The H' lowers the energy levels for any sign λ, further the larger n, the greater the energy shift:

$$E_n - E_{n-1} = \hbar\omega\left[1 - \tfrac{15}{2}\lambda^2 n\right].$$

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6. 2. Degenerate Perturbation Theory

Suppose now that E_n^0 is degenerate; $g_n^0 > 1$. Then

$$H_0|\psi_n^{(0)}\rangle = \epsilon_n^{(0)}|\psi_n^{(0)}\rangle$$

$$= E_n^0|\psi_n^{(0)}\rangle$$

is not sufficient to determine $|\psi_n^{(0)}\rangle$. Indeed, $|\psi_n^{(0)}\rangle$ can be any linear combination of the $|\varphi_{n,\ell}\rangle$, $\ell = 1, \ldots, g_n^0$. Since

$$H_0|\varphi_{n,\ell}\rangle = E_n^0|\varphi_{n,\ell}\rangle;$$ such a linear combination will have energy E_n^0. Thus

$$|\psi_n^{(0)}\rangle = \sum_{\ell=1}^{g_n^0} a_{n\ell}|\varphi_{n,\ell}\rangle$$

and

$$H_0|\psi_n^{(0)}\rangle = E_n^0|\psi_n^{(0)}\rangle.$$

When $\lambda \neq 0$, H' will act, in general, to remove the degeneracy, part or all, of the E_n^0 eigenvalue. We can then use the first order Schrödinger equation to find $|\psi_n^{(0)}\rangle$. Recall this equation

$$(H_0 - \epsilon_n^{(0)})|\psi_n^{(1)}\rangle + (\hat{H}' - \epsilon_n^{(1)})|\psi_n^{(0)}\rangle = 0,$$

with $\epsilon_n^{(0)} = E_n^0$ this is

$$(H_0 - E_n^0)|\psi_n^{(1)}\rangle + (\hat{H}' - \epsilon_n^{(1)})|\psi_n^{(0)}\rangle = 0.$$

Again, projecting this onto the $|\varphi_{n,\ell}\rangle$ state gives

$$\underbrace{\langle\varphi_{n,\ell}|(H_0 - E_n^0)|\psi_n^{(1)}\rangle}_{=0} + \langle\varphi_{n,\ell}|\hat{H}' - \epsilon_n^{(1)}|\psi_n^{(0)}\rangle$$
$$= 0$$

$$\Rightarrow \langle\varphi_{n,\ell}|\hat{H}'|\psi_n^{(0)}\rangle = \epsilon_n^{(1)}\langle\varphi_{n,\ell}|\psi_n^{(0)}\rangle$$

Substituting the expansion for $|\psi_n^{(0)}\rangle$

$$|\psi_n^{(0)}\rangle = \sum_{\ell=1}^{g_n^0} a_{n\ell}|\varphi_{n,\ell}\rangle$$

with

$$a_{n\ell} = \langle\varphi_{n,\ell}|\psi_n^{(0)}\rangle$$

we have

$$\sum_{k=1}^{g_n^0} \langle \varphi_{n,l} | \hat{H}' | \varphi_{n,k} \rangle 4_{nk} = \epsilon_n^{(1)} 4_{nl}$$

Defining the matrix elements of $\hat{H}'$ in this g_n^0-dimensional subspace as

$$\hat{H}'_{lk} \equiv \langle \varphi_{n,l} | \hat{H}' | \varphi_{n,k} \rangle$$

we see this becomes of <u>matrix</u> eigenvalue equation

$$\boxed{\sum_{k=1}^{g_n^0} \hat{H}'_{lk} 4_{nk} = \epsilon_n^{(1)} 4_{nl}}$$

$(\hat{H}')_{lk}$ is a $g_n^0 \times g_n^0$ matrix and the $(4_n)_l$ are components of a g_n^0-dimensional column vector, the eigenvectors of the matrix $(\hat{H}')_{lk}$ with eigenvalues $\epsilon_n^{(1)}$.

The eigenvalues $\epsilon_n^{(1)}$ of $(\hat{H}')_{lk}$ will give the $O(\lambda)$ energy shifts

for the n^{th} level. Hence we see that to determine the zeroth order eigenstates $|\psi_n^{(0)}\rangle$, i.e. $(\psi_n)_\ell$ and the first order energy shifts, i.e. $\epsilon_n^{(1)}$, we must solve the $g_n \times g_n$ - matrix eigenvalue problem. Thus we need only to diagonalize the H' operator on the degenerate subspace spanned by the E_n^0 degenerate eigenvectors $|\psi_{n,\ell}\rangle$ in this order. We do not have to worry about mixing to the whole Hilbert space, only this degenerate subspace.

From a practical point of view we can most easily diagonalize H' restricted to this subspace by choosing a convenient set of basis vectors of H_0; $\{|\psi_{n,\ell}\rangle\}$. For instance if there is a Hermitian operator A that commutes with H_0 and H'

$$[H_0, A] = 0 = [H', A],$$

then the $|\psi_{n,k}\rangle$ should also be

chosen to be its eigenstates (since $[A, H_0] = 0$ this is allowed)

$$A|\varphi_{n,\ell}\rangle = a_\ell |\varphi_{n,\ell}\rangle .$$

Since $[A, H'] = 0 \Rightarrow$

$$\langle \varphi_{n,\ell} | [A, \hat{H}'] | \varphi_{n,k} \rangle = 0$$

$$= (a_\ell - a_k) \langle \varphi_{n,\ell} | \hat{H}' | \varphi_{n,k} \rangle$$

$$\Rightarrow \quad (\hat{H}')_{\ell k} = \langle \varphi_{n,\ell} | \hat{H}' | \varphi_{n,k} \rangle = 0$$

unless $\ell = k$, that is $(\hat{H}')_{\ell k}$ is automatically diagonal in this basis. Of course, often the case is not this, but that $[A, H'] \neq 0$ and we must work to diagonalize $(\hat{H}')_{\ell k}$.

If the energy shift eigenvalues $E_n^{(1)}$ are all different, the degenerate energy level E_n^0 has been completely split by H' at first order.

The $|\psi_n^{(0)}\rangle$, i.e. ψ_{nl}, are completely determined (up to normalization). We can now use the non-degenerate perturbation theory techniques to calculate all the higher order effects.

On the other hand, it could be that not all of the g_n^0-fold degeneracy of E_n^0 is removed. It could be that some or even all of the g_n^0 eigenvalues $\epsilon_n^{(1)}$ are the same. We can label the eigenvalues $\epsilon_n^{(1)}$ by $\epsilon_{nj}^{(1)}$ with $j = 1, \ldots, f_n^{(1)}$ different

where $f_n^{(1)} \leq g_n^0$. If $f_n^{(1)} = g_n^0$ we have g_n^0 distinct energy shifts — the degeneracy is completely removed. If $f_n^{(1)} < g_n^0$, the degeneracy, to first order, is only partially removed (if $f_n^{(1)} = 1$, the degeneracy is not removed at all).

So again we now choose a particular $\epsilon_{nj}^{(1)}$. If $\epsilon_{nj}^{(1)}$ is non-degenerate the corresponding

eigenvector $\psi_{n\ell}$ ($|\psi_n^{(0)}\rangle$) is uniquely determined and we proceed to higher orders via non-degenerate perturbation theory.

If $\epsilon_{nj}^{(1)}$ is g_{nj}-fold degenerate we now must consider diagonalizing the g_{nj}-dimensional problem. That is $|\psi_n^{(0)}\rangle$ now belongs to a g_{nj}-dimensional subspace of the original g_n-dimensional subspace and we must proceed to 2nd order perturbation theory to determine the $|\psi_n^{(0)}\rangle$ in terms of the $|\psi_{n,\ell}\rangle$.

To be specific, let's consider the case where $f_{nj}^{(1)} = 1$, that is H' in first order does not remove any of the g_n-fold degeneracy of E_n^0. Thus $\langle \hat{H}' \rangle_{kk}$ has only one eigenvalue $\epsilon_n^{(1)}$ and it occurs g_n times. As is often the case and to simplify the ensuing notation we now realize this by assuming that H' vanishes between the g_n - E_n^0 eigenstates.

Let $\langle \psi_{n,k} | H' | \psi_{n,\ell} \rangle = 0$.

So the eigenvalue $\epsilon_n^{(1)} = 0$ and the ψ_{nk} are undetermined in 1st order.

This being the case consider the λ^2 Schrödinger equation

$$(H_0 - E_n^0)|\psi_n^{(2)}\rangle + (\hat{H}' - \cancel{\epsilon_n^{(1)}}^{\,0})|\psi_n^{(1)}\rangle = \epsilon_n^{(2)}|\psi_n^{(0)}\rangle$$

As usual we project this onto the g_n^0-dimensional subspace spanned by $\{|\varphi_{n,k}\rangle \; k = 1, \ldots, g_n^0\}$

$$\underbrace{\langle\varphi_{n,k}|(H_0 - E_n^0)|\psi_n^{(2)}\rangle}_{=0} + \langle\varphi_{n,k}|\hat{H}'|\psi_n^{(1)}\rangle = \epsilon_n^{(2)}\langle\varphi_{n,k}|\psi_n^{(0)}\rangle$$

$$\Rightarrow \boxed{\langle\varphi_{n,k}|\hat{H}'|\psi_n^{(1)}\rangle = \epsilon_n^{(2)}\langle\varphi_{n,k}|\psi_n^{(0)}\rangle}$$

Inserting a complete set of states on the LHS

$$1 = \sum_{l=1}^{g_n^0} |\varphi_{n,l}\rangle\langle\varphi_{n,l}| + \sum_{m\neq n}\sum_{l=1}^{g_m^0} |\varphi_{m,l}\rangle\langle\varphi_{m,l}|$$

we find

$$\sum_{l=1}^{g_n^0} \langle \varphi_{n,k}|\hat{H}'|\varphi_{n,l}\rangle\langle\varphi_{n,l}|\psi_n^{(1)}\rangle + \sum_{m\neq n}\sum_{l=1}^{g_m^0}\langle\varphi_{n,k}|\hat{H}'|\varphi_{m,l}\rangle\langle\varphi_{m,l}|\psi_n^{(1)}\rangle = \epsilon_n^{(2)}\langle\varphi_{n,k}|\psi_n^{(0)}\rangle$$

but $\langle\varphi_{n,k}|\hat{H}'|\varphi_{n,l}\rangle = 0$ by assumption,

Thus

$$\boxed{\sum_{m\neq n}\sum_{l=1}^{g_m^0}\langle\varphi_{n,k}|\hat{H}'|\varphi_{m,l}\rangle\langle\varphi_{m,l}|\psi_n^{(1)}\rangle = \epsilon_n^{(2)}\langle\varphi_{n,k}|\psi_n^{(0)}\rangle}$$

To continue further we need the components of $|\psi_n^{(1)}\rangle$ in the space orthogonal to the g_n^0 dimensional subspace. As usual this can be determined from the λ' equation projected onto this complementary space spanned by the $\{|\varphi_{m,l}\rangle \ni m\neq n\}$. The λ' Schrödinger equation is

$$(H_0 - E_n^0)|\psi_n^{(1)}\rangle + (\hat{H}' - \epsilon_n^{(1)})|\psi_n^{(0)}\rangle = 0$$

Projecting onto $|\varphi_{m,\ell}\rangle$

$$\underbrace{\langle\varphi_{m,\ell}|H_0 - E_n^0|\psi_n^{(1)}\rangle}_{=\langle\varphi_{m,\ell}|E_m^0} + \langle\varphi_{m,\ell}|\hat{H}'|\psi_n^{(0)}\rangle = 0$$

Since $E_m^0 \neq E_n^0$ we find

$$\boxed{\langle\varphi_{m,\ell}|\psi_n^{(1)}\rangle = \frac{\langle\varphi_{m,\ell}|\hat{H}'|\psi_n^{(0)}\rangle}{E_n^0 - E_m^0}}$$

Thus we obtain an eigenvalue equation

$$\sum_{m\neq n}\sum_{k=1}^{g_m} \frac{\langle\varphi_{n,k}|\hat{H}'|\varphi_{m,\ell}\rangle\langle\varphi_{m,\ell}|\hat{H}'|\psi_n^{(0)}\rangle}{E_n^0 - E_m^0} = \epsilon_n^{(2)}\langle\varphi_{n,k}|\psi_n^{(0)}\rangle$$

Recalling that $|\psi_n^{(0)}\rangle = \sum_{j=1}^{g_n} a_{nj}|\varphi_{nj}\rangle$

we finally secure the matrix eigenvalue equation

$$\sum_{j=1}^{g_n^0} \left\{ \sum_{m\neq n}^{} \sum_{k=1}^{g_m^0} \frac{\langle \varphi_{n,k} | \hat{H}' | \varphi_{m,\ell} \rangle \langle \varphi_{m,\ell} | \hat{H}' | \varphi_{n,j} \rangle}{E_n^0 - E_m^0} \right\} a_{nj}$$

$$\equiv \left(\hat{H}'_{(2)}\right)_{kj} = \epsilon_n^{(2)} a_{nk}$$

Thus

$$\sum_{j=1}^{g_n^0} \left(\hat{H}'_{(2)}\right)_{kj} a_{nj} = \epsilon_n^{(2)} a_{nk}$$

we obtain a $g_n^0 \times g_n^0$ matrix eigenvalue equation for the second order energy shifts $\epsilon_n^{(2)}$ and zeroth order eigenstate a_{nk}. In second order we see that $\left(\hat{H}'_{(2)}\right)_{kj}$ now has in it information about the matrix elements of $\hat{H}'$ between the complementary subspaces $m \neq n$.

In first order, we only had $\hat{H}'$ connecting states in the g^0_n-dimensional degenerate subspace. Clearly, this gets complicated rapidly.

As previously, the eigenvalues $\epsilon_n^{(2)}$ are the second order energy shifts. If these are g^0_n-different eigenvalues, then the E^0_n degeneracy is completely broken in 2nd order. If some of the $\epsilon_n^{(2)}$ eigenvalues remain degenerate, we must proceed to third order perturbation theory to try to remove it. For the non-degenerate $\epsilon_n^{(2)}$ eigenvalues, we can proceed to higher order calculations using the non-degenerate perturbation theory techniques.

At degenerate energies or close to them (i.e. where $(E^0_n - E^0_m)^{-1}$ gets very large) the Rayleigh-Schrödinger perturbation scheme is quite complicated. As well, higher order expressions for the energy levels and eigenstates become [illegible]

[illegible] with free Hamiltonian $H_0 = \begin{pmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{pmatrix}$. This will allow us to adjust $\epsilon_{1,2}$ to make the problem non-degenerate ($\epsilon_1 \neq \epsilon_2$) or degenerate ($\epsilon_1 \to \epsilon_2 = \epsilon$)

So choose as the H' the

perturbing Hamiltonian $H' = \begin{bmatrix} 0 & v \\ v^* & 0 \end{bmatrix}$
so that $H = H_0 + H'$.

This problem can be solved exactly.
The energy eigenvalues are

$$\det \begin{vmatrix} \epsilon_1 - E & v \\ v^* & \epsilon_2 - E \end{vmatrix} = 0$$

$$\Rightarrow \quad E^2 - (\epsilon_1 + \epsilon_2)E + \epsilon_1\epsilon_2 - |v|^2 = 0$$

$$\Rightarrow$$

$$E = \tfrac{1}{2}(\epsilon_1 + \epsilon_2) \pm \tfrac{1}{2}\sqrt{(\epsilon_1 - \epsilon_2)^2 + 4|v|^2}$$

Thus the exact energy eigenvalues are

$$E_1 = \tfrac{1}{2}(\epsilon_1 + \epsilon_2) + \tfrac{1}{2}\sqrt{(\epsilon_1 - \epsilon_2)^2 + 4|v|^2}$$

$$E_2 = \tfrac{1}{2}(\epsilon_1 + \epsilon_2) - \tfrac{1}{2}\sqrt{(\epsilon_1 - \epsilon_2)^2 + 4|v|^2} \; .$$

The unperturbed Hamiltonian H_0 has energy eigenvalues

$$E_1^0 = \epsilon_1$$

$$E_2^0 = \epsilon_2$$

The unperturbed eigenstates are

$$|\psi_1\rangle = \begin{pmatrix}1\\0\end{pmatrix} \; ; \; |\psi_2\rangle = \begin{pmatrix}0\\1\end{pmatrix}$$

Since $\langle \psi_{1,2} | H' | \psi_{1,2} \rangle = 0$, we must use second order R-S perturbation theory to find, for instance,

$$E_1^{R\text{-}S} = \epsilon_1 + \cancel{\langle \psi_1 | H' | \psi_1 \rangle}^{\to 0} + \frac{|\langle \psi_1 | H' | \psi_2 \rangle|^2}{E_1^0 - E_2^0}$$

$$= \epsilon_1 + \frac{\left|\begin{pmatrix}1 & 0\end{pmatrix}\begin{pmatrix}0 & V\\ V^* & 0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix}\right|^2}{\epsilon_1 - \epsilon_2}$$

$$E_1^{R\text{-}S} = \epsilon_1 + \frac{|V|^2}{\epsilon_1 - \epsilon_2} \quad \left(\text{likewise we find } E_2^{R\text{-}S} = \epsilon_2 - \frac{|V|^2}{\epsilon_1 - \epsilon_2} \right)$$

clearly for almost degenerate unperturbed energy levels or degenerate ones! $\epsilon_1 \approx \epsilon_2$ this becomes non-sense, we must use the complicated degenerate R-SPT

for $\frac{|V|}{|\epsilon_1 - \epsilon_2|} \ll 1$, this is correct to second order for E_1, as seen by expanding the exact energy eigenvalues.

Consider the degenerate R-S perturbation theory. So $\epsilon_1 = \epsilon_2 = \epsilon$ and $|\varphi_1\rangle$ both have energy ϵ, $H_0|\varphi_i\rangle = \epsilon|\varphi_i\rangle$

Thus the eigenstates of the system $|\psi''\rangle$ are given by

$$|\psi''\rangle = C_1|\varphi_1\rangle + C_2|\varphi_2\rangle$$

and we must use the 1st order R-S equation to find C_1, C_2 and $\epsilon^{(1)}$ this is simply the equations on page

$$\sum_{k=1}^{2} H'_{lk} C_k = (E - E^0) C_l$$

with $E^0 = \epsilon$ and $H'_{lk} = \langle\varphi_l|H'|\varphi_k\rangle$

$$= \begin{pmatrix} 0 & v \\ v^* & 0 \end{pmatrix}$$

So

$$\begin{pmatrix} 0 & v \\ v^* & 0 \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = (E-\epsilon)\begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

$$\Rightarrow \quad \left.\begin{aligned} v C_2 &= (E-\epsilon) C_1 \\ v^* C_1 &= (E-\epsilon) C_2 \end{aligned}\right\} \Rightarrow \boxed{E - \epsilon = \pm |v|}$$

Thus the interacting energy levels are

$$E_1 = \epsilon + |V|$$
$$E_2 = \epsilon - |V|$$

the exact results.

The eigenstates corresponding to these energies are found from the above equation

$$V C_2 = (E - \epsilon) C_1$$

Then, with $|\psi_{\frac{1}{2}}^{II}\rangle$ corresponding to E_2 we have

$$C_{12} = \frac{E_1 - \epsilon}{V} C_{11} = \frac{|V|}{V} C_{11}$$

$$C_{22} = \frac{E_2 - \epsilon}{V} C_{21} = -\frac{|V|}{V} C_{21}.$$

Normalizing $\langle \psi_{\frac{1}{2}}^{II} | \psi_{\frac{1}{2}}^{II} \rangle = 1 \Rightarrow$

$$|C_{11}|^2 + |C_{12}|^2 = 1 = |C_{21}|^2 + |C_{22}|^2$$

$$\Rightarrow \boxed{C_{11} = \frac{1}{\sqrt{2}} = C_{21}}$$

So $|\psi_1''\rangle = c_{11}|\varphi_1\rangle + c_{12}|\varphi_2\rangle$

$= \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ \frac{|v|}{v}\end{pmatrix}$ corresponding

to energy E_1 and

$|\psi_2''\rangle = c_{21}|\varphi_1\rangle + c_{22}|\varphi_2\rangle$

$= \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ -\frac{|v|}{v}\end{pmatrix}$ corresponding

to energy E_2.

Note: Since these energies are exact, $|\psi_{1,2}''\rangle$ are exact

$$H|\psi_{1,2}''\rangle = E_{1,2}|\psi_{1,2}''\rangle.$$

And clearly $\langle\psi_1''|\psi_2''\rangle = 0$ as it must.