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 nondegenerate and degenerate levels.

- Suppose that the unperturbed Hamiltonian H_0 has discrete eigenvalues ε_n and orthonormal eigenkets $|n\rangle$. For each unperturbed eigenstate, we can define a pair of complementary projection operators,

$$P_n = |n\rangle\langle n| \quad \text{and} \quad Q_n = I - P_n = \sum_{m \neq n} P_m. \tag{1}$$

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

- We write the perturbed eigenproblem for $H = H_0 + \lambda H_1$ (where $0 \leq \lambda \leq 1$) in the form

$$(E_n - H_0)|\psi_n\rangle = \lambda H_1 |\psi_n\rangle. \tag{2}$$

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

$$Q_n|\psi_n\rangle = \lambda R_n H_1 |\psi_n\rangle, \tag{3}$$

  where

$$R_n = (E_n - H_0)^{-1} Q_n = Q_n (E_n - H_0)^{-1}, \tag{4}$$

  which has a spectral representation

$$R_n = \sum_{m \neq n} \frac{P_m}{E_n - \varepsilon_m}.$$

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

- Using Eqs. (1) and (3), and adopting the usual convention $\langle n|\psi_n\rangle = 1$, we can write

$$|\psi_n\rangle = (P_n + Q_n)|\psi_n\rangle = |n\rangle + \lambda R_n H_1 |\psi_n\rangle. \tag{5}$$

  This equation can be solved iteratively in powers of λ. Inserting $|\psi_n\rangle$ correct through order λ^{j-1} on the right-hand side of Eq. (5) yields the order-λ^j result on the left:

$$\begin{aligned}
&\text{To order } \lambda^0: \quad && |\psi_n\rangle = |n\rangle \\
&\text{To order } \lambda^1: \quad && |\psi_n\rangle = |n\rangle + \lambda R_n H_1 |n\rangle, \\
&\text{To order } \lambda^2: \quad && |\psi_n\rangle = |n\rangle + \lambda R_n H_1 |n\rangle + (\lambda R_n H_1)^2 |n\rangle, \\
& && \ldots
\end{aligned}$$

  Thus, the full solution is

$$|\psi_n\rangle = \sum_{j=0}^{\infty} (\lambda R_n H_1)^j |n\rangle \equiv (1 - \lambda R_n H_1)^{-1} |n\rangle. \tag{6}$$

Substituting the spectral representation of R_n into Eq. (6), we obtain

$$\begin{aligned}|\psi_n\rangle &= |n\rangle + \lambda \sum_{m_1 \neq n} |m_1\rangle \frac{\langle m_1|H_1|n\rangle}{E_n - \varepsilon_{m_1}} + \lambda^2 \sum_{m_1 \neq n} \sum_{m_2 \neq n} |m_1\rangle \frac{\langle m_1|H_1|m_2\rangle\langle m_2|H_1|n\rangle}{(E_n - \varepsilon_{m_1})(E_n - \varepsilon_{m_2})} + \ldots \\ &\quad + \lambda^j \sum_{m_1 \neq n} \sum_{m_2 \neq n} \sum_{m_3 \neq n} \cdots \sum_{m_j \neq n} |m_1\rangle \frac{\langle m_1|H_1|m_2\rangle\langle m_2|H_1|m_3\rangle \cdots \langle m_j|H_1|n\rangle}{(E_n - \varepsilon_{m_1})(E_n - \varepsilon_{m_2}) \cdots (E_n - \varepsilon_{m_j})} + \ldots \end{aligned} \tag{7}$$

- We can obtain E_n by applying $\langle n|$ to Eq. (2), and recalling that $\langle n|\psi_n\rangle = 1$:

$$E_n = \varepsilon_n + \lambda \langle n|H_1|\psi_n\rangle, \tag{8}$$

or, making use of Eq. (7),

$$\begin{aligned}E_n &= \varepsilon_n + \lambda\langle n|H_1|n\rangle + \lambda^2 \sum_{m_1 \neq n} \frac{\langle n|H_1|m_1\rangle\langle m_1|H_1|n\rangle}{E_n - \varepsilon_{m_1}} + \ldots \\ &\quad + \lambda^{j+1} \sum_{m_1 \neq n} \sum_{m_2 \neq n} \cdots \sum_{m_j \neq n} \frac{\langle n|H_1|m_1\rangle\langle m_1|H_1|m_2\rangle \cdots \langle m_j|H_1|n\rangle}{(E_n - \varepsilon_{m_1})(E_n - \varepsilon_{m_2}) \cdots (E_n - \varepsilon_{m_j})} + \ldots \end{aligned} \tag{9}$$

- The BW formulation has the advantages that (i) the terms of order λ^2 and higher in Eq. (7), and the terms of order λ^3 and higher in Eq. (9) are much simpler than their counterparts in RS perturbation theory, and (ii) there is no need for special versions of these equations to handle degeneracies among unperturbed states.

- A disadvantage of the BW approach is that the perturbed energy E_n appears on both sides of Eq. (9). One way around this is to substitute a trial value of E_n on the right-hand side, then iterate Eq. (9) to convergence. Alternatively, one can substitute lower-order approximations for E_n on the right side of Eq. (9). For example, if the unperturbed problem has no degeneracy, so that $|\varepsilon_m - \varepsilon_n| = O(\lambda^0)$ for $m \neq n$, then

$$\begin{aligned}E_n &= \varepsilon_n + \lambda\langle n|H_1|n\rangle + \lambda^2 \sum_{m_1 \neq n} \frac{\langle n|H_1|m_1\rangle\langle m_1|H_1|n\rangle}{\varepsilon_n + \lambda\langle n|H_1|n\rangle - \varepsilon_{m_1}} \\ &\quad + \lambda^3 \sum_{m_1 \neq n} \sum_{m_2 \neq n} \frac{\langle n|H_1|m_1\rangle\langle m_1|H_1|m_2\rangle}{(\varepsilon_n - \varepsilon_{m_1})(\varepsilon_n - \varepsilon_{m_2})} + O\left(\lambda^4\right). \end{aligned} \tag{10}$$

- A condition for convergence of the BW perturbation series is $\lambda|\langle m|H_1|m'\rangle| \ll |E_n - \varepsilon_m|$ for every pair of states $|m \neq n\rangle$ and $|m'\rangle$ that can be reached from $|n\rangle$ under repeated application of H_1. (State $|m\rangle$ can be reached from $|n\rangle$ under H_1 if there is any nonvanishing product of matrix elements $\langle m|H_1|m_1\rangle\langle m_1|H_1|m_2\rangle \cdots \langle m_{j-1}|H_1|m_j\rangle\langle m_j|H_1|n\rangle$.)

  This convergence condition is clearly violated if the exact eigenvalue E_n happens to equal any unperturbed eigenvalue ε_m, where $m \neq n$ and the state $|m\rangle$ can be reached from $|n\rangle$ under repeated application of H_1. In such cases, the operator R_n defined in Eq. (4) does not exist. One can still get an approximate eigenenergy by solving Eq. (9) to order λ^j, but this value will not converge to E_n with increasing j.

  To avoid this, and other problems arising from degeneracy (or near-degeneracy) of the unperturbed eigenvalues, it is often necessary to diagonalize H_1 in each nearly-degenerate subspace before applying BW theory.

- 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.