

Time-Independent Perturbation Theory & Applications

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Abstract

We begin with the formal setup, derive the first- and second-order corrections for the non-degenerate case, then address the breakdown of this formalism in the presence of degeneracy, finally the systematic approach for handling degenerate states by diagonalizing the perturbation within the degenerate subspace. The theory is illustrated with a detailed example: the Stark effect in the hydrogen atom, where we analyze both the non-degenerate ground state (quadratic effect) and the degenerate first-excited state (linear effect). We also include an outlook on time-dependent perturbation theory and an interpretation of Fermi's Golden Rule plus an Appendix. Thank AI Gemini.

1 Foundations & Non-Degenerate Theory

1.1 The Formal Setup

Perturbation theory is a systematic method to find approximate solutions for more complex systems, assuming their Hamiltonian H can be written as the sum of a solvable part H_0 and a "small" correction H' .

We write the full Hamiltonian as:

$$H = H_0 + \lambda H'$$

Here:

- H_0 is the **unperturbed Hamiltonian**. We assume we know its complete, orthonormal set of eigenstates $|n^{(0)}\rangle$ and eigenvalues $E_n^{(0)}$:

$$H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle$$

- H' is the **perturbation**.
- λ is a dimensionless bookkeeping parameter, $0 \leq \lambda \leq 1$. We will treat it as small and find solutions as a power series in λ . At the end of the calculation, we set $\lambda = 1$.

We seek the eigenstates $|n\rangle$ and eigenvalues E_n of the full Hamiltonian, $H|n\rangle = E_n|n\rangle$. We assume the solutions are analytic in λ and can be expanded in a Taylor series:

$$\begin{aligned} E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \mathcal{O}(\lambda^3) \\ |n\rangle &= |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \mathcal{O}(\lambda^3) \end{aligned}$$

Substituting these series into the full Schrödinger equation $(H_0 + \lambda H')|n\rangle = E_n|n\rangle$ gives:

$$(H_0 + \lambda H')(|n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \dots) = (E_n^{(0)} + \lambda E_n^{(1)} + \dots)(|n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \dots)$$

We then collect terms with the same power of λ to create a hierarchy of equations:

$$\begin{aligned} \mathcal{O}(\lambda^0) : \quad & H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle \\ \mathcal{O}(\lambda^1) : \quad & H_0 |n^{(1)}\rangle + H' |n^{(0)}\rangle = E_n^{(0)} |n^{(1)}\rangle + E_n^{(1)} |n^{(0)}\rangle \\ \mathcal{O}(\lambda^2) : \quad & H_0 |n^{(2)}\rangle + H' |n^{(1)}\rangle = E_n^{(0)} |n^{(2)}\rangle + E_n^{(1)} |n^{(1)}\rangle + E_n^{(2)} |n^{(0)}\rangle \end{aligned}$$

The $\mathcal{O}(\lambda^0)$ equation is just the unperturbed Schrödinger equation, which is a useful sanity check. Our goal is to solve the $\mathcal{O}(\lambda^1)$ and $\mathcal{O}(\lambda^2)$ equations for the energy and state corrections.

1.2 First-Order Corrections (Non-Degenerate)

We begin by assuming the energy level $E_n^{(0)}$ is **non-degenerate**.

1.2.1 First-Order Energy $E_n^{(1)}$

To find the first-order energy correction $E_n^{(1)}$, we rearrange the $\mathcal{O}(\lambda^1)$ equation:

$$(H_0 - E_n^{(0)}) |n^{(1)}\rangle = (E_n^{(1)} - H') |n^{(0)}\rangle$$

Now, we project this equation onto the unperturbed state $\langle n^{(0)}|$:

$$\langle n^{(0)}| (H_0 - E_n^{(0)}) |n^{(1)}\rangle = \langle n^{(0)}| (E_n^{(1)} - H') |n^{(0)}\rangle$$

On the Left-Hand Side (LHS), H_0 is Hermitian, so $\langle n^{(0)}| H_0 = E_n^{(0)} \langle n^{(0)}|$.

$$\text{LHS} = (E_n^{(0)} \langle n^{(0)}| - E_n^{(0)} \langle n^{(0)}|) |n^{(1)}\rangle = 0$$

On the Right-Hand Side (RHS), $E_n^{(1)}$ is a scalar, and $\langle n^{(0)}|n^{(0)}\rangle = 1$.

$$\text{RHS} = E_n^{(1)} \langle n^{(0)}|n^{(0)}\rangle - \langle n^{(0)}| H' |n^{(0)}\rangle = E_n^{(1)} - \langle n^{(0)}| H' |n^{(0)}\rangle$$

Setting LHS = RHS gives $0 = E_n^{(1)} - \langle n^{(0)}| H' |n^{(0)}\rangle$, which yields the first-order energy correction:

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

The first-order shift in energy is simply the expectation value of the perturbation in the *unperturbed* state.

1.2.2 First-Order State $|n^{(1)}\rangle$

To find the state correction $|n^{(1)}\rangle$, we can expand it in the complete basis of H_0 eigenstates: $|n^{(1)}\rangle = \sum_k c_k |k^{(0)}\rangle$. We are free to choose the normalization of the new state $|n\rangle$. We adopt the convention $\langle n^{(0)}|n\rangle = 1$. This implies:

$$\langle n^{(0)}|(|n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \dots)\rangle = 1 \implies 1 + \lambda \langle n^{(0)}|n^{(1)}\rangle + \mathcal{O}(\lambda^2) = 1$$

This forces $\langle n^{(0)}|n^{(1)}\rangle = 0$, meaning the first-order correction is orthogonal to the zeroth-order state. Therefore, in the expansion $|n^{(1)}\rangle = \sum_k c_k |k^{(0)}\rangle$, the coefficient c_n must be zero. We only sum over $k \neq n$:

$$|n^{(1)}\rangle = \sum_{k \neq n} c_k |k^{(0)}\rangle$$

To find the coefficients c_k , we project the $\mathcal{O}(\lambda^1)$ equation onto a *different* unperturbed state $\langle m^{(0)}|$ (where $m \neq n$):

$$\langle m^{(0)}|(H_0 - E_n^{(0)})|n^{(1)}\rangle = \langle m^{(0)}|(E_n^{(1)} - H')|n^{(0)}\rangle$$

$$\text{LHS} = (E_m^{(0)} - E_n^{(0)}) \langle m^{(0)}|n^{(1)}\rangle = (E_m^{(0)} - E_n^{(0)})c_m$$

$$\text{RHS} = E_n^{(1)} \langle m^{(0)}|n^{(0)}\rangle - \langle m^{(0)}|H'|n^{(0)}\rangle = -\langle m^{(0)}|H'|n^{(0)}\rangle$$

Equating these gives $c_m = \frac{\langle m^{(0)}|H'|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}$. Summing over all $k \neq n$ gives the full state correction:

$$|n^{(1)}\rangle = \sum_{k \neq n} \frac{\langle k^{(0)}|H'|n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}} |k^{(0)}\rangle \quad (2)$$

This shows that the perturbation "mixes" the unperturbed state $|n^{(0)}\rangle$ with other states $|k^{(0)}\rangle$. The mixing is large if the matrix element $\langle k^{(0)}|H'|n^{(0)}\rangle$ is large and the energy denominator $E_n^{(0)} - E_k^{(0)}$ is small.

1.3 Second-Order Corrections (Non-Degenerate)

To find the second-order energy $E_n^{(2)}$, we project the $\mathcal{O}(\lambda^2)$ equation onto $\langle n^{(0)}|$:

$$\langle n^{(0)}|(H_0 - E_n^{(0)})|n^{(2)}\rangle = \langle n^{(0)}|(E_n^{(1)} - H')|n^{(1)}\rangle + \langle n^{(0)}|E_n^{(2)}|n^{(0)}\rangle$$

The LHS is again zero by the same logic as before.

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

Using our normalization $\langle n^{(0)}|n^{(1)}\rangle = 0$, this simplifies to:

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

This is an exact expression, but not useful until we substitute our result for $|n^{(1)}\rangle$ from Eq. (2):

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

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

This gives the final, useful formula for the second-order energy correction:

$$E_n^{(2)} = \sum_{k \neq n} \frac{|\langle k^{(0)} | H' | n^{(0)} \rangle|^2}{E_n^{(0)} - E_k^{(0)}} \quad (3)$$

Note that for the ground state ($n = 0$), the denominator $E_0^{(0)} - E_k^{(0)}$ is always negative. Since the numerator is always non-negative, $E_0^{(2)}$ is always less than or equal to zero. The second-order correction **always** pushes the ground state energy down.

2 Degenerate Perturbation Theory

2.1 The Problem with Degeneracy

The formulas we derived, specifically Eq. (2) and Eq. (3), are built on the assumption of non-degeneracy. Look at the denominators: $E_n^{(0)} - E_k^{(0)}$.

- **The Breakdown:** If the unperturbed energy level $E_n^{(0)}$ is degenerate, there exists at least one other state $|k^{(0)}\rangle \neq |n^{(0)}\rangle$ such that $E_n^{(0)} = E_k^{(0)}$. This causes the denominators to become zero, and the theory breaks down.
- **The Conceptual Problem:** If H_0 has a d -fold degenerate subspace D with energy $E_n^{(0)}$, then *any* linear combination of the degenerate basis vectors $\{|n_1^{(0)}\rangle, \dots, |n_d^{(0)}\rangle\}$ is also an eigenstate of H_0 . Which one should we use as our $|n^{(0)}\rangle$?

The answer is that the perturbation H' will "choose" the correct basis. The perturbation often "lifts the degeneracy" by splitting the d degenerate states into d states with (slightly) different energies. Our task is to find this "good" basis *before* applying the perturbation formulas.

2.2 Finding the "Good" Basis

Let $\{|n_a^{(0)}\rangle\}$ be an arbitrary orthonormal basis for the d -fold degenerate subspace D . The "correct" or "good" zeroth-order state, $|\psi^{(0)}\rangle$, will be some linear combination of these:

$$|\psi^{(0)}\rangle = \sum_{a \in D} c_a |n_a^{(0)}\rangle$$

Let's return to the $\mathcal{O}(\lambda^1)$ equation:

$$(H_0 - E_n^{(0)}) |n^{(1)}\rangle = (E_n^{(1)} - H') |\psi^{(0)}\rangle$$

The operator on the LHS, $(H_0 - E_n^{(0)})$, is singular. Its kernel (null space) is the entire degenerate subspace D . For this equation to have a solution for $|n^{(1)}\rangle$ (a solvability condition), the vector on the RHS must be orthogonal to the kernel of the LHS.

Therefore, we must project the RHS onto *every* basis vector $|n_b^{(0)}\rangle \in D$ and set the result to zero:

$$\langle n_b^{(0)} | (E_n^{(1)} - H') |\psi^{(0)}\rangle = 0 \quad \text{for all } b \in D$$

Now, we substitute our expansion for $|\psi^{(0)}\rangle$:

$$\begin{aligned} \langle n_b^{(0)} | (E_n^{(1)} - H') \left(\sum_{a \in D} c_a |n_a^{(0)}\rangle \right) &= 0 \\ \sum_{a \in D} \left(E_n^{(1)} \langle n_b^{(0)} | n_a^{(0)}\rangle - \langle n_b^{(0)} | H' | n_a^{(0)}\rangle \right) c_a &= 0 \end{aligned}$$

Let's define the matrix $H'_{ba} = \langle n_b^{(0)} | H' | n_a^{(0)}\rangle$. Since $\langle n_b^{(0)} | n_a^{(0)}\rangle = \delta_{ba}$, we have:

$$\sum_{a \in D} (E_n^{(1)} \delta_{ba} - H'_{ba}) c_a = 0$$

This is a $d \times d$ matrix eigenvalue problem. In matrix notation:

$$\begin{pmatrix} H'_{11} & H'_{12} & \cdots \\ H'_{21} & H'_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} = E_n^{(1)} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}$$

Or more compactly: $\mathbf{H}'^{(D)} \mathbf{c} = E_n^{(1)} \mathbf{c}$.

2.3 Procedure and Second-Order Corrections

This result gives us a clear procedure for degenerate perturbation theory:

1. Identify the d -fold degenerate subspace D for the energy $E_n^{(0)}$.
2. Construct the $d \times d$ matrix of the perturbation, $H'_{ba} = \langle n_b^{(0)} | H' | n_a^{(0)}\rangle$, using any convenient basis $\{|n_a^{(0)}\rangle\}$ for that subspace.
3. **Diagonalize this matrix.**
4. The **eigenvalues** of this matrix are the **first-order energy corrections**, $E_n^{(1)}$.
5. The corresponding **eigenvectors** \mathbf{c} give the coefficients for the **"good" basis states**, $|\psi^{(0)}\rangle = \sum_a c_a |n_a^{(0)}\rangle$.

If the eigenvalues $E_n^{(1)}$ are all distinct, the degeneracy is fully lifted at first order. If some are still the same, the degeneracy is only partially lifted.

Once the "good" basis $\{|\psi_j^{(0)}\rangle\}$ is found, the higher-order corrections can be calculated using the non-degenerate formulas, with one crucial modification: the sums must exclude the *entire* degenerate subspace D .

$$E_j^{(2)} = \sum_{k \notin D} \frac{|\langle k^{(0)} | H' | \psi_j^{(0)} \rangle|^2}{E_j^{(0)} - E_k^{(0)}}$$

3 Example: The Stark Effect in Hydrogen

The Stark effect describes the splitting of atomic energy levels in an external electric field (i.e. in the \mathbf{z} direction).

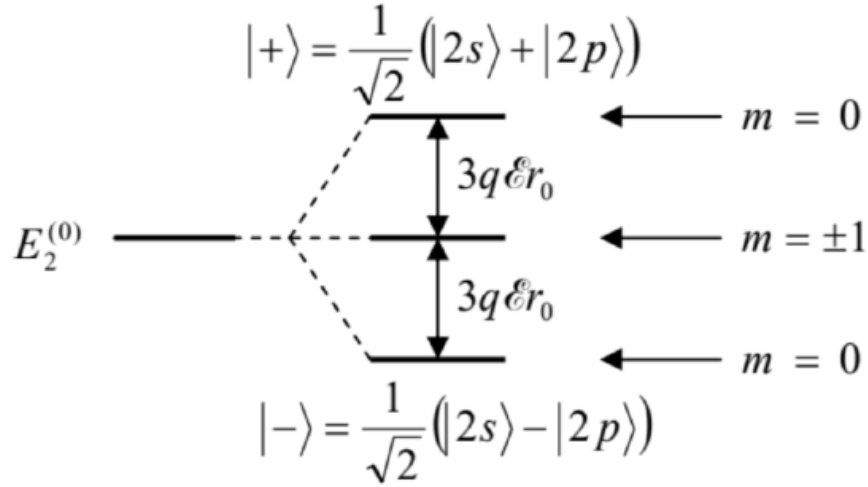


Figure 1: 4 fold degeneracy of $n = 2$ levels of H atoms splits under external electric field in the \mathbf{z} direction, where $|\psi_{100}\rangle$; $|2s\rangle$ denotes ψ_{200} & $|2p\rangle$ being $\psi_{210}, \psi_{211}, \psi_{21-1}$ collectively.

3.1 Problem Setup

Consider a hydrogen atom in a uniform electric field $\mathcal{E} = \mathcal{E}\hat{z}$ ($z = r\cos\theta$)

- H_0 : The unperturbed hydrogen Hamiltonian. Eigenstates $|n, l, m\rangle$ and energies $E_n^{(0)}$.
- H' : The perturbation. This is the potential energy of the electron's dipole moment $\mathbf{d} = -e\mathbf{r}$ in the field.

$$H' = -\mathbf{d} \cdot \mathcal{E} = -(-e\mathbf{r}) \cdot (\mathcal{E}\hat{z}) = e\mathcal{E}z$$

3.2 Ground State (n=1) - Non-Degenerate Case

The $n = 1$ ground state is $|1, 0, 0\rangle$ (or $|1s\rangle$), which is non-degenerate (ignoring spin). We can use the non-degenerate formulas directly.

First-Order Energy Shift:

$$E_{1s}^{(1)} = \langle 1, 0, 0 | H' | 1, 0, 0 \rangle = e\mathcal{E} \langle 1, 0, 0 | z | 1, 0, 0 \rangle$$

This expectation value is the integral $\int |\psi_{100}(\mathbf{r})|^2 z d^3r$. We can solve this by a symmetry argument:

- The wavefunction ψ_{100} is spherically symmetric, so $|\psi_{100}|^2$ is an **even** function under parity ($\mathbf{r} \rightarrow -\mathbf{r}$).
- The operator z is an **odd** function ($z \rightarrow -z$).
- The integrand is (even) \times (odd) = **odd**.
- The integral of an odd function over all space (a symmetric interval) is identically **zero**.

Thus, $E_{1s}^{(1)} = 0$. There is **no linear Stark effect** for the ground state.

The energy shift is dominated by the second-order correction, $E_{1s}^{(2)} \propto \mathcal{E}^2$. This is the **quadratic Stark effect**, where the field first *induces* a dipole moment, which then interacts with the field.

3.3 First Excited State (n=2) - Degenerate Case

The $n = 2$ level is **4-fold degenerate**. The basis for this subspace is:

$$D = \{|2, 0, 0\rangle, |2, 1, 1\rangle, |2, 1, 0\rangle, |2, 1, -1\rangle\}$$

We must build the 4×4 matrix $H'_{ba} = \langle \psi_b | e\mathcal{E}z | \psi_a \rangle$ and diagonalize it.

Simplifying the Matrix: We can use symmetries to simplify the 4×4 matrix.

1. **L_z Symmetry:** Consider the L_z operator. We find that $[H', L_z] = [e\mathcal{E}z, L_z] = e\mathcal{E}[z, L_z] = 0$. Since $[H_0, L_z] = 0$ and $[H', L_z] = 0$, H' cannot connect states with different m eigenvalues.

$$\langle n', l', m' | H' | n, l, m \rangle = 0 \quad \text{unless } m' = m$$

This means our 4×4 matrix is **block-diagonal**. The $m = 1$, $m = -1$, and $m = 0$ sectors are all separate.

2. **Parity Symmetry:** All diagonal elements $H'_{aa} = \langle \psi_a | H' | \psi_a \rangle$ are zero by the same parity argument we used for the ground state. The states $|n, l, m\rangle$ have definite parity $(-1)^l$, so $|\psi_{nlm}|^2$ is even. The integrand $|\psi_{nlm}|^2 z$ is odd, so the integral is zero.

Our 4×4 matrix, ordered by $\{|2, 1, 1\rangle, |2, 1, -1\rangle, |2, 0, 0\rangle, |2, 1, 0\rangle\}$, becomes:

$$\mathbf{H}^{(D)} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & W \\ 0 & 0 & W & 0 \end{pmatrix}$$

Where the only non-zero element is $W = \langle 2, 0, 0 | H' | 2, 1, 0 \rangle$. This integral is (even) \times (odd) \times (odd) = even, so it is **non-zero**. A full calculation yields $W = 3e\mathcal{E}a_0$.

Diagonalization: The $m = 1$ and $m = -1$ states are already "good" states and have an energy shift of $E^{(1)} = 0$. We only need to diagonalize the 2×2 $m = 0$ block:

$$\det \begin{pmatrix} -E^{(1)} & W \\ W & -E^{(1)} \end{pmatrix} = 0 \implies (E^{(1)})^2 - W^2 = 0 \implies E^{(1)} = \pm W$$

Results:

- **Energies:** The 4-fold degenerate $n = 2$ level splits into three distinct energies:
 - $E^{(1)} = +W$ (for one $m = 0$ state)
 - $E^{(1)} = -W$ (for the other $m = 0$ state)
 - $E^{(1)} = 0$ (for the $m = \pm 1$ states, which remain degenerate)

This shift, proportional to \mathcal{E} , is the **linear Stark effect**.

- **"Good" States:** The eigenvectors for the $m = 0$ block are:

$$\begin{aligned} - E^{(1)} = +W &\implies |\psi_+\rangle = \frac{1}{\sqrt{2}}(|2, 0, 0\rangle + |2, 1, 0\rangle) \\ - E^{(1)} = -W &\implies |\psi_-\rangle = \frac{1}{\sqrt{2}}(|2, 0, 0\rangle - |2, 1, 0\rangle) \end{aligned}$$

The field polarizes the atom by mixing the s and p orbitals, creating permanent dipole moments.

4 Outlook: Time-Dependent Perturbation Theory

4.1 The Time-Dependent Problem

So far, H' has been time-independent. What if the perturbation itself is a function of time?

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

A key example is an atom interacting with an oscillating electromagnetic field (light). In this case, energy is no longer conserved, and the system does not have stationary states. We can no longer ask "What are the new energy eigenvalues?" Instead, the key question becomes:

If the system starts in an H_0 eigenstate $|i\rangle$ at $t = 0$, what is the probability of finding it in another eigenstate $|f\rangle$ at a later time t ?

We are now solving for **transition probabilities**, $P_{i \rightarrow f}(t)$.

4.2 Fermi's Golden Rule

A (lengthy) derivation using time-dependent perturbation theory leads to one of the most important results in quantum mechanics. For a weak perturbation that can cause transitions from an initial state $|i\rangle$ to a *continuum* of final states $|f\rangle$, the **transition rate** $\Gamma_{i \rightarrow f}$ (probability per unit time) is constant.

$$\Gamma_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle f | H' | i \rangle|^2 \rho(E_f) \quad (4)$$

This is **Fermi's Golden Rule**. The terms are:

- $\Gamma_{i \rightarrow f}$: The transition rate, in units of (probability / time) or (transitions / time).
- $|\langle f | H' | i \rangle|^2$: The **matrix element** (squared). This measures the *strength of coupling* between the initial and final states. If this matrix element is zero (e.g., due to a symmetry), the transition is "forbidden" (a **selection rule**).
- $\rho(E_f)$: The **density of final states**, i.e., the number of available states per unit energy at the final energy E_f .

The rule also implicitly contains an energy-conserving delta function, $\delta(E_f - E_i - E_{\text{photon}})$, which ensures that the transition only occurs if the final state energy matches the initial state energy plus the energy added by the perturbation.

This single formula is the foundation for understanding almost all light-matter interactions, including:

- Absorption and emission of light by atoms (spectroscopy).
- Particle scattering cross-sections.
- Electron-phonon interactions in solids.

5 Appendix: The Solvability Condition (Fredholm Alternative)

In the derivation of degenerate perturbation theory, we encountered the equation:

$$(H_0 - E_n^{(0)}) |n^{(1)}\rangle = (E_n^{(1)} - H') |\psi^{(0)}\rangle \quad (5)$$

We stated that for a solution $|n^{(1)}\rangle$ to exist, the vector on the right-hand side (RHS) must be orthogonal to the kernel (or null space) of the operator on the left-hand side (LHS). This concept, known as the **Fredholm Alternative**, is a fundamental result from linear algebra.

5.1 What is the Kernel (Null Space)?

The **kernel** of a linear operator A , denoted $\text{Ker}(A)$, is the set of all vectors $|v\rangle$ that the operator maps to the zero vector.

$$\text{Ker}(A) = \{|v\rangle \mid A|v\rangle = 0\}$$

If the kernel contains more than just the zero vector, the operator A is called **singular**. This means A is not invertible (it has at least one zero eigenvalue).

5.1.1 The Kernel in Our Problem

In our case, the operator on the LHS is $A = (H_0 - E_n^{(0)})$. The kernel of this operator is the set of all vectors $|\psi\rangle$ such that:

$$(H_0 - E_n^{(0)})|\psi\rangle = 0 \quad \implies \quad H_0|\psi\rangle = E_n^{(0)}|\psi\rangle$$

By definition, the kernel of our operator is the set of all eigenstates of H_0 with the eigenvalue $E_n^{(0)}$. This is precisely the **degenerate subspace** D for that energy.

5.2 The Solvability Condition with an Example

The Fredholm Alternative states that for a singular operator A , the equation $A|x\rangle = |b\rangle$ has a solution for the unknown vector $|x\rangle$ *if and only if* the vector $|b\rangle$ is orthogonal to the kernel of A .

$$\text{A solution } |x\rangle \text{ exists} \iff \langle v|b\rangle = 0 \text{ for all } |v\rangle \in \text{Ker}(A)$$

5.2.1 A Finite-Dimensional Example

Let's consider a simple 3D vector space. We want to solve $A|x\rangle = |b\rangle$ where A is a singular matrix. Let A be a projection onto the xy -plane:

$$A = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

This matrix is singular (its determinant is 0).

1. Find the Kernel of A: We look for all vectors $|v\rangle = (v_1, v_2, v_3)^T$ such that $A|v\rangle = 0$.

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix} = \begin{pmatrix} v_1 \\ v_2 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

This requires $v_1 = 0$ and $v_2 = 0$. The vector $|v\rangle$ must be of the form $(0, 0, v_3)^T$. Thus, the kernel is the z -axis, spanned by the basis vector $|v_k\rangle = (0, 0, 1)^T$.

2. Find the Solvability Condition: Now let's see when $A|x\rangle = |b\rangle$ has a solution.

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} x_1 \\ x_2 \\ 0 \end{pmatrix} = \begin{pmatrix} b_1 \\ b_2 \\ b_3 \end{pmatrix}$$

This system of equations ($x_1 = b_1$, $x_2 = b_2$, $0 = b_3$) only has a solution if $\mathbf{b}_3 = \mathbf{0}$.

3. Compare the Conditions:

- The direct condition for a solution is $b_3 = 0$.
- The "orthogonality" condition is that $|b\rangle$ must be orthogonal to the kernel $|v_k\rangle$.

$$\langle v_k | b \rangle = \begin{pmatrix} 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \\ b_3 \end{pmatrix} = b_3$$

The condition $\langle v_k | b \rangle = 0$ implies $\mathbf{b}_3 = \mathbf{0}$.

The two conditions are identical. This demonstrates why the "orthogonality" condition is the key to solvability.

5.3 Tying It Back to Perturbation Theory

We now apply this logic to our main equation, Eq. (5).

- $\mathbf{A} = (H_0 - E_n^{(0)})$ is our singular operator.
- $|\mathbf{x}\rangle = |n^{(1)}\rangle$ is the unknown vector we want to find.
- $|\mathbf{b}\rangle = (E_n^{(1)} - H') |\psi^{(0)}\rangle$ is the vector on the RHS.
- $\text{Ker}(\mathbf{A}) = D$, the degenerate subspace, spanned by $\{|n_a^{(0)}\rangle\}$.

For a solution $|n^{(1)}\rangle$ to exist, the vector $|b\rangle$ *must* be orthogonal to the kernel D . This means $|b\rangle$ must be orthogonal to *every* basis vector $|n_b^{(0)}\rangle$ that spans the kernel.

$$\langle n_b^{(0)} | b \rangle = 0 \quad \text{for all } |n_b^{(0)}\rangle \in D$$

Substituting our expression for $|b\rangle$:

$$\langle n_b^{(0)} | (E_n^{(1)} - H') |\psi^{(0)}\rangle = 0$$

This equation is the *solvability condition*. We are not "projecting" the equation arbitrarily; we are *enforcing* the mathematical condition required for the existence of the first-order state correction $|n^{(1)}\rangle$. This condition is what allows us to find the unknown energy corrections $E_n^{(1)}$ and the "good" basis states $|\psi^{(0)}\rangle$.