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Degenerate Perturbation Theory
(Corrected)

The treatment of degenerate perturbation theory presented in class is written out here in detail. The appendix presents the underlying algebraic mechanism on which perturbation theory is based.

1 General framework and strategy

We begin with a Hamiltonian H which can be decomposed into an operator H_0 with known eigenvectors and eigenvalues and a second perturbing piece V:

$$H = H_0 + \lambda V. \tag{1}$$

The eigenvectors and eigenvalues of H and H_0 are defined as follows:

$$\begin{aligned} H_0|\phi_n\rangle &= E_n^{(0)}|\phi_n\rangle & (2)\\ H|\psi_n\rangle &= E_n|\psi_n\rangle. & (3) \end{aligned}$$

For simplicity we will assume that all of the eigenvalues $E_n^{(0)}$ are distinct with the exception of a group of N_{deg} vectors which share the same eigenvalue $E_n^{(0)} = E_{\text{deg}}^{(0)}$. We will label these N_{deg} degenerate eigenvectors as $\{|\phi_{n_i}\rangle\}_{1\le i\le N_{\text{deg}}}$ and define the set made up of the N_{deg} indices of these degenerate states as $W_{\text{deg}} = \{n_i\}_{1\le i\le N_{\text{deg}}}$. We should recognize that there may be many possible choices for the basis of eigenvectors which lie in this N_{deg} subspace of degenerate states. However, this subspace itself is well-defined and is denoted V_{deg} as is the projection operator P_{deg} onto this subspace:

$$P_{\text{deg}} = \sum_{i=1}^{N_{\text{deg}}} |\phi_{n_i}\rangle\langle\phi_{n_i}|. \tag{4}$$

Our objective is to express the exact eigenvalues and eigenstates of H in terms of those of H_0 as a power series in the small parameter λ. In order to easily express such a relationship we need to coordinate the labeling of the

perturbed ($|\psi_n\rangle$) and unperturbed ($|\phi_n\rangle$) eigenstates. For $n \notin W_{\rm deg}$ this is easy. We simply use the label n for the perturbed $|\psi_n\rangle$ whose eigenvalue E_n obeys:

$$\lim_{\lambda\to 0} E(\lambda)_n = E_n^{(0)}. \tag{5}$$

Since each energy $E_n^{(0)}$ corresponds to a unique index n there is no ambiguity. However, for the $N_{\rm deg}$ perturbed eigenstates whose energies approach $E_{\rm deg}^{(0)}$ as $\lambda \to 0$ there is no guarantee that their $\lambda \to 0$ limit will match up with a particular unperturbed eigenstate $|\phi_n\rangle$. In general we expect that if we were to label the $N_{\rm deg}$ states whose energies approach $E_{\rm deg}^{(0)}$ as $\{|\psi_{n_i}\rangle\}_{1\le i\le N_{\rm deg}}$, we would find:

$$\lim_{\lambda\to 0} |\psi_{n_i}\rangle = \sum_{j=1}^{N_{\rm deg}} C_{ji} |\phi_{n_j}\rangle. \tag{6}$$

Later in our procedure we will go back and redefine the unperturbed states $|\phi_{n_i}\rangle$ so that the C matrix above is the unit matrix: $C_{ji} = \delta_{ij}$ which implies a smooth limit as $\lambda \to 0$ relating our $|\psi_n\rangle$ and $|\phi_n\rangle$, consistent with the perturbative expansion that we were able to derive in the case of no degeneracy. However, at present we do not have enough information to make this redefinition of the $|\phi_{n_i}\rangle$ states and must take a less convenient approach in order to make an expansion in λ possible.

We introduce a new basis for the $N_{\rm deg}$-dimensional subspace spanned by the perturbed eigenvectors $|\psi_{n_i}\rangle$, denoted $|\widetilde{\psi}_{n_i}\rangle$ which are no longer eigenvectors of H but instead obey the conditions:

$$\lim_{\lambda\to 0} |\widetilde{\psi}_{n_i}\rangle = |\phi_{n_j}\rangle \tag{7}$$

$$\langle\widetilde{\psi}_{n_i}|\phi_{n_j}\rangle \quad \text{is real and positive if } i = j \text{ and vanishes if } i \neq j. \tag{8}$$

These conditions are analogues of our standard condition that $\langle\phi_n|\psi_n\rangle$ is real and positive, needed to define the phase of the perturbed states $|\psi_n\rangle$. For simplicity of notation we will also define:

$$|\widetilde{\psi}_n\rangle = |\psi_n\rangle \tag{9}$$

when $n \notin W_{\rm deg}$. We will learn more about the relationship between the two sets of states $|\widetilde{\psi}_{n_i}\rangle$ and $|\phi_{n_i}\rangle$ for $1 \le i \le N_{\rm deg}$ as we develop the perturbation series which expresses the former in terms of the latter.

Our new states $|\widetilde{\psi}_{n_i}\rangle$ are now easily related to our unperturbed states and "almost" diagonalize H:

$$H|\widetilde{\psi}_n\rangle = \sum_{n'} E_{nn'}|\widetilde{\psi}_{n'}\rangle, \tag{10}$$

where

$$E_{nn'} = \begin{cases} \delta_{nn'}E_n & n \text{ or } n' \notin W_{\rm deg} \\ E_{nn'} & \text{otherwise} \end{cases} \tag{11}$$

Now we have a problem that can be solved in perturbation theory and which has reduced H to a matrix which is entirely diagonal except for a finite $N_{\rm deg} \times N_{\rm deg}$ block which must be diagonalized by hand. We will now show how the states $|\widetilde{\psi}_n\rangle$ and the nearly diagonal matrix $E_{nn'}$ can be worked out to first and second order in λ. The final diagonalization of the $N_{\rm deg} \times N_{\rm deg}$ matrix $E_{n_i n_j}$ must be carried out by some method other than perturbation theory.

Just as in the non-degenerate case we start with the eigenvalue equation, Eq. (10), take its matrix element on the left with $\langle\phi_n|$ and insert a sum over a complete set of unperturbed states between $(H + \lambda V)$ and $|\widetilde{\psi}_n\rangle$:

$$\langle\phi_{n'}|\Big(H_0 + \lambda V\Big)\Big(\sum_{n''}|\phi_{n''}\rangle\langle\phi_{n''}|\Big)|\widetilde{\psi}_n\rangle = \sum_{n''}\langle\phi_{n'}|\widetilde{\psi}_{n''}\rangle E_{n''n}. \tag{12}$$

Next we introduce expansions in λ for both $E_{n'n}$ and $\langle\phi_{n'}|\widetilde{\psi}_n\rangle = S_{n'n}$:

$$E_{n'',n} = \delta_{n'n}E^{(0)}_n + \lambda E^{(1)}_{n'n} + \lambda^2 E^{(2)}_{n'n} \tag{13}$$

$$\langle\phi_{n'}|\widetilde{\psi}_n\rangle = \delta_{n'n} + \lambda S^{(1)}_{n'n} + \lambda^2\lambda S^{(2)}_{n'n} \tag{14}$$

and substitute them into Eq. (12). Note that the matrices $E^{(1)}_{n'n}$ and $E^{(2)}_{n'n}$ will be diagonal except for the same $N_{\rm deg} \times N_{\rm deg}$ non-diagonal block which appears in $E_{n'n}$. We obtain the following equation:

$$\sum_{n''}\Big(E^{(0)}_{n'}\delta_{n'n''} + \lambda V_{n'n''}\Big)\Big(\delta_{n''n} + \lambda S^{(1)}_{n''n} + \lambda^2 S^{(2)}_{n''n}\Big) \tag{15}$$

$$= \sum_{n''}\Big(\delta_{n'n''} + \lambda S^{(1)}_{n'n''} + \lambda^2 S^{(2)}_{n'n''}\Big)\Big(\delta_{n''n}E^{(0)}_n + \lambda E^{(1)}_{n''n} + \lambda^2 E^{(2)}_{n''n})\Big).$$

2 First-order degenerate perturbation theory

We can next determine the matrices $S^{(1)}_{nn'}$ and $E^{(1)}_{nn'}$ by starting with Eq. (15) and collecting all terms that are first order in λ:

$$E^{(0)}_{n'} S^{(1)}_{n'n} + V_{n'n} = E^{(1)}_{n'n} + S^{(1)}_{n'n} E^{(0)}_{n}. \tag{16}$$

If either n or n' are not in the set $W_{\rm deg}$ of degenerate states, then the consequences are exactly as we found in non-degenerate perturbation theory. For $n \neq n'$ this equation can be solved for $S^{(1)}_{n'n}$ without any need for a non-zero off-diagonal element $E^{(1)}_{n'n}$. When $n = n'$, $E^{(1)}_{nn}$ is determined and $S^{(1)}_{nn}$ is left unconstrained. However, as in the non-degenerate case our condition ${\rm Im}(S^{(1)}_{nn})$ and the unit norm of the state $|\psi_n\rangle$ combine to determine $S^{(1)}_{nn} = 0$. Thus, to first order in λ and for either $n \notin W_{\rm deg}$ or $n' \notin W_{\rm deg}$ we have:

$$E^{(1)}_{n'n} = \delta_{n'n} V_{nn} \tag{17}$$

$$S^{(1)}_{n'n} = \frac{V_{n'n}}{E^{(0)}_{n} - E^{(0)}_{n'}}. \tag{18}$$

For both $n = n_i$ and $n' = n_j$ in $W_{\rm deg}$, then $S^{(1)}_{n_i n_j}$ cancels between the left and right sides of Eq. (16) and we are left with a formula for which there is a non-diagonal matrix $E^{(1)}_{n_i n_j}$ connecting degenerate states:

$$E^{(1)}_{n_i n_j} = V_{n_i n_j} \tag{19}$$

and through first order the matrix $E_{n'n} = \langle \widetilde{\psi}_{n'} | H | \widetilde{\psi}_n \rangle$ is given by:

$$E_{n'n} = \delta_{n'n} E^{(0)}_{n} + \lambda E^{(1)}_{n'n}, \tag{20}$$

where $E^{(1)}_{n'n}$ is a diagonal matrix with diagonal element V_{nn} when either n or n' lies outside of $W_{\rm deg}$ while if $n, n' \in W_{\rm deg}$ then $E^{(1)}_{n'n}$ is the $N_{\rm deg} \times N_{\rm deg}$ matrix $V_{n'n}$. The last step is to perform a unitary transformation on the original, $N_{\rm deg}$, unperturbed vectors $|\phi_{n_i}\rangle_{1 \leq i \leq N_{\rm deg}}$ to diagonalize this $N_{\rm deg} \times N_{\rm deg}$ matrix $V_{n_i n_j}$. To avoid making the notation excessively complex, we will use the same notation, $|\phi_{n_i}\rangle_{1 \leq i \leq N_{\rm deg}}$, for this new choice of the degenerate, unperturbed eigenvectors $|\phi_{n_i}\rangle$.

This choice ensures that the matrix $E^{(1)}_{nn'}$ is diagonal, the goal of first-order perturbation theory. This has been achieved by a more physical choice

of the unperturbed eigenvectors $|\phi_n\rangle$, informed by the properties of the perturbing matrix $V_{nn'}$. With this informed choice of the eigenstates $|\phi_{n_i}\rangle$ the corresponding perturbed states $|\widetilde{\psi}_{n_i}\rangle$ which lie in the subspace $V_{\rm deg}$ and which approaches the state $|\phi_{n_i}\rangle$ as $\lambda \to 0$, as in Eq. (8), are now also eigenstates of H to first order.

In the discussion of second order degenerate perturbation theory below we will assume that this diagonalization has been performed so that in our transformed basis:

$$E^{(1)}_{n_i n_j} = V_{n_i n_j} = V_{n_i n_i}\delta_{n_i n_j}. \tag{21}$$

for $1 \leq i, j \leq N_{\rm deg}$.

Because the matrix $S^{(1)}_{n_i n_j}$ drops out of Eq. (16), it has not been determined. For the first-order, non-degenerate case only $S^{(1)}_{nn}$ was left undetermined at this step. However, our phase conventions for the perturbed states $|\psi_n\rangle$ and the unit normalization of those states required $S^{(1)}_{nn} = 0$. The analogous choice is available here. As in the non-degenerate case we must ensure that our new states $|\widetilde{\psi}_n\rangle$ are orthonormal which will be achieved if the transformation matrix S is unitary:

$$\sum_{n''} S_{n'n''}\left(S^\dagger\right)_{n''n} = \delta_{n'n}. \tag{22}$$

To first order this equation becomes a condition on $S^{(1)}_{n'n}$:

$$S^{(1)}_{n'n} + \left(S^{(1)^\dagger}\right)_{n'n} = 0. \tag{23}$$

One can see that this equation is automatically obeyed if n or n' are not elements of $W_{\rm deg}$ but must be imposed if both n and n' belong to $W_{\rm deg}$:

$$S^{(1)}_{n_i n_j} + \left(S^{(1)^\dagger}\right)_{n_i n_j} = 0. \tag{24}$$

Thus, we are permitted to use an arbitrary anti-hermitian matrix $S^{(1)}_{n_i n_j}$, if we wish. This amounts to permitting a first-order unitary rotation among our $N_{\rm deg}$ degenerate states $|\phi_{n_i}\rangle$. Since such a first order shift would serve no purpose, we adopt this simplest convention

$$S^{(1)}_{n_i n_j} = 0 \quad 1 \leq i, j \leq N_{\rm deg}. \tag{25}$$

This is precisely the first-order component of the condition which we imposed when defining the states $|\widetilde{\psi}_{n_i}\rangle$ in Eq. (8)

Finally we should observe that the new, first order eigenstates $|\psi_n\rangle$ determined by $S^{(1)}$ when n is not in the degenerate set $W_{\rm deg}$ are actually independent of the basis used for the degenerate set of states $\{|\phi_{n_i}\rangle\}_{n_i \in W_{\rm deg}}$. so that our first-order expression for these states is unaffected by any final diagonalization steps taken in this subspace to deal with the first-order degeneracy:

$$\begin{aligned} |\psi_n\rangle &= |\psi_n\rangle + \sum_{n'} |\phi_{n'}\rangle S^{(1)}_{n'n} \qquad (26) \\ &= |\psi_n\rangle + \sum_{n'} |\phi_{n'}\rangle \frac{V_{n'n}}{E^{(0)}_n - E^{(0)}_{n'}} \\ &= |\psi_n\rangle + \sum_{n' \notin W_{\rm deg}} |\phi_{n'}\rangle \frac{V_{n'n}}{E^{(0)}_n - E^{(0)}_{n'}} + \frac{1}{E^{(0)}_n - E^{(0)}_{\rm deg}} \sum_{n' \in W_{\rm deg}} |\phi_{n'}\rangle V_{n'n} \\ &= |\psi_n\rangle + \sum_{n' \notin W_{\rm deg}} |\phi_{n'}\rangle \frac{V_{n'n}}{E^{(0)}_n - E^{(0)}_{n'}} + \frac{1}{E^{(0)}_n - E^{(0)}_{\rm deg}} P_{\rm deg} V |\phi_n\rangle. \end{aligned}$$

3 Second-order degenerate perturbation theory

Extending this procedure to second order is a simple repetition of the steps just taken. However, the off-diagonal elements of $E_{n'n}$ which appear will now be second order terms — terms which must be computed and are less obvious than the simple off-diagonal elements of $V_{n'n}$. Just as before we start with our general equation, Eq (15) and pick out the terms which are of order λ^2:

$$E^{(0)}_{n'} S^{(2)}_{n'n} + \sum_{n''} V_{n'n''} S^{(1)}_{n''n} = E^{(2)}_{n'n} + \sum_{n''} S^{(1)}_{n'n''} E^{(1)}_{n''n} + S^{(2)}_{n'n} E^{(0)}_n. \qquad (27)$$

Just as in the first-order case, this is easily solved for $S^{(2)}_{n'n}$ and the diagonal, second order energy matrix $E^{(2)}_{n'n}$ determined if either n' or n is not an element

of $W_{\rm deg}$:

$$E^{(2)}_{n'n} = \delta_{n'n}\sum_{n''} V_{nn''}S^{(1)}_{n''n} = \delta_{n'n}\sum_{n''\neq n}\frac{V_{nn''}V_{n''n}}{E^{(0)}_n - E^{(0)}_{n''}} \tag{28}$$

$$S^{(2)}_{n'n} = \frac{1}{E^{(0)}_n - E^{(0)}_{n'}}\sum_{n''}\Big(V_{n'n''}S^{(1)}_{n''n} - S^{(1)}_{n'n''}E^{(1)}_{n''n}\Big) \tag{29}$$

$$= \frac{1}{E^{(0)}_n - E^{(0)}_{n'}}\left(\sum_{n''\neq n} V_{n'n''}\frac{V_{n''n}}{E^{(0)}_n - E^{(0)}_{n''}} - \frac{V_{n'n}}{E^{(0)}_n - E^{(0)}_{n'}}V_{nn}\right).$$

For the case when both $n' = n_i$ and $n = n_j$ lie in the degenerate set $W_{\rm deg}$, the second order matrices $S^{(2)}_{n_in_j}$ in Eq. (27) will cancel between the left- and right-hand sides and cannot be used to remove the off-diagonal terms. In this case Eq. (27) can be written as an equation for the $N_{\rm deg}\times N_{\rm deg}$, second-order matrix $E^{(2)}_{n_in_j}$:

$$E^{(2)}_{n_in_j} = \sum_{n''}\Big\{V_{n_in''}S^{(1)}_{n''n_j} - S^{(1)}_{n_in''}E^{(1)}_{n''n_j}\Big\} \tag{30}$$

$$= \sum_{n''} V_{n_in''}S^{(1)}_{n''n_j} - S^{(1)}_{n_in_j}V_{n_jn_j} \tag{31}$$

using $n' = n_i$ and $n = n_j$ with $1 \le i, j \le N_{\rm deg}$ and assuming that the first order matrix $E^{(1)}_{n''n_j}$ has already been diagonalized as part of the first-order solution.

We should consider three possibilities:

1. There are no second-order terms connecting the degenerate states. In this case the full matrix $E^{(2)}_{n'n}$ will have only diagonal terms and we have succeeded in diagonalizing H through second order in λ.

2. The degeneracy has been lifted at first order. In this case all of the elements of the now diagonal matrix $V_{n_in_j}$ are distinct so $V_{n_in_i} = V_{n_jn_j}$ implies that $i = j$. In this case the fundamental problem posed by degenerate perturbation theory, how to determine which combination of the unperturbed states $|\phi_{n_i}\rangle$ correspond to the perturbed states has been resolved and we should expect no further difficulties. In fact, this is the case because although we cannot use the matrix $S^{(2)}_{n_in_j}$ to remove the second-order off-diagonal terms which have appeared, we can make

use of the first order matrix $S^{(1)}_{n_i n_j}$ (which so far has not been used and simply set to zero for convenience) to remove the off-diagonal elements of $E^{(2)}_{n_i n_j}$. That this is possible can be seen by rewriting Eq. (31) to show explicitly these so far unconstrained elements of $S^{(1)}_{n_i n_j}$:

$$E^{(2)}_{n_i n_j} = \sum_{n' \notin W_{\rm deg}} V_{n_i n'} S^{(1)}_{n' n_j} + V_{n_i n_i} S^{(1)}_{n_i n_j} - S^{(1)}_{n_i n_j} V_{n_j n_j}. \tag{32}$$

Since the matrix element $S^{(1)}_{n_i n_j}$ has not previously been constrained and was set to zero only for simplicity, it can now be chosen to make this off-diagonal term $E^{(2)}_{n_i n_j} = 0$:

$$\begin{aligned} S^{(1)}_{n_i n_j} &= \frac{1}{V_{n_j n_j} - V_{n_i n_i}} \sum_{n' \notin W_{\rm deg}} V_{n_i n'} S^{(1)}_{n' n_j} & (33) \\ &= \frac{1}{V_{n_j n_j} - V_{n_i n_i}} \sum_{n' \notin W_{\rm deg}} V_{n_i n'} \frac{V_{n' n_j}}{E^{(0)}_{n_j} - E^{(0)}_{n'}}. & (34) \end{aligned}$$

This is indeed first-order in V as required and has the form of an interesting ratio of a second-order divided by a first-order piece. Thus, if unique, non-degenerate states are resolved at first order in λ then no further difficulties arise at order λ^2. The equations which must be obeyed to make $E^{(2)}_{n_i n_j}$ diagonal can be solved and end up determining the previous unspecified coefficients $S^{(1)}_{n_i n_j}$.

3. The $N_{\rm deg}$ degenerate states $|\phi_{n_i}\rangle$ remain degenerate at first order. Under these circumstances both the matrix elements $S^{(1)}_{n_i n_j}$ and $S^{(2)}_{n_i n_j}$ cancel from the expression giving $E^{(2)}_{n_i n_j}$ which implies that no choices remain to remove the off-diagonal terms from $E^{(2)}_{n_i n_j}$. As a result to second order in perturbation theory the matrix

$$E_{n' n} = \delta_{n' n} \left(E^{(0)}_n + \lambda V_{nn} \right) + \lambda E^{(2)}_{n' n}, \tag{35}$$

where $E^{(2)}_{n' n}$ is diagonal except for the $N_{\rm deg} \times N_{\rm deg}$ block:

$$E^{(2)}_{n_i n_j} = \sum_{n' \notin W_{\rm deg}} V_{n_i n'} S^{(1)}_{n' n_j} = \sum_{n' \notin W_{\rm deg}} V_{n_i n'} \frac{V_{n' n_j}}{E^{(0)}_{n_j} - E^{(0)}_{n'}} \tag{36}$$

which must be diagonalized explicitly, without the further use of perturbation theory. **Equation (36) gives the standard, $N_{\rm deg} \times N_{\rm deg}$ matrix that must be diagonalized for a correct calculation of the second order energy in this third case, where degenerate second-order perturbation theory is needed.**

Finally we should observe that the second order energy shift $E_n^{(2)}$ given in Eq. (28) for states $|\phi_n\rangle$ where n is not in the degenerate set $W_{\rm deg}$ are actually independent of the basis used for the degenerate set of states $\{|\phi_{n_i}\rangle\}_{n_i \in W_{\rm deg}}$ so these energies are unaffected by any final diagonalization steps taken in this subspace to deal with the second order degeneracy:

$$E_n^{(2)} = \sum_{n'' \neq n} \frac{V_{nn''}V_{n''n}}{E_n^{(0)} - E_{n''}^{(0)}} \tag{37}$$

$$= \sum_{\substack{n'' \neq n \\ n'' \notin W_{\rm deg}}} \frac{V_{nn''}V_{n''n}}{E_n^{(0)} - E_{n''}^{(0)}} + \sum_{\substack{n'' \neq n \\ n'' \in W_{\rm deg}}} \frac{V_{nn''}V_{n''n}}{E_n^{(0)} - E_{n''}^{(0)}} \tag{38}$$

$$= \sum_{\substack{n'' \neq n \\ n'' \notin W_{\rm deg}}} \frac{V_{nn''}V_{n''n}}{E_n^{(0)} - E_{n''}^{(0)}} + \frac{\langle\phi_n|VP_{\rm deg}V|\phi_n\rangle}{E_n^{(0)} - E_{\rm deg}^{(0)}}. \tag{39}$$

A How Perturbation Theory Works

A.1 The strategy of perturbation theory

The basic algebraic structure upon which perturbation theory is built is the problem of diagonalizing a simple 2×2 matrix with small off-diagonal matrix elements, which can be removed by a small rotation. Consider a pair of states $|\phi_n\rangle$ and $|\phi_{n'}\rangle$ and the 2×2 matrix

$$\begin{pmatrix} \langle\phi_{n'}|H_0+V|\phi_{n'}\rangle & \langle\phi_{n'}|H_0+V|\phi_n\rangle \\ \langle\phi_n|H_0+V|\phi_{n'}\rangle & \langle\phi_n|H_0+V|\phi_n\rangle \end{pmatrix} = \begin{pmatrix} E_{n'}^{(0)} + V_{n'n'} & V_{n'n} \\ V_{nn'} & E_n^{(0)} + V_{nn} \end{pmatrix}.$$

For simplicity we have now removed the parameter λ by setting it to one so that we are now counting powers of V. If we make a small rotation that mixes the states $|\phi_n\rangle$ and $|\phi_{n'}\rangle$ and defines a new basis:

$$|\chi_n\rangle = |\phi_n\rangle + \varepsilon_{n'n}^{(1)}|\phi_{n'}\rangle \tag{40}$$

$$|\chi_{n'}\rangle = |\phi_{n'}\rangle - \varepsilon_{n'n}^{(1)\,*}|\phi_n\rangle, \tag{41}$$

these new states will also be orthonormal through first order in the small complex parameter $\varepsilon^{(1)}_{n'n}$. This rotation will spoil the diagonal character of H_0 and generate two off-diagonal terms so in this new basis H_0+V becomes:

$$\begin{pmatrix} \langle\chi_{n'}|H_0+V|\chi_{n'}\rangle & \langle\chi_{n'}|H_0+V|\chi_n\rangle \\ \langle\chi_n|H_0+V|\chi_{n'}\rangle & \langle\chi_n|H_0+V|\chi_n\rangle \end{pmatrix} = \tag{42}$$
$$\begin{pmatrix} E^{(0)}_{n'}+V_{n'n'} & (E^{(0)}_{n'}-E^{(0)}_n)\varepsilon^{(1)}_{n'n}+V_{n'n} \\ (E^{(0)}_{n'}-E^{(0)}_n)\varepsilon^{(1)\,*}_{nn'}+V_{nn'} & E^{(0)}_n+V_{nn} \end{pmatrix}.$$

where we are now treating both V and $\varepsilon^{(1)}_{n'n}$ as small and working to first order in both. The off-diagonal terms are proportional to the energy difference $E^{(0)}_{n'}-E^{(0)}_n$ because if the energies $E^{(0)}_{n'}$ and $E^{(0)}_n$ were equal we would be rotating the identity matrix which would remain the identity matrix with no off-diagonal terms.

The entire strategy of non-degenerate perturbation theory is simply to choose $\varepsilon^{(1)}_{n'n}$ to remove the off-diagonal elements of V:

$$\varepsilon^{(1)}_{n'n} = \frac{V_{n'n}}{E^{(0)}_n - E^{(0)}_{n'}}, \tag{43}$$

our standard first-order perturbation theory result. While we have focused on a single 2×2 block, this strategy will remove every off-diagonal element of V since to first order in V these individual rotations will not interfere with each other and will separately remove each off-diagonal element. (Note, here the coefficient $\varepsilon^{(1)}_{n'n}$ is the same as the usual quantity $\lambda S^{(1)}_{n'n}$ of Eq. (18). We chose to introduce a new symbol in the current session to make it clear that this discussion was independent of our earlier treatment.)

In this simple way we have removed the off-diagonal matrix elements of V. However, in the process we have generated a large number of second-order off-diagonal terms so that in this new basis H_0+V is diagonal only to first order. We can then follow the same strategy and make further small rotations between each pair, now with parameters $\varepsilon^{(2)}_{n'n}$ that are second order in V and chosen to remove these second order terms in exactly the same way that the $\varepsilon^{(1)}_{n'n}$ above removed the first order terms. We can then continue in exactly this way to remove to any desired order the off-diagonal terms in H_0+V, provided such terms connect non-degenerate states.

While this approach gives considerable insight into the workings of perturbation theory and a very clear idea of the off-diagonal terms that must

eliminated "by-hand" when this approach cannot be used because of degeneracy, it is more complex in practice than the approach worked out in this note. Never-the-less, it may be instructive to see how this works at second order.

A.2 This strategy applied to second order

We use the matrix S defined in Eq. (14) and then multiply the matrix Eq. (15) from the left by S^{-1} to obtain:

$$\sum_{n_1 n_2} \left(S^{-1}\right)_{n' n_1} \left(H_0 + \lambda V\right)_{n_1 n_2} S_{n_2 n} = E_{n' n} \tag{44}$$

where the object is to choose the second-order term, $S^{(2)}$, in S to remove the second-order, off-diagonal terms in $E_{n'n}$ generated by the first-order rotation S^1. These off-diagonal terms in $E^{(2)}$ that must be removed by the choice of $S^{(2)}$ (or by hand in the case of degeneracy) can be worked out directly from Eq. (44). The first step is to evaluate S^{-1} to second order:

$$S^{-1} = \frac{1}{1 + \lambda S^{(1)} + \lambda^2 S^{(2)}} = 1 - \lambda S^{(1)} - \lambda^2 S^{(2)} + \lambda^2 \left(S^{(1)}\right)^2 \tag{45}$$

using the usual formula for a geometric series to second order. Collecting all of the second-order terms in Eq. (45) when evaluated between the states $|\phi_{n'}\rangle$ and $|\phi_n\rangle$ but not yet including the effects of $S^{(2)}$ we find:

$$\begin{aligned} E^{(2)}_{n'n} &= \left(-S^{(1)} V + S^{(1)} S^{(1)} H_0 + V S^{(1)} - S^{(1)} H_0 S^{(1)}\right)_{n'n} && (46) \\ &= -\sum_{n'' \neq n'} \frac{V_{n'n''}}{E^{(0)}_{n''} - E^{(0)}_{n'}} V_{n''n} + \sum_{n'' \neq n', n} \frac{V_{n'n''}}{E^{(0)}_{n''} - E^{(0)}_{n'}} \frac{V_{n''n}}{E^{(0)}_{n} - E^{(0)}_{n''}} E^{(0)}_n \\ &+ \sum_{n'' \neq n} V_{n'n''} \frac{V_{n''n}}{E^{(0)}_{n} - E^{(0)}_{n''}} - \sum_{n'' \neq n, n'} \frac{V_{n'n''}}{E^{(0)}_{n''} - E^{(0)}_{n'}} E^{(0)}_{n''} \frac{V_{n''n}}{E^{(0)}_{n} - E^{(0)}_{n''}}. && (47) \end{aligned}$$

While working with S^{-1} is more complicated than the presentation in class and earlier in this note, this equation can be simplified to give the same result. Sepcifically, the second and fourth terms in Eq. (47) can be combined and then used to cancel all but the $n'' = n$ part of the first term, leaving exactly the second-order, off-diagonal term which $S^{(2)}_{n'n}$ is chosen to cancel in

our usual treatment of Rayleigh-Schrödinger perturbation theory:

$$
\begin{aligned}
E^{(2)}_{n'n} &= -\sum_{n''\neq n'} \frac{V_{n'n''}}{E^{(0)}_{n''}-E^{(0)}_{n'}} V_{n''n} + \sum_{n''\neq n} V_{n'n''}\frac{V_{n''n}}{E^{(0)}_{n}-E^{(0)}_{n''}} \\
&\quad + \sum_{n''\neq n,n'} \frac{V_{n'n''}}{E^{(0)}_{n''}-E^{(0)}_{n'}}(E^{(0)}_{n}-E^{(0)}_{n''})\frac{V_{n''n}}{E^{(0)}_{n}-E^{(0)}_{n''}} \qquad (48) \\
&= \sum_{n''} V_{n'n''}\frac{V_{n''n}}{E^{(0)}_{n}-E^{(0)}_{n''}} - \frac{V_{n'n}}{E^{(0)}_{n}-E^{(0)}_{n'}} V_{nn} \qquad (49)
\end{aligned}
$$

This result for $E^{(2)}_{n'n}$ also agrees with that found in Eq. (36) since for the case where $|\phi_{n'}\rangle$ and $|\phi_n\rangle$ are degenerate, $S^{(1)}_{n_2 n_1} = 0$ and it is this term which produced the right hand term in Eq. (49), which is absent from Eq. (36).

We should observe that $E^{(2)}_{n'n}$ given by Eq. (49) is not hermitian as should be expected since our approximation for $S = 1 + \lambda S^{(1)}$ is not unitary at second order.