+ \sum_{j\neq i} |\psi_j^{(0)}\rangle \frac{\langle\psi_j^{(0)}|V|\psi_i^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}} + \sum_{j,k\neq i} |\psi_j^{(0)}\rangle \frac{\langle\psi_j^{(0)}|V|\psi_k^{(0)}\rangle\langle\psi_k^{(0)}|V|\psi_i^{(0)}\rangle}{\left(E_i^{(0)} - E_j^{(0)}\right)\left(E_i^{(0)} - E_k^{(0)}\right)} \\ &- \sum_{j\neq i} |\psi_j^{(0)}\rangle \frac{\langle\psi_j^{(0)}|V|\psi_i^{(0)}\rangle\langle\psi_i^{(0)}|V|\psi_i^{(0)}\rangle}{\left(E_i^{(0)} - E_j^{(0)}\right)^2}\end{aligned} \tag{9.10}$$

and

$$E_i = E_i^{(0)} + \langle\psi_i^{(0)}|V|\psi_i^{(0)}\rangle + \sum_{j\neq i}\frac{|\langle\psi_i^{(0)}|V|\psi_j^{(0)}\rangle|^2}{E_i^{(0)} - E_j^{(0)}}. \tag{9.11}$$

The second order states $|\psi_i\rangle$ are not normalized any more,

$$\langle\psi_i|\psi_j\rangle = \delta_{ij} + \mathcal{O}(\lambda^2)\delta_{ij}.$$

Normalization is preserved in first order due to

$$\langle\psi_i^{(0)}|\psi_j^{(1)}\rangle + \langle\psi_i^{(1)}|\psi_j^{(0)}\rangle = 0,$$

but in second order we have

$$\langle\psi_i^{(0)}|\psi_j^{(2)}\rangle + \langle\psi_i^{(1)}|\psi_j^{(1)}\rangle + \langle\psi_i^{(2)}|\psi_j^{(0)}\rangle = \sum_{k\neq i}\frac{|\langle\psi_i^{(0)}|V|\psi_k^{(0)}\rangle|^2}{\left(E_i^{(0)} - E_k^{(0)}\right)^2}\delta_{ij}.$$

However, we can add to the leading term $|\psi_i^{(0)}\rangle$ in $|\psi_i\rangle$ a term of the form $|\psi_i^{(0)}\rangle\mathcal{O}(\lambda^2)$ and still preserve the master equation (9.3) to second order. We can therefore rescale (9.10) by a factor $[1 + \mathcal{O}(\lambda^2)]^{-1/2}$ to a normalized second order state

$$\begin{aligned}|\psi_i\rangle = {}& |\psi_i^{(0)}\rangle - \frac{1}{2}|\psi_i^{(0)}\rangle\sum_{j\neq i}\frac{|\langle\psi_i^{(0)}|V|\psi_j^{(0)}\rangle|^2}{\left(E_i^{(0)} - E_j^{(0)}\right)^2} + \sum_{j\neq i}|\psi_j^{(0)}\rangle\frac{\langle\psi_j^{(0)}|V|\psi_i^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}}\\ &+ \sum_{j,k\neq i}|\psi_j^{(0)}\rangle\frac{\langle\psi_j^{(0)}|V|\psi_k^{(0)}\rangle\langle\psi_k^{(0)}|V|\psi_i^{(0)}\rangle}{\left(E_i^{(0)} - E_j^{(0)}\right)\left(E_i^{(0)} - E_k^{(0)}\right)}\\ &- \sum_{j\neq i}|\psi_j^{(0)}\rangle\frac{\langle\psi_j^{(0)}|V|\psi_i^{(0)}\rangle\langle\psi_i^{(0)}|V|\psi_i^{(0)}\rangle}{\left(E_i^{(0)} - E_j^{(0)}\right)^2}.\end{aligned} \tag{9.12}$$

Now the second order shift is not orthogonal to $|\psi_i^{(0)}\rangle$ any more, but we still have a solution of equation (9.3) to second order.

9.2 Time-independent perturbation theory with degenerate energy levels

Now we admit degeneracy of energy levels of our unperturbed Hamiltonian H_0. Time-independent perturbation theory in the previous section repeatedly involved division by energy differences $[E_i^{(0)} - E_j^{(0)}]_{i\neq j}$. This will not be possible any more for pairs of degenerate energy levels, and we have to carefully reconsider each step in the previous derivation if degeneracies are involved.

The full Hamiltonian and the 0-th order results are now

$$H = H_0 + \lambda V,\ H_0|\psi_{j\alpha}^{(0)}\rangle = E_j^{(0)}|\psi_{j\alpha}^{(0)}\rangle,$$

where Greek indices denote sets of degeneracy indices. For example, if H_0 would correspond to a hydrogen atom, the quantum number j would correspond to the principal quantum number n of a bound state or the wave number k of a spherical Coulomb wave, and the degeneracy index α would correspond to the set of angular momentum quantum number, magnetic quantum number, and spin projection, $\alpha = \{\ell, m_\ell, m_s\}$. For the same reasons as in equation (9.9), the energy level for which we wish to calculate an approximation must be discrete, i.e. the techniques developed in this chapter can be used to study perturbations of the bound states of hydrogen atoms, but not perturbations of Coulomb waves.

We denote the degeneracy subspace to the energy level $E_j^{(0)}$ as $\mathcal{E}_j$ and the projector on $\mathcal{E}_j$ is

$$\mathcal{P}_j^{(0)} = \sum_\alpha |\psi_{j\alpha}^{(0)}\rangle\langle\psi_{j\alpha}^{(0)}|.$$

As in the previous section, we wish to calculate approximations for the energy level $E_{i\alpha}$ and corresponding eigenstates $|\psi_{i\alpha}\rangle$, $H|\psi_{i\alpha}\rangle = E_{i\alpha}|\psi_{i\alpha}\rangle$, which arise from the energy level $E_i^{(0)}$ and the eigenstates $|\psi_{i\alpha}^{(0)}\rangle$ due to the perturbation V. The energy level $E_i^{(0)}$ may split into several energy levels $E_{i\alpha}$ because the perturbation might lift the degeneracy of $E_i^{(0)}$. We will actually assume that the perturbation V lifts the degeneracy of the energy level $E_i^{(0)}$ already at first order, $E_{i\alpha}^{(1)} \neq E_{i\beta}^{(1)}$ if $\alpha \neq \beta$.

The Rayleigh-Ritz-Schrödinger *ansatz* is

$$|\psi_{i\alpha}\rangle = \sum_{n\geq 0}\lambda^n|\psi_{i\alpha}^{(n)}\rangle,\ \ \langle\psi_{i\alpha}^{(0)}|\psi_{i\alpha}^{(n\geq 1)}\rangle = 0,\ \ E_{i\alpha} = \sum_{n\geq 0}\lambda^n E_{i\alpha}^{(n)}. \tag{9.13}$$

Substitution into the full time-independent Schrödinger equation yields

$$\begin{aligned}\sum_{n\geq 0}\lambda^n H_0|\psi_{i\alpha}^{(n)}\rangle + \sum_{n\geq 0}\lambda^{n+1}V|\psi_{i\alpha}^{(n)}\rangle &= \sum_{m,n\geq 0}\lambda^{m+n}E_{i\alpha}^{(m)}|\psi_{i\alpha}^{(n)}\rangle \\ &= \sum_{n\geq 0}\sum_{m=0}^{n}\lambda^n E_{i\alpha}^{(m)}|\psi_{i\alpha}^{(n-m)}\rangle.\end{aligned}$$

This is yields in $(n+1)$-st order for $n \geq 0$

$$H_0|\psi_{i\alpha}^{(n+1)}\rangle + V|\psi_{i\alpha}^{(n)}\rangle = \sum_{m=0}^{n+1}E_{i\alpha}^{(m)}|\psi_{i\alpha}^{(n-m+1)}\rangle. \tag{9.14}$$

We determine the corrections $|\psi_{i\alpha}^{(n\geq 1)}\rangle$ to the wave functions through their projections $\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n\geq 1)}\rangle$ onto the basis of unperturbed states. Projection of equation (9.14) yields

$$E_j^{(0)}\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n+1)}\rangle + \langle\psi_{j\beta}^{(0)}|V|\psi_{i\alpha}^{(n)}\rangle = \sum_{m=0}^{n} E_{i\alpha}^{(m)}\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n-m+1)}\rangle + E_{i\alpha}^{(n+1)}\delta_{ij}\delta_{\alpha\beta}. \tag{9.15}$$

First order corrections to the energy levels

The first order equations ($n = 0$ in equation (9.15)) yield for $j = i$ and $\beta = \alpha$ the equation

$$E_{i\alpha}^{(1)} = \langle\psi_{i\alpha}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle, \tag{9.16}$$

while $j = i$, $\alpha \neq \beta$ imposes a consistency condition on the choice of basis of unperturbed states,

$$\langle\psi_{i\beta}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle\Big|_{\beta\neq\alpha} = 0, \tag{9.17}$$

This condition means that we have to diagonalize V first *within each degeneracy subspace* $\mathcal{E}_i$ in the sense

$$V|\psi_{i\alpha}^{(0)}\rangle = E_{i\alpha}^{(1)}|\psi_{i\alpha}^{(0)}\rangle + \sum\!\!\!\!\!\!\int_{j\neq i}\sum_{\beta}|\psi_{j\beta}^{(0)}\rangle\langle\psi_{j\beta}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle, \tag{9.18}$$

before we can use the perturbation *ansatz* (9.13), and according to (9.16) the first order energy corrections $E_{i\alpha}^{(1)}$ are the corresponding eigenvalues in the i-th degeneracy subspace. If the first order energy corrections $E_{i\alpha}^{(1)}$ are all we care about, this means that we can calculate them from the eigenvalue conditions

$$\det\Big[\langle\psi_{i\beta}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle - E_{i\alpha}^{(1)}\delta_{\alpha\beta}\Big] = 0, \tag{9.19}$$

using any initial choice of unperturbed orthogonal energy eigenstates. But that would achieve only a very limited objective.

As also indicated in equation (9.18), diagonalization within the subspaces means only diagonalization of the operators $\mathcal{P}_i^{(0)}V\mathcal{P}_i^{(0)}$, which does *not* amount to total diagonalization of V,

$$\sum_i \mathcal{P}_i^{(0)}V\mathcal{P}_i^{(0)} \neq V = \sum_{i,j}\mathcal{P}_i^{(0)}V\mathcal{P}_j^{(0)}.$$

We still will have non-vanishing transition matrix elements $\langle\psi_{j\beta}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle \neq 0$ between different degeneracy subspaces $i \neq j$.

First order corrections to the energy eigenstates

Setting $i \neq j$ in equation (9.15) yields a part of the first order corrections to the wave functions,

$$\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(1)}\rangle = \frac{\langle\psi_{j\beta}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}}. \tag{9.20}$$

However, this yields only the projections $\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(1)}\rangle$ of the first order corrections $|\psi_{i\alpha}^{(1)}\rangle$ onto the unperturbed states for $j \neq i$. We need to use $j = i$ in the second order equations to calculate the missing terms $\langle\psi_{i\beta}^{(0)}|\psi_{i\alpha}^{(1)}\rangle$, $(\beta \neq \alpha)$, for the first order corrections.

Equation (9.15) yields for $n = 1, j = i$ and $\beta \neq \alpha$ the equation

$$\langle\psi_{i\beta}^{(0)}|V|\psi_{i\alpha}^{(1)}\rangle\Big|_{\beta\neq\alpha} = E_{i\alpha}^{(1)}\ \langle\psi_{i\beta}^{(0)}|\psi_{i\alpha}^{(1)}\rangle\Big|_{\beta\neq\alpha}$$

and after substitution of equations (9.16, 9.17, 9.20)

$$\begin{aligned}\left(E_{i\alpha}^{(1)} - E_{i\beta}^{(1)}\right)\ \langle\psi_{i\beta}^{(0)}|\psi_{i\alpha}^{(1)}\rangle\Big|_{\beta\neq\alpha} &= \sum\!\!\!\!\!\!\int_{j\neq i}\sum_{\gamma}\langle\psi_{i\beta}^{(0)}|V|\psi_{j\gamma}^{(0)}\rangle\langle\psi_{j\gamma}^{(0)}|\psi_{i\alpha}^{(1)}\rangle \\ &= \sum\!\!\!\!\!\!\int_{j\neq i}\sum_{\gamma}\frac{\langle\psi_{i\beta}^{(0)}|V|\psi_{j\gamma}^{(0)}\rangle\langle\psi_{j\gamma}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}},\end{aligned}$$

i.e. we find the missing pieces of the first order corrections to the states

$$\begin{aligned}\langle\psi_{i\beta}^{(0)}|\psi_{i\alpha}^{(1)}\rangle\Big|_{\beta\neq\alpha} &= \frac{1}{\langle\psi_{i\alpha}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle - \langle\psi_{i\beta}^{(0)}|V|\psi_{i\beta}^{(0)}\rangle} \\ &\quad\times\sum\!\!\!\!\!\!\int_{j\neq i}\sum_{\gamma}\frac{\langle\psi_{i\beta}^{(0)}|V|\psi_{j\gamma}^{(0)}\rangle\langle\psi_{j\gamma}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}}\end{aligned} \tag{9.21}$$

if V has removed the degeneracy between $|\psi_{i\alpha}\rangle$ and $|\psi_{i\beta}\rangle$ in first order, $E_{i\alpha}^{(1)} \neq E_{i\beta}^{(1)}$.

Recursive solution of equation (9.15) for $n \geq 1$

We first rewrite equation (9.15) by inserting

$$1 = \sum\!\!\!\!\!\!\int_{k,\gamma}|\psi_{k\gamma}^{(0)}\rangle\langle\psi_{k\gamma}^{(0)}|$$

in the matrix element of V, and using equations (9.16, 9.17):

$$\begin{aligned}
&E_j^{(0)}\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n+1)}\rangle + E_{j\beta}^{(1)}\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n)}\rangle + \sum\!\!\!\!\!\!\!\int_{k\neq j}\sum_{\gamma}\langle\psi_{j\beta}^{(0)}|V|\psi_{k\gamma}^{(0)}\rangle\langle\psi_{k\gamma}^{(0)}|\psi_{i\alpha}^{(n)}\rangle \\
&= E_i^{(0)}\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n+1)}\rangle + E_{i\alpha}^{(1)}\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n)}\rangle + \Theta(n\geq 2)\sum_{m=2}^{n}E_{i\alpha}^{(m)}\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n-m+1)}\rangle \\
&\quad + E_{i\alpha}^{(n+1)}\delta_{ij}\delta_{\alpha\beta}.
\end{aligned} \tag{9.22}$$

Substitution of $j = i$ and $\beta = \alpha$ yields

$$E_{i\alpha}^{(n+1)} = \sum\!\!\!\!\!\!\!\int_{k\neq i}\sum_{\gamma}\langle\psi_{i\alpha}^{(0)}|V|\psi_{k\gamma}^{(0)}\rangle\langle\psi_{k\gamma}^{(0)}|\psi_{i\alpha}^{(n)}\rangle, \tag{9.23}$$

where equations (9.13, 9.17) have been used. The second order correction is in particular with equation (9.20):

$$E_{i\alpha}^{(2)} = \sum\!\!\!\!\!\!\!\int_{j\neq i}\sum_{\beta}\frac{|\langle\psi_{j\beta}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle|^2}{E_i^{(0)} - E_j^{(0)}}. \tag{9.24}$$

We find again that the second order correction to the ground state energy is always negative.

For the higher order shifts of the states we find for $j \neq i$ in equation (9.22)

$$\begin{aligned}
&\left(E_i^{(0)} - E_j^{(0)}\right)\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n+1)}\rangle = \langle\psi_{j\beta}^{(0)}|V|\psi_{i\alpha}^{(n)}\rangle - \sum_{m=1}^{n}E_{i\alpha}^{(m)}\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n-m+1)}\rangle \\
&= \langle\psi_{j\beta}^{(0)}|V|\psi_{i\alpha}^{(n)}\rangle - \langle\psi_{i\alpha}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n)}\rangle \\
&\quad - \Theta(n\geq 2)\sum_{m=1}^{n-1}\sum\!\!\!\!\!\!\!\int_{k\neq i}\sum_{\gamma}\langle\psi_{i\alpha}^{(0)}|V|\psi_{k\gamma}^{(0)}\rangle\langle\psi_{k\gamma}^{(0)}|\psi_{i\alpha}^{(m)}\rangle\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n-m)}\rangle,
\end{aligned} \tag{9.25}$$

which gives us the contributions $\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n+1)}\rangle\Big|_{j\neq i}$ to the $(n+1)$-st order wave function corrections.

Substitution of $i = j$, $\alpha \neq \beta$ yields finally

$$\begin{aligned}
&\left(E_{i\alpha}^{(1)} - E_{i\beta}^{(1)}\right)\langle\psi_{i\beta}^{(0)}|\psi_{i\alpha}^{(n\geq 1)}\rangle\Big|_{\beta\neq\alpha} = \sum\!\!\!\!\!\!\!\int_{k\neq i}\sum_{\gamma}\langle\psi_{i\beta}^{(0)}|V|\psi_{k\gamma}^{(0)}\rangle\langle\psi_{k\gamma}^{(0)}|\psi_{i\alpha}^{(n)}\rangle \\
&- \Theta(n\geq 2)\sum_{m=2}^{n}E_{i\alpha}^{(m)}\langle\psi_{i\beta}^{(0)}|\psi_{i\alpha}^{(n-m+1)}\rangle = \sum\!\!\!\!\!\!\!\int_{k\neq i}\sum_{\gamma}\langle\psi_{i\beta}^{(0)}|V|\psi_{k\gamma}^{(0)}\rangle\langle\psi_{k\gamma}^{(0)}|\psi_{i\alpha}^{(n)}\rangle \\
&- \Theta(n\geq 2)\sum_{m=1}^{n-1}\sum\!\!\!\!\!\!\!\int_{k\neq i}\sum_{\gamma}\langle\psi_{i\alpha}^{(0)}|V|\psi_{k\gamma}^{(0)}\rangle\langle\psi_{k\gamma}^{(0)}|\psi_{i\alpha}^{(m)}\rangle\langle\psi_{i\beta}^{(0)}|\psi_{i\alpha}^{(n-m)}\rangle.
\end{aligned} \tag{9.26}$$

This gives us the missing pieces $\langle\psi_{i\beta}^{(0)}|\psi_{i\alpha}^{(n)}\rangle\Big|_{\beta\neq\alpha}$ of the n-th order wave function correction for $E_{i\alpha}^{(1)} \neq E_{i\beta}^{(1)}$.

Summary of first order shifts of the level $E_i^{(0)}$ *if the perturbation lifts the degeneracy of the level*

We must diagonalize the perturbation operator V within the degeneracy subspace $\mathcal{E}_i$ in the sense of (9.18), i.e. we must choose the unperturbed eigenstates $|\psi_{i\alpha}^{(0)}\rangle$ such that the equation

$$\langle\psi_{i\alpha}^{(0)}|V|\psi_{i\beta}^{(0)}\rangle = E_{i\alpha}^{(1)}\delta_{\alpha\beta} \tag{9.27}$$

also holds for $\alpha \neq \beta$.

The projections of the first order shifts of the energy eigenstates onto states in other degeneracy sectors are

$$\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(1)}\rangle\Big|_{j\neq i} = \frac{\langle\psi_{j\beta}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}}, \tag{9.28}$$

and the projections within the degeneracy sector are

$$\begin{aligned}\langle\psi_{i\beta}^{(0)}|\psi_{i\alpha}^{(1)}\rangle\Big|_{\beta\neq\alpha} &= \frac{1}{\langle\psi_{i\alpha}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle - \langle\psi_{i\beta}^{(0)}|V|\psi_{i\beta}^{(0)}\rangle}\\ &\quad\times\sum_{j\neq i}\sum_{\gamma}\frac{\langle\psi_{i\beta}^{(0)}|V|\psi_{j\gamma}^{(0)}\rangle\langle\psi_{j\gamma}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}}.\end{aligned} \tag{9.29}$$

This requires that the first order shifts have completely removed the degeneracies in the i-th energy level, $E_{i\beta}^{(1)} \neq E_{i\alpha}^{(1)}$ for $\beta \neq \alpha$.

9.3 Problems

9.1. A one-dimensional harmonic oscillator is perturbed by a term

$$V = \lambda[(a^+)^2 + a^2]^2.$$

Calculate the first and second order corrections to the ground state energy and wave function.

9.2. An atom on a surface is prevented from moving along the surface through a two-dimensional potential

$$V(x,y)=\frac{1}{2}m\omega^2(x^2+y^2)+Ax^4+By^4,\quad A\geq 0,\quad B\geq 0.$$

Find an approximation H_0 for the Hamiltonian of the atom where you can write down exact energy levels and eigenstates for the atom.

Use the remaining terms in $H-H_0$ to calculate first order corrections to the energy levels and eigenstates of the atom.

9.3. Which results do you get for the perturbed system from 9.2 in second order perturbation theory?

9.4. Suppose that the perturbation V has removed all degeneracies in all energy levels of an unperturbed system. Show that all the first order states $|\psi_{i\alpha}^{(0)}\rangle+|\psi_{i\alpha}^{(1)}\rangle$ are orthonormal in first order.

9.5. A hydrogen atom is perturbed by a static electric field $\boldsymbol{E}=\mathcal{E}\boldsymbol{e}_z$ in z direction. This field induces an extra potential

$$V=-e\Phi=e\mathcal{E}z \tag{9.30}$$

in the Hamiltonian for relative motion.

9.5a. Calculate the shift of the ground state energy up to second order in $\mathcal{E}$.

9.5b. Calculate the shift of the ground state wave function up to second order in $\mathcal{E}$.

9.5c. Which constraints on $\mathcal{E}$ do you find from the requirement of applicability of perturbation theory?

9.6. Calculate the first order shifts of the $n=2$ level of hydrogen under the perturbation (9.30).

9.7. A two-level system has two energy eigenstates $|E_\pm\rangle$ with energies

$$H_0|E_\pm\rangle=\left(E_0\pm\frac{\Delta E}{2}\right)|E_\pm\rangle,\quad \Delta E\neq 0.$$

We can use 2-spinor notation such that a general state in the two-level system is

$$|\psi\rangle=\sum_\pm|E_\pm\rangle\langle E_\pm|\psi\rangle\to\psi=\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix},\quad \psi_1=\langle E_+|\psi\rangle,\quad \psi_2=\langle E_-|\psi\rangle.$$

The Hamiltonian in 2-spinor notation is

$$H_0=E_0\underline{1}+\frac{\Delta E}{2}\underline{\sigma}_3.$$

We now perturb the Hamiltonian $H_0 \to H = H_0 + V$ through a term

$$V = \frac{V_1}{2}\underline{\sigma}_1 + \frac{V_2}{2}\underline{\sigma}_2.$$

9.7a. Calculate the first order corrections to the energy levels and eigenstates due to the perturbation V.

9.7b. Calculate the second order corrections to the energy levels and eigenstates due to the perturbation V.

9.7c. The Hamiltonian H is a hermitian 2 × 2 matrix which can be diagonalized exactly.

Calculate the exact energy levels and eigenstates of H. Compare with the perturbative results from 9.7a and 9.7b.

9.8. Which consistency conditions in the degeneracy subspace $\mathcal{E}_i$ would you find if the perturbation V does *not* remove the degeneracy in that subspace in first order?

Solution. The derivation of (9.21) shows that if we still have $E^{(1)}_{i\alpha} = E^{(1)}_{i\beta}$ for all degeneracy indices in $\mathcal{E}_i$, consistency of the second order equation requires that not just the operator $V^{(1)}_i = \mathcal{P}^{(0)}_i V \mathcal{P}^{(0)}_i$ is diagonal, but also that the operator

$$V^{(2)}_i = \mathcal{P}^{(0)}_i V \frac{1 - \mathcal{P}^{(0)}_i}{E^{(0)}_i - H_0} V \mathcal{P}^{(0)}_i$$

is diagonal. However, consistency of the simultaneous diagonalization of $V^{(1)}_i$ and $V^{(2)}_i$ then also implies the condition

$$\left[V^{(1)}_i, V^{(2)}_i\right] = \mathcal{P}^{(0)}_i V \left(\mathcal{P}^{(0)}_i V \frac{1 - \mathcal{P}^{(0)}_i}{E^{(0)}_i - H_0} - \frac{1 - \mathcal{P}^{(0)}_i}{E^{(0)}_i - H_0} V \mathcal{P}^{(0)}_i\right) V \mathcal{P}^{(0)}_i = 0.$$

If V preserves the degeneracy in $\mathcal{E}_i$, but these consistency conditions cannot be met, then $H = H_0 + V$ apparently does not have a complete set of eigenstates which scale analytically under scaling $V \to \lambda V$ of the perturbation.