Chapter 7: Perturbation Theory

Quantum Mechanics

1 Perturbation Equation

Remark 1.1 (Working Treatment of Operator Domains). [rem:operator-domain-convention] Fix a Hilbert space $\mathcal{H}$. Throughout this chapter, formally write $A : \mathcal{H} \to \mathcal{H}$ for an operator $A \in \mathscr{O}$. This notation is literal for finite-dimensional matrix operators. For differential operators, it suppresses domain restrictions: all expressions are understood on a suitable common domain where the indicated operations are defined. Detailed operator domains and self-adjointness will be addressed when revising Chapters 2 and 3 rigorously

Definition 1.1 (Unperturbed Hamiltonian). [def:unperturbed-hamiltonian] An *unperturbed Hamiltonian* $\hat{H}_0 \in \mathscr{O}$ is a reference time-independent Hamiltonian, quantum-mechanics whose eigenstates and corresponding energies are taken as known for the perturbation calculation

Definition 1.2 (Perturbation Operator). [def:perturbation] Given an unperturbed Hamiltonian $\hat{H}_0$ and the physical time-independent Hamiltonian $\hat{H} \in \mathscr{O}$ on the same state space $\mathcal{H}$, the *perturbation operator* is their difference:

$$\hat{H}' \equiv \hat{H} - \hat{H}_0$$

Definition 1.3 (Perturbation Family). [def:perturbation-family] Fix an unperturbed Hamiltonian $\hat{H}_0$ and its perturbation operator $\hat{H}'$. Let $I \subseteq \mathbb{R}$ be an interval containing 0 and 1. The *perturbation family* determined by these operators is the function

$$\hat{H}_{\text{fam}} : I \to \mathscr{O} \equiv \lambda \mapsto \hat{H}_0 + \lambda \cdot \hat{H}'.$$

Require each $\hat{H}_{\text{fam}}(\lambda)$ to be Hermitian, with domain restrictions suppressed as in the working treatment of operator domains

Convention 1.1 (Perturbation Terminology). [conv:perturbation-terminology] For the perturbation family, use the following terminology:
$\hat{H}$**:** the full physical Hamiltonian, also called the *perturbed Hamiltonian.*
$\hat{H}_0$**:** the unperturbed Hamiltonian, whose eigenstates and energies are taken as known.
$\hat{H}'$**:** the perturbation operator, equal to $\hat{H} - \hat{H}_0$.
λ**:** the dimensionless *perturbation parameter*, treated as small when deriving corrections. The value 0 gives the reference Hamiltonian, and 1 gives the full physical Hamiltonian

Remark 1.2 (Prime on $\hat{H}'$ Is a Label, Not a Derivative). [rem:perturbation-prime-notation]

Definition 1.4 (Reference Eigenpair). [def:reference-eigenpair] A *reference eigenpair* of an unperturbed Hamiltonian $\hat{H}_0$ is a known pair $(\psi_n^{(0)}, E_n^{(0)}) \in \mathcal{H} \times \mathbb{R}$ satisfying

$$\psi_n^{(0)} \neq 0, \qquad \hat{H}_0\big(\psi_n^{(0)}\big) = E_n^{(0)} \cdot \psi_n^{(0)}$$

Definition 1.5 (Eigenvector Branch). [def:eigenvector-branch] Given a perturbation family and a reference eigenpair $(\psi_n^{(0)}, E_n^{(0)})$, an *eigenvector branch* is a continuous function $\phi : I \to \mathcal{H}$ with $\phi(0) = \psi_n^{(0)}$ and, for every $\lambda \in I$,

$$\phi(\lambda) \neq 0, \qquad \exists e \in \mathbb{R}, \quad \hat{H}_{\text{fam}}(\lambda)\big(\phi(\lambda)\big) = e \cdot \phi(\lambda)$$

Definition 1.6 (Eigenvalue Branch). [def:eigenvalue-branch] For a chosen eigenvector branch ϕ_n, its *eigenvalue branch* is the function $\varepsilon_n : I \to \mathbb{R}$ satisfying

$$\hat{H}_{\text{fam}}(\lambda)\big(\phi_n(\lambda)\big) = \varepsilon_n(\lambda) \cdot \phi_n(\lambda) \qquad (\lambda \in I)$$

Remark 1.3 (Choosing a Branch). [rem:eigenvector-branch-choice] The eigenvector-branch definition specifies possible functions without asserting existence or uniqueness. If one exists, fix a choice ϕ_n; the index n labels its reference eigenpair. For this choice, each $\varepsilon_n(\lambda)$ exists and is unique: two candidate eigenvalues e, f satisfy $(e - f) \cdot \phi_n(\lambda) = 0$, so $e = f$. In particular, $\varepsilon_n(0) = E_n^{(0)}$

Convention 1.2 (State and Energy Notation). [conv:eigenpair-notation]

$$\psi_n^{(0)} = \phi_n(0), \qquad E_n^{(0)} = \varepsilon_n(0).$$

$$\psi_n^{\text{phys}} \equiv \phi_n(1), \qquad E_n^{\text{phys}} \equiv \varepsilon_n(1)$$

Definition 1.7 (State Coefficient Sequence). [def:perturbative-expansion]

$$\psi_n : \mathbb{N}_0 \to \mathcal{H} \equiv k \mapsto \psi_n^{(k)}$$

Definition 1.8 (Energy Coefficient Sequence). [def:energy-perturbative-expansion]

$$E_n : \mathbb{N}_0 \to \mathbb{R} \equiv k \mapsto E_n^{(k)}$$

Hypothesis 1.1 (Existence of a Perturbative Expansion). [hypo:perturbative-expansion-existence] *For a chosen eigenvector branch ϕ_n and its eigenvalue branch ε_n, assume there exist a state coefficient sequence ψ_n, an energy coefficient sequence E_n, and a neighborhood J of 0 in I such that the following local function rules hold for $\lambda \in J$:*

$$\phi_n : I \to \mathcal{H}, \qquad \lambda \mapsto \sum_0^\infty \big(k \mapsto \lambda^k \cdot \psi_n(k)\big)\,.$$

$$\varepsilon_n : I \to \mathbb{R}, \qquad \lambda \mapsto \sum_0^\infty \big(k \mapsto \lambda^k \cdot E_n(k)\big)\,.$$

Moreover, for each $A \in \{\hat{H}_0, \hat{H}'\}$, all indicated operator applications are defined and

$$A \circ \phi_n : I \to \mathcal{H}, \qquad \lambda \mapsto \sum_0^\infty \big(k \mapsto \lambda^k \cdot A\big(\psi_n(k)\big)\big)\,.$$

For every $\lambda \in J$, all vector series above converge in the norm of $\mathcal{H}$, and the scalar series converges in $\mathbb{R}$

Remark 1.4 (Scope of the Expansion Hypothesis). [rem:expansion-convergence] The expansion hypothesis assumes convergence near $\lambda = 0$; matching coefficients alone does not prove convergence. Validity at the physical endpoint $\lambda = 1$ requires separate justification

Theorem 1.1 (Perturbation Equation (Summation Form)). [thm:perturbation-equation] *Under the expansion hypothesis, for $\lambda \in I$ sufficiently close to 0,*

$$\begin{aligned}&\left(\hat{H}_0 + \lambda \cdot \hat{H}'\right)\left(\sum_0^\infty \big(k \mapsto \lambda^k \cdot \psi_n(k)\big)\right)\\ &\quad = \left(\sum_0^\infty \big(j \mapsto \lambda^j \cdot E_n(j)\big)\right) \cdot \left(\sum_0^\infty \big(k \mapsto \lambda^k \cdot \psi_n(k)\big)\right)\end{aligned}$$

Proof. Substitute $\hat{H}_{\text{fam}}(\lambda) = \hat{H}_0 + \lambda \cdot \hat{H}'$ and the assumed expansions into the TISE □

Convention 1.3 (Perturbation Order Notation). [conv:order-k-correction] Parenthesized superscripts denote perturbative order:

$$\psi_n^{(k)} \equiv \psi_n(k), \qquad E_n^{(k)} \equiv E_n(k).$$

For $k \geq 1$, these are the *k-th-order state and energy correction coefficients*. The zeroth-order terms form the reference eigenpair:

$$\psi_n^{(0)} = \phi_n(0), \qquad E_n^{(0)} = \varepsilon_n(0)$$

Definition 1.9 (Order-by-Order Perturbation System). [def:order-matched-system] For coefficient sequences ψ_n, E_n, the *order-by-order perturbation system* consists of

$$\hat{H}_0\big(\psi_n(0)\big) = E_n(0) \cdot \psi_n(0)$$

and, for every $k \in \mathbb{N}_{>0}$,

$$\hat{H}_0\big(\psi_n(k)\big) + \hat{H}'\big(\psi_n(k-1)\big) = \sum_0^k \big(j \mapsto E_n(j) \cdot \psi_n(k-j)\big)$$

Theorem 1.2 (Equivalence of Perturbation Equations). [thm:order-matched-equations] *Under the expansion hypothesis, the sequences $\psi_n \equiv i \mapsto \psi_n^{(i)}$ and $E_n \equiv i \mapsto E_n^{(i)}$ satisfy all equations of the order-by-order system if and only if (ϕ_n, ε_n) solves the summation-form equation for every $\lambda \in I$ sufficiently close to 0*

Proof. **TODO** □

Remark 1.5 (Recovering the Summation Equation). [rem:recovering-summation-equation] Multiply the order-k equation by λ^k and sum its left-hand and right-hand sides separately over all orders. Here k is the correction order, while n labels the reference state. The shifted perturbation sum becomes

$$\sum_1^\infty \Big(k \mapsto \lambda^k \cdot \hat{H}'\big(\psi_n(k-1)\big)\Big) = \lambda \cdot \hat{H}'\big(\phi_n(\lambda)\big),$$

and the summed right-hand side becomes $\varepsilon_n(\lambda) \cdot \phi_n(\lambda)$. Thus

$$\left(\hat{H}_0 + \lambda \cdot \hat{H}'\right)\big(\phi_n(\lambda)\big) = \varepsilon_n(\lambda) \cdot \phi_n(\lambda)$$

Corollary 1.1 (Zeroth-, First-, and Second-Order Equations). [cor:equations-through-second-order]

$$\begin{aligned}
\hat{H}_0\big(\psi_n^{(0)}\big) &= E_n^{(0)} \cdot \psi_n^{(0)}, \\
\hat{H}_0\big(\psi_n^{(1)}\big) + \hat{H}'\big(\psi_n^{(0)}\big) &= E_n^{(0)} \cdot \psi_n^{(1)} + E_n^{(1)} \cdot \psi_n^{(0)}, \\
\hat{H}_0\big(\psi_n^{(2)}\big) + \hat{H}'\big(\psi_n^{(1)}\big) &= E_n^{(0)} \cdot \psi_n^{(2)} + E_n^{(1)} \cdot \psi_n^{(1)} + E_n^{(2)} \cdot \psi_n^{(0)}
\end{aligned}$$

Proof. Take orders $0, 1, 2$ in the order-by-order system □

Definition 1.10 (k-th-Order Approximation). [def:perturbative-approximation] Let $\psi_n^{(k)}$ and $E_n^{(k)}$ be the solution for the order-by-order system at order k
The *k-th-order perturbative approximation* to the eigenpair $(\phi_n(\lambda), \varepsilon_n(\lambda))$ is

$$\phi_n^{(k)} \equiv \sum_0^k \big(i \mapsto \psi_n^{(i)}\big), \qquad \varepsilon_n^{(k)} \equiv \sum_0^k \big(i \mapsto E_n^{(i)}\big)$$

Remark 1.6 (Validity of the Approximation). [rem:perturbative-validity] Since the equation works at λ sufficiently close to 0, the k-th-order approximation shall be significant small when k is bigger

2 First-Order Perturbation Theory

Theorem 2.1 (First Order Energy Correction). [thm:first-order-energy-correction] *Under the expansion hypothesis, let the reference eigenstate be normalized: $\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle = 1$. Then*

$$E_n^{(1)} = \langle\psi_n^{(0)}|\,\hat{H}'\,|\psi_n^{(0)}\rangle$$

Proof. According to the first order equation, we have

$$\hat{H}_0\,|\psi_n^{(1)}\rangle + \hat{H}'\,|\psi_n^{(0)}\rangle = E_n^{(0)}\,|\psi_n^{(1)}\rangle + E_n^{(1)}\,|\psi_n^{(0)}\rangle$$

Since $\psi_n^{(0)}$ is a non-zero eigenvector, we can multiply its bra vector to both sides, ie

$$\langle\psi_n^{(0)}|\,\hat{H}_0\,|\psi_n^{(1)}\rangle + \langle\psi_n^{(0)}|\,\hat{H}'\,|\psi_n^{(0)}\rangle = \langle\psi_n^{(0)}|\,E_n^{(0)}\,|\psi_n^{(1)}\rangle + \langle\psi_n^{(0)}|\,E_n^{(1)}\,|\psi_n^{(0)}\rangle$$

Notice $E_n^{(0)}$ is an real number, and according to the normalization axiom,

$$\langle\psi_n^{(0)}|\,E_n^{(1)}\,|\psi_n^{(0)}\rangle = E_n^{(1)}\,\langle\psi_n^{(0)}\mid\psi_n^{(0)}\rangle = E_n^{(1)}$$

According to the TISE, $H\,|\psi\rangle = E\,|\psi\rangle$, we subsitute that relationship into $\langle\psi_n^{(0)}|\,\hat{H}_0$

$$\langle\psi_n^{(0)}|\,\hat{H}_0\,|\psi_n^{(1)}\rangle = \langle\psi_n^{(0)}|\,\hat{E}_0\,|\psi_n^{(1)}\rangle = E_0\,\langle\psi_n^{(0)}\mid\psi_n^{(1)}\rangle$$

Subsitute back, we can get

$$E_0\,\langle\psi_n^{(0)}\mid\psi_n^{(1)}\rangle + \langle\psi_n^{(0)}|\,\hat{H}'\,|\psi_n^{(0)}\rangle = \langle\psi_n^{(0)}|\,E_n^{(0)}\,|\psi_n^{(1)}\rangle + E_n^{(1)}$$

Notice that $E_0\,\langle\psi_n^{(0)}\mid\psi_n^{(1)}\rangle = \langle\psi_n^{(0)}|\,E_n^{(0)}\,|\psi_n^{(1)}\rangle$, cancel out the term,

$$E_n^{(1)} = \langle\psi_n^{(0)}|\,\hat{H}'\,|\psi_n^{(0)}\rangle$$

□

Theorem 2.2 (First Order State Correction). [thm:first-order-state-correction] *Under the expansion hypothesis, suppose the reference eigenstates are orthonormal and $\psi_n^{(1)}$ admits a norm-convergent expansion in them. Let $E_n^{(0)}$ be nondegenerate, and choose $\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle = 0$. Then*

$$\psi_n^{(1)} = \sum_{m\neq n}\left(m \mapsto \frac{\langle\psi_m^{(0)}|\,\hat{H}'\,|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}\cdot\psi_m^{(0)}\right),$$

where the sum runs over $m \in \mathbb{N}_1$ with $m \neq n$

Proof. According to the first order equation, and multiply $\langle\psi_m^{(0)}|$ (the bra of a reference eigenstate) on both sides, we have

$$\begin{aligned}&\langle\psi_m^{(0)}|\,\hat{H}_0\,|\psi_n^{(1)}\rangle + \langle\psi_m^{(0)}|\,\hat{H}'\,|\psi_n^{(0)}\rangle\\ &\quad= \langle\psi_m^{(0)}|\,E_n^{(0)}\,|\psi_n^{(1)}\rangle + \langle\psi_m^{(0)}|\,E_n^{(1)}\,|\psi_n^{(0)}\rangle\end{aligned}$$

Rearranging the equation, we can get

$$\langle\psi_m^{(0)}|\,\hat{H}_0\,|\psi_n^{(1)}\rangle - E_n^{(0)}\cdot\langle\psi_m^{(0)}|\psi_n^{(1)}\rangle = E_n^{(1)}\cdot\langle\psi_m^{(0)}|\psi_n^{(0)}\rangle - \langle\psi_m^{(0)}|\,\hat{H}'\,|\psi_n^{(0)}\rangle$$

Apply Hermiticity and the reference eigenvalue equation, we get

$$\langle\psi_m^{(0)}|\,\hat{H}_0\,|\psi_n^{(1)}\rangle = \langle\hat{H}_0\psi_m^{(0)}\mid\psi_n^{(1)}\rangle = E_m^{(0)}\,\langle\psi_m^{(0)}\mid\psi_n^{(1)}\rangle$$

Also, according orthonormality,

$$E_n^{(1)} \cdot \langle \psi_m^{(0)} | \psi_n^{(0)} \rangle = E_n^{(1)} \cdot \delta_{n,m}$$

Let $\{\psi_m^{(0)} : m \in \mathbb{N}_1\}$ be linearly independent reference solutions. For fixed n, assume there exists a coefficient function $c_n : \mathbb{N}_1 \to \mathbb{C}$ such that

$$\psi_n^{(1)} = \sum^{\infty} \left(m \mapsto c_n(m) \cdot \psi_m^{(0)} \right)$$

with convergence in the norm of $\mathcal{H}$. Which means that

$$c_m \equiv c_n(m) = \langle \psi_m^{(0)} \mid \psi_n^{(1)} \rangle$$

Plug back in, we get

$$E_m^{(0)} \cdot c_m - E_n^{(0)} \cdot c_m = E_n^{(1)} \cdot \delta_{n,m} - \langle \psi_m^{(0)} | \, \hat{H}' \, | \psi_n^{(0)} \rangle$$

Choose $c_n(n) = 0$. **TODO**: justify this normalization and phase choice
For $m \neq n$ with $E_m^{(0)} \neq E_n^{(0)}$, solve for c_m, we have

$$c_m = \frac{E_n^{(1)} \cdot \delta_{n,m} - \langle \psi_m^{(0)} | \, \hat{H}' \, | \psi_n^{(0)} \rangle}{E_m^{(0)} - E_n^{(0)}}$$

Since $m \neq n$, $\delta_{n,m} = 0$. Hence

$$c_m = -\frac{\langle \psi_m^{(0)} | \, \hat{H}' \, | \psi_n^{(0)} \rangle}{E_m^{(0)} - E_n^{(0)}} = \frac{\langle \psi_m^{(0)} | \, \hat{H}' \, | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}.$$

Substituting these coefficients into the expansion and using $c_n(n) = 0$ gives

$$\psi_n^{(1)} = \sum_{m \neq n} \left(m \mapsto \frac{\langle \psi_m^{(0)} | \, \hat{H}' \, | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \cdot \psi_m^{(0)} \right)$$

□

Remark 2.1 (Normalization and Phase). [rem:eigenpair-choices] An eigenvector branch is not unique: for any continuous function $c : I \to \mathbb{C} \setminus \{0\}$ with $c(0) = 1$, the branch

$$\widetilde{\phi}_n : I \to \mathcal{H} \equiv \lambda \mapsto c(\lambda) \cdot \phi_n(\lambda)$$

has the same starting vector and eigenvalue branch by linearity. Unit normalization leaves a parameter-dependent phase undetermined

3 Second-Order Perturbation Theory

Theorem 3.1 (Second Order Energy Correction). [thm:second-order-energy-correction] *Under the assumptions and normalization choice of the first-order state correction, with $\hat{H}'$ Hermitian,*

$$E_n^{(2)} = \sum_{m \neq n} \left(m \mapsto \frac{\left| \langle \psi_m^{(0)} | \, \hat{H}' \, | \psi_n^{(0)} \rangle \right|^2}{E_n^{(0)} - E_m^{(0)}} \right)$$

where the sum runs over $m \in \mathbb{N}_1$ with $m \neq n$

Proof. **TODO** □

4 Degenerate Perturbation Theory

Definition 4.1 (Good Basis). [def:good-basis] Let the degenerate eigenspace of the unperturbed Hamiltonian be

$$V_{E_0} \equiv \{\psi \in \mathcal{H} : \hat{H}_0(\psi) = E_0 \cdot \psi\}, \qquad \dim V_{E_0} = d \geq 2.$$

A *good basis* is an orthonormal basis $B = \{\chi_r^{(0)} : r \in \{1, \ldots, d\}\}$ of V_{E_0}, where for each r there exists an eigenvector branch ϕ_r, satisfying the expansion hypothesis, with corresponding eigenvalue branch ε_r such that

$$\phi_r(0) = \chi_r^{(0)}, \qquad \varepsilon_r(0) = E_0$$

Definition 4.2 (Good States). [def:good-states] The *good states* are the states in a good basis B, ie, each $\chi_r^{(0)} \in B$ is a good state

Corollary 4.1 (Common Unperturbed Energy). [cor:good-states-common-energy] *Given a good basis B of V_{E_0} and a coefficient function $c : \{1, \ldots, d\} \to \mathbb{C}$, let*

$$\psi \equiv \sum_1^d \left(r \mapsto c(r) \cdot \chi_r^{(0)}\right).$$

If $\psi \neq 0$, it is an eigenstate of $\hat{H}_0$ with energy E_0:

$$\hat{H}_0(\psi) = E_0 \cdot \psi.$$

Thus all good states and their nonzero linear combinations have the same unperturbed energy

Proof. Since each $\chi_r^{(0)} \in V_{E_0}$, we have $\hat{H}_0(\chi_r^{(0)}) = E_0 \cdot \chi_r^{(0)}$. By linearity,

$$\begin{aligned}\hat{H}_0(\psi) &= \sum_1^d \left(r \mapsto c(r) \cdot \hat{H}_0(\chi_r^{(0)})\right) \\ &= E_0 \cdot \sum_1^d \left(r \mapsto c(r) \cdot \chi_r^{(0)}\right) = E_0 \cdot \psi\end{aligned}$$

□

Theorem 4.1 (Existence of a Good Basis). [thm:good-basis-existence] *Suppose $\mathcal{H}$ is finite-dimensional and $\hat{H}_0, \hat{H}'$ are Hermitian. Then every degenerate eigenspace V_{E_0} of $\hat{H}_0$ has a good basis for the perturbation family*

Proof. **TODO** Rellich's theorem for analytic Hermitian matrix families, operator theory □

Infinite-dimensional extension: state the additional spectral and operator-domain assumptions and justify existence of the branches, functional-analysis. **TODO**

Definition 4.3 (Perturbation Matrix Constructor). [def:perturbation-matrix-constructor] Fix $\hat{H}'$. Let $\mathcal{B}(V_{E_0})$ denote the ordered orthonormal bases $A : \{1, \ldots, d\} \to V_{E_0}$ of V_{E_0}. The *perturbation matrix constructor* is

$$\text{pertmat} : \mathcal{B}(V_{E_0}) \to \mathbb{C}^{d \times d} \equiv A \mapsto \left(\langle A(r)| \hat{H}' |A(s)\rangle\right)_{r,s=1}^{d}.$$

The input basis need not be a good basis

Definition 4.4 (Perturbation Matrix). [def:perturbation-matrix] For $A \in \mathcal{B}(V_{E_0})$, its *perturbation matrix* is the matrix generated by the perturbation matrix constructor:

$$W \equiv \text{pertmat}(A)$$

Theorem 4.2 (Degenerate First-Order Equation). [thm:degenerate-first-order-equation] *Let $A(r) = \psi_r^{(0)}$ be an ordered orthonormal basis of V_{E_0}, and let $W \equiv \text{pertmat}(A)$. If $B(i) = \chi_i^{(0)}$ is an ordered good basis, then for each fixed i, with corresponding first-order energy correction $E_i^{(1)}$, write*

$$\chi_i^{(0)} = \sum_1^d \left(s \mapsto c(s) \cdot \psi_s^{(0)}\right), \qquad c : \{1, \dots, d\} \to \mathbb{C}.$$

Then its coefficient column satisfies

$$W\mathbf{c} = E_i^{(1)} \cdot \mathbf{c}, \qquad \mathbf{c} \neq 0.$$

In particular, giving the good basis B to the constructor yields

$$[\text{pertmat}(B)]_{ri} = E_i^{(1)} \cdot \delta_{r,i}, \qquad r, i \in \{1, \dots, d\}$$

Proof. Given a degenerate eigenspace V_{E_0} of dimension $d \geq 2$, we have the unperturbed orthonormal degenerate eigenstates $\{\psi_s^{(0)} : s \in \{1, \dots, d\}\}$ with the same eigenvalue E_0
Given an orthonormal basis A, for the chosen good state $\chi_i^{(0)}$, there exists a coefficient function $c : \{1, \dots, d\} \to \mathbb{C}$ such that

$$\chi_i^{(0)} = \sum_1^d \left(s \mapsto c(s) \cdot \psi_s^{(0)}\right)$$

Where we get the original first order equation and multiply $\langle \psi_r^{(0)}|$ on both sides, we have

$$\langle \psi_r^{(0)}| \hat{H}_0 |\chi_i^{(1)}\rangle + \langle \psi_r^{(0)}| \hat{H}' |\chi_i^{(0)}\rangle = \langle \psi_r^{(0)}| E_i^{(0)} |\chi_i^{(1)}\rangle + \langle \psi_r^{(0)}| E_i^{(1)} |\chi_i^{(0)}\rangle$$

Notice that all states in A have the same unperturbed energy E_0 as the degenerate eigenstates, we can obtain:

$$\langle \psi_r^{(0)}| \hat{H}_0 |\chi_i^{(1)}\rangle = \langle \hat{H}_0 \psi_r^{(0)} \mid \chi_i^{(1)}\rangle = E_i^{(0)} \langle \psi_r^{(0)} \mid \chi_i^{(1)}\rangle$$

Plug in and extract the real number out, we have:

$$E_i^{(0)} \langle \psi_r^{(0)} \mid \chi_i^{(1)}\rangle + \langle \psi_r^{(0)}| \hat{H}' |\chi_i^{(0)}\rangle = E_i^{(0)} \langle \psi_r^{(0)} \mid \chi_i^{(1)}\rangle + E_i^{(1)} \langle \psi_r^{(0)} \mid \chi_i^{(0)}\rangle$$

Which means

$$\langle \psi_r^{(0)}| \hat{H}' |\chi_i^{(0)}\rangle = E_i^{(1)} \langle \psi_r^{(0)} \mid \chi_i^{(0)}\rangle$$

Plug in the expansion of $\chi_i^{(0)}$, we have

$$\langle \psi_r^{(0)}| \hat{H}' |\sum_1^d \left(s \mapsto c(s) \cdot \psi_s^{(0)}\right)\rangle = E_i^{(1)} \langle \psi_r^{(0)} \mid \sum_1^d \left(s \mapsto c(s) \cdot \psi_s^{(0)}\right)\rangle$$

Due to linearity,

$$\sum_1^d \left(s \mapsto \langle \psi_r^{(0)}| \hat{H}' |c(s) \cdot \psi_s^{(0)}\rangle\right) = E_i^{(1)} \sum_1^d \left(s \mapsto \langle \psi_r^{(0)} \mid c(s) \cdot \psi_s^{(0)}\rangle\right)$$

$$\sum_1^d \left(s \mapsto c(s) \langle \psi_r^{(0)}| \hat{H}' |\psi_s^{(0)}\rangle\right) = E_i^{(1)} \sum_1^d \left(s \mapsto c(s) \langle \psi_r^{(0)} \mid \psi_s^{(0)}\rangle\right)$$

Notice that $\langle \psi_r^{(0)} \mid \psi_s^{(0)} \rangle = \delta_{r,s}$, we have

$$\sum_1^d \left(s \mapsto c(s) \langle \psi_r^{(0)} | \hat{H}' | \psi_s^{(0)} \rangle \right) = E_i^{(1)} c(r)$$

We treat each $c(r), r \in \{1, 2, ..., d\}$ as a variable, then we can assemble a linear system of equations, to solve c pointwise.

$$\begin{bmatrix} \langle \psi_1^{(0)} | \hat{H}' | \psi_1^{(0)} \rangle & \langle \psi_1^{(0)} | \hat{H}' | \psi_2^{(0)} \rangle & \cdots & \langle \psi_1^{(0)} | \hat{H}' | \psi_d^{(0)} \rangle \\ \langle \psi_2^{(0)} | \hat{H}' | \psi_1^{(0)} \rangle & \langle \psi_2^{(0)} | \hat{H}' | \psi_2^{(0)} \rangle & \cdots & \langle \psi_2^{(0)} | \hat{H}' | \psi_d^{(0)} \rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle \psi_d^{(0)} | \hat{H}' | \psi_1^{(0)} \rangle & \langle \psi_d^{(0)} | \hat{H}' | \psi_2^{(0)} \rangle & \cdots & \langle \psi_d^{(0)} | \hat{H}' | \psi_d^{(0)} \rangle \end{bmatrix} \begin{bmatrix} c(1) \\ c(2) \\ \vdots \\ c(d) \end{bmatrix} = E_i^{(1)} \begin{bmatrix} c(1) \\ c(2) \\ \vdots \\ c(d) \end{bmatrix}$$

According to the definition of the perturbation matrix, let

$$W \equiv \text{pertmat}(A), \qquad \mathbf{c} \equiv \begin{bmatrix} c(1) \\ c(2) \\ \vdots \\ c(d) \end{bmatrix}.$$

Then the linear system becomes

$$W\mathbf{c} = E_i^{(1)} \cdot \mathbf{c}.$$

Since $\chi_i^{(0)} \neq 0$, $\mathbf{c} \neq 0$. Thus $E_i^{(1)}$ is an eigenvalue of W, and $\mathbf{c}$ is a corresponding eigenvector. Finding $\mathbf{c}$ is equivalent to finding c, since its r-th entry is $c(r)$
Giving the ordered good basis $B(r) = \chi_r^{(0)}$ to the constructor instead, the projected equation above gives

$$[\text{pertmat}(B)]_{ri} = \langle \chi_r^{(0)} | \hat{H}' | \chi_i^{(0)} \rangle = E_i^{(1)} \cdot \langle \chi_r^{(0)} \mid \chi_i^{(0)} \rangle = E_i^{(1)} \cdot \delta_{r,i}.$$

Thus $W_B \equiv \text{pertmat}(B)$ is diagonal. It is the matrix in basis B; $W = \text{pertmat}(A)$ is the matrix in basis A □

Theorem 4.3 (First-Order Converse)**.** [thm:degenerate-first-order-converse] *Let A and W be as in the degenerate first-order equation. Assume V_{E_0} has a good basis and W has d distinct eigenvalues. Given $c : \{1, \ldots, d\} \to \mathbb{C}$, let*

$$\chi^{(0)} \equiv \sum_1^d \left(s \mapsto c(s) \cdot \psi_s^{(0)} \right), \qquad \sum_1^d \left(s \mapsto |c(s)|^2 \right) = 1.$$

If $W\mathbf{c} = e \cdot \mathbf{c}$, then $\chi^{(0)}$ is a good state, with first-order energy correction e

Proof. **TODO** □

Remark 4.1 (Why the Converse Needs a Proof). [rem:converse-not-automatic] The converse does not follow just by reversing the previous implication, since that proof already assumed the $\chi_i^{(0)}$ were good states

Theorem 4.4 (Constructing a Good Basis)**.** [thm:good-basis-from-perturbation-matrix] *Choose an ordered orthonormal basis $A(s) = \psi_s^{(0)}$ of V_{E_0} and calculate $W \equiv \text{pertmat}(A)$. Assume V_{E_0} has a good basis and W has d distinct eigenvalues $e_1, \ldots, e_d$. Choose orthonormal eigenvectors $\mathbf{c}_1, \ldots, \mathbf{c}_d$ satisfying*

$$W\mathbf{c}_i = e_i \cdot \mathbf{c}_i, \qquad i \in \{1, \ldots, d\}.$$

Write their entries as a function

$$c : \{1, \dots, d\} \times \{1, \dots, d\} \to \mathbb{C}, \qquad \mathbf{c}_i = \begin{bmatrix} c(i,1) \\ \vdots \\ c(i,d) \end{bmatrix}.$$

Then

$$\chi_i^{(0)} \equiv \sum_1^d \left(s \mapsto c(i,s) \cdot \psi_s^{(0)} \right), \qquad i \in \{1, \dots, d\},$$

form an ordered good basis $B(i) = \chi_i^{(0)}$, with corresponding first-order energy corrections $E_i^{(1)} = e_i$. Its perturbation matrix satisfies

$$[\mathrm{pertmat}(B)]_{ij} = e_i \cdot \delta_{i,j}, \qquad i, j \in \{1, \dots, d\}$$

Proof. Each $\chi_i^{(0)}$ is a good state with first-order energy correction e_i by the first-order converse. Since A and the coefficient vectors are orthonormal,

$$\langle \chi_i^{(0)} \mid \chi_j^{(0)} \rangle = \sum_1^d \left(s \mapsto c(i,s)^* \cdot c(j,s) \right) = \delta_{i,j}.$$

Thus the d states form an orthonormal basis of the d-dimensional space V_{E_0}, hence a good basis. The degenerate first-order equation applied in this good basis shows that $\mathrm{pertmat}(B)$ has diagonal entries e_i □