3.19. Level-Shifts and Perturbed Wave Functions from Schrodinger Equation

Consider the perturbed Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{V} \tag{3.523}$$

Let

$$\hat{H}_0 \mid n\rangle = E_0^{(n)} \mid n\rangle \qquad \hat{H} \left| \psi^{(n)} \right\rangle = E^{(n)} \left| \psi^{(n)} \right\rangle \tag{3.524}$$

where $\{ \mid n\rangle \}$ is orthonormal and complete. $\left\{ \left| \psi^{(n)} \right\rangle \right\}$ is orthogonal with normalization

$$\left\langle n \middle| \psi^{(n)} \right\rangle \equiv a_n^{(n)} = 1 \tag{3.525}$$

Completeness of $\{ \mid n\rangle \}$ means

$$\left\langle \psi^{(m)} \middle| \psi^{(n)} \right\rangle = \sum_k \left\langle \psi^{(m)} \middle| k \right\rangle \left\langle k \middle| \psi^{(n)} \right\rangle$$

$$= \sum_k a_k^{(m)*} a_k^{(n)} \quad \propto \delta_{mn} \tag{3.525a}$$

where

$$a_k^{(n)} \equiv \left\langle k \middle| \psi^{(n)} \right\rangle \tag{3.527}$$

Likewise,

$$\left| \psi^{(n)} \right\rangle = \sum_m \mid m\rangle \left\langle m \middle| \psi^{(n)} \right\rangle$$

$$= \sum_m a_m^{(n)} \left| m \right\rangle$$

$$= \mid n\rangle + \sum_{m \neq n} a_m^{(n)} \left| m \right\rangle \tag{3.526}$$

$\langle m \mid$(3.524) gives

$$\left\langle m \middle| \hat{H} \middle| \psi^{(n)} \right\rangle = E^{(n)} \left\langle m \middle| \psi^{(n)} \right\rangle$$

Using (3.527), we have

$$\left\langle m \right| \left(\hat{H}_0 + \hat{V} \right) \left| \psi^{(n)} \right\rangle = E^{(n)} a_m^{(n)}$$

$$E_0^{(m)} a_m^{(n)} + \left\langle m \middle| \hat{V} \middle| \psi^{(n)} \right\rangle = E^{(n)} a_m^{(n)} \tag{3.528}$$

Replacing $\left| \psi^{(n)} \right\rangle$ with (3.526) gives

$$E_0^{(m)} a_m^{(n)} + \left\langle m \middle| \hat{V} \middle| n \right\rangle + \sum_{k \neq n} a_k^{(n)} \left\langle m \middle| \hat{V} \middle| k \right\rangle = E^{(n)} a_m^{(n)} \tag{3.529}$$

Using (3.525) on the case $m = n$, we have

$$E_0^{(n)} + \left\langle n \middle| \hat{V} \middle| n \right\rangle + \sum_{k \neq n} a_k^{(n)} \left\langle n \middle| \hat{V} \middle| k \right\rangle = E^{(n)} \tag{3.530}$$

(3.529)$-a_m^{(n)}$(3.530) gives

$$\left(E_0^{(m)} - E_0^{(n)} \right) a_m^{(n)} + \left\langle m \middle| \hat{V} \middle| n \right\rangle + \sum_{k \neq n} a_k^{(n)} \left\langle m \middle| \hat{V} \middle| k \right\rangle$$

$$-a_m^{(n)} \left\langle n \middle| \hat{V} \middle| n \right\rangle - \sum_{k \neq n} a_k^{(n)} a_m^{(n)} \left\langle n \middle| \hat{V} \middle| k \right\rangle = 0$$

$$\to \qquad a_m^{(n)} = \frac{1}{E_0^{(n)} - E_0^{(m)}} \left\{ \left[\langle m \mid - a_m^{(n)} \langle n \mid \right] \hat{V} \mid n \rangle \right.$$

$$\left. + \sum_{k \neq n} a_k^{(n)} \left[\langle m \mid - a_m^{(n)} \langle n \mid \right] \hat{V} \mid k \rangle \right\} \tag{3.531}$$

(3.531) can be solved iteratively in powers of V. To help keep track of things, we set

$$\hat{V} \to g\,\hat{V}$$

and write

$$a_m^{(n)} = \sum_{l=1}^{\infty} (-g)^l \, a_{m,l}^{(n)} \qquad \text{for } m \neq n \tag{3.532}$$

$$E^{(n)} = E_0^{(n)} - \sum_{l=1}^{\infty} (-g)^l \, E_l^{(n)} \tag{3.533}$$

where l represents the order of perturbation.

Putting (3.532-3) into (3.530), we have

$$g\left\langle n \mid \hat{V} \mid n \right\rangle - \sum_{k \neq n} \sum_{l=1}^{\infty} (-g)^{l+1} a_{k,l}^{(n)} \left\langle n \mid \hat{V} \mid k \right\rangle = -\sum_{l=1}^{\infty} (-g)^l E_l^{(n)}$$

$$\to \qquad g\left\langle n \mid \hat{V} \mid n \right\rangle - \sum_{l=2}^{\infty} (-g)^l \sum_{k \neq n} a_{k,l-1}^{(n)} \left\langle n \mid \hat{V} \mid k \right\rangle = -\sum_{l=1}^{\infty} (-g)^l E_l^{(n)} \tag{3.533a}$$

Equating the coefficients of g^l, we get

$$E_1^{(n)} = \left\langle n \mid \hat{V} \mid n \right\rangle \tag{3.534}$$

$$E_l^{(n)} = \sum_{k \neq n} a_{k,l-1}^{(n)} \left\langle n \mid \hat{V} \mid k \right\rangle \qquad \text{for} \quad l > 1 \tag{3.535}$$

Similarly, putting (3.532-3) into (3.531), we have

$$\sum_{l=1}^{\infty} (-g)^l a_{m,l}^{(n)} = \frac{1}{E_0^{(n)} - E_0^{(m)}} \left\{ \left[g\langle m \mid + \sum_{l=2}^{\infty} (-g)^l a_{m,l-1}^{(n)} \langle n \mid \right] \hat{V} \mid n \rangle \right. \tag{3.535a}$$

$$\left. - \sum_{k \neq n} \sum_{l=2}^{\infty} (-g)^l a_{k,l-1}^{(n)} \left[\langle m \mid - \sum_{l'=1}^{\infty} (-g)^{l'} a_{m,l'}^{(n)} \langle n \mid \right] \hat{V} \mid k \rangle \right\}$$

Equating the coefficients of g^l, we get

$$a_{m,1}^{(n)} = \frac{1}{E_0^{(m)} - E_0^{(n)}} \left\langle m \mid \hat{V} \mid n \right\rangle \tag{3.536}$$

and for $l > 1$,

$$a_{m,l}^{(n)} = \frac{1}{E_0^{(m)} - E_0^{(n)}} \left\{ -a_{m,l-1}^{(n)} \left\langle n \mid \hat{V} \mid n \right\rangle + \sum_{k \neq n} a_{k,l-1}^{(n)} \left\langle m \mid \hat{V} \mid k \right\rangle \right. \tag{3.537}$$

$$\left. - \sum_{k \neq n} \sum_{l'=1}^{l-2} a_{k,l-l'-1}^{(n)} a_{m,l'}^{(n)} \left\langle n \mid \hat{V} \mid k \right\rangle \right\}$$

where the last term is obtained using

$$\sum_{l=2}^{\infty} (-g)^l a_{k,l-1}^{(n)} \sum_{l'=1}^{\infty} (-g)^{l'} a_{m,l'}^{(n)} = \sum_{l=2}^{\infty} \sum_{l'=1}^{\infty} (-g)^{l+l'} a_{k,l-1}^{(n)} a_{m,l'}^{(n)}$$

$$= \sum_{l''=3}^{\infty} \sum_{l'''=1}^{l''-2} (-g)^{l''} a_{k,l''-l'''-1}^{(n)} a_{m,l'''}^{(n)}$$

where

$$l'' = l + l' \qquad\qquad l''' = l'$$

$$\to \qquad l - 1 = l'' - l''' - 1 \geq 1$$

and we've reset $l'' \to l$ and $l''' \to l'$ in (3.537).

Note that the last term in (3.537) kicks in only for $l \geq 3$.

Using (3.534-5), we can write (3.537) as

$$a_{m,l}^{(n)} = \frac{1}{E_0^{(m)} - E_0^{(n)}} \left\{ -a_{m,l-1}^{(n)} E_1^{(n)} + \sum_{k \neq n} a_{k,l-1}^{(n)} \left\langle m \mid \hat{V} \mid k \right\rangle - \sum_{l'=1}^{l-2} a_{m,l'}^{(n)} E_{l-l'}^{(n)} \right\}$$

$$= \frac{1}{E_0^{(m)} - E_0^{(n)}} \left\{ \sum_{k \neq n} a_{k,l-1}^{(n)} \left\langle m \mid \hat{V} \mid k \right\rangle - \sum_{l'=1}^{l-1} a_{m,l'}^{(n)} E_{l-l'}^{(n)} \right\} \qquad (3.538)$$

(3.534,5,6 & 8) are equivalent to expansions (3.515-6). For example, with $l = 2$, (3.535) gives

$$E_2^{(n)} = \sum_{k \neq n} a_{k,1}^{(n)} \left\langle n \mid \hat{V} \mid k \right\rangle$$

$$= \sum_{k \neq n} \frac{1}{E_0^{(k)} - E_0^{(n)}} \left\langle k \mid \hat{V} \mid n \right\rangle \left\langle n \mid \hat{V} \mid k \right\rangle \quad \text{[(3.536) used.]} \; (3.539)$$

which is simply $\Delta_2 E_n$ in (3.515).

For a polynomial potential $\hat{V}$,

$$\left\langle n \mid \hat{V} \mid k \right\rangle = 0 \text{ for } \mid n - k \mid > M$$

where M is some positive integer. The recursive relations thus contain only finite numbers of terms and hence be solved exactly.