

Time-Independent Perturbation Theory

Quantum Mechanics II

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The Hamiltonian of interest is expressed as the sum of an unperturbed Hamiltonian $\hat{H}^{(0)}$ and a perturbation $\delta\hat{H}$:

$$\hat{H} = \hat{H}^{(0)} + \delta\hat{H}.$$

- Both $\hat{H}^{(0)}$ and $\delta\hat{H}$ are time-independent and Hermitian.
- To systematically study the perturbation, we introduce a family of λ -dependent Hamiltonians:

$$\hat{H}(\lambda) = \hat{H}^{(0)} + \lambda\delta\hat{H},$$

where $\lambda \in [0, 1]$.

Note that the perturbations **do not create new states**; they only modify the eigenstates of the $\hat{H}^{(0)}$ theory. In perturbation theory we will be assuming that the state space of $\hat{H}^{(0)}$, called $\mathcal{H}$, is also the state space of $\hat{H}(\lambda)$. The eigenstates of $\hat{H}(\lambda)$ are ultimately going to be expressed as superpositions of $\hat{H}^{(0)}$ eigenstates.

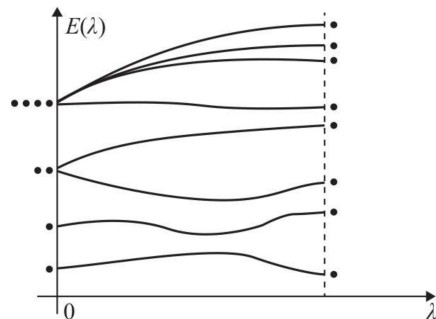


Figure: The energy eigenvalues of $\hat{H}(\lambda)$ change as λ goes from 0 to 1. On the $\lambda = 0$ vertical axis, the $\hat{H}^{(0)}$ eigenstates are represented by heavy dots. For $\lambda = 1$, the dots have shifted.

Nondegenerate Perturbation Theory

Nondegenerate Perturbation Theory

We begin by describing the unperturbed Hamiltonian $\hat{H}^{(0)}$, which has a discrete spectrum of eigenstates. The state space $\mathcal{H}$ is spanned by an orthonormal basis of energy eigenstates $\{|k^{(0)}\rangle\}$.

- The eigenvalue equation for the unperturbed Hamiltonian:

$$\hat{H}^{(0)}|k^{(0)}\rangle = E_k^{(0)}|k^{(0)}\rangle, \quad \langle k^{(0)}|l^{(0)}\rangle = \delta_{kl}.$$

- Here, $k \in \mathbb{Z}$ is a label that indexes the eigenstates. The superscript 0 denotes the unperturbed system.
- The eigenvalues $E_k^{(0)}$ are ordered as:

$$E_0^{(0)} \leq E_1^{(0)} \leq E_2^{(0)} \leq \dots$$

- Equalities between energies may occur if the states are degenerate.
- For nondegenerate perturbation theory, we focus on a single nondegenerate state $|n^{(0)}\rangle$ with a fixed n . This state satisfies:

$$\dots < E_{n-1}^{(0)} < E_n^{(0)} < E_{n+1}^{(0)} < \dots$$

- If the chosen state is the ground state, we take $n = 0$, yielding: $E_0^{(0)} < E_1^{(0)}$.

Perturbed States and Energies

- When the perturbation is turned on ($\lambda \neq 0$), the eigenstate $|n^{(0)}\rangle$ of $\hat{H}^{(0)}$ becomes a perturbed eigenstate $|n\rangle_\lambda$ of $\hat{H}(\lambda)$ with energy $E_n(\lambda)$:

$$\hat{H}(\lambda)|n\rangle_\lambda = E_n(\lambda)|n\rangle_\lambda. \quad (1)$$

- At $\lambda = 0$, the perturbed state and energy revert to their unperturbed values:

$$|n\rangle_{\lambda=0} = |n^{(0)}\rangle, \quad E_n(\lambda=0) = E_n^{(0)}.$$

- Both the state $|n\rangle_\lambda$ and energy $E_n(\lambda)$ can be expanded in a Taylor series in λ . For any function $f(\lambda)$, we write:

$$f(\lambda) = \sum_{n=0}^{\infty} \frac{1}{n!} f^{(n)}(0) \lambda^n = f(0) + f'(0)\lambda + \frac{1}{2}f''(0)\lambda^2 + \frac{1}{3!}f'''(0)\lambda^3 + \dots$$

- Here, $f(0), f'(0), \dots$ are coefficients independent of λ , representing the function's value and derivatives at $\lambda = 0$.

- The perturbed states $|n\rangle_\lambda$ and energies $E_n(\lambda)$ can be expanded in powers of λ :

$$|n\rangle_\lambda = |n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \lambda^3|n^{(3)}\rangle + \dots,$$

$$E_n(\lambda) = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + \dots.$$

- The superscripts denote the power of λ that accompanies them. For example:

- $|n^{(1)}\rangle, |n^{(2)}\rangle, \dots$: Corrections to the state $|n^{(0)}\rangle$.
- $E_n^{(1)}, E_n^{(2)}, \dots$: Corrections to the energy $E_n^{(0)}$.

- These expansions imply that the perturbed states and energies vary continuously as functions of λ . Our goal is to calculate:

$$|n^{(1)}\rangle, |n^{(2)}\rangle, \dots, \quad \text{and} \quad E_n^{(1)}, E_n^{(2)}, \dots$$

- Since we assume that the state space $\mathcal{H}$ of $\hat{H}^{(0)}$ is also the state space of $\hat{H}(\lambda)$, the states $|n^{(k)}\rangle$ above will be determined in terms of superpositions of $\hat{H}^{(0)}$ eigenstates.
- We will not impose the requirement that $|n\rangle_\lambda$ is normalized. It suffices that $|n\rangle_\lambda$ is normalizable, which it will be for sufficiently small perturbations.

Perturbation Expansions

- For $\lambda = 1$, the expansions from the Taylor series give:

$$|n\rangle = |n^{(0)}\rangle + |n^{(1)}\rangle + |n^{(2)}\rangle + |n^{(3)}\rangle + \dots,$$

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + E_n^{(3)} + \dots.$$

- To proceed, we rewrite the Schrödinger equation (1) in the form:

$$\left[\hat{H}^{(0)} + \lambda \delta \hat{H} - E_n(\lambda) \right] |n\rangle_\lambda = 0.$$

- Using the expansions for $|n\rangle_\lambda$ and $E_n(\lambda)$, we arrive at:

$$\begin{aligned} & \left[\left(\hat{H}^{(0)} - E_n^{(0)} \right) - \lambda \left(E_n^{(1)} - \delta \hat{H} \right) - \lambda^2 E_n^{(2)} - \lambda^3 E_n^{(3)} - \dots - \lambda^k E_n^{(k)} + \dots \right] \\ & \times \left[|n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \lambda^3 |n^{(3)}\rangle + \dots + \lambda^k |n^{(k)}\rangle + \dots \right] = 0. \end{aligned}$$

- Expanding the equation into a power series in λ , we collect terms corresponding to each power of λ . Setting each coefficient to zero yields the following conditions:

$$\lambda^0 : (\hat{H}^{(0)} - E_n^{(0)})|n^{(0)}\rangle = 0,$$

$$\lambda^1 : (\hat{H}^{(0)} - E_n^{(0)})|n^{(1)}\rangle = (E_n^{(1)} - \delta\hat{H})|n^{(0)}\rangle,$$

$$\lambda^2 : (\hat{H}^{(0)} - E_n^{(0)})|n^{(2)}\rangle = (E_n^{(1)} - \delta\hat{H})|n^{(1)}\rangle + E_n^{(2)}|n^{(0)}\rangle,$$

$$\lambda^3 : (\hat{H}^{(0)} - E_n^{(0)})|n^{(3)}\rangle = (E_n^{(1)} - \delta\hat{H})|n^{(2)}\rangle + E_n^{(2)}|n^{(1)}\rangle + E_n^{(3)}|n^{(0)}\rangle,$$

$\vdots$

$$\lambda^k : (\hat{H}^{(0)} - E_n^{(0)})|n^{(k)}\rangle = (E_n^{(1)} - \delta\hat{H})|n^{(k-1)}\rangle + E_n^{(2)}|n^{(k-2)}\rangle + \dots + E_n^{(k)}|n^{(0)}\rangle.$$

- Each equation is a condition for the vanishing of the coefficient of a specific power of λ .
 - For λ^0 , this corresponds to the unperturbed Hamiltonian.
 - For λ^1 , the equation allows determination of $|n^{(1)}\rangle$ and $E_n^{(1)}$.
 - Higher-order equations ($\lambda^2, \lambda^3, \dots$) can be solved iteratively.
- The corrections are manifestly λ -independent since λ is merely a parameter for organizing the expansion.

A usefull choice: Orthogonality of State Corrections

- Without loss of generality, we can assume that all the state corrections $|n^{(k)}\rangle$, with $k \geq 1$, contain no vector along the unperturbed state $|n^{(0)}\rangle$. Explicitly:

$$\langle n^{(0)} | n^{(k)} \rangle = 0, \quad k \geq 1.$$

- To show this, suppose the state corrections $|n^{(k)}\rangle$ have components along $|n^{(0)}\rangle$. That is:

$$|n^{(k)}\rangle = |n^{(k)}\rangle' - a_k |n^{(0)}\rangle, \quad k \geq 1.$$

- Then the solution for the full corrected state is

$$|n\rangle_\lambda = (1 - a_1\lambda - a_2\lambda^2 - \dots) |n^{(0)}\rangle + \lambda |n^{(1)}\rangle' + \lambda^2 |n^{(2)}\rangle' + \dots$$

- Change its normalization :

$$|n\rangle'_\lambda = |n^{(0)}\rangle + \frac{1}{(1 - a_1\lambda - a_2\lambda^2 - \dots)} \left[\lambda |n^{(1)}\rangle' + \lambda^2 |n^{(2)}\rangle' + \dots \right].$$

- Expanding the denominator via a Taylor series gives:

$$|n'_\lambda\rangle = |n^{(0)}\rangle + \lambda |n^{(1)}\rangle' + \lambda^2 \left(|n^{(2)}\rangle' + a_1 |n^{(1)}\rangle' \right) + \dots$$

Solving the Equations in Perturbation Theory

- Start from the Schrödinger equation:

$$\langle n^{(0)} | \left(\hat{H}^{(0)} - E_n^{(0)} \right) | n^{(0)} \rangle = 0$$

- **First-order correction:** From the λ term, energy correction is:

$$E_n^{(1)} = \langle n^{(0)} | \delta \hat{H} | n^{(0)} \rangle$$

- **Second-order correction:** Using λ^2 , we find:

$$E_n^{(2)} = \langle n^{(0)} | \delta \hat{H} | n^{(1)} \rangle$$

- **Recursive relation for higher-order corrections:**

$$E_n^{(k)} = \langle n^{(0)} | \delta \hat{H} | n^{(k-1)} \rangle$$

- Corrections to the states arise from solving:

$$(\hat{H}^{(0)} - E_n^{(0)}) | n^{(1)} \rangle = -(\delta \hat{H} - E_n^{(1)}) | n^{(0)} \rangle$$

$$(\hat{H}^{(0)} - E_n^{(0)}) | n^{(2)} \rangle = -(\delta \hat{H} - E_n^{(1)}) | n^{(1)} \rangle + E_n^{(2)} | n^{(0)} \rangle$$

- **Key insight:** Energy corrections $E_n^{(k)}$ are determined recursively, and Hermiticity ensures all corrections are real.

First Correction to the State in Perturbation Theory

- To find the first correction $|n^{(1)}\rangle$, we start from the λ term:

$$\left(\hat{H}^{(0)} - E_n^{(0)}\right) |n^{(1)}\rangle = \left(E_n^{(1)} - \delta\hat{H}\right) |n^{(0)}\rangle$$

- By acting with $\langle k^{(0)}|$ ($k \neq n$) on both sides, we get:

$$\langle k^{(0)}| \left(\hat{H}^{(0)} - E_n^{(0)}\right) |n^{(1)}\rangle = \langle k^{(0)}| \left(E_n^{(1)} - \delta\hat{H}\right) |n^{(0)}\rangle, \quad k \neq n$$

- On simplifying, using orthonormality and $\langle n^{(0)}|n^{(0)}\rangle = 1$, we obtain:

$$(E_k^{(0)} - E_n^{(0)})\langle k^{(0)}|n^{(1)}\rangle = -\langle k^{(0)}|\delta\hat{H}|n^{(0)}\rangle$$

- Define shorthand for the matrix elements of $\delta\hat{H}$ in the original basis:

$$\delta\hat{H}_{km} \equiv \langle k^{(0)}|\delta\hat{H}|m^{(0)}\rangle, \quad \text{and Hermiticity implies: } \delta\hat{H}_{km} = (\delta\hat{H}_{mk})^*$$

- Substituting this into the equation, we have:

$$\langle k^{(0)}|n^{(1)}\rangle = \frac{-\delta\hat{H}_{kn}}{E_k^{(0)} - E_n^{(0)}}, \quad k \neq n$$

- The result highlights that $|n^{(1)}\rangle$ is determined entirely by the unperturbed energies $E_k^{(0)}$, $E_n^{(0)}$, and the matrix elements of the perturbation operator $\delta\hat{H}$.

Summary of First and Second Order Corrections

- Using the orthogonality assumption and completeness relation, we write the first-order correction to the state:

$$|n^{(1)}\rangle = \sum_{k \neq n} |k^{(0)}\rangle \frac{\langle k^{(0)} | \delta \hat{H} | n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}}$$

- The first-order correction has contributions from all basis states $|k^{(0)}\rangle$ except $|n^{(0)}\rangle$.
- The second-order correction to the energy follows from:

$$E_n^{(2)} = \sum_{k \neq n} \frac{|\langle n^{(0)} | \delta \hat{H} | k^{(0)} \rangle|^2}{E_n^{(0)} - E_k^{(0)}}$$

where $\delta \hat{H}_{nk} = \langle n^{(0)} | \delta \hat{H} | k^{(0)} \rangle$.

- In summary, the perturbed states and energies for $\hat{H}(\lambda) = \hat{H}^{(0)} + \lambda \delta \hat{H}$ are:

$$|n\rangle = |n^{(0)}\rangle + \lambda \sum_{k \neq n} |k^{(0)}\rangle \frac{\delta \hat{H}_{kn}}{E_n^{(0)} - E_k^{(0)}} + \mathcal{O}(\lambda^2)$$

$$E_n = E_n^{(0)} + \lambda \langle n^{(0)} | \delta \hat{H} | n^{(0)} \rangle + \lambda^2 \sum_{k \neq n} \frac{|\delta \hat{H}_{kn}|^2}{E_n^{(0)} - E_k^{(0)}} + \mathcal{O}(\lambda^3)$$

Remarks on Ground State Energy

- The energy of the (nondegenerate) ground state to first order in λ **overstates** the exact ground state energy.
- Consider the ground state energy $E_0^{(0)} + \lambda E_0^{(1)}$ to first order in λ . Writing this in terms of expectation values, with $|0^{(0)}\rangle$ denoting the unperturbed ground state:

$$E_0^{(0)} + \lambda E_0^{(1)} = \langle 0^{(0)} | \hat{H}(\lambda) | 0^{(0)} \rangle$$

where $\hat{H}(\lambda) = \hat{H}^{(0)} + \lambda \delta \hat{H}$. By the variational principle, this value overstates the ground state energy $E_0(\lambda)$:

$$E_0^{(0)} + \lambda E_0^{(1)} \geq E_0(\lambda).$$

- The second-order correction to the ground state energy is always **negative**, as given by:

$$E_0^{(2)} = -\lambda^2 \sum_{k \neq 0} \frac{|\delta \hat{H}_{k0}|^2}{E_k^{(0)} - E_0^{(0)}} < 0.$$

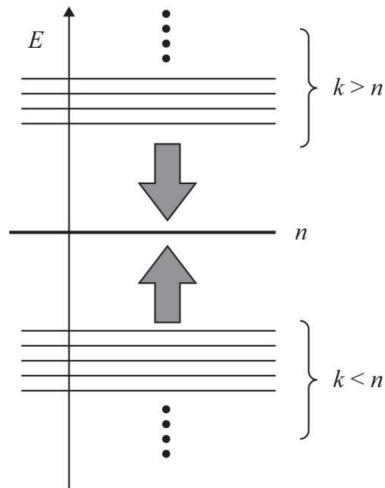
Here, each term in the sum is negative since the unperturbed excited state energies $E_k^{(0)}$ (for $k \neq 0$) exceed the unperturbed ground state energy $E_0^{(0)}$.

Second-Order Energy Corrections and Level Repulsion

- The second-order correction to the energy of the $|n^{(0)}\rangle$ eigenstate exhibits **level repulsion**:
 - Levels with $k > n$ **push the energy down**.
 - Levels with $k < n$ **push the energy up**.
- The correction is given by:

$$\begin{aligned} E_n^{(2)} &= -\lambda^2 \sum_{k \neq n} \frac{|\delta \hat{H}_{kn}|^2}{E_k^{(0)} - E_n^{(0)}} \\ &= -\lambda^2 \sum_{k > n} \frac{|\delta \hat{H}_{kn}|^2}{E_k^{(0)} - E_n^{(0)}} + \lambda^2 \sum_{k < n} \frac{|\delta \hat{H}_{kn}|^2}{E_n^{(0)} - E_k^{(0)}}. \end{aligned}$$

- The first term on the right-hand side corresponds to the **negative contribution** from higher-energy states.
- The second term corresponds to the **positive contribution** from lower-energy states.



Degenerate Perturbation Theory

Degenerate Perturbation Theory: Toy Model

- Consider $\hat{H}(\lambda) = \hat{H}^{(0)} + \lambda\delta\hat{H}$, where:

$$\hat{H}^{(0)} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \delta\hat{H} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

- $\hat{H}^{(0)}$ has degenerate eigenvalues:

$$|1^{(0)}\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |2^{(0)}\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad E_1^{(0)} = E_2^{(0)} = 1.$$

- Perturbation breaks degeneracy. Exact eigenvalues:

$$E = 1 \pm \lambda.$$

Degenerate Perturbation Theory: First-Order Predictions

- First-order energy corrections predicted by nondegenerate theory:

$$E_1(\lambda) = E_1^{(0)} + \lambda \delta \hat{H}_{11} = 1 + \lambda \cdot 0 = 1,$$

$$E_2(\lambda) = E_2^{(0)} + \lambda \delta \hat{H}_{22} = 1 + \lambda \cdot 0 = 1.$$

- First-order predictions are incorrect:
 - The eigenvalues remain degenerate, which is inconsistent with the perturbation.
 - Exact eigenvalues are:

Eigenvalues: $1 + \lambda, 1 - \lambda$.

- Exact eigenvectors of $\hat{H}(\lambda)$:

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}.$$

- Key point:
 - We must choose the basis in the degenerate subspace of $\hat{H}(0)$ to get states that vary continuously as $\lambda \rightarrow 0$.

Degenerate Perturbation Theory: Resolving the Ambiguity

- Degenerate eigenstates of $\hat{H}^{(0)}$ span a subspace:

$$\text{Span: } |1^{(0)}\rangle, |2^{(0)}\rangle.$$

- Perturbation $\delta\hat{H}$ defines a **good basis** within this subspace.
- Diagonalize $\delta\hat{H}$ in the degenerate subspace:

$$\delta\hat{H} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

- Good basis:

$$|1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad |2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}.$$

- Energy corrections:

$$E_1(\lambda) = 1 + \lambda, \quad E_2(\lambda) = 1 - \lambda.$$

Summary of Degenerate Perturbation Theory

- Key ideas:
 - Degenerate eigenstates require a careful choice of zeroth-order states.
 - Good basis is determined by diagonalizing $\delta\hat{H}$ in the degenerate subspace.
- Implications:
 - Breaks degeneracy to first order.
 - Corrects zeroth-order states for higher-order consistency.
- Example illustrated:
 - Toy model shows exact solution matches perturbative results after choosing the good basis.

Degenerate Subspace and Basis Setup

- We focus on a degenerate subspace of eigenvectors of $\hat{H}^{(0)}$, where $N > 1$ eigenstates share the same eigenvalue $E_n^{(0)}$.
- In the eigenbasis, $\hat{H}^{(0)}$ is diagonal:

$$\hat{H}^{(0)} = \text{diag}(E_1^{(0)}, E_2^{(0)}, \dots, \underbrace{E_n^{(0)}, \dots, E_n^{(0)}}_N, \dots).$$

- Arbitrary orthonormal basis vectors are chosen for the degenerate subspace V_N :

$$|n^{(0)}; 1\rangle, |n^{(0)}; 2\rangle, \dots, |n^{(0)}; N\rangle,$$

satisfying

$$\langle n^{(0)}; p | n^{(0)}; q \rangle = \delta_{pq}, \quad \hat{H}^{(0)} |n^{(0)}; k\rangle = E_n^{(0)} |n^{(0)}; k\rangle.$$

- The degenerate subspace $\mathbb{V}_N$ is:

$$\mathbb{V}_N = \text{span} \left\{ |n^{(0)}; k\rangle, k = 1, \dots, N \right\}.$$

State Space Decomposition

- The total state space $\mathcal{H}$ is decomposed as a direct sum:

$$\mathcal{H} = \mathbb{V}_N \oplus V_{\perp},$$

where $V_{\perp}$ is the orthogonal complement of $\mathbb{V}_N$.

- Basis for $V_{\perp}$ is denoted by $|p^{(0)}\rangle$ ($p \in \mathbb{Z}$), satisfying: $\langle p^{(0)} | n^{(0)}; k \rangle = 0$.
- Key distinctions:
 - States in $\mathbb{V}_N$: $|n^{(0)}; k\rangle$ (two labels, degenerate subspace).
 - States in $V_{\perp}$: $|p^{(0)}\rangle$ (single label, orthogonal to V_N).
- Since the basis states $|n^{(0)}; k\rangle$ of $\mathbb{V}_N$ were chosen arbitrarily, they are generally **not** good zeroth-order states.
- A perturbation $\delta\hat{H}$ that breaks the degeneracy will select the good basis.
- The basis vectors in the good basis are linear combinations of the basis vectors $|n^{(0)}; k\rangle$, but we must find those linear combinations.
- In degenerate perturbation theory, the zeroth-order states are **not obvious**!

Good Basis

- Express the good basis vectors $|\psi_I^{(0)}\rangle$ in terms of the original basis vectors:

$$|\psi_I^{(0)}\rangle = \sum_{k=1}^N |n^{(0)}; k\rangle a_{Ik}^{(0)}, \quad I = 1, \dots, N.$$

- If the degeneracy is broken by $\delta\hat{H}$ the states will be automatically orthonormal:

$$\langle\psi_I^{(0)}|\psi_J^{(0)}\rangle = \delta_{IJ}.$$

As soon as these states are perturbed, their energies are different, and thus they are necessarily orthonormal. If they are orthonormal for arbitrarily small perturbations, they will remain orthonormal for zero perturbation.

- Expand states and energies in powers of λ :

$$\begin{aligned} |\psi_I\rangle_\lambda &= |\psi_I^{(0)}\rangle + \lambda|\psi_I^{(1)}\rangle + \lambda^2|\psi_I^{(2)}\rangle + \dots, \\ E_{nI}(\lambda) &= \textcolor{red}{E}_n^{(0)} + \lambda E_{nI}^{(1)} + \lambda^2 E_{nI}^{(2)} + \dots. \end{aligned}$$

The energy expansion accounts for the degeneracy: the index I does not appear in the **zeroth-order energies**.

Degenerate Perturbation Theory: Order-by-Order Equations

- Introducing the above expansions into the Schrödinger equation:

$$\hat{H}(\lambda) |\psi_I\rangle_\lambda = E_{nl}(\lambda) |\psi_I\rangle_\lambda.$$

- Order-by-order equations:

$$\begin{aligned}\lambda^0 : \quad & (\hat{H}^{(0)} - E_n^{(0)}) |\psi_I^{(0)}\rangle = 0, \quad \textbf{trivial} \\ \lambda^1 : \quad & (\hat{H}^{(0)} - E_n^{(0)}) |\psi_I^{(1)}\rangle = (E_{nl}^{(1)} - \delta \hat{H}) |\psi_I^{(0)}\rangle, \\ \lambda^2 : \quad & (\hat{H}^{(0)} - E_n^{(0)}) |\psi_I^{(2)}\rangle = E_{nl}^{(1)} |\psi_I^{(1)}\rangle + E_{nl}^{(2)} |\psi_I^{(0)}\rangle - \delta \hat{H} |\psi_I^{(1)}\rangle.\end{aligned}\tag{2}$$

- Project the λ^1 equation onto $|n^{(0)}; \ell\rangle$ (LHS vanishes):

$$0 = \langle n^{(0)}; \ell | (E_{nl}^{(1)} - \delta \hat{H}) |\psi_I^{(0)}\rangle.$$

Then, insert $|\psi_I^{(0)}\rangle = \sum_{k=1}^N |n^{(0)}; k\rangle a_{lk}^{(0)}$

$$0 = \sum_{k=1}^N \left(E_{nl}^{(1)} a_{lk}^{(0)} \delta_{\ell k} - \langle n^{(0)}; \ell | \delta \hat{H} | n^{(0)}; k \rangle a_{lk}^{(0)} \right).$$

- Define the matrix elements of $\delta\hat{H}$ in the degenerate subspace:

$$\delta\hat{H}_{n\ell,nk} \equiv \langle n^{(0)}; \ell | \delta\hat{H} | n^{(0)}; k \rangle. \quad [\delta\hat{H}]_{\ell k} \equiv \delta\hat{H}_{n\ell,nk}.$$

where we define the $N \times N$ matrix $[\delta\hat{H}]$ as the restriction of $\delta\hat{H}$ to the degenerate subspace.

- Matrix equation:

$$\sum_{k=1}^N \left([\delta\hat{H}]_{\ell k} a_{lk}^{(0)} - E_{nl}^{(1)} \delta_{\ell k} a_{lk}^{(0)} \right) = 0.$$

$$\left([\delta\hat{H}] - E_{nl}^{(1)} \mathbb{1} \right) a_l^{(0)} = 0.$$

$a_l^{(0)}$ is the eigenvector of $[\delta\hat{H}]$ with eigenvalue $E_{nl}^{(1)}$.

- We have therefore determined the good basis and the leading energy corrections: **the good basis is that composed by the eigenvectors of $[\delta\hat{H}]$, with energy corrections given by the associated eigenvalues.**

Summary of Results for the Good Basis

- In the good basis, the perturbation $\delta\hat{H}$ is diagonal:

$$\delta\hat{H}_{IJ} = E_{nI}^{(1)}\delta_{IJ}.$$

- The eigenvalues of $\delta\hat{H}$ give the first-order corrections to the energy:

$$E_{nI}^{(1)} = \delta\hat{H}_{II}.$$

- Full expression for energy corrections:

$$E_{nI} = E_n^{(0)} + \lambda\delta\hat{H}_{II} + \mathcal{O}(\lambda^2).$$

- The basis $|\psi_I^{(0)}\rangle, I = 1, \dots, N$ makes $\delta\hat{H}$ diagonal in the space $\mathbb{V}_N$.

Remarks on Degenerate Perturbation Theory (1)

- The relation

$$E_{nl}^{(1)} = \delta \hat{H}_{ll}$$

is **always true**, even if the degeneracy is not lifted. The degeneracy is lifted when all eigenvalues of $[\delta \hat{H}]$ are different:

$$E_{nl}^{(1)} \neq E_{nJ}^{(1)}, \quad \text{whenever } l \neq J, \quad l, J = 1, \dots, N.$$

- If the degeneracy is lifted, the basis states $|\psi_l^{(0)}\rangle$ that make $\delta \hat{H}$ diagonal in $\mathbb{V}_N$ are confirmed to form a **good basis**. These states get deformed continuously as λ becomes nonzero.
- If the degeneracy is not lifted to first order, $[\delta \hat{H}]$ has degeneracies, and the eigenvectors are not uniquely fixed. The determination of the good basis has to be attempted to second order.

Remarks on Degenerate Perturbation Theory (2)

- The perturbation $\delta\hat{H}$ is diagonalized in the subspace $\mathbb{V}_N$, but $\delta\hat{H}$ is **not diagonal** on the whole state space; it is only diagonal within $\mathbb{V}_N$.

- Action of $\delta\hat{H}$ on the basis states:

$$\delta\hat{H}|\psi_I^{(0)}\rangle = \sum_J |\psi_J^{(0)}\rangle \langle \psi_J^{(0)} | \delta\hat{H} | \psi_I^{(0)} \rangle + \sum_P |\psi_P^{(0)}\rangle \langle \psi_P^{(0)} | \delta\hat{H} | \psi_I^{(0)} \rangle.$$

- Expanding terms, we find:

$$\delta\hat{H}|\psi_I^{(0)}\rangle = |\psi_I^{(0)}\rangle E_{nI}^{(1)} + \sum_P |\psi_P^{(0)}\rangle \langle \psi_P^{(0)} | \delta\hat{H} | \psi_I^{(0)} \rangle.$$

- This shows that the states $|\psi_I^{(0)}\rangle$ are **almost eigenstates** of $\delta\hat{H}$, with eigenvalues equal to the first-order energy corrections.
- The failure arises from an extra state along $V_\perp$.

Remarks on Degenerate Perturbation Theory (3)

- Rule: **The matrix $[\delta\hat{H}]$ is diagonal for a choice of basis in $\mathbb{V}_N$ if for any two different basis vectors there is a Hermitian operator $\hat{K}$ that commutes with δH for which the two basis vectors are $\hat{K}$ eigenstates with different eigenvalues.**
- This rule can be established as follows:
 - Assume we are testing a $\mathbb{V}_N$ basis $|n^{(0)}; k\rangle$, with $k = 1, \dots, N$.
 - Take two basis states $|n^{(0)}; p\rangle$ and $|n^{(0)}; q\rangle$, with $p \neq q$, and assume these states have different $\hat{K}$ eigenvalues k_p and k_q .
 - Since $[\delta\hat{H}, \hat{K}] = 0$, we have:

$$0 = \langle n^{(0)}; p | [\delta\hat{H}, \hat{K}] | n^{(0)}; q \rangle = (k_q - k_p) \langle n^{(0)}; p | \delta\hat{H} | n^{(0)}; q \rangle.$$

- Since $k_p \neq k_q$, this implies:

$$\langle n^{(0)}; p | \delta\hat{H} | n^{(0)}; q \rangle = 0.$$

Remarks on Degenerate Perturbation Theory (3)

- This implies that the off-diagonal matrix element of $\delta\hat{H}$ vanishes.
- For any pair of basis vectors where such an operator $\hat{K}$ exists, all off-diagonal matrix elements of $\delta\hat{H}$ vanish.
- In practical applications:
 - A single operator K is often sufficient to verify a good basis, provided it has distinct eigenvalues for each basis vector.
 - In more complex cases, several Hermitian operators $(\hat{K}_1, \hat{K}_2, \dots)$ may be required to test subsets of off-diagonal matrix elements.

Corrections to 1st-Order States and 2nd-Order Energies

- To find the first-order state corrections and second-order energy corrections, we analyze equations (2) in two steps:
 - 1 Use the order λ equation to calculate the components of $|\psi_I^{(1)}\rangle$ in $\mathcal{V}_\perp$.
 - 2 Form the overlap of the order λ^2 equation with $\langle\psi_K^{(0)}|$ to determine the second-order energy correction $E_{nI}^{(2)}$ and the component of $|\psi_I^{(1)}\rangle$ in $\mathbb{V}_N$.
- It may be surprising that we need to go to **second order in λ** to complete the determination of the **first-order correction** to the state.
- This analysis will make it clear why this is necessary.

Corrections to 1st-Order States and Step 1

Step 1: Acting on the order λ equation in (2) with $\langle p^{(0)} |$ gives:

$$(E_p^{(0)} - E_n^{(0)}) \langle p^{(0)} | \psi_I^{(1)} \rangle = \langle p^{(0)} | (E_n^{(1)} - \delta \hat{H}) | \psi_I^{(0)} \rangle = -\langle p^{(0)} | \delta \hat{H} | \psi_I^{(0)} \rangle,$$

where we used the orthogonality of $V_\perp$ and $\mathbb{V}_N$.

Define:

$$\delta \hat{H}_{pI} \equiv \langle p^{(0)} | \delta \hat{H} | \psi_I^{(0)} \rangle,$$

leading to:

$$\langle p^{(0)} | \psi_I^{(1)} \rangle = -\frac{\delta \hat{H}_{pI}}{E_p^{(0)} - E_n^{(0)}}.$$

State Correction in $V_\perp$:

$$|\psi_I^{(1)}\rangle_{V_\perp} = -\sum_p \frac{|p^{(0)}\rangle \delta \hat{H}_{pI}}{E_p^{(0)} - E_n^{(0)}}.$$

The order λ equation provides no further information about the component of $|\psi_I^{(1)}\rangle$ along the degenerate subspace $\mathbb{V}_N$, completing **Step 1**.

Corrections (Step 2)

Step 2: Having determined the component of $|\psi_I^{(1)}\rangle$ in $V_\perp$, we now write:

$$|\psi_I^{(1)}\rangle = - \sum_p \frac{|p^{(0)}\rangle \delta \hat{H}_{pI}}{E_p^{(0)} - E_n^{(0)}} + |\psi_I^{(1)}\rangle_{\mathbb{V}_N}.$$

Hitting the order λ^2 equation with $\langle \psi_K^{(0)} |$, the LHS vanishes:

$$0 = - \langle \psi_K^{(0)} | \left(E_{nI}^{(1)} - \delta \hat{H} \right) \sum_p |p^{(0)}\rangle \frac{\delta \hat{H}_{pI}}{E_p^{(0)} - E_n^{(0)}} + \langle \psi_K^{(0)} | \left(E_{nI}^{(1)} - \delta \hat{H} \right) |\psi_I^{(1)}\rangle_{\mathbb{V}_N} + E_{nI}^{(2)} \delta_{KI} \quad (3)$$

Simplifying the 2nd term using $\delta \hat{H}$ being diagonal in $\mathbb{V}_N$:

$$\langle \psi_K^{(0)} | \delta \hat{H} | \psi_I^{(1)} \rangle_{\mathbb{V}_N} = E_{nK}^{(1)} \langle \psi_K^{(0)} | \psi_I^{(1)} \rangle_{\mathbb{V}_N} = E_{nK}^{(1)} \langle \psi_K^{(0)} | \psi_I^{(1)} \rangle.$$

We obtain:

$$\sum_p \frac{\delta \hat{H}_{Kp} \delta \hat{H}_{pI}}{E_p^{(0)} - E_n^{(0)}} + (E_{nI}^{(1)} - E_{nK}^{(1)}) \langle \psi_K^{(0)} | \psi_I^{(1)} \rangle + E_{nI}^{(2)} \delta_{KI} = 0.$$

- The second-order correction to the energy is found by setting $K = I$ and using $\delta\hat{H}_{Ip} = (\delta\hat{H}_{pI})^*$:

$$E_{nI}^{(2)} = - \sum_p \frac{|\delta\hat{H}_{pI}|^2}{E_p^{(0)} - E_n^{(0)}}.$$

- For $I \neq K$, the equation determines the component of $|\psi_I^{(1)}\rangle$ along $|\psi_K^{(0)}\rangle$:

$$\sum_p \frac{\delta\hat{H}_{Kp}\delta\hat{H}_{pI}}{E_p^{(0)} - E_n^{(0)}} + (E_{nI}^{(1)} - E_{nK}^{(1)})\langle\psi_K^{(0)}|\psi_I^{(1)}\rangle = 0.$$

- Solving for $\langle \psi_K^{(0)} | \psi_I^{(1)} \rangle_{\mathbb{V}_N}$, we have:

$$\langle \psi_K^{(0)} | \psi_I^{(1)} \rangle = -\frac{1}{E_{nI}^{(1)} - E_{nK}^{(1)}} \sum_p \frac{\delta \hat{H}_{Kp} \delta \hat{H}_{pI}}{E_p^{(0)} - E_n^{(0)}}, \quad I \neq K.$$

- Therefore, the first-order correction to the state in $\mathbb{V}_N$ is:

$$|\psi_I^{(1)}\rangle_{\mathbb{V}_N} = -\sum_{K \neq I} |\psi_K^{(0)}\rangle \frac{1}{E_{nI}^{(1)} - E_{nK}^{(1)}} \sum_p \frac{\delta \hat{H}_{Kp} \delta \hat{H}_{pI}}{E_p^{(0)} - E_n^{(0)}}.$$

It may seem that this first-order correction to the state is higher order: its numerator contains two powers of $\delta \hat{H}$. But this expression also has a denominator $E_{nI}^{(1)} - E_{nK}^{(1)}$ in which each term is of order $\delta \hat{H}$. All in all, the correction to the state is properly first order in $\delta \hat{H}$.

Summary of Degenerate Perturbation Theory

- Summarizing our results, we have the following expressions for degenerate perturbation theory with degeneracies lifted at $O(\lambda)$:

$$|\psi_I\rangle_\lambda = |\psi_I^{(0)}\rangle - \lambda \left(\sum_p \frac{\delta \hat{H}_{pI}}{E_p^{(0)} - E_n^{(0)}} |p^{(0)}\rangle + \sum_{K \neq I} \frac{|\psi_K^{(0)}\rangle}{E_{nI}^{(1)} - E_{nK}^{(1)}} \sum_p \frac{\delta \hat{H}_{Kp} \delta \hat{H}_{pI}}{E_p^{(0)} - E_n^{(0)}} \right) + O(\lambda^2),$$

$$E_n(\lambda) = E_n^{(0)} + \lambda \delta \hat{H}_{II} - \lambda^2 \sum_p \frac{|\delta \hat{H}_{pI}|^2}{E_p^{(0)} - E_n^{(0)}} + O(\lambda^3), \quad E_{nI}^{(1)} = \delta \hat{H}_{II}.$$

- These expressions summarize the corrections to states and energies for degenerate perturbation theory.