Chapter 5

Perturbation Theory

5.1 Non-Degenerate Perturbation Theory

Often, the Hamiltonians of physical systems don't lend themselves to convenient analytic solutions. However, there exist ways to start from a known "base" Hamiltonian with known solutions, and then add in a second "perturbation" Hamiltonian which modifies the eigenstates and eigenvalues of the Schrödinger equation. However, since the base eigenstates span the Hilbert space, the new eigenstates can always be written as superpositions of the original ones. The goal of perturbation theory is to iteratively determine higher and higher order corrections to the original state, and by extension also the energy levels of the new perturbed Hamiltonian.

5.1.1 Setting up the problem

Perturbation theory can get very confusing without an adequate notational scheme. To start, we will define the notation used in the remainder of our treatment. We assume that we start with a solved Hamiltonian H_0, meaning that we will consider its energy eigenvalues $E_n^{(0)}$ and eigenstates $|n^{(0)}\rangle$ to be known. Specifically, the time-independent Schrödinger equation for this system is

$$H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle ., \tag{5.1}$$

where the eigenstates form an orthonormal basis such that $\langle k^{(0)}|n^{(0)}\rangle = 0$. We then add a perturbation Hamiltonian V to this system such that the total Hamiltonian becomes $H(\lambda) = H_0 + \lambda V$. The perturbed system obeys a new Schrödinger equation, and we define the new system's energy eigenstates in the following way::

$$\begin{aligned} H(\lambda) |n\rangle_\lambda &= (H_0 + \lambda V) |n\rangle_\lambda = E_n(\lambda) |n\rangle_\lambda \\ |n\rangle_\lambda &= |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots \\ E_n(\lambda) &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \end{aligned} \tag{5.2}$$

Here we have introduced the parameter $0 \leq \lambda \leq 1$ which allows us to track the number of times the perturbation has entered into any given term. The explicit goal of perturnation

theory will be to solve for the energy $E_n(\lambda)$ of a particular state (labeled n) up to a specific order λ in the perturbation, and similarly for the state $|n\rangle_\lambda$. This means that we will need to solve for the energy shifts $E_n^{(1)}$, $E_n^{(2)}$, ... and the eigenstate corrections $|n^{(1)}\rangle$, $|n^{(2)}\rangle$, ... up to the desired order in the perturbation. The known quantities which are allowed to appear in the solutions are the base Hamiltonian H_0, its eigenvalues $E_n^{(0)}$, its states $|n^{(0)}\rangle$, and the perturbation Hamiltonian V.

The perturbative solutions we derive must be valid for a "tunable" λ, and therefore we can group all terms of the same order in λ together to generate an infinite number of simultaneous equations. If the perturbation is weak, the eigenvalues and eigenstates should stay similar to their unperturbed values, and higher order terms will be progressively smaller. Note that we will not require the states $|n\rangle_\lambda$ to be normalized. Rather, they can be normalized at the end.

Grouping terms of the full Schrödinger equation by the order of λ, we can write the infinite set of equations explicitly:

$$\begin{aligned}
\lambda^0 &: \quad (H_0 - E_n^{(0)})\,|n^{(0)}\rangle = 0 \\
\lambda^1 &: \quad (H_0 - E_n^{(0)})\,|n^{(1)}\rangle = -V\,|n^{(0)}\rangle + E_n^{(1)}\,|n^{(0)}\rangle \\
\lambda^2 &: \quad (H_0 - E_n^{(0)})\,|n^{(2)}\rangle = -V\,|n^{(1)}\rangle + E_n^{(1)}\,|n^{(1)}\rangle + E_n^{(2)}\,|n^{(0)}\rangle \\
&\vdots \qquad\qquad\qquad\qquad \vdots \\
\lambda^k &: \quad (H_0 - E_n^{(0)})\,|n^{(k)}\rangle = -V\,|n^{(k-1)}\rangle + \sum_{m=0}^{k-1} E_n^{(k-m)}\,|n^{(m)}\rangle
\end{aligned} \tag{5.3}$$

Here we have placed the highest order state on the left-hand side, and all lower states on the right. It's clear that the equation for λ^0 order just reproduces the unperturbed Schrödinger equation, and is automatically satisfied by our initial assumptions.

5.1.2 Solving for the energy shifts

More interestingly, taking the inner product of the left-hand side of Eq. 5.3 (order λ^k) with $|n^{(0)}\rangle$ we see that

$$\langle n^{(0)}|(H_0 - E_n^{(0)})|n^{(k)}\rangle = 0, \tag{5.4}$$

where we have used the hermiticity of H_0 to obtain $\langle n^{(0)}|\,H_0 = \langle n^{(0)}|\,E_n^{(0)}$. Using this result, and taking the same inner product with the right-hand side of this equation, and moving the V term over, results in:

$$\langle n^{(0)}|V|n^{(k-1)}\rangle = \sum_{m=0}^{k-1} E_n^{(k-m)}\,\langle n^{(0)}|n^{(m)}\rangle = E_n^{(k)} + \sum_{m=1}^{k-1} E_n^{(k-m)}\,\langle n^{(0)}|n^{(m)}\rangle \tag{5.5}$$

We now assert that, without any loss of generality, we can construct our solutions such that $\langle n^{(0)}|n^{(m)}\rangle = \delta_{0m}$. In other words, the perturbative changes to the eigenstates have no component along the original eigenstate. We can show this is true by writing down the

expression for $|n\rangle_\lambda$, but for now assuming that the perturbative solutions do have components along $|n^{(0)}\rangle$ and writing this down explicitly as:

$$|n\rangle'_\lambda = |n^{(0)}\rangle + \sum_{k=1}^{\infty} \lambda^k (|n^{(k)}\rangle' + c_k |n^{(0)}\rangle) \tag{5.6}$$

$$= \left[1 + \sum_{k=1}^{\infty} \lambda^k c_k\right] |n^{(0)}\rangle + \sum_{k=1}^{\infty} \lambda^k |n^{(k)}\rangle' \tag{5.7}$$

Recall that we explicitly do not require $|n\rangle'_\lambda$ to be normalized, and so we are free to divide the entire state by the term in square brackets to obtain an equally valid state:

$$|n\rangle_\lambda = \left[1 + \sum_{k=1}^{\infty} \lambda^k c_k\right]^{-1} |n\rangle'_\lambda \tag{5.8}$$

$$= |n^{(0)}\rangle + \sum_{k=1}^{\infty} \lambda^k \left[1 + \sum_{k=1}^{\infty} \lambda^k c_k\right]^{-1} |n^{(k)}\rangle' \tag{5.9}$$

$$= |n^{(0)}\rangle + \sum_{k=1}^{\infty} \lambda^k |n^{(k)}\rangle \tag{5.10}$$

where the $|n^{(k)}\rangle$ have been shown to have no component along $|n^{(0)}\rangle$ for $k \neq 0$.

This means that the right-most term in Eq. 5.5 vanishes to yield the expressions for the k-th order energy level shift of $|n\rangle_\lambda$:

$$E_n^{(k)} = \langle n^{(0)}|V|n^{(k-1)}\rangle \tag{5.11}$$

An interesting feature of this result is that it is only necessary to know the $(k-1)$-th order correction to the eigenstate in order to calculate the k-th order energy shift. For the case where $k = 1$, we find the explicit expression for the first order energy shift:

$$E_n^{(1)} = \langle n^{(0)}|V|n^{(0)}\rangle\,, \tag{5.12}$$

which is simply the expectation value of the perturbation Hamiltonian in the unperturbed state. For notational simplicity, we will use the notation $\langle k^{(0)}|V|n^{(0)}\rangle = V_{kn}$ going forward.

5.1.3 First-order state correction

Going back to the λ^1 order expression in Eq. 5.3, and now taking the inner product of both sides with $|k^{(0)}\rangle$ where $k \neq n$:

$$\langle k^{(0)}|H_0 - E_n^{(0)}|n^{(1)}\rangle = -\langle k^{(0)}|V|n^{(0)}\rangle + \langle k^{(0)}|E_n^{(1)}|n^{(0)}\rangle \tag{5.13}$$

The last term on the right is zero, so we obtain:

$$\langle k^{(0)}|n^{(1)}\rangle = \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} \tag{5.14}$$

This expression gives us the component of $|n^{(1)}\rangle$ along every base state $|k^{(0)}\rangle$ for $k \neq n$ which, along with $\langle n^{(0)}|n^{(1)}\rangle = 0$, allows us to write down the explicit expression for the first-order change to the state:

$$|n^{(1)}\rangle = \sum_{k\neq n} |k^{(0)}\rangle \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} \tag{5.15}$$

We can now insert this expression into Eq. 5.11 for $k = 2$ to obtain the second order energy shift:

$$E_n^{(2)} = \langle n^{(0)}|V|n^{(1)}\rangle = \sum_{k\neq n} \frac{|V_{kn}|^2}{E_n^{(0)} - E_k^{(0)}} \tag{5.16}$$

It's clear that Eq. 5.15 and Eq. 5.16 only hold when the $E_n^{(0)} \neq E_k^{0)}$ for any k. In other words, the state $|n^{(0)}\rangle$ must be non-degenerate with any other state in the Hilbert space. These expressions also make it clear what it means for a perturbation to be "weak": The magnitude of the perturbation Hamiltonian elements must be small compared to the base Hamiltonian's energy differences (and notably not the energy values themselves!).

We can continue this procedure, taking the inner product of the λ^2 equation from Eq. 5.3 with $|k^{(0)}\rangle$ $(k \neq n)$ to find $|n^{(2)}\rangle$, use this state to find $E_n^{(3)}$, and so on until our mental fortitude to do algebra gives out. In summary, the changes to the state and energy of a non-degenerate eigenstate $|n^{(0)}\rangle$ of the base Hamiltonian are given by:

$$\begin{aligned} |n\rangle_\lambda &= |n^{(0)}\rangle + \lambda \sum_{k\neq n} |k^{(0)}\rangle \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} + \mathcal{O}(\lambda^2) \\ E_n(\lambda) &= E_n^{(0)} + \lambda V_{nn} + \lambda^2 \sum_{k\neq n} \frac{|V_{kn}|^2}{E_n^{(0)} - E_k^{(0)}} + \mathcal{O}(\lambda^3) \end{aligned} \tag{5.17}$$

5.2 Degenerate Perturbation Theory

The expressions in Eq. 5.17 hold as long as the state $|n^{(0)}\rangle$ for which we are trying to calculate the corrections is not degenerate with another state. It bears emphasizing that it is perfectly allowable for other states to be degenerate to each other. The non-degeneracy requirement is only for the state being corrected. For example, if the matrix representation for a specific H_0 is:

$$H_0 = \hbar \begin{pmatrix} 0 & 0 & 0 \\ 0 & \omega_1 & 0 \\ 0 & 0 & \omega_1 \end{pmatrix} \qquad |0\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \qquad |1\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \qquad |2\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \tag{5.18}$$

we can still use non-degenerate perturbation theory to calculate perturbations due to an arbitrary V for state $|0\rangle$, even though states $|1\rangle$ and $|2\rangle$ are degenerate. However, we cannot use it to calculate the changes to $|1\rangle$ or $|2\rangle$.

In order to proceed for these degenerate states, we will first restrict ourselves to states in the degenerate subspace D_N, where the N index refers to the number of degenerate states in the subspace. That is to say, there are N states, all with eigenvalue $E_n^{(0)}$, in the subspace D_N.

We will label these states $|n^{(0)}, k\rangle$, where $1 \leq k \leq N$. The two separate indices n, k denote that we are talking about states in the degenerate subspace, and can easily be distinguished from states $|m^{(0)}\rangle$, with a single index, in the space outside the degenerate subspace. We know that the $|n^{(0)}, k\rangle$ states span the degenerate subspace, and the $|m^{(0)}\rangle$ states span the space outside of the degenerate subspace, and so the combined set of states span the entire Hilbert space.

5.2.1 Setting up the problem

We will make similar assumptions to those we made for the non-degenerate case. Specifically, we will require the base states in the degenerate subspace to be orthonormal:

$$\langle n^{(0)}, k | n^{(0)}, l \rangle = \delta_{kl}, \tag{5.19}$$

and, as in the non-degenerate case, we require that $|n^{(q)}, k\rangle$ has no component along $|n^{(0)}, k\rangle$:

$$\langle n^{(0)}, k | n^{(q)}, k \rangle = \delta_{0q}. \tag{5.20}$$

By definition, we also know that:

$$H_0 \, |n^{(0)}, k\rangle = E_n^{(0)} \, |n^{(0)}, k\rangle \tag{5.21}$$

We also know that the states which span the degenerate subspace are orthonormal to the states outside of it, and so:

$$\langle m^{(0)} | n^{(0)}, k \rangle = 0 \tag{5.22}$$

We know set up our system of equations similarly to how we set up Eq. 5.3 for the non-degenerate case. Using this notation, we define the perturbed eigenstates and eigenvalues to be:

$$\begin{aligned} |n, k\rangle_\lambda &= |n^{(0)}, k\rangle + \lambda \, |n^{(1)}, k\rangle + \lambda^2 \, |n^{(2)}, k\rangle + \dots \\ E_{n,k}(\lambda) &= E_n^{(0)} + \lambda E_{n,k}^{(1)} + \lambda^2 E_{n,k}^{(2)} + \dots \end{aligned} \tag{5.23}$$

Applying these equations to the Schrödinger equation in the degenerate subspace:

$$H(\lambda) \, |n, k\rangle_\lambda = E_{n,k}(\lambda) \, |n, k\rangle_\lambda \tag{5.24}$$

we obtain the infinite set of simultaneous equations for the degenerate subspace:

$$\begin{aligned} \lambda^0 : &\quad (H_0 - E_n^{(0)}) \, |n^{(0)}, k\rangle = 0 \\ \lambda^1 : &\quad (H_0 - E_n^{(0)}) \, |n^{(1)}, k\rangle = -V \, |n^{(0)}, k\rangle + E_{n,k}^{(1)} \, |n^{(0)}, k\rangle \\ \lambda^2 : &\quad (H_0 - E_n^{(0)}) \, |n^{(2)}, k\rangle = -V \, |n^{(1)}, k\rangle + E_{n,k}^{(1)} \, |n^{(1)}, k\rangle + E_{n,k}^{(2)} \, |n^{(0)}, k\rangle \\ &\vdots \qquad\qquad\qquad\qquad \vdots \\ \lambda^q : &\quad (H_0 - E_n^{(0)}) \, |n^{(q)}, k\rangle = -V \, |n^{(q-1)}, k\rangle + \sum_{m=0}^{q-1} E_{n,k}^{(q-m)} \, |n^{(m)}, k\rangle \end{aligned} \tag{5.25}$$

While this set of equations looks virtually identical Eq. 5.3, there are some subtle differences on the restrictions placed on these states which have a significant impact.

5.2.2 Solving for the first-order energy shift

If we now take the inner product of the left-hand side of Eq. 5.25 with any state in the degenerate subspace $|n^{(0)}, l\rangle$, we see that the expression vanishes due to the energy degeneracy of all these states:

$$\langle n^{(0)}, l|(H_0 - E_n^{(0)})|n^{(q)}, k\rangle = (E_n^{(0)} - E_n^{(0)}) \langle n^{(0)}, l|n^{(q)}, k\rangle = 0 \tag{5.26}$$

Now examine the right-hand side of the λ^1 order specifically, and remembering the orthonormality of the base states in the degenerate subspace, we see that:

$$\langle n^{(0)}, l|V|n^{(0)}, k\rangle = E_{n,k}^{(1)}\delta_{lk}. \tag{5.27}$$

This seemingly simple equation is actually quite profound. It makes it clear that, in the degenerate subspace, the correct choice of basis is that which diagonalizes the perturbation Hamiltonian V! Since these states do not (usually) correspond to the basis states we chose for H_0, we ran into trouble. However, in the degenerate subspace we know that, by definition, H_0 is proportional to the identity operator (i.e. $H_0 = E_n^{(0)}\mathbb{1}$). This means that, in the degenerate subspace, H_0 and V commute, and are therefore simultaneously diagonalizable. For these reasons, any eigenstates of V is therefore also an eigenstate of H_0. We are therefore free to use the correct basis states which satisfy Eq. 5.27, but we can only do this in the degenerate subspace. Outside of this, we continue to use the original basis states.

Of course we need to remember that the states in the degenerate subspace will still couple to states outside of it, due to the perturbation Hamiltonian. This should not be surprising. We can see what this means mathematically by looking at what happens when V acts on state $|n^{(0)}, k\rangle$ and explicitly writing out the identity operator in terms of states in D and outside of D:

$$\begin{aligned} V|n^{(0)}, k\rangle &= \sum_{l=1}^{N} |n^{(0)}, l\rangle \langle n^{(0)}, l|V|n^{(0)}, k\rangle + \sum_p |p^{(0)}\rangle \langle p^{(0)}|V|n^{(0)}, k\rangle \\ &= E_{n,k}^{(1)}|n^{(0)}, k\rangle + \sum_p |p^{(0)}\rangle V_{p,nk} \end{aligned} \tag{5.28}$$

where we have used the notation $V_{p,nk} = \langle n^{(0)}, l|V|n^{(0)}, k\rangle$. Without the second term on the right-hand side, $|n^{(0)}, k\rangle$ would be an eigenstate of V. However, clearly there are terms which couple this state to states outside of the degenerate subspace and ruin the fun.

While Eq. 5.27 is always true, it may not always successfully lift the degeneracy between the states. Mathematically, we know that the degeneracy is completely lifted if $E_{n,l}^{(1)} \neq E_{n,k}^{(1)}$ for all $l \neq k$. If this does not hold, we will need to determine if an appropriate basis can be determined to second order.

5.2.3 Second-order energy shift and first-order state correction

Solving for the first-order corrections to the eigenstate is more involved in the degenerate case, mostly due to having to take into account states in- and outside the degenerate subspace.

We start by taking the inner product of $|p^{(0)}\rangle$ with the λ^1 terms in Eq. 5.25:

$$\langle p^{(0)}|(H_0 - E_n^{(0)}|n^{(1)}, k\rangle = \langle p^{(0)}|V|n^{(0)}, k\rangle \tag{5.29}$$

which we can rewrite as:

$$(E_n^{(0)} - E_p^{(0)})\,\langle p^{(0)}|n^{(1)}, k\rangle = V_{p,nk} \tag{5.30}$$

This expression has given us the projection of our state on all the states outside of $\hat{D}_N$, but we still need the projection on the states in $\hat{D}_N$. Explicitly, we can write this as:

$$|n^{(1)}, k\rangle = \sum_p |p^{(0)}\rangle \frac{V_{p,nk}}{E_n^{(0)} - E_p^{(0)}} + \left\{|n^{(1)}, k\rangle\right\}_{\hat{D}_N} \tag{5.31}$$

where the term in curly brackets is meant to denote the part of the state in $\hat{D}_N$ projected on the $|n^{(0)}, k\rangle$ states.

To continue, we need to take the inner product of $|n^{(0)}, l\rangle$ with the λ^2 terms in Eq. 5.25, recalling that the left-hand side vanishes for these states:

$$\langle n^{(0)}, l|(V - E_{n,k}^{(1)})|n^{(1)}, k\rangle = \langle n^{(0)}, l|E_{n,k}^{(2)}|n^{(0)}, k\rangle\,. \tag{5.32}$$

We can insert Eq. 5.31 to obtain:

$$\langle n^{(0)}, l|\,(V - E_{n,k}^{(1)}) \sum_p |p^{(0)}\rangle \frac{V_{p,nk}}{E_n^{(0)} - E_p^{(0)}} + \langle n^{(0)}, l|\,(V - E_{n,k}^{(1)}) \left\{|n^{(1)}, k\rangle\right\}_{\hat{D}_N} = E_{n,k}^{(2)}\delta_{lk} \tag{5.33}$$

The $E_{n,k}^{(1)}$ part in the first term on the left-hand side vanishes because $\langle n^{(0)}, l|p^{(0)}\rangle = 0$. Also, we apply Eq. 5.28 to obtain:

$$\begin{aligned}\sum_p \frac{V_{nl,p}V_{p,nk}}{E_n^{(0)} - E_p^{(0)}} + \left[E_{n,l}^{(1)}\,\langle n^{(0)}, l| + \sum_p \langle p^{(0)}|\,V_{nl,p}\right] \left\{|n^{(1)}, k\rangle\right\}_{\hat{D}_N} \\ -E_{n,k}^{(1)}\,\langle n^{(0)}, l|\left\{|n^{(1)}, k\rangle\right\}_{\hat{D}_N} = E_{n,k}^{(2)}\delta_{lk}\end{aligned} \tag{5.34}$$

The term proportional to $\langle p^{(0)}|$ vanishes because it is orthogonal to all states in $\hat{D}_N$ by definition, and so we are left with:

$$\sum_p \frac{V_{nl,p}V_{p,nk}}{E_n^{(0)} - E_p^{(0)}} + (E_{n,l}^{(1)} - E_{n,k}^{(1)})\,\langle n^{(0)}, l|\left\{|n^{(1)}, k\rangle\right\}_{\hat{D}_N} = E_{n,k}^{(2)}\delta_{lk} \tag{5.35}$$

If we set $l = k$, we obtain the second-order energy shift:

$$\sum_p \frac{V_{nk,p}V_{p,nk}}{E_n^{(0)} - E_p^{(0)}} = E_{n,k}^{(2)} \tag{5.36}$$

Alternatively, for $l \neq k$:

$$\frac{1}{E_{n,k}^{(1)} - E_{n,l}^{(1)}} \sum_p \frac{V_{nl,p}V_{p,nk}}{E_n^{(0)} - E_p^{(0)}} = \langle n^{(0)}, l|\left\{|n^{(1)}, k\rangle\right\}_{\hat{D}_N} \tag{5.37}$$

Here it is important to note that we have implicitly assumed that $E^{(1)}_{n,k} \neq E^{(1)}_{n,l}$ as long as $l \neq k$. This means that we must ensure that the diagonalization we performed in the degenerate subspace has fully lifted the degeneracy.

Since we now have the projection of $|n^{(1)}, k\rangle$ along states in the degenerate subspace (Eq. 5.37) as well as outside the degenerate subspace (Eq. 5.31), we can put them together for the state correction to first order in λ:

$$|n,k\rangle_\lambda = |n^{(0)},k\rangle + \lambda\left[\sum_p \frac{|p^{(0)}\rangle\, V_{p,nk}}{E^{(0)}_n - E^{(0)}_p} + \sum_l \frac{|n^{(0)},l\rangle}{E^{(1)}_{n,k} - E^{(1)}_{n,l}} \sum_p \frac{V_{nl,p}V_{p,nk}}{E^{(0)}_n - E^{(0)}_p}\right] + \mathcal{O}(\lambda^2) \quad (5.38)$$

as well as the energy shift to second order in λ:

$$E_{n,k}(\lambda) = E^{(0)}_n + \lambda V_{nk,nk} + \lambda^2 \sum_p \frac{V_{nk,p}V_{p,nk}}{E^{(0)}_n - E^{(0)}_p} + \mathcal{O}(\lambda^3) \quad (5.39)$$

5.3 Time-Dependent Perturbation Theory

In time-dependent perturbation theory we still assume a known, time-independent H_0 with the same properties as we assumed in the time-independent case. However, now the perturbation is assumed to be explicitly dependent on time. The Hamiltonian is then:

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t). \quad (5.40)$$

The important distinction to be made here is that, due to the time dependence of the perturbation, $\hat{H}(t)$ no longer has energy eigenstates. This means that the Schrödinger equation maintains the time derivative:

$$i\hbar\frac{d}{dt}|\psi(t)\rangle = \hat{H}(t)\,|\psi(t)\rangle = (\hat{H}_0 + \hat{V}(t))\,|\psi(t)\rangle \quad (5.41)$$

5.3.1 Interaction Picture

We will first rewrite the problem in a way that makes a perturbative approach much easier and convenient. To do this, we will move to the *interaction picture*. Recall that the two most commonly used pictures in quantum mechanics are the Schrödinger picture, where the states are time dependent but the operators are constant, and the Heisenberg picture, where the states are constant but the operators are time dependent. The interaction picture lies somewhere in the middle. We define a new state $|\widetilde{\psi}(t)\rangle$ such that:

$$|\widetilde{\psi}(t)\rangle = \exp\left(\frac{i\hat{H}_0 t}{\hbar}\right)|\psi(t)\rangle \iff |\psi(t)\rangle = \exp\left(\frac{-i\hat{H}_0 t}{\hbar}\right)|\widetilde{\psi}(t)\rangle \quad (5.42)$$

Taking this new state's time derivative gives:

$$\begin{aligned}\frac{d}{dt}\left|\widetilde{\psi}(t)\right\rangle &= \exp\left(\frac{i\hat{H}_0 t}{\hbar}\right)\left(\frac{\partial}{\partial t}\left|\psi(t)\right\rangle + \frac{i\hat{H}_0}{\hbar}\left|\psi(t)\right\rangle\right) \\ &= \exp\left(\frac{i\hat{H}_0 t}{\hbar}\right)\left(\frac{1}{i\hbar}\right)\left(\hat{H}_0 + \hat{V}(t)\right)\left|\psi(t)\right\rangle - \frac{\hat{H}_0}{i\hbar}\left|\widetilde{\psi}(t)\right\rangle \\ &= \exp\left(\frac{i\hat{H}_0 t}{\hbar}\right)\frac{\hat{V}(t)}{i\hbar}\exp\left(\frac{-i\hat{H}_0 t}{\hbar}\right)\left|\widetilde{\psi}(t)\right\rangle\end{aligned} \tag{5.43}$$

This equation is essentially another Schrödinger equation:

$$i\hbar\frac{d}{dt}\left|\widetilde{\psi}(t)\right\rangle = \widetilde{V}(t)\left|\widetilde{\psi}(t)\right\rangle \tag{5.44}$$

where

$$\begin{aligned}\widetilde{V}(t) &= \exp\left(\frac{i\hat{H}_0 t}{\hbar}\right)\hat{V}(t)\exp\left(\frac{-i\hat{H}_0 t}{\hbar}\right) \\ \left|\widetilde{\psi}(t)\right\rangle &= \exp\left(\frac{i\hat{H}_0 t}{\hbar}\right)\left|\psi(t)\right\rangle\end{aligned} \tag{5.45}$$

5.3.2 Setting up the perturbations

We will introduce the perturbation parameter λ in a way that is identical to the time-independent case. The time-dependent Hamiltonian is

$$\hat{H}(t) = \hat{H}_0 + \lambda\hat{V}(t) \tag{5.46}$$

which means that, in the interaction picture, the Schrödinger equation is

$$i\hbar\frac{d}{dt}\left|\widetilde{\psi}(t)\right\rangle = \lambda\widetilde{V}(t)\left|\widetilde{\psi}(t)\right\rangle \tag{5.47}$$

We will also write the desired solution, including λ:

$$\left|\widetilde{\psi}(t)\right\rangle_\lambda = \left|\widetilde{\psi}^{(0)}(t)\right\rangle + \lambda\left|\widetilde{\psi}^{(1)}(t)\right\rangle + \lambda^2\left|\widetilde{\psi}^{(2)}(t)\right\rangle + \ldots \tag{5.48}$$

which we will insert on the left- and right-hand side of the Schrödinger equation:

$$\begin{aligned}&i\hbar\frac{d}{dt}\left|\widetilde{\psi}^{(0)}(t)\right\rangle + i\hbar\lambda\frac{d}{dt}\left|\widetilde{\psi}^{(1)}(t)\right\rangle + i\hbar\lambda^2\frac{d}{dt}\left|\widetilde{\psi}^{(2)}(t)\right\rangle + \ldots \\ &= \lambda\widetilde{V}(t)\left|\widetilde{\psi}^{(0)}(t)\right\rangle + \lambda^2\widetilde{V}(t)\left|\widetilde{\psi}^{(1)}(t)\right\rangle + \lambda^3\widetilde{V}(t)\left|\widetilde{\psi}^{(2)}(t)\right\rangle + \ldots\end{aligned} \tag{5.49}$$

Unsurprisingly, we again end up with an infinite set of equations by equating all the terms in the same order of λ:

$$\begin{aligned}
\lambda^0 &: \quad i\hbar\frac{d}{dt}|\widetilde{\psi}^{(0)}(t)\rangle = 0 \\
\lambda^1 &: \quad i\hbar\frac{d}{dt}|\widetilde{\psi}^{(1)}(t)\rangle = \widetilde{V}(t)\,|\widetilde{\psi}^{(0)}(t)\rangle \\
\lambda^2 &: \quad i\hbar\frac{d}{dt}|\widetilde{\psi}^{(2)}(t)\rangle = \widetilde{V}(t)\,|\widetilde{\psi}^{(1)}(t)\rangle \\
&\vdots \qquad\qquad\qquad \vdots \\
\lambda^k &: \quad i\hbar\frac{d}{dt}|\widetilde{\psi}^{(k)}(t)\rangle = \widetilde{V}(t)\,|\widetilde{\psi}^{(k-1)}(t)\rangle
\end{aligned} \tag{5.50}$$

It is clear that, given a known perturbation order's state correction, we need to integrate it to obtain the next order's state correction.

Therefore we can write the initial conditions as

$$|\widetilde{\psi}(0)\rangle = |\psi(0)\rangle = |\widetilde{\psi}^{(0)}(0)\rangle + \lambda\,|\widetilde{\psi}^{(1)}(0)\rangle + \lambda^2\,|\widetilde{\psi}^{(2)}(0)\rangle \tag{5.51}$$

which we know must hold true, no matter the value of λ. Therefore:

$$\begin{aligned}
|\widetilde{\psi}^{(0)}(0)\rangle &= |\psi(0)\rangle \\
|\widetilde{\psi}^{(k)}(0)\rangle &= 0 \quad \text{for } k \neq 0
\end{aligned} \tag{5.52}$$

5.3.3 Solutions of time-dependent perturbation theory

The λ^0 term in Eq. 5.50 clearly shows that the zero-order perturbation is a constant, and from Eq 5.52 we now know its initial condition. Therefore this term is solved:

$$|\widetilde{\psi}^{(0)}(t)\rangle = |\widetilde{\psi}^{(0)}(0)\rangle = |\psi(0)\rangle \tag{5.53}$$

Moving right along to the λ^1 equation, we then get:

$$i\hbar\frac{d}{dt}|\widetilde{\psi}^{(1)}(t)\rangle = \widetilde{V}(t)\,|\psi(0)\rangle \tag{5.54}$$

which is easily integrated to obtain:

$$|\widetilde{\psi}^{(1)}(t)\rangle = \frac{1}{i\hbar}\int_0^t V(t')\,|\psi(0)\rangle\,dt' \tag{5.55}$$

Plugging this into the λ^2 equation, we see that:

$$i\hbar\frac{d}{dt}|\widetilde{\psi}^{(2)}(t)\rangle = \widetilde{V}(t)\,|\widetilde{\psi}^{(1)}(t)\rangle \tag{5.56}$$

which we can again integrate to obtain

$$|\widetilde{\psi}^{(2)}(t)\rangle = \frac{1}{i\hbar}\int_0^t V(t')\,|\widetilde{\psi}^{(1)}(t')\rangle\,dt' \tag{5.57}$$

We can use our previous result for $|\widetilde{\psi}^{(1)}(t)\rangle$ to get the iterated integral expression:

$$|\widetilde{\psi}^{(2)}(t)\rangle = \frac{1}{(i\hbar)^2}\int_0^t V(t')\int_0^{t'} V(t'')\,|\psi(0)\rangle\,dt''dt' \tag{5.58}$$

It is in principle, though often not in practice, simple enough to extrapolate the higher order iterative integral solutions for $|\widetilde{\psi}^{(k)}(t)\rangle$. The overall solution to the Schrödinger equation is then:

$$|\psi(t)\rangle_\lambda = \exp\left(\frac{-iH_0t}{\hbar}\right)\left(|\psi(0)\rangle + \lambda\,|\widetilde{\psi}^{(1)}(t)\rangle + \lambda^2\,|\widetilde{\psi}^{(2)}(t)\rangle + \dots\right) \tag{5.59}$$

5.3.4 Explicit time-dependent coefficients

Just like in the time-independent perturbation case, we expand the solution of the time-dependent perturbation using the basis states for the unperturbed Hamiltonian $|n^{(0)}\rangle$, but letting the coefficients of the expansion be time-dependent,

$$|\psi(t)\rangle = \sum_n c_n(t)\,|n^{(0)}\rangle\,, \tag{5.60}$$

where

$$c_n(t) = \langle n^{(0)}|\psi(t)\rangle\,. \tag{5.61}$$

In the same basis, the perturbation Hamiltonian can be represented as a matrix element

$$\langle n^{(0)}|\hat{V}(t)|k^{(0)}\rangle = \hat{V}_{nk}(t). \tag{5.62}$$

We note that $\langle n^{(0)}|\hat{H}_0|k^{(0)}\rangle = E_n^{(0)}\delta_{nk}$, and because $|n^{(0)}\rangle$ is an orthonormal basis set,

$$\sum_k |k^{(0)}\rangle\,\langle k^{(0)}| = \hat{I}. \tag{5.63}$$

Moving to interaction picture in this model is to allow $c_n(t)$ to be decomposed of the trivial time evolution corresponding to $\hat{H}_0$ for each coefficient and capturing the remainder in a slowly-varying envelop $b_n(t)$, *i.e.*, letting

$$c_n(t) = b_n(t)e^{-iE_n^{(0)}t/\hbar}. \tag{5.64}$$

The perturbation equation with the scaling parameter λ now reads

$$i\hbar e^{-iE_n^{(0)}t/\hbar}\frac{d}{dt}b_n(t) = \sum_k \lambda\hat{V}_{nk}(t)b_k(t)e^{-iE_k^{(0)}t/\hbar}. \tag{5.65}$$

Multiplying both sides by $e^{iE_n^{(0)}t/\hbar}$ and introducing the Bohr angular frequency $\omega_{nk} \equiv (E_n^{(0)} - E_k^{(0)})/\hbar$, the differential equation for the time-dependent coefficients become

$$i\hbar\frac{d}{dt}b_n(t) = \lambda\sum_k e^{i\omega_{nk}t}\hat{V}_{nk}(t)b_k(t). \tag{5.66}$$

Expanding the $b_n(t)$ with the small parameter λ as

$$b_n(t) = b_n^{(0)}(t) + \lambda b_n^{(1)}(t) + \lambda^2 b_n^{(2)}(t) + \ldots \tag{5.67}$$

For zeroth order, we get

$$i\hbar\frac{d}{dt}b_n^{(0)}(t) = 0. \tag{5.68}$$

For higher order, we get

$$i\hbar\frac{d}{dt}b_n^{(r)}(t) = \sum_k e^{i\omega_{nk}t}\hat{V}_{nk}(t)b_k^{(r-1)}(t). \tag{5.69}$$

This is an explicit equivalent to Eq. 5.50.