messy near or at degenerate energy levels, the B-W scheme will handle these cases more simply.

6.2. Brillouin-Wigner Stationary State Perturbation Theory

As we saw above, the unperturbed energy differences in denominators led to a ~~breakdown~~ of the non-degenerate R-S perturbation theory at or close to degenerate energy levels. In general then we would like to avoid such denominators. At the same time, we would like to develop a general expression for the eigenvalue equation, applicable even in the degenerate case. Recall in that case we must determine which vectors the $|\Psi_n\rangle$ go into at $\lambda = 0$.

Thus we can first consider an expansion not in $\frac{1}{E_n^0 - E_m^0}$ but

$\frac{1}{E_n - E_n^0}$, which does not blow up at degenerate values, since we assume $E_n \neq E_n^0$.

So as usual we begin with the Schrödinger equation

$$H|\psi_n\rangle = (H_0 + H')|\psi_n\rangle = E_n|\psi_n\rangle.$$

rather than expanding $E_n = E_n^0 + \cdots$ as before we write this as

$$(E_n - H_0)|\psi_n\rangle = H'|\psi_n\rangle$$

which yields the equation

$$\boxed{|\psi_n\rangle = (E_n - H_0)^{-1} H' |\psi_n\rangle}$$

Since H_0 has eigenvalues $\{E_n^0\}$, $\dfrac{1}{E_n - H_0}$ is well behaved. In order to find a more explicit equation for E_n as well as $|\psi_n\rangle$ we project this equation onto the various subspaces of the unperturbed Hamiltonian. In particular we can expand $|\psi_n\rangle$ in terms of the H_0 eigen-basis

$$|\psi_n\rangle = \sum_{k=1}^{g_n} C_{nk}|\varphi_{n,k}\rangle + \sum_{m\neq n}\sum_{l=1}^{g_m} C_{ml}|\varphi_{m,l}\rangle .$$

In the degenerate case we must find an eigenvalue equation for the C_{nk} at $\lambda = 0$.

(Note: $C_{nk} = C_{nk}(\lambda)$ here, as $\lambda \to 0$ the $C_{ml} \to 0$, $m \neq n$, while the C_{nk} go to a particular set, $C_{nk} \xrightarrow[\lambda\to 0]{} 2\mathcal{l}_{nk}$, as $|\psi_n\rangle \to |\psi_n^{(0)}\rangle$. For $\lambda \neq 0$, we denote the component of $|\psi_n\rangle$ in the degenerate subspace by $|\psi_n''\rangle$

$$|\psi_n''\rangle = \sum_{k=1}^{g_n} C_{nk}|\varphi_{n,k}\rangle .$$

So

$$|\psi_n^{(0)}\rangle = \lim_{\lambda\to 0} |\psi_n''\rangle \ .)$$

We can introduce the projector P_n onto the g_n-degenerate subspace, call it $\mathcal{H}_n^0$, of eigenvalue E_n^0.

$$P_n \equiv \sum_{k=1}^{g_n} |\varphi_{n,k}\rangle\langle\varphi_{n,k}| \ .$$

So since the $\{|\varphi_{n,l}\rangle\}$ are orthonormal we have

$$P_n P_n = P_n$$

$$P_m P_n = 0 \quad \text{if } m \neq n$$

and summing over all n we recover completeness

$$\mathbb{1} = \sum_n P_n .$$

The projector onto the ~~space~~ orthogonal to $\mathcal{H}_n^0$, that is the complement of $\mathcal{H}_n^0$ is

$$Q_n \equiv 1 - P_n$$

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

note $Q_n Q_n = Q_n$, $Q_n P_n = 0$, and

$$P_n = 1 - Q_n$$

$$= 1 - \sum_{m \neq n} \sum_{l=1}^{g_m} |\varphi_{m,l}\rangle\langle\varphi_{m,l}| .$$

The projection of $|\psi_n\rangle$ onto $\mathcal{H}_n^0$ is

$$|\psi_n^{\parallel}\rangle \equiv P_n |\psi_n\rangle$$

and as $\lambda \to 0$ $\quad |\psi_n\rangle \xrightarrow{\lambda\to 0} |\psi_n^{\shortparallel}\rangle\Big|_{\lambda=0} = \sum_{k=1}^{g_n} \psi_{nk} |\varphi_{n,k}\rangle$

a particular vector in $\mathcal{H}_n^0$.

Thus in our Schrödinger equation, we would like to separate out this projection of $|\psi_n\rangle$ onto $\mathcal{H}_n^0$ and perturb about it.
~~Thus~~

$$|\psi_n\rangle = P_n|\psi_n\rangle + (1-P_n)|\psi_n\rangle$$

$$= |\psi_n^{\shortparallel}\rangle + (1-P_n)|\psi_n\rangle$$

but the Schrödinger equation is

$$|\psi_n\rangle = (E_n - H_0)^{-1} H' |\psi_n\rangle,$$

substituting into the second term on the RHS $\Rightarrow$

$$\boxed{|\psi_n\rangle = |\psi_n^{\shortparallel}\rangle + (1-P_n)(E_n - H_0)^{-1} H' |\psi_n\rangle}$$

Now we note that

$$P_n H_0 = \sum_{k=1}^{g_n} |\varphi_{n,k}\rangle \underbrace{\langle\varphi_{n,k}| H_0}_{= E_n^0 \langle\varphi_{n,k}|}$$

$$= E_n^0 \sum_{k=1}^{g_n} |\varphi_{n,k}\rangle\langle\varphi_{n,k}|$$

So
$$\boxed{P_n H_0 = H_0 P_n = E_n^0 P_n}$$

Thus
$$(1-P_n)(E_n - H_0)^{-1} = (E_n - H_0)^{-1}(1-P_n)$$
$$= (E_n - H_0)^{-1} \sum_{m\neq n}{}' \sum_{l=1}^{g_m}{}' |\varphi_{m,l}\rangle\langle\varphi_{m,l}|$$
$$\boxed{= \sum_{m\neq n}{}' \sum_{l=1}^{g_m}{}' \frac{|\varphi_{m,l}\rangle\langle\varphi_{m,l}|}{E_n - E_m^0} = (1-P_n)(E_n - H_0)^{-1}}$$

where we used $H_0|\varphi_{m,l}\rangle = E_m^0|\varphi_{m,l}\rangle$.

Since $E_n \neq E_m^0$ by assumption, this is a well defined sum. So the Schrödinger equation, in the form above, is well defined (naturally). So we need now to extract more explicitly 3 things 1) an expression for E_n, 2) an equation determining $|\psi_n^{\prime\prime}\rangle$ and therefore Z_{nk}, 3) an equation determining the component of $|\psi_n\rangle$ $\perp$ to $\mathcal{H}_n^0$.

Considering the last first. The Schrödinger equation

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

$$\equiv |\psi_n''\rangle + R_n H'|\psi_n\rangle$$

with

$$R_n \equiv (1-P_n)(E_n-H_0)^{-1}$$

$$= \sum_{m\neq n}{}' \sum_{\ell=1}^{g_m}{}' \frac{|\varphi_{m,\ell}\rangle\langle\varphi_{m,\ell}|}{E_n - E_m^0}$$

Can be solved recursively, or more formerly we can re-write this as

$$[1-R_nH']|\psi_n\rangle = |\psi_n''\rangle$$

$$\Rightarrow \boxed{\begin{aligned}|\psi_n\rangle &= [1-R_nH']^{-1}|\psi_n''\rangle \\ &= |\psi_n''\rangle + R_nH'|\psi_n''\rangle \\ &\quad + (R_nH')^2|\psi_n''\rangle + \cdots\end{aligned}}$$

This is the Brillouin-Wigner Perturbation expansion for $|\psi_n\rangle$

Note: $|\psi_n\rangle = |\psi_n^{\parallel}\rangle + |\psi_n^{\perp}\rangle$ with

$$|\psi_n^{\parallel}\rangle = P_n|\psi_n\rangle \text{ and } |\psi_n^{\perp}\rangle = Q_n|\psi_n\rangle$$

Since $R_n = Q_n(E_n - H_0)^{-1}$ we have that the above equation gives $|\psi_n^{\perp}\rangle$ in terms of $|\psi_n^{\parallel}\rangle$

$$\boxed{\begin{aligned} |\psi_n^{\perp}\rangle &= Q_n|\psi_n\rangle \\ &= [R_nH' + (R_nH')^2 + \cdots]|\psi_n^{\parallel}\rangle \\ &= \frac{R_nH'}{1-R_nH'}|\psi_n^{\parallel}\rangle . \end{aligned}}$$

Secondly we can find an eigenvalue equation for $|\psi_n^{\parallel}\rangle$ by projecting the Schrödinger equation onto ψ_n;

$$H'|\psi_n\rangle = (E_n - H_0)|\psi_n\rangle$$

Now operate with P_n

$$\begin{aligned} P_nH'|\psi_n\rangle &= P_n(E_n - H_0)|\psi_n\rangle \\ &= (E_n - H_0)P_n|\psi_n\rangle \end{aligned}$$

$$P_n H' |\Psi_n\rangle = (E_n - E_n^0) P_n |\Psi_n\rangle = (E_n - E_n^0) |\Psi_n''\rangle$$

where we used $H_0 P_n = E_n^0 P_n$.

Relating $|\Psi_n\rangle$ on the LHS to $|\Psi_n''\rangle$ by the equation for $|\Psi_n^+\rangle$:

$$|\Psi_n\rangle = [1 - R_n H']^{-1} |\Psi_n''\rangle$$

we have

$$\boxed{\left(P_n H' [1 - R_n H']^{-1}\right) |\Psi_n''\rangle = (E_n - E_n^0) |\Psi_n''\rangle}$$

Thus we have an eigenvalue equation for the energy shifts $(E_n - E_n^0)$ and the eigenstates $|\Psi_n''\rangle$.

A more direct formula for the energy levels can be obtained by simply projecting the Schrödinger equation onto $\mathcal{H}_n^0$ as above

$$E_n |\psi_n''\rangle = E_n^0 |\psi_n''\rangle + P_n H' |\psi_n\rangle$$

taking the inner product with any vector in $\mathcal{H}_n^0$ $\Rightarrow$

$$\boxed{E_n = E_n^0 + \frac{\langle a_n^0 | H' | \psi_n\rangle}{\langle a_n^0 | \psi_n\rangle}}$$

with $|a_n^0\rangle \in \mathcal{H}_n^0$ so $P_n |a_n^0\rangle = |a_n^0\rangle$.

Substituting the expansion for $|\psi_n\rangle$ we have

$$E_n = E_n^0 + \frac{\langle a_n^0 | H' | \psi_n''\rangle}{\langle a_n^0 | \psi_n''\rangle} + \frac{\langle a_n^0 | H' R_n H' | \psi_n''\rangle}{\langle a_n^0 | \psi_n''\rangle}$$

$$+ \ldots$$

Using the formula for R_n (page -887-)

$\Rightarrow$

$$\boxed{E_n = E_n^0 + \frac{\langle a_n^0 | H' | \psi_n''\rangle}{\langle a_n^0 | \psi_n''\rangle} + \sum_{m \neq n} \sum_{l=1}^{g_m} \frac{\langle a_n^0 | H' | \varphi_{m,l}\rangle \langle \varphi_{m,l} | H' | \psi_n''\rangle}{\langle a_n^0 | \psi_n''\rangle (E_n - E_m^0)} + \ldots}$$

Choosing $|a_n^o\rangle = |\psi_n''\rangle$ and normalizing $\langle\psi_n''|\psi_n''\rangle = 1$, this looks simpler

$$\boxed{E_n = E_n^o + \langle\psi_n''|H'|\psi_n''\rangle + \sum_{m\neq n}' \sum_{l=1}^{g_m} \frac{|\langle\psi_n''|H'|\varphi_{m,l}\rangle|^2}{(E_n - E_m^o)} + \cdots}$$

Since it is $(E_n - E_m^o)$ that appears in this formula there are no difficulties ~~even~~ for degenerate E_n^o eigenvalues. Of course the appearance of E_n in the RHS defines E_n only implicitly. The utility of the formula occurs when evaluating the equations numerically. One puts in a trial value for E_n on the RHS and determines the E_n on the LHS. This process can be continued until the ~~two~~ values converge.

Likewise the equation for $|\Psi_n\rangle$:

$$|\Psi_n\rangle = [1 - R_n H']^{-1} |\Psi_n''\rangle$$

is exact. Of course we can only solve it approximately. Namely, expanding the inverse to obtain

$$|\Psi_n\rangle = |\Psi_n''\rangle + R_n H' |\Psi_n''\rangle + (R_n H')^2 |\Psi_n''\rangle + \cdots$$

$$= |\Psi_n''\rangle + \sum_{m \neq n}{}' \sum_{l=1}^{g_m}{}' \frac{\langle \varphi_{m,l} | H' | \Psi_n'' \rangle}{E_n - E_m^0} |\varphi_{m,l}\rangle$$

$$+ \sum_{\substack{m \neq n \\ m' \neq n}}{}' \sum_{l=1}^{g_m}{}' \sum_{l'=1}^{g_{m'}}{}' \frac{\langle \varphi_{m,l} | H' | \varphi_{m',l'} \rangle \langle \varphi_{m',l'} | H' | \Psi_n'' \rangle}{(E_n - E_m^0)(E_n - E_{m'}^0)} \times |\varphi_{m,l}\rangle$$

$$+ \cdots .$$

Again it is $(E_n - E_m^0)$ that occurs in the denominators providing applicability for even degenerate ~~E_n~~^{0} eigenvalues.

For non-degenerate E_n^0 we have that $|\Psi_n''\rangle = |\varphi_n\rangle$ and

$$E_n = E_n^0 + \langle \varphi_n | H' \frac{1}{1 - R_n H'} | \varphi_n \rangle$$

$$E_n = E_n^0 + \langle \varphi_n | H' | \varphi_n \rangle + \sum_{m\neq n}' \sum_{l=1}^{g_m} \frac{|\langle \varphi_n | H' | \varphi_{m,l} \rangle|^2}{E_n - E_m^0} + \cdots$$

The R-S expansion can be obtained if we further expand $E_n = E_n^0 + \lambda \epsilon_n^{(1)} + \cdots$
So

$$\lambda \epsilon_n^{(1)} + \lambda^2 \epsilon_n^{(2)} + \cdots = \langle \varphi_n | \lambda \hat{H}' | \varphi_n \rangle + \sum_{m\neq n}' \sum_{l=1}^{g_m} \lambda^2 \frac{|\langle \varphi_n | \hat{H}' | \varphi_{m,l} \rangle|^2}{E_n^0 - E_m^0} + \cdots$$

recovering the result we found earlier. For higher order corrections this is messier.

For degenerate eigenvalues E_n^0 we must determine the $|\Psi_n^0\rangle$ state as well as $E_n - E_n^0$.

Recalling the eigenvalue equation on page -889- for $|\Psi_n''\rangle$

$$P_n H' \frac{1}{1-R_n H'} |\Psi_n''\rangle = (E_n - E_n^0) |\Psi_n''\rangle$$

where $$|\Psi_n''\rangle = \sum_{k=1}^{g_n} C_{nk} |\varphi_{n,k}\rangle$$

we have

$$\sum_{k=1}^{g_n} \langle \varphi_{n,l} | H' \frac{1}{1-R_n H'} |\varphi_{n,k}\rangle C_{nk} = (E_n - E_n^0) C_{nl}$$

$$\Rightarrow$$

$$\sum_{k=1}^{g_n} \left\{ \langle \varphi_{n,l} | H' | \varphi_{n,k}\rangle + \sum_{m \neq n} \sum_{j=1}^{g_m} \frac{\langle \varphi_{n,l} | H' | \varphi_{m,j}\rangle \langle \varphi_{m,j} | H' | \varphi_{n,k}\rangle}{E_n - E_m^0} + \cdots \right\} C_{nk} = (E_n - E_n^0) C_{nl}$$

As before this is a complicated equation since E_n appears on the LHS, thus we can only solve it approximately.

One approximation is the R-S scheme

Then we expand in powers of λ

So we find to order λ^2 (note: $C_{nl}^{(0)} = \mathcal{U}_{nl}$)

$$\sum_{k=1}^{g_n} \left[\lambda \hat{H}'_{lk} + \lambda^2 \hat{H}'_{(2)lk}\right]\left[\mathcal{U}_{nk} + \lambda C_{nk}^{(1)}\right]$$

$$= \left[\lambda \epsilon_n^{(1)} + \lambda^2 \epsilon_n^{(2)}\right]\left[\mathcal{U}_{nk} + \lambda C_{nk}^{(1)}\right]$$

$\Rightarrow$

$$1) \sum_{k=1}^{g_n} \hat{H}'_{lk}\, \mathcal{U}_{nk} = \epsilon_n^{(1)} \mathcal{U}_{nl}$$

$$2) \hat{H}'_{(2)lk}\, \mathcal{U}_{nk} = \epsilon_n^{(2)} \mathcal{U}_{nl} + \left(\hat{H}'_{lk} - \epsilon_n^{(1)} \delta_{lk}\right) C_{nk}^{(1)}$$

These are just our previous equations in R-S degenerate perturbation theory.

Of course the B-W expansion for the energy

$$E_n = E_n^0 + \langle \mathcal{U}_n'' | H' | \mathcal{U}_n'' \rangle + \sum_{m \neq n}' \sum_{l=1}^{g_m} \frac{|\langle \mathcal{U}_n'' | H' | \varphi_{m,l} \rangle|^2}{(E_n - E_m^0)} + \cdots$$

and the eigenstate

$$|\mathcal{U}_n\rangle = |\mathcal{U}_n''\rangle + R_n H' |\mathcal{U}_n''\rangle + \cdots$$

although more difficult to solve than the R-S approximation (we are summing an infinite (large) number of R-S terms) ~~they~~ yield more accurate approximations to the energy levels.

Since these equations only implicitly define E_n due to its appearance on both sides of the equation they are known as <u>self consistent</u> determinations of E_n. In fact this is how we described the use of the energy level equation. We guess a value for E_n, plug it into the equation and see if the E_n we calculate is the same. If not we continue the process until the results converge, they have been self-consistently determined.

Finally, let's consider a simple example comparing the R-S and B-W schemes! which begins as a non-degenerate system whose parameters we can adjust to make degenerate.

<u>Example</u>: Consider a 2-level system with free Hamiltonian

$$H_0 = \begin{pmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{pmatrix} \quad \text{and}$$

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

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

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

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

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 Ho has energy eigenvalues

$$E_1^0 = \epsilon_1$$

$$E_2^0 = \epsilon_2$$

The unperturbed eigenstates are

$$|\varphi_1\rangle = \begin{pmatrix}1\\0\end{pmatrix} \; ; \; |\varphi_2\rangle = \begin{pmatrix}0\\1\end{pmatrix}$$

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

$$E_1^{R\text{-}S} = \epsilon_1 + \cancelto{0}{\langle\varphi_1|H'|\varphi_1\rangle} + \frac{|\langle\varphi_1|H'|\varphi_2\rangle|^2}{E_1^0 - E_2^0}$$

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

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

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 eigenvalue.

Consider the degenerate R-S perturbation theory. So $\epsilon_1 = \epsilon_2 = \epsilon$ and $|\varphi_1\rangle$ both have energy ϵ, $H_0|\varphi_{\frac{1}{2}}\rangle = \epsilon|\varphi_{\frac{1}{2}}\rangle$

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 -895- or page -871-

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

with $E^0 = \epsilon$ and $H'_{\ell k} = \langle \varphi_\ell | H' | \varphi_k \rangle$

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

So

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

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

Thus the interacting energy levels are

$$\boxed{\begin{aligned} E_1 &= \epsilon + |v| \\ E_2 &= \epsilon - |v| \end{aligned}}$$

the exact results.

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

$$v\, C_2 = (E - \epsilon)\, C_1$$

Then, with $|\psi''_{\frac{1}{2}}\rangle$ corresponding to $E_{\frac{1}{2}}$ 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 $\langle \psi''_{\frac{1}{2}} | \psi''_{\frac{1}{2}} \rangle = 1 \Rightarrow$

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

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

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, $|\psi_{\substack{1\\2}}''\rangle$ are exact

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

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

On the other hand B-W perturbation theory has

$$E_1^{B\text{-}W} = \epsilon_1 + \cancelto{0}{\langle\varphi_1|H'|\varphi_1\rangle} + \frac{|\langle\varphi_1|H'|\varphi_2\rangle|^2}{E_1^{B\text{-}W}-\epsilon_2}$$

$$= \epsilon_1 + \frac{\left|\begin{pmatrix}1 & 0\end{pmatrix}\begin{pmatrix}0 & v\\ v^* & 0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix}\right|^2}{E_1-\epsilon_2}$$

$$E_1^{B\text{-}W} = \epsilon_1 + \frac{|v|^2}{E_1^{B\text{-}W}-\epsilon_2}$$

and likewise $$E_2^{B\text{-}W} = \epsilon_2 + \frac{|v|^2}{E_2^{B\text{-}W}-\epsilon_1}.$$

Thus multiplying these equations out we see that

$$E_{\substack{1\\2}}^{B\text{-}W} = \tfrac{1}{2}(\epsilon_1+\epsilon_2) \pm \tfrac{1}{2}\sqrt{(\epsilon_1-\epsilon_2)^2+4|v|^2}$$

$$= E_{\substack{1\\2}}$$ the exact solutions!!

In the degenerate $\epsilon_1=\epsilon_2=\epsilon$ limit

They are $E_{\substack{1\\2}} = \epsilon \pm |v|$, the exact result.