Stationary State Perturbation Theory

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Consider the perturbed Hamiltonian
$$\widehat{H} = \widehat{H}_0 + \lambda \widehat{H}_1.$$
$\widehat{H}_0$ is the unperturbed Hamiltonian whose (complete and orthonormal) eigenstates $|n^{(0)}\rangle$ and eigenvalues $E_n^{(0)}$ are known, and $\widehat{H}_1$ is a weak perturbation. λ is a perturbative parameter which *slowly* turns the perturbation on, with values from 0 ($\widehat{H} = \widehat{H}_0$) to 1 ($\widehat{H} = \widehat{H}_0 + \widehat{H}_1$). Note: sometimes, λ can be "built into" the perturbing Hamiltonian.

1 NON-DEGENERATE CASE

- ***Known***: the EVP of unperturbed Hamiltonian,
$$\widehat{H}_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle \tag{1}$$
Note: the weakness of $\widehat{H}_1$ is such that $|\lambda \langle k^{(0)}|\widehat{H}_1|n^{(0)}\rangle| \ll |E_n^{(0)} - E_k^{(0)}|$.

- ***Goal***: the *perturbed* eigenkets and eigenvalues
$$\widehat{H}|\psi_n\rangle = E_n|\psi_n\rangle \tag{2}$$
Note that, as the perturbation is turned off ($\lambda \to 0$), the EVP is reduced to that of the unperturbed system i.e. $|\psi_n\rangle \to |n^{(0)}\rangle$ and $E_n \to E_n^{(0)}$.

- **Seek**:
$$|\psi_n\rangle \stackrel{!}{=} |n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + ... = \sum_{p=0}^{\infty} \lambda^p |n^{(p)}\rangle \tag{3}$$
$$E_n \stackrel{!}{=} E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ... = \sum_{p=0}^{\infty} \lambda^p E_n^{(p)} \tag{4}$$

Note: the perturbed state $|\psi_n\rangle$ cannot be rigorously normalized, since it is an infinite series. An approximate normalization condition ($\langle\psi_n|\psi_n\rangle \overset{!}{\approx} 1$) can be imposed up to the desired correction order. For example, if the 1st-order correction is sufficient, terms $\mathcal{O}(\lambda^2)$ and higher are neglected; for the 2nd-order, terms $\mathcal{O}(\lambda^3)$ and higher are neglected a.s.o.

The solutions are found by expressing $\widehat{H}|\psi_n\rangle = E_n|\psi_n\rangle$ in powers of λ using Eqs. 3 and 4 i.e.

$$\begin{aligned}\widehat{H}|\psi_n\rangle &= (\widehat{H}_0 + \lambda\widehat{H}_1)\sum_{p=0}^{\infty}\lambda^p|n^{(p)}\rangle \\ &\overset{!}{=} \sum_{q=0}^{\infty}\lambda^q E_n^{(q)}\sum_{r=0}^{\infty}\lambda^r|n^{(r)}\rangle = \sum_{q=0}^{\infty}\sum_{r=0}^{\infty}\lambda^{q+r}E_n^{(q)}|n^{(r)}\rangle \end{aligned} \tag{5}$$

Identify the coefficients of the different powers of λ on the LHS and RHS:

$$\begin{aligned}
\lambda^0 : &\quad \widehat{H}_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle \\
\lambda^1 : &\quad \widehat{H}_0|n^{(1)}\rangle + \widehat{H}_1|n^{(0)}\rangle = E_n^{(0)}|n^{(1)}\rangle + E_n^{(1)}|n^{(0)}\rangle \\
\lambda^2 : &\quad \widehat{H}_0|n^{(2)}\rangle + \widehat{H}_1|n^{(1)}\rangle = E_n^{(0)}|n^{(2)}\rangle + E_n^{(1)}|n^{(1)}\rangle + E_n^{(2)}|n^{(0)}\rangle \\
\ldots & \\
\lambda^j : &\quad \widehat{H}_0|n^{(j)}\rangle + \widehat{H}_1|n^{(j-1)}\rangle = \sum_{p=0}^{j}E_n^{(p)}|n^{(j-p)}\rangle.
\end{aligned} \tag{6}$$

The corrections to the energy eigenvalues are obtained by projecting the EVP (Equation 5) onto the unperturbed state $|n^{(0)}\rangle$ and using Eqs. 6 to identify the powers of λ:

$$\begin{aligned}\langle n^{(0)}|\widehat{H}|\psi_n\rangle &= \sum_{p=0}^{\infty}\Big(\lambda^p\langle n^{(0)}|\widehat{H}_0|n^{(p)}\rangle + \lambda^{p+1}\langle n^{(0)}|\widehat{H}_1|n^{(p)}\rangle\Big) \\ &= \sum_{q=0}^{\infty}\sum_{r=0}^{\infty}\lambda^{q+r}E_n^{(q)}\,\langle n^{(0)}|n^{(r)}\rangle. \end{aligned} \tag{7}$$

The first-order corrections

For the energy correction, focus on the λ^1–terms on either side of Eq. 7:

$$\begin{aligned}\langle n^{(0)}|\widehat{H}_0|n^{(1)}\rangle + \langle n^{(0)}|\widehat{H}_1|n^{(0)}\rangle &= E_n^{(0)}\langle n^{(0)}|n^{(1)}\rangle + E_n^{(1)}\underbrace{\langle n^{(0)}|n^{(0)}\rangle}_{1} \\ \cancel{E_n^{(0)}\langle n^{(0)}|n^{(1)}\rangle} + \langle n^{(0)}|\widehat{H}_1|n^{(0)}\rangle &= \cancel{E_n^{(0)}\langle n^{(0)}|n^{(1)}\rangle} + E_n^{(1)}, \end{aligned} \tag{8}$$

which leads to

$$E_n^{(1)} = \langle n^{(0)}|\widehat{H}_1|n^{(0)}\rangle \tag{9}$$

Eq 9 shows that the 1-st order correction to the n-th energy eigenvalue is essentially the diagonal element of the peturbation Hamiltonian, in the basis formed by the unperturbed states ("unperturbed basis"), namely $\{|n^{(0)}\rangle\}$. Thus, to first order, the perturbed n-th energy level is

$$\boxed{E_n = E_n^{(0)} + \lambda\,\langle n^{(0)}|\widehat{H}_1|n^{(0)}\rangle + \mathcal{O}(\lambda^2).}$$

To obtain the 1-st order correction to the eigenstate, $|n^{(1)}\rangle$, start by expressing it in the unperturbed basis:

$$\begin{aligned} |n^{(1)}\rangle &= \sum_k |k^{(0)}\rangle\langle k^{(0)}|n^{(1)}\rangle \\ &= |n^{(0)}\rangle\,\underbrace{\langle n^{(0)}|n^{(1)}\rangle}_{?} + \sum_{k\neq n} |k^{(0)}\rangle\,\underbrace{\langle k^{(0)}|n^{(1)}\rangle}_{?} \end{aligned} \tag{10}$$

At this point, we have to evaluate $\langle n^{(0)}|n^{(1)}\rangle$ and $\langle k^{(0)}|n^{(1)}\rangle$ to first order in λ. For $\langle n^{(0)}|n^{(1)}\rangle$, we impose that the perturbed state $|\psi_n\rangle$ be normalized to unity i.e.

$$\begin{aligned} 1 \overset{!}{=} \langle\psi_n|\psi_n\rangle &= \sum_{p=0}^{\infty} \lambda^p \langle n^{(p)}| \sum_{r=0}^{\infty} \lambda^r |n^{(r)}\rangle = \sum_{p=0}^{\infty}\sum_{r=0}^{\infty} \lambda^{p+r}\langle n^{(p)}|n^{(r)}\rangle \\ &= \underbrace{\langle n^{(0)}|n^{(0)}\rangle}_{1} + \lambda\left(\langle n^{(0)}|n^{(1)}\rangle + \langle n^{(1)}|n^{(0)}\rangle\right) + \mathcal{O}(\lambda^2) \end{aligned} \tag{11}$$

The term in parentheses in Eq. 11 can thus be set to zero; furthermore, since it is the sum of $\langle n^{(0)}|n^{(1)}\rangle$ and its complex conjugate, $\langle n^{(0)}|n^{(1)}\rangle \overset{!}{\approx} 0$. For $\langle k^{(0)}|n^{(1)}\rangle$, project the λ^1–term of Eqs. 6 onto the unperturbed state $|k^{(0)}\rangle$:

$$\langle k^{(0)}|\widehat{H}_0|n^{(1)}\rangle + \langle k^{(0)}|\widehat{H}_1|n^{(0)}\rangle = E_n^{(0)}\langle k^{(0)}|n^{(1)}\rangle + E_n^{(1)}\,\underbrace{\langle k^{(0)}|n^{(0)}\rangle}_{\delta_{kn}}$$

Using the EVP for $\widehat{H}_0$ and Eq. 9, one obtains

$$E_k^0\langle k^{(0)}|n^{(1)}\rangle + \langle k^{(0)}|\widehat{H}_1|n^{(0)}\rangle = E_n^{(0)}\langle k^{(0)}|n^{(1)}\rangle + \langle n^{(0)}|\widehat{H}_1|n^{(0)}\rangle\delta_{kn}$$

$$\left(E_n^0 - E_k^0\right)\langle k^{(0)}|n^{(1)}\rangle = \langle k^{(0)}|\widehat{H}_1|n^{(0)}\rangle - \langle n^{(0)}|\widehat{H}_1|n^{(0)}\rangle\,\delta_{kn} \tag{12}$$

If $k = n$, Eq. 12 is trivial; for $k \neq n$, it becomes

$$\langle k^{(0)}|n^{(1)}\rangle = \frac{\langle k^{(0)}|\widehat{H}_1|n^{(0)}\rangle}{E_n^0 - E_k^0}. \tag{13}$$

Hence, to first order of λ, the n-th perturbed eigenstate is

$$\boxed{|\psi_n\rangle = |n^{(0)}\rangle + \lambda \sum_{k\neq n} |k^{(0)}\rangle \frac{\langle k^{(0)}|\widehat{H}_1|n^{(0)}\rangle}{E_n^0 - E_k^0} + \mathcal{O}(\lambda^2),} \tag{14}$$

where the sum contains the off-diagonal matrix elements of the perturbation Hamiltonian, $(H_1)^0_{kn} \equiv \langle k^{(0)}|\widehat{H}_1|n^{(0)}\rangle$, in the unperturbed basis.

The second-order correction to the energy

For the energy correction, consider the λ^2–terms on both sides of Eq. 7:

$$\begin{aligned}
\langle n^{(0)}|\widehat{H}_0|n^{(2)}\rangle + \langle n^{(0)}|\widehat{H}_1|n^{(1)}\rangle &= E_n^{(0)}\langle n^{(0)}|n^{(2)}\rangle + E_n^{(1)}\langle n^{(0)}|n^{(1)}\rangle + E_n^{(2)} \underbrace{\langle n^{(0)}|n^{(0)}\rangle}_{1} \\
\cancel{E_n^{(0)}\langle n^{(0)}|n^{(2)}\rangle} + \langle n^{(0)}|\widehat{H}_1|n^{(1)}\rangle &= \cancel{E_n^{(0)}\langle n^{(0)}|n^{(2)}\rangle} + E_n^{(2)},
\end{aligned} \tag{15}$$

which leads to

$$\begin{aligned}
E_n^{(2)} &= \langle n^{(0)}|\widehat{H}_1|n^{(1)}\rangle \\
&= \langle n^{(0)}|\widehat{H}_1 \mathbb{1}^{(0)}|n^{(1)}\rangle = \sum_{k=0}^{\infty} \langle n^{(0)}|\widehat{H}_1|k^{(0)}\rangle\langle k^{(0)}|n^{(1)}\rangle \\
&= \langle n^{(0)}|\widehat{H}_1|n^{(0)}\rangle \underbrace{\langle n^{(0)}|n^{(1)}\rangle}_{\overset{!}{\approx} 0} + \sum_{k\neq n} \langle n^{(0)}|\widehat{H}_1|k^{(0)}\rangle \underbrace{\langle k^{(0)}|n^{(1)}\rangle}_{\text{use Eq. 13}} \\
&\approx \sum_{k\neq n} \langle n^{(0)}|\widehat{H}_1|k^{(0)}\rangle \frac{\langle k^{(0)}|\widehat{H}_1|n^{(0)}\rangle}{E_n^0 - E_k^0}.
\end{aligned}$$

Hence

$$E_n^{(2)} = \sum_{k\neq n} \frac{|\langle k^{(0)}|\widehat{H}_1|n^{(0)}\rangle|^2}{E_n^0 - E_k^0}. \tag{16}$$

The perturbed n-th energy level is thus, to second order,

$$\boxed{E_n = E_n^{(0)} + \lambda\, \langle n^{(0)}|\widehat{H}_1|n^{(0)}\rangle + \lambda^2 \sum_{k\neq n} \frac{|\langle k^{(0)}|\widehat{H}_1|n^{(0)}\rangle|^2}{E_n^0 - E_k^0} + \mathcal{O}(\lambda^3).}$$

2 DEGENERATE CASE

- $\widehat{H}_0$ is the unperturbed operator, whose eigenvalues are degenerate (see below).
- $\widehat{H}_1$ is a small perturbation.

As usual, we use the bookkeeping parameter $0 \leq \lambda \leq 1$, such that $\widehat{H} = \widehat{H}_0 + \lambda \widehat{H}_1$. In other words, as $\lambda = 0 \to 1$, $\widehat{H}_0 \to \widehat{H}_0 + \widehat{H}_1$

- ***Known***: $\widehat{H}_0 |n_\alpha^{(0)}\rangle = E_n^{(0)} |n_\alpha^{(0)}\rangle$ ($\alpha = 1...N$, $n = 1, 2, ...$)

  The α subscript denotes the degeneracy of the n^{th} unperturbed state. We assume the n^{th} level is N–fold degenerate i.e. there are N states with energy $E_n^{(0)}$.

- ***Goal***: $\widehat{H} |\Psi_{n_\alpha}\rangle \stackrel{!}{=} E_n |\Psi_{n_\alpha}\rangle$, with $\langle \Psi_{n_\alpha} | \Psi_{n_\alpha} \rangle \stackrel{!}{\approx} 1$, to the desired perturbation order ($\alpha = 1...N$, $n = 1, 2, ...$).

- **Seek** the appropriate linear combination of the unperturbed ($j = 0$) degenerate ($\alpha = 1...N$) states and perturbed ($j \geq 1$) non-degenerate states:

$$|\Psi_{n_\alpha}\rangle \stackrel{!}{=} \sum_{\beta=1}^{N} c_{\alpha\beta} |n_{\alpha\beta}^{(0)}\rangle + \sum_{j=1}^{\infty} \lambda^j |n_\alpha^{(j)}\rangle \tag{17}$$

$$E_n \stackrel{!}{=} E_n^{(0)} + \sum_{j=1}^{\infty} \lambda^j E_n^{(j)} \tag{18}$$

  In Eq. 17 above, $\sum_{\beta=1}^{N} c_{\alpha\beta} |n_{\alpha\beta}^{(0)}\rangle \equiv |n_\alpha^{(0)}\rangle$ is the unique linear combination that diagonalizes $\widehat{H}$ in the subspace formed by the degenerate eigenstates of $\widehat{H}_0$.

Notation *The superscripts in parentheses (e.g. $n^{(j)}$, $E_n^{(j)}$) denote the* order *of the perturbation; superscripts without parentheses (e.g. λ^j) denote exponents. Additionally, Greek subscripts represent the degenerate states ($\alpha, \beta = 1...N$)*

The needed EVP for the perturbed Hamiltonian can be written as

$$(\widehat{H}_0 + \lambda \widehat{H}_1) \left(\sum_{\beta=1}^{N} c_{\alpha\beta} |n_{\alpha\beta}^{(0)}\rangle + \sum_{j=1}^{\infty} \lambda^j |n_\alpha^{(j)}\rangle \right)$$

$$\stackrel{!}{=} \left(E_n^{(0)} + \sum_{j=1}^{\infty} \lambda^j E_n^{(j)} \right) \left(\sum_{\beta=1}^{N} c_{\alpha\beta} |n_{\alpha\beta}^{(0)}\rangle + \sum_{j=1}^{\infty} \lambda^j |n_\alpha^{(j)}\rangle \right) \tag{19}$$

Expand product and identify coefficients of λ^j $(j = 1, 2, ...)$:

$\lambda^0: \quad \widehat{H}_0 |n_\alpha^{(0)}\rangle = E_n^{(0)} |n_\alpha^{(0)}\rangle$

$\lambda^1: \quad \widehat{H}_0 |n_\alpha^{(1)}\rangle + \widehat{H}_1 \sum_{\beta=1}^{N} c_{\alpha\beta} |n_{\alpha\beta}^{(0)}\rangle = E_n^{(0)} |n_\alpha^{(1)}\rangle + E_n^{(1)} \sum_{\beta=1}^{N} c_{\alpha\beta} |n_{\alpha\beta}^{(0)}\rangle$

$\lambda^2: \quad \widehat{H}_0 |n_\alpha^{(2)}\rangle + \widehat{H}_1 |n_\alpha^{(1)}\rangle = E_n^{(0)} |n_\alpha^{(2)}\rangle + E_n^{(1)} |n_\alpha^{(1)}\rangle + E_n^{(2)} \sum_{\beta=1}^{N} c_{\alpha\beta} |n_{\alpha\beta}^{(0)}\rangle \; ...$

$\lambda^j: \quad \widehat{H}_0 |n_\alpha^{(j)}\rangle + \widehat{H}_1 |n_\alpha^{(j-1)}\rangle = \sum_{l=0}^{j-1} E_n^{(l)} |n_\alpha^{(j-l)}\rangle + E_n^{(j)} \sum_{\beta=1}^{N} c_{\alpha\beta} |n_{\alpha\beta}^{(0)}\rangle.$

(Note: for $j = 1$, the zeroth-order "perturbation" is actually $\sum_{\beta=1}^{N} c_{\alpha\beta} |n_{\alpha\beta}^{(0)}\rangle$.)

Now project the λ^j term on the $\langle n_\gamma^0|$ degenerate state, using $\langle n_\gamma^{(0)} | n_\alpha^{(0)}\rangle = \delta_{\gamma\alpha}$. After some algebra:

$$\langle n_\gamma^{(0)} | \widehat{H}_0 | n_\alpha^{(j)}\rangle + \langle n_\gamma^{(0)} | \widehat{H}_1 | n_\alpha^{(j-1)}\rangle = \sum_{l=1}^{j-1} E_n^{(l)} \langle n_\gamma^{(0)} | n_\alpha^{(j-l)}\rangle + E_n^{(j)} \; c_{\alpha\gamma} \tag{20}$$

The first-order energy correction $E_n^{(1)}$ is obtained from Eq. 20 as follows:

$$\langle n_\gamma^{(0)} | \widehat{H}_1 \sum_{\beta=1}^{N} c_{\alpha\beta} | n_{\alpha\beta}^{(0)}\rangle = E_n^{(1)} \; c_{\alpha\gamma}$$

$$\sum_{\beta=1}^{N} c_{\alpha\beta} \langle n_\gamma^{(0)} | \widehat{H}_1 | n_{\alpha\beta}^{(0)}\rangle = E_n^{(1)} \; \sum_{\beta=1}^{N} c_{\alpha\beta} \; \delta_{\beta\gamma}$$

$$\sum_{\beta=1}^{N} c_{\alpha\beta} \left(\langle n_\gamma^{(0)} | \widehat{H}_1 | n_{\alpha\beta}^{(0)}\rangle - E_n^{(1)} \delta_{\beta\gamma} \right) = 0$$

$$\rightarrow \quad \boxed{(H_1)_{\gamma\beta} \equiv \langle n_\gamma^{(0)} | \widehat{H}_1 | n_\beta^{(0)}\rangle = E_n^{(1)} \delta_{\gamma\beta}} \qquad (\gamma, \beta = 1...N) \tag{21}$$

Equation 21 means that the first-order energy corrections are obtained by diagonalizing the perturbation $\widehat{H}_1$ in the degenerate subspace of the unperturbed Hamiltonian $\widehat{H}_0$.