Degenerate Perturbation Theory

Suppose we are dealing with a system where the unperturbed levels are degenerate so that the Schrodinger equation is

$H^0\Phi^0_{\mu n} = E^0_\mu \Phi^0_{\mu n}$ where $\Phi^0_{\mu n}$ is p fold degenerate, $n = 1, 2, \cdots, p$.
If we add the perturbation and go through the analysis as we did for the non-degenerate theory we find the equation determining the first order correction

$\hat{H}^0 \mathbf{\Phi}^{(1)}_{\mu n} + \hat{V}\mathbf{\Phi}^0_{\mu n} = E^{(1)}_{\mu n}\mathbf{\Phi}^0_{\mu n} + E^0_\mu \mathbf{\Phi}^{(1)}_{\mu n}$ and if we then multiply by $\Phi^{0*}_{\mu m}$ and integrate we have

$$\left\langle \mathbf{\Phi}^0_{\mu m} \middle| \hat{H}^0 \middle| \mathbf{\Phi}^{(1)}_{\mu n} \right\rangle + \left\langle \mathbf{\Phi}^0_{\mu m} \middle| \hat{V} \middle| \mathbf{\Phi}^0_{\mu n} \right\rangle = E^{(1)}_{\mu n} \left\langle \mathbf{\Phi}^0_{\mu m} \middle| \mathbf{\Phi}^0_{\mu n} \right\rangle + E^0_\mu \left\langle \mathbf{\Phi}^0_{\mu m} \middle| \mathbf{\Phi}^{(1)}_{\mu n} \right\rangle$$

which simplifies to

$\left\langle \mathbf{\Phi}^0_{\mu m} \middle| \hat{V} \middle| \mathbf{\Phi}^0_{\mu n} \right\rangle = E^{(1)}_{\mu n}\delta_{nm}$ which says that the perturbation does not couple the degenerate states of the μ^{th} level which may or may not be true. This possible contradiction is rooted in the degeneracy of the μ^{th} level and may be removed as follows. Because of the degeneracy the eignfunctions for the μ^{th} level may be written as

$\varphi^0_{\mu k} = \sum_{n=1}^{p} \Phi^0_{\mu n} C_{nk}$ where the coefficients C_{nk} form the elements of a *pxp* matrix $\mathbf{C}$. While the coefficients are arbitrary we will choose $\mathbf{C}$ to be unitary so that the functions $\varphi^0_{\mu k}$ are orthonormal in the degenerate sub-space. If we carried out the perturbation analysis with the $\varphi^0_{\mu k}$ functions we arrive at

$$\left\langle \varphi^0_{\mu m} \middle| \hat{V} \middle| \varphi^0_{\mu n} \right\rangle = \left\langle \sum_{k=1}^{p} \mathbf{\Phi}^0_{\mu k} C_{km} \middle| \hat{V} \middle| \sum_{l=1}^{p} \mathbf{\Phi}^0_{\mu n} C_{nl} \right\rangle = \sum_{k=1}^{p} \sum_{l=1}^{p} C_{km} V^{\mu}_{kn} C_{nl} = E^{(1)}_{\mu n}\delta_{nm}$$

Since $C_{nl} = \mathbf{C}_{nl}$ & $C_{mk} = \left(\mathbf{C}^T\right)_{mk}$, where $\mathbf{C}^T$ is the transpose of $\mathbf{C}$, we may write the above in matrix form $\mathbf{C}^T\mathbf{V}^{\mu}\mathbf{C} = \mathbf{E}_{\mu}^{(1)}$ where $\mathbf{E}_{\mu}^{(1)}$ is a diagonal matrix with the elements $E_{\mu n}^{(1)}\delta_{nm}$. So if we choose the zero order functions so that they diagonalize the matrix of the perturbation in the degenerate subspace we will have no contradiction and can continue as in the nondegenerate case. For example, the first order correction to the wavefunction for the m^{th} state of the μ^{th} level would be

$$\varphi_{\mu m}^{(1)} = \sum_{\nu \neq \mu} \sum_{k=1}^{p_\nu} \frac{\left\langle \varphi_{\mu m}^0 \middle| \hat{V} \middle| \varphi_{\nu k}^0 \right\rangle \varphi_{\nu k}^0}{E_{\mu}^0 - E_{\nu}^0}$$

with the associate first order change in the energy

$$E_{\mu m}^{(1)} = \left\langle \varphi_{\mu m}^0 \middle| \hat{V} \middle| \varphi_{\mu m}^0 \right\rangle$$