PHY202 – Quantum Mechanics

Summary of Topic 12: First Order Time Independent Perturbation Theory

Assume ϕ_n complete set of orthonormal eigenfunctions of Hamiltonian $\hat{H}_0$ for which an exact solution exists:

$$\hat{H}_0\phi_n = E_n^{(0)}\phi_n. \tag{1}$$

The true Hamiltonian of the system $\hat{H}$ differs from $\hat{H}_0$ by a small perturbation $\hat{H}_1$:

$$\hat{H} = \hat{H}_0 + \hat{H}_1, \tag{2}$$

such that

$$(\hat{H}_0 + \hat{H}_1)\psi_n = E_n\psi_n. \tag{3}$$

If this is not solvable exactly then let us write:

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + ... \tag{4}$$

$$\psi_n = N\left(\phi_n + \sum_{k\neq n} c_{nk}\phi_k\right) \tag{5}$$

$$c_{nk} = c_{nk}^{(1)} + c_{nk}^{(2)} + ... \tag{6}$$

Now substitute $\lambda\hat{H}_1$ for $\hat{H}_1$ where λ is a small number (which will cancel later) in powers of which we will expand $\hat{H}$. Then write:

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \tag{7}$$

$$\psi_n = N(\lambda)\left(\phi_n + \sum_{k\neq n} c_{nk}(\lambda)\phi_k\right) \tag{8}$$

$$c_{nk}(\lambda) = \lambda c_{nk}^{(1)} + \lambda^2 c_{nk}^{(2)} + \dots \tag{9}$$

$$\tag{10}$$

Therefore we have:

$$(\hat{H}_0 + \lambda\hat{H}_1)\left(\phi_n + \sum_{k\neq n} c_{nk}(\lambda)\phi_k\right) = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ...)\left(\phi_n + \sum_{k\neq n} c_{nk}(\lambda)\phi_k\right) \tag{11}$$

This must hold for all λ so we now compare coefficients of λ:

$$\lambda^0 \quad : \quad \hat{H}_0\phi_n = E_n^{(0)}\phi_n \tag{12}$$

$$\lambda^1 \quad : \quad \lambda\hat{H}_1\phi_n + \hat{H}_0\lambda\sum_{k\neq n} c_{nk}^{(1)}\phi_k = \lambda E_n^{(1)}\phi_n + \lambda E_n^{(0)}\sum_{k\neq n} c_{nk}^{(1)}\phi_k \tag{13}$$

$$\lambda^2 \quad : \quad \hat{H}_0\sum_{k\neq n}\lambda^2 c_{nk}^{(2)}\phi_k + \lambda\hat{H}_1\sum_{k\neq n}\lambda c_{nk}^{(1)}\phi_k = E_n^{(0)}\sum_{k\neq n}\lambda^2 c_{nk}^{(2)}\phi_k + \lambda E_n^{(1)}\sum_{k\neq n}\lambda c_{nk}^{(1)}\phi_k + \lambda^2 E_n^{(2)}\phi_n \tag{14}$$

Now pre-multiply by ϕ_n^* or ϕ_k^* and integrate over all space, and use orthonormality of the ϕ_n. The λ^0 term is just the unperturbed eigenvalue equation. For λ^1 and using ϕ_n^* one gets:

$$\langle\phi_n|\lambda\hat{H}_1|\phi_n\rangle = \lambda E_n^{(1)}. \tag{15}$$

For λ^1 and using ϕ_k^* one gets:

$$\langle\phi_k|\lambda\hat{H}_1|\phi_n\rangle + E_k^{(0)}\lambda c_{nk}^{(1)} = E_n^{(0)}\lambda c_{nk}^{(1)}. \tag{16}$$

Hence we get

$$\lambda E_n^{(1)} = \langle\phi_n|\lambda\hat{H}_1|\phi_n\rangle \tag{17}$$

$$\lambda c_{nk}^{(1)} = \frac{\langle\phi_k|\lambda\hat{H}_1|\phi_n\rangle}{E_n^{(0)} - E_k^{(0)}} \tag{18}$$

For λ^2 abd using ϕ_n^* one gets:

$$\sum_{k\neq n}\lambda c_{nk}^{(1)}\langle\phi_n|\lambda\hat{H}_1|\phi_k\rangle = \lambda^2 E_N^{(2)}, \tag{19}$$

which can be used to find the second order correction to the wavefunction (not shown) and the second order correction to the energy:

$$\lambda^2 E_n^{(2)} = \sum_{k\neq n}\frac{|\langle\phi_k|\lambda\hat{H}_1|\phi_n\rangle|^2}{E_n^{(0)} - E_k^{(0)}}. \tag{20}$$

The normalisation factor $N(\lambda)$ is not required for these calculations but can be shown to be equal to unity to first order in λ (i.e. no terms in λ^0 or λ^1).

Dividing these results by λ we finally get:

$$E_n^{(1)} = \langle\phi_n|\hat{H}_1|\phi_n\rangle \tag{21}$$

$$c_{nk}^{(1)} = \frac{\langle\phi_k|\hat{H}_1|\phi_n\rangle}{E_n^{(0)} - E_k^{(0)}} \tag{22}$$

$$E_n^{(2)} = \sum_{k\neq n}\frac{|\langle\phi_k|\hat{H}_1|\phi_n\rangle|^2}{E_n^{(0)} - E_k^{(0)}}. \tag{23}$$

So the first order perturbation of the energy of the state is just given by the expectation value of the perturbation of the Hamiltonian, using the eigenfunctions of the unperturbed Hamiltonian as a basis.