<u>Perturbation Theory (cont'd)</u>

Insert

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} \qquad (1)$$

$$\psi_n = \varphi_n^{(0)} + \lambda\varphi_n^{(1)} + \lambda^2\varphi_n^{(2)} \qquad (2)$$

into

$$\left(H_0 + \lambda V - E_n\right)\psi_n = 0 \qquad (3)$$

and separate terms according to powers of λ.

$$\lambda^0 : \left(H_0 - E_n^{(0)}\right)\varphi_n^{(0)} \quad ✓ \text{ by assumption} \qquad (4)$$

$$\lambda^1 : H_0\varphi_n^{(1)} + V\varphi_n^{(0)} = E_n^{(0)}\varphi_n^{(1)} + E_n^{(1)}\varphi_n^{(0)} \qquad (5)$$

First require $\left\langle\varphi_n^{(0)}\middle|\varphi_n^{(1)}\right\rangle = 0$ (see below) and project with $\left\langle\varphi_n^{(0)}\right|$ on eq. (5). Result is

$$\left\langle\varphi_n^{(0)}\middle|H_0\middle|\varphi_n^{(1)}\right\rangle + \left\langle\varphi_n^{(0)}\middle|V\middle|\varphi_n^{(0)}\right\rangle = E_n^{(0)}\left\langle\varphi_n^{(0)}\middle|\varphi_n^{(1)}\right\rangle + E_n^{(1)}\left\langle\varphi_n^{(0)}\middle|\varphi_n^{(0)}\right\rangle.$$

Making use of the requirement $\left\langle\varphi_n^{(0)}\middle|\varphi_n^{(1)}\right\rangle = 0$ and that $\left\langle\varphi_n^{(0)}\middle|\varphi_n^{(0)}\right\rangle = 1$, we have the final result

$$E_n^{(1)} = \left\langle\varphi_n^{(0)}\middle|V\middle|\varphi_n^{(0)}\right\rangle \qquad \text{(I)}$$

To proceed project with $\left\langle\varphi_\ell^{(0)}\right|$ on eq. (5). Doing that we have

$$\left\langle\varphi_\ell^{(0)}\middle|H_0\middle|\varphi_n^{(1)}\right\rangle + \left\langle\varphi_\ell^{(0)}\middle|V\middle|\varphi_n^{(0)}\right\rangle = E_n^{(0)}\left\langle\varphi_\ell^{(0)}\middle|\varphi_n^{(1)}\right\rangle \quad \text{(Recalling that } \left\langle\varphi_\ell^{(0)}\middle|\varphi_n^{(0)}\right\rangle = 0\text{).} \qquad (6)$$

Now, since the $\{\varphi_n^{(0)}\}$ for a complete, orthonormal set, we have

$$\varphi_n^{(1)} = \sum_{\ell \neq n} C_{n,\ell}\varphi_\ell^{(0)} \; ; \; C_{n,\ell} = \left\langle \varphi_\ell^{(0)} \middle| \varphi_n^{(1)} \right\rangle \tag{7}$$

and so

$$\left\langle \varphi_\ell^{(0)} \middle| H_0 \middle| \varphi_n^{(1)} \right\rangle = E_\ell^{(0)} C_{n,\ell}$$

and thus from (6), we have

$$E_\ell^{(0)} C_{n,\ell} + V_{\ell,n} = E_n^{(0)} C_{n,\ell}; \; V_{\ell,n} \equiv \left\langle \varphi_\ell^{(0)} \middle| V \middle| \varphi_n^{(0)} \right\rangle$$ and thus

$$C_{n,\ell} = \frac{V_{\ell,n}}{E_n^{(0)} - E_\ell^{(0)}}.$$ Finally then

$$\varphi_n^{(1)} = \sum_{\ell \neq n} \frac{V_{\ell,n}}{E_n^{(0)} - E_\ell^{(0)}} \varphi_\ell^{(0)} \qquad \text{II.}$$

Thus, $\psi_n \approx \varphi_n^{(0)} + \sum_{\ell \neq n} \frac{V_{\ell,n}}{E_n^{(0)} - E_\ell^{(0)}} \varphi_\ell^{(0)}$ and this explains why the term $\ell = n$ is missing from the summation over ℓ.

Similar manipulations give $$E_n^{(2)} = \sum_{\ell \neq n} \frac{V_{\ell,n}^* V_{\ell,n}}{E_n^{(0)} - E_\ell^{(0)}} \qquad \text{III.}$$