Degenerate Rayleigh-Schrödinger Perturbation Theory

- Assume that we know the stationary states of the unperturbed Hamiltonian H_0, namely the kets $|n, r\rangle$ satisfying $H_0|n, r\rangle = \varepsilon_n|n, r\rangle$. The integer index r ($1 \le r \le g_n$) is used to distinguish among the g_n eigenstates of energy ε_n. (For simplicity, we assume that the vector space is has a finite or countably infinite dimension. The extension to continuous vector spaces is straightforward.)

- We seek stationary solutions $|\psi_{n,r}\rangle$ of the perturbed problem

$$(H_0 + \lambda H_1)|\psi_{n,r}\rangle = E_{n,r}|\psi_{n,r}\rangle \tag{1}$$

in the form of power-series expansions

$$|\psi_{n,r}\rangle = \sum_{j=0}^{\infty} \lambda^j |\psi_{n,r}^{(j)}\rangle, \qquad E_{n,r} = \sum_{j=0}^{\infty} \lambda^j E_{n,r}^{(j)}. \tag{2}$$

Let us insert Eqs. (2) into Eq. (1), and collect terms having the same power of λ.

- At order λ^0 we have $(H_0 - E_{n,r}^{(0)})|\psi_{n,r}^{(0)}\rangle = 0$, which is satisfied by any linear combination of the unperturbed eigenkets of energy ε_n, i.e.,

$$|\psi_{n,r}^{(0)}\rangle = \sum_{t=1}^{g_n} (c_{n,r})_t |n, t\rangle, \qquad \text{with} \qquad E_{n,r}^{(0)} = \varepsilon_n.$$

Orthonormality requires that $\langle \psi_{n,r}^{(0} | \psi_{n,s}^{(0)}\rangle = \sum_{t=1}^{g_n} (c_{n,r})_t^* (c_{n,s})_t = \delta_{r,s}$.

- At order λ^1 we find $(H_0 - E_{n,r}^{(0)})|\psi_{n,r}^{(1)}\rangle = (E_{n,r}^{(1)} - H_1)|\psi_{n,r}^{(0)}\rangle$. Acting from the left with $\langle m, s|$, we obtain

$$(\varepsilon_m - \varepsilon_n)\langle m, s|\psi_{n,r}^{(1)}\rangle = \delta_{m,n} E_{n,r}^{(1)} (c_{n,r})_s - \sum_{t=1}^{g_n} \langle m, s|H_1|n, t\rangle (c_{n,r})_t. \tag{3}$$

- For $m = n$, Eq. (3) yields

$$\sum_{t=1}^{g_n} \langle n, s|H_1|n, t\rangle (c_{n,r})_t = E_{n,r}^{(1)} (c_{n,r})_s,$$

which is the matrix eigenequation for H_1 in the g_n-dimensional subspace spanned by the unperturbed states of energy ε_n. It is perfectly consistent with the λ^0 result to choose the $|\psi_{n,r}^{(0)}\rangle$'s to be the eigenkets of this problem. We will assume henceforth that this is the case, so that

$$\langle \psi_{n,s}^{(0)}|H_0 + \lambda H_1|\psi_{n,r}^{(0)}\rangle = (\varepsilon_n + \lambda E_{n,r}^{(1)})\delta_{s,r}, \tag{4}$$

where the first-order correction to the unperturbed energy is

$$E_{n,r}^{(1)} = \langle \psi_{n,r}^{(0)}|H_1|\psi_{n,r}^{(0)}\rangle. \tag{5}$$

Note that we *cannot* assume that $|\psi^{(0)}_{n,r}\rangle$ is an eigenket of H_1 in the full vector space. Equation (4) implies only that

$$H_1|\psi^{(0)}_{n,r}\rangle = E^{(1)}_{n,r}|\psi^{(0)}_{n,r}\rangle + \sum_{m\neq n}\sum_{t=1}^{g_m}|\psi^{(0)}_{m,t}\rangle\langle\psi^{(0)}_{m,t}|H_1|\psi^{(0)}_{n,r}\rangle. \tag{6}$$

- For $m \neq n$, Eq. (3) yields

$$\langle m,s|\psi^{(1)}_{n,r}\rangle = \sum_{t=1}^{g_n}\frac{\langle m,s|H_1|n,t\rangle}{\varepsilon_n-\varepsilon_m}(c_{n,r})_t = \frac{\langle m,s|H_1|\psi^{(0)}_{n,r}\rangle}{\varepsilon_n-\varepsilon_m}.$$

  or

$$\langle\psi^{(0)}_{m,s}|\psi^{(1)}_{n,r}\rangle = \frac{\langle\psi^{(0)}_{m,s}|H_1|\psi^{(0)}_{n,r}\rangle}{\varepsilon_n-\varepsilon_m}, \qquad m\neq n. \tag{7}$$

- If $g_n = 1$, we can drop the second label for each eigenket. Then Eqs. (5) and (7) reduce to the standard results of nondegenerate perturbation theory.

- Conversely, it appears from Eqs. (5) and (7) that the perturbative solution of the degenerate problem to order λ^1 can be obtained from that of a nondegenerate problem by substituting $|n\rangle \to |\psi^{(0)}_{n,r}\rangle$ and $\sum_m \to \sum_m\sum_{t=1}^{g_m}$. However, this conclusion is premature because Eq. (3) does not determine $\langle n,s|\psi^{(1)}_{n,r}\rangle$, or alternatively, $\langle\psi^{(0)}_{n,s}|\psi^{(1)}_{n,r}\rangle$. We will now correct this omission.

- Following a convention from the nondegenerate theory, we enforce $\langle\psi^{(0)}_{n,r}|\psi_{n,r}\rangle = 1$. Thus, $\langle\psi^{(0)}_{n,r}|\psi^{(j)}_{n,r}\rangle = 0$ for all $j > 0$, which includes as a special case

$$\langle\psi^{(0)}_{n,r}|\psi^{(1)}_{n,r}\rangle = 0.$$

- To determine $\langle\psi^{(0)}_{n,s}|\psi^{(1)}_{n,r}\rangle$ for $s \neq r$, it is necessary to proceed to order λ^2 in the expansion of Eq. (1):

$$(H_0 - E^{(0)}_{n,r})|\psi^{(2)}_{n,r}\rangle = (E^{(1)}_{n,r} - H_1)|\psi^{(1)}_{n,r}\rangle + E^{(2)}_{n,r}|\psi^{(0)}_{n,r}\rangle.$$

  Acting from the left with $\langle\psi^{(0)}_{n,s}|$, we eliminate all but the term involving $|\psi^{(1)}_{n,r}\rangle$. Then, using the adjoint of Eq. (6) with s replacing r, we obtain

$$0 = (E^{(1)}_{n,r} - E^{(1)}_{n,s})\langle\psi^{(0)}_{n,s}|\psi^{(1)}_{n,r}\rangle - \sum_{m\neq n}\sum_{t=1}^{g_m}\langle\psi^{(0)}_{n,s}|H_1|\psi^{(0)}_{m,t}\rangle\langle\psi^{(0)}_{m,t}|\psi^{(1)}_{n,r}\rangle,$$

  where the last inner product on the right-hand side can be evaluated using Eq. (7). Provided that $E^{(1)}_{n,r} \neq E^{(1)}_{n,s}$, we can conclude that

$$\langle\psi^{(0)}_{n,s}|\psi^{(1)}_{n,r}\rangle = \sum_{m\neq n}\sum_{t=1}^{g_m}\frac{\langle\psi^{(0)}_{n,s}|H_1|\psi^{(0)}_{m,t}\rangle\langle\psi^{(0)}_{m,t}|H_1|\psi^{(0)}_{n,r}\rangle}{(E^{(1)}_{n,r}-E^{(1)}_{n,s})(\varepsilon_n-\varepsilon_m)}, \qquad s\neq r.$$

- Summary: In cases of degeneracy, it is necessary to work at least to second order in λ to obtain $|\psi_{n,r}\rangle$ correct to first order. [If H_1 does not lift the degeneracy between $|\psi^{(0)}_{n,r}\rangle$ and $|\psi^{(0)}_{n,s}\rangle$ (i.e., $E^{(1)}_{n,r} = E^{(1)}_{n,s}$), then one must work to third order or higher.]