## Degenerate Rayleigh-Schrödinger Perturbation Theory

- Suppose that we know the eigensolution of the unperturbed Hamiltonian $H_0$ in a vector space of finite or countably infinite dimension: a set of discrete eigenvalues $\varepsilon_n$ and their eigenkets $|n,r\rangle$, satisfying $H_0|n,r\rangle = \varepsilon_n|n,r\rangle$. The integer label $r$ ($1 \le r \le g_n$) is used to distinguish among the $g_n$ eigenstates of energy $\varepsilon_n$.

- We seek stationary solutions of the perturbed problem

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

in the form

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

Since different powers of $\lambda$ are linearly independent, the coefficients of each power of $\lambda$ must be the same on the two sides of Eq. (1).

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

$$|\psi_{n,r}^{(0)}\rangle = \sum_{t=1}^{g_n} c_{n,r,t}|n,t\rangle, \qquad \text{with} \qquad E_{n,r}^{(0)} = \varepsilon_n. \tag{3}$$

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 $\lambda^1$ 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

$$(\varepsilon_m - \varepsilon_n)\langle m,s|\psi_{n,r}^{(1)}\rangle = \delta_{m,n}E_{n,r}^{(1)}c_{n,r,s} - \sum_{t=1}^{g_n}\langle m,s|H_1|n,t\rangle c_{n,r,t}. \tag{4}$$

- For $m = n$, Eq. (4) reduces to

$$\sum_{t=1}^{g_n}\langle n,s|H_1|n,t\rangle c_{n,r,t} = E_{n,r}^{(1)}c_{n,r,s}, \tag{5}$$

which is the eigenequation for $H_1$ projected into the subspace $\mathcal{V}_n$ spanned by the unperturbed states of energy $\varepsilon_n$. (Think of $\langle n,s|H_1|n,t\rangle$ as a $g_n \times g_n$ matrix, and $c_{n,r,t}$ as a column vector with rows labeled $t = 1, 2, \ldots, g_n$.)

We simultaneously satisfy Eqs. (3) and (5) by choosing the $|\psi_{n,r}^{(0)}\rangle$'s to be the exact (i.e., nonperturbative) eigenkets of $H = H_0 + \lambda H_1$ projected into $\mathcal{V}_n$. Then

$$\langle\psi_{n,s}^{(0)}|H_0 + \lambda H_1|\psi_{n,r}^{(0)}\rangle = \left(\varepsilon_n + \lambda E_{n,r}^{(1)}\right)\delta_{s,r}, \tag{6}$$

where the first-order energy correction is

$$E_{n,r}^{(1)} = \langle\psi_{n,r}^{(0)}|H_1|\psi_{n,r}^{(0)}\rangle. \tag{7}$$

Note that we *cannot* assume that $|\psi_{n,r}^{(0)}\rangle$ is an eigenket of $H_1$ or $H$ in the full vector space. Equation (6) implies only that

$$H_1|\psi_{n,r}^{(0)}\rangle = E_{n,r}^{(1)}|\psi_{n,r}^{(0)}\rangle + \sum_{m\neq n}\sum_{t=1}^{g_m}|\psi_{m,t}^{(0)}\rangle\langle\psi_{m,t}^{(0)}|H_1|\psi_{n,r}^{(0)}\rangle. \tag{8}$$

- For $m \neq n$, Eq. (4) yields

$$\langle m,s|\psi_{n,r}^{(1)}\rangle = \sum_{t=1}^{g_n} \frac{\langle m,s|H_1|n,t\rangle}{\varepsilon_n - \varepsilon_m} c_{n,r,t} = \frac{\langle m,s|H_1|\psi_{n,r}^{(0)}\rangle}{\varepsilon_n - \varepsilon_m}. \tag{9}$$

or

$$\langle \psi_{m,s}^{(0)}|\psi_{n,r}^{(1)}\rangle = \frac{\langle \psi_{m,s}^{(0)}|H_1|\psi_{n,r}^{(0)}\rangle}{\varepsilon_n - \varepsilon_m}, \qquad m \neq n. \tag{10}$$

- If $g_n = 1$, we can drop the second label for each eigenket. Then Eqs. (7) and (10) reduce to the standard results of nondegenerate Rayleigh-Schrödinger perturbation theory.

- Conversely, it appears from Eqs. (7) and (10) that the perturbative solution of the degenerate problem to order $\lambda^1$ can be obtained from that of a nondegenerate problem by substituting $|n\rangle \to |\psi_{n,r}^{(0)}\rangle$ and $\sum_m \to \sum_m \sum_{t=1}^{g_m}$. However, this conclusion is premature because Eq. (4) does not determine $\langle n,s|\psi_{n,r}^{(1)}\rangle$, or alternatively, $\langle \psi_{n,s}^{(0)}|\psi_{n,r}^{(1)}\rangle$. We will now rectify this omission.

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

$$\langle \psi_{n,r}^{(0)}|\psi_{n,r}^{(1)}\rangle = 0. \tag{11}$$

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

$$(H_0 - E_{n,r}^{(0)})|\psi_{n,r}^{(2)}\rangle = (E_{n,r}^{(1)} - H_1)|\psi_{n,r}^{(1)}\rangle + E_{n,r}^{(2)}|\psi_{n,r}^{(0)}\rangle. \tag{12}$$

Acting from the left with $\langle \psi_{n,s}^{(0)}|$, replacing $\langle \psi_{n,s}^{(0)}|H_1$ using the adjoint of Eq. (8) with $r \to s$, and then applying Eq. (10), we obtain

$$0 = (E_{n,r}^{(1)} - E_{n,s}^{(1)})\langle \psi_{n,s}^{(0)}|\psi_{n,r}^{(1)}\rangle - \sum_{m\neq n}\sum_{t=1}^{g_m} \frac{\langle \psi_{n,s}^{(0)}|H_1|\psi_{m,t}^{(0)}\rangle\langle \psi_{m,t}^{(0)}|H_1|\psi_{n,r}^{(0)}\rangle}{\varepsilon_n - \varepsilon_m} + E_{n,r}^{(2)}\delta_{r,s}. \tag{13}$$

Setting $s = r$ yields the second-order energy correction:

$$E_{n,r}^{(2)} = \sum_{m\neq n}\sum_{t=1}^{g_m} = \frac{\left|\langle \psi_{m,t}^{(0)}|H_1|\psi_{n,r}^{(0)}\rangle\right|^2}{\varepsilon_n - \varepsilon_m}. \tag{14}$$

For $s \neq r$, and provided that $E_{n,r}^{(1)} \neq E_{n,s}^{(1)}$, we can conclude from Eq. (13) that

$$\langle \psi_{n,s}^{(0)}|\psi_{n,r}^{(1)}\rangle = \sum_{m\neq n}\sum_{t=1}^{g_m} \frac{\langle \psi_{n,s}^{(0)}|H_1|\psi_{m,t}^{(0)}\rangle\langle \psi_{m,t}^{(0)}|H_1|\psi_{n,r}^{(0)}\rangle}{(E_{n,r}^{(1)} - E_{n,s}^{(1)})(\varepsilon_n - \varepsilon_m)}, \qquad s \neq r. \tag{15}$$

- If $E_{n,r}^{(1)} = E_{n,s}^{(1)}$ for any $s \neq r$, then one can try to diagonalize $H_1$ exactly in a subspace larger than $\mathcal{V}_n$, e.g., $\mathcal{V}_n \oplus \mathcal{V}_p$, where $\varepsilon_p \neq \varepsilon_n$. Provided that there is no residual degeneracy within this expanded subspace, a modified version of the perturbation theory above can still be used to find $|\psi_{n,r}^{(1)}\rangle$.

- **Summary:** If the unperturbed eigenvalue $\varepsilon_n$ is degenerate, it is necessary to diagonalize $H$ exactly within a subspace of the full problem so as to break the degeneracy and thereby identify a suitable basis for use in perturbation theory. Furthermore, one must work to second order in $\lambda$ to obtain the eigenkets $|\psi_{n,r}\rangle$ correct to first order.