Brillouin-Wigner Perturbation Theory

Brillouin-Wigner (BW) perturbation theory is less widely used than the Rayleigh-Schrödinger (RS) version. At first order in the perturbation, the two theories are equivalent. However, BW perturbation theory extends more easily to higher orders, and avoids the need for separate treatment of non-degenerate and degenerate levels.

- Assume that we know the stationary states of the unperturbed Hamiltonian H_0, namely the kets $|n\rangle$ satisfying $H_0|n\rangle = \varepsilon_n|n\rangle$. For each unperturbed state, we can define a projection operator

  $$Q_n = I - |n\rangle\langle n| = \sum_{m\neq n} |m\rangle\langle m|.$$

  Using the spectral representation $H_0 = \sum_n \varepsilon_n|n\rangle\langle n|$, one can see that $[H_0, Q_n] = 0$.

- Let us write the perturbed eigenproblem in the form

  $$(E_n - H_0)|\psi_n\rangle = H_1|\psi_n\rangle. \tag{1}$$

  Acting with Q_n from the left, and taking advantage of $[H_0, Q_n] = 0$,

  $$Q_n|\psi_n\rangle = R_n H_1|\psi_n\rangle,$$

  where

  $$R_n = (E_n - H_0)^{-1}Q_n = Q_n(E_n - H_0)^{-1},$$

  which has a spectral representation

  $$R_n = \sum_{m\neq n} \frac{|m\rangle\langle m|}{E_n - \varepsilon_m}.$$

  Note that R_n is not a projection operator because $R_n^2 \neq R_n$.

- Adopting the usual convention $\langle n|\psi_n\rangle = 1$, we can write

  $$|\psi_n\rangle = |n\rangle + Q_n|\psi_n\rangle = |n\rangle + R_n H_1|\psi_n\rangle. \tag{2}$$

  Assuming that H_1 is small, this equation can be solved iteratively in powers of H_1. The wave function correct through order j, $|\psi_n^{(j)}\rangle$, can be obtained from Eq. (2) by inserting $|\psi_n^{(j-1)}\rangle$ on the right-hand side:

  $$\begin{aligned}
  |\psi_n^{(0)}\rangle &= |n\rangle, \\
  |\psi_n^{(1)}\rangle &= |n\rangle + R_n H_1|n\rangle, \\
  |\psi_n^{(2)}\rangle &= |n\rangle + R_n H_1|n\rangle + (R_n H_1)^2|n\rangle, \\
  &\text{etc}
  \end{aligned}$$

In other words,

$$|\psi_n\rangle = \sum_{j=0}^{\infty}(R_n H_1)^j|n\rangle \equiv (1 - R_n H_1)^{-1}|n\rangle, \tag{3}$$

where the first equality serves to define $(1 - R_n H_1)^{-1}$.

Substituting the spectral representation of R_n into Eq. (3), we obtain

$$\begin{aligned} |\psi_n\rangle &= |n\rangle + \sum_{m\neq n}|m\rangle\frac{\langle m|H_1|n\rangle}{E_n - \varepsilon_m} + \sum_{m\neq n}\sum_{l\neq n}|m\rangle\frac{\langle m|H_1|l\rangle\langle l|H_1|n\rangle}{(E_n-\varepsilon_m)(E_n-\varepsilon_l)} \\ &\quad + \sum_{m\neq n}\sum_{l\neq n}\sum_{k\neq n}|m\rangle\frac{\langle m|H_1|l\rangle\langle l|H_1|k\rangle\langle k|H_1|n\rangle}{(E_n-\varepsilon_m)(E_n-\varepsilon_l)(E_n-\varepsilon_k)} + \ldots \end{aligned} \tag{4}$$

- We can obtain E_n by applying $\langle n|$ to Eq. (1):

  $$(E_n - \varepsilon_n)\langle n|\psi_n\rangle = \langle n|H_1|\psi_n\rangle.$$

  Since $\langle n|\psi_n\rangle = 1$,

  $$E_n = \varepsilon_n + \langle n|H_1|\psi_n\rangle, \tag{5}$$

  or, making use of Eq. (4),

  $$\begin{aligned} E_n &= \varepsilon_n + \langle n|H_1|n\rangle + \sum_{m\neq n}\frac{\langle n|H_1|m\rangle\langle m|H_1|n\rangle}{E_n-\varepsilon_m} \\ &\quad + \sum_{m\neq n}\sum_{l\neq n}\frac{\langle n|H_1|m\rangle\langle m|H_1|l\rangle\langle l|H_1|n\rangle}{(E_n-\varepsilon_m)(E_n-\varepsilon_l)} \\ &\quad + \sum_{m\neq n}\sum_{l\neq n}\sum_{k\neq n}\frac{\langle n|H_1|m\rangle\langle m|H_1|l\rangle\langle l|H_1|k\rangle\langle k|H_1|n\rangle}{(E_n-\varepsilon_m)(E_n-\varepsilon_l)(E_n-\varepsilon_k)} + \ldots \end{aligned} \tag{6}$$

- The BW formulation has the advantages that the expressions given in Eqs (4) and (6) are much simpler than those produced by RS perturbation theory, and there is no need to devise a special treatment of degeneracies $\varepsilon_m = \varepsilon_n$.

  A disadvantage of the BW approach is that the perturbed energy appears on the right-hand side of Eq. (6). This is therefore really a polynomial equation for E_n, which can be nontrivial to solve.

  One has to weigh up the pros and cons of the BW and RS methods in deciding which one to use for a particular problem.