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The Case of Nearly Degenerate Levels

[Alternatively, the results of this section can also be used for precisely degenerate levels in case (3), when $H^{(1)}$ does not remove the degeneracy and hence does not give the *proper* or *stabilized* zeroth-order state vectors.]

If for some specific pair of levels, n and m, $(E_n^{(0)} - E_m^{(0)})$ is accidentally very small (the case of an accidental near degeneracy), particularly if $\langle m^{(0)}|H^{(1)}|n^{(0)}\rangle$ is of the same order of magnitude as $(E_n^{(0)} - E_m^{(0)})$, our perturbation theory formulae would give a very poor approximation for this pair of levels. A technique that can deal with this situation is the following: We shall make a unitary transformation on the original perturbed Hamiltonian, H, to transform it to a new Hamiltonian, H', to eliminate the off-diagonal matrix elements that connect the nearly degenerate levels to all other levels, or at least make these off-diagonal matrix elements small enough in orders of powers of λ, so they will not contribute to the energies of states n and m to some particular order in λ. An elegant way to achieve this follows in the next section.

A Perturbation Theory by Similarity Transformation

We shall try to find a unitary operator, U, generated by a hermitian operator, G, such that H is transformed into H'

$$H' = UHU^{\dagger} = U(H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \cdots)U^{\dagger}, \qquad \text{with} \quad U = e^{i\lambda G}, \quad (1)$$

where the parameter, λ, in U is the parameter of smallness in the perturbation expansion. (The eigenvalues of a hermitian operator are invariant to similarity transformations.) In particular, if we succeed in choosing a G such that the first-order matrix elements of H' connecting states n and m to states $k \neq n, m$ are all equal to zero, the 2×2 matrix for H' in the n, m subspace will give us the energies correct to order λ^2. The surviving off-diagonal matrix elements (of order λ^2) connecting states n and m to states $k \neq n, m$ would contribute to the energies E_n and E_m only through their squares, divided by zeroth-order energy differences. The strategy then will be to find a G with matrix elements such that $\langle k^{(0)}|H'^{(1)}|n^{(0)}\rangle = 0$, and $\langle k^{(0)}|H'^{(1)}|m^{(0)}\rangle = 0$ (with similar zeros for the transposed matrix elements of $H'^{(1)}$) for all $k \neq n, m$.

$$\begin{aligned} H' &= (1 + i\lambda G - \frac{\lambda^2}{2}G^2 + \cdots)(H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \cdots) \\ &\quad \times (1 - i\lambda G - \frac{\lambda^2}{2}G^2 + \cdots) \\ &= H^{(0)} + \lambda(H^{(1)} + i[G, H^{(0)}]) + \lambda^2(H^{(2)} + i[G, H^{(1)}] \\ &\qquad - \tfrac{1}{2}[G, [G, H^{(0)}]]) + \cdots \\ &= H^{(0)} + \lambda H'^{(1)} + \lambda^2 H'^{(2)} + \cdots \ . \end{aligned} \tag{2}$$

Now, we shall choose G such that, with $k \neq n, m$,

$$\begin{aligned} \langle k^{(0)}|H'^{(1)}|n^{(0)}\rangle &= \langle k^{(0)}|H^{(1)}|n^{(0)}\rangle + i\langle k^{(0)}|[G, H^{(0)}]|n^{(0)}\rangle = 0 \\ &= \langle k^{(0)}|H^{(1)}|n^{(0)}\rangle + i(E_n^{(0)} - E_k^{(0)})\langle k^{(0)}|G|n^{(0)}\rangle. \end{aligned} \tag{3}$$

With a similar relation for the km^{th} matrix element, this equation leads to

$$\begin{aligned} \langle k^{(0)}|G|n^{(0)}\rangle &= i\frac{\langle k^{(0)}|H^{(1)}|n^{(0)}\rangle}{(E_n^{(0)} - E_k^{(0)})}, \quad \langle k^{(0)}|G|m^{(0)}\rangle = i\frac{\langle k^{(0)}|H^{(1)}|m^{(0)}\rangle}{(E_m^{(0)} - E_k^{(0)})}, \\ \langle n^{(0)}|G|k^{(0)}\rangle &= i\frac{\langle n^{(0)}|H^{(1)}|k^{(0)}\rangle}{(E_k^{(0)} - E_n^{(0)})}, \quad \langle m^{(0)}|G|k^{(0)}\rangle = i\frac{\langle m^{(0)}|H^{(1)}|k^{(0)}\rangle}{(E_k^{(0)} - E_m^{(0)})}. \end{aligned} \tag{4}$$

All remaining matrix elements of G will be set equal to zero. In particular,

$$\langle n^{(0)}|G|n^{(0)}\rangle = \langle m^{(0)}|G|m^{(0)}\rangle = \langle n^{(0)}|G|m^{(0)}\rangle = 0. \tag{5}$$

Now,

$$\begin{aligned} &\langle n^{(0)}|H'^{(1)}|n^{(0)}\rangle = \langle n^{(0)}|H^{(1)}|n^{(0)}\rangle \\ &+ i\sum_{k\neq n,m}\Big[\langle n^{(0)}|G|k^{(0)}\rangle\langle k^{(0)}|H^{(0)}|n^{(0)}\rangle - \langle n^{(0)}|H^{(0)}|k^{(0)}\rangle\langle k^{(0)}|G|n^{(0)}\rangle\Big] \\ &= \langle n^{(0)}|H^{(1)}|n^{(0)}\rangle. \end{aligned} \tag{6}$$

Similarly,

$$\begin{aligned} \langle m^{(0)}|H'^{(1)}|m^{(0)}\rangle &= \langle m^{(0)}|H^{(1)}|m^{(0)}\rangle, \\ \langle n^{(0)}|H'^{(1)}|m^{(0)}\rangle &= \langle n^{(0)}|H^{(1)}|m^{(0)}\rangle. \end{aligned} \tag{7}$$

For

$$H'^{(2)} = H^{(2)} + i(GH^{(1)} - H^{(1)}G) - \frac{1}{2}\Big(G^2H^{(0)} - 2GH^{(0)}G + H^{(0)}G^2\Big), \tag{8}$$

let us first calculate the nm^{th} matrix element

$$\begin{aligned}
&\langle n^{(0)}|H'^{(2)}|m^{(0)}\rangle = \langle n^{(0)}|H^{(2)}|m^{(0)}\rangle \\
&+ i\sum_{k\neq n,m}\Big[\langle n^{(0)}|G|k^{(0)}\rangle\langle k^{(0)}|H^{(1)}|m^{(0)}\rangle - \langle n^{(0)}|H^{(1)}|k^{(0)}\rangle\langle k^{(0)}|G|m^{(0)}\rangle\Big] \\
&-\tfrac{1}{2}\sum_{k\neq n,m}\Big[\langle n^{(0)}|G|k^{(0)}\rangle\langle k^{(0)}|G|m^{(0)}\rangle\langle m^{(0)}|H^{(0)}|m^{(0)}\rangle \\
&-2\langle n^{(0)}|G|k^{(0)}\rangle\langle k^{(0)}|H^{(0)}|k^{(0)}\rangle\langle k^{(0)}|G|m^{(0)}\rangle \\
&+\langle n^{(0)}|H^{(0)}|n^{(0)}\rangle\langle n^{(0)}|G|k^{(0)}\rangle\langle k^{(0)}|G|m^{(0)}\rangle\Big] \\
&= \langle n^{(0)}|H^{(2)}|m^{(0)}\rangle + \sum_{k\neq n,m}\langle n^{(0)}|H^{(1)}|k^{(0)}\rangle\langle k^{(0)}|H^{(1)}|m^{(0)}\rangle\times \\
&\left[\left(\frac{1}{(E_n^{(0)}-E_k^{(0)})}+\frac{1}{(E_m^{(0)}-E_k^{(0)})}\right)-\tfrac{1}{2}\left(\frac{E_m^{(0)}-2E_k^{(0)}+E_n^{(0)}}{(E_n^{(0)}-E_k^{(0)})(E_m^{(0)}-E_k^{(0)})}\right)\right].
\end{aligned} \tag{9}$$

Now, using the trivial identity

$$\frac{1}{(E_n^{(0)}-E_k^{(0)})}+\frac{1}{(E_m^{(0)}-E_k^{(0)})}=\frac{(E_n^{(0)}+E_m^{(0)}-2E_k^{(0)})}{(E_n^{(0)}-E_k^{(0)})(E_m^{(0)}-E_k^{(0)})}, \tag{10}$$

and defining the average energy for the pair of levels $\bar{E}_{n,m}^{(0)} = \frac{1}{2}(E_n^{(0)}+E_m^{(0)})$, we obtain

$$\begin{aligned}
&\langle n^{(0)}|H'^{(2)}|m^{(0)}\rangle = \langle n^{(0)}|H^{(2)}|m^{(0)}\rangle \\
&+\sum_{k\neq n,m}\langle n^{(0)}|H^{(1)}|k^{(0)}\rangle\langle k^{(0)}|H^{(1)}|m^{(0)}\rangle\frac{(\bar{E}_{n,m}^{(0)}-E_k^{(0)})}{(E_n^{(0)}-E_k^{(0)})(E_m^{(0)}-E_k^{(0)})}.
\end{aligned} \tag{11}$$

By setting $m = n$ in this expression, we can also immediately get the matrix element $\langle n^{(0)}|H'^{(2)}|n^{(0)}\rangle$, and similarly by setting $n = m$, we get $\langle m^{(0)}|H'^{(2)}|m^{(0)}\rangle$. With these results, the 2×2 submatrix of H' connecting the two states $|n\rangle$ and $|m\rangle$ is

$$\begin{pmatrix} H'_{nn} & H'_{nm} \\ H'_{mn} & H'_{mm}\end{pmatrix},$$

where, with an obvious shorthand matrix notation for the matrix elements, we have (through second order)

$$\begin{aligned}
H'_{nn} &= E_n^{(0)} + \lambda H_{nn}^{(1)} + \lambda^2\left[H_{nn}^{(2)} + \sum_{k\neq n,m}\frac{|H_{kn}^{(1)}|^2}{(E_n^{(0)}-E_k^{(0)})}\right] \\
H'_{nm} &= \lambda H_{nm}^{(1)} + \lambda^2\left[H_{nm}^{(2)} + \sum_{k\neq n,m}\frac{H_{nk}^{(1)}H_{km}^{(1)}(\bar{E}_{n,m}^{(0)}-E_k^{(0)})}{(E_n^{(0)}-E_k^{(0)})(E_m^{(0)}-E_k^{(0)})}\right] \\
H'_{mn} &= \lambda H_{mn}^{(1)} + \lambda^2\left[H_{mn}^{(2)} + \sum_{k\neq n,m}\frac{H_{mk}^{(1)}H_{kn}^{(1)}(\bar{E}_{n,m}^{(0)}-E_k^{(0)})}{(E_n^{(0)}-E_k^{(0)})(E_m^{(0)}-E_k^{(0)})}\right] \\
H'_{mm} &= E_m^{(0)} + \lambda H_{mm}^{(1)} + \lambda^2\left[H_{mm}^{(2)} + \sum_{k\neq n,m}\frac{|H_{km}^{(1)}|^2}{(E_m^{(0)}-E_k^{(0)})}\right].
\end{aligned} \tag{12}$$

To get the energies to second order, it is now only necessary to diagonalize this 2×2 matrix, leading to

$$E = E_{\pm} = \frac{1}{2}\left((H'_{nn} + H'_{mm}) \pm \sqrt{(H'_{nn} - H'_{mm})^2 + 4|H'_{nm}|^2}\right). \tag{13}$$

This result is quite general. Note: If the two levels n and m are not nearly degenerate, the result applies for a *single* level, say, the n^{th} one, and in that case, we have simply regained the result of nondegenerate-level perturbation theory. The result also applies to a pair of exactly degenerate levels. In that case, with $\bar{E}^{(0)}_{nm} = E^{(0)}_n = E^{(0)}_m$, the off-diagonal matrix element has a term

$$\sum_{k \neq n,m} \frac{H^{(1)}_{nk} H^{(1)}_{km}}{(E^{(0)}_n - E^{(0)}_k)}.$$

This equation will be important in case (3), in which $H^{(1)}_{nm}$ is zero and does not remove the degeneracy in first order, and in the case in which $H^{(1)}$ does not lead to the *proper* zeroth-order state vectors. Finally, the diagonal and off-diagonal matrix elements given by eq. (12) can be used in the case in which the degeneracy or near degeneracy is greater than two-fold.

B An Example: Two Coupled Harmonic Oscillators with $\omega_1 \approx 2\omega_2$

Let us consider the Hamiltonian for two coupled nearly harmonic oscillators with cubic and quartic coupling terms

$$\begin{aligned} H &= \tfrac{1}{2}\hbar\omega_1(p_x^2 + x^2) + \tfrac{1}{2}\hbar\omega_2(p_y^2 + y^2) \\ &\quad + \lambda\hbar\omega_c xy^2 + \lambda^2(\hbar\omega_d x^4 + \hbar\omega_e y^4 + \hbar\omega_f x^2 y^2), \end{aligned} \tag{14}$$

where x, p_x, y, p_y, are dimensionless variables as for the 1-D oscillator. It is assumed $\omega_1 \approx 2\omega_2$. States with $|n_1 n_2\rangle$ are then nearly degenerate with states $|(n_1 - 1)(n_2 + 2)\rangle$. Using matrix elements of x, x^2, x^4 from earlier chapters, and combining these to yield, e.g.,

$$\langle (n_1 - 1)(n_2 + 2)|xy^2|n_1 n_2\rangle = \sqrt{\frac{n_1(n_2 + 1)(n_2 + 2)}{8}}, \tag{15}$$

we get, for the nearly degenerate levels $n_1 n_2 = 10$ and $n_1 n_2 = 02$, the 2×2 matrix for H':

$$\begin{aligned} H'_{10,10} &= \tfrac{3}{2}\hbar\omega_1 + \tfrac{1}{2}\hbar\omega_2 - \lambda^2 \frac{(\hbar\omega_c)^2}{\hbar\omega_1}\left(\frac{1}{8} + \frac{\omega_1}{2(\omega_1 + 2\omega_2)}\right), \\ &\quad + \lambda^2 \tfrac{1}{4}(15\hbar\omega_d + 3\hbar\omega_e + 3\hbar\omega_f), \\ H'_{10,02} &= H'_{02,10} = \tfrac{1}{2}\lambda\hbar\omega_c, \\ H'_{02,02} &= \tfrac{1}{2}\hbar\omega_1 + \tfrac{5}{2}\hbar\omega_2 - \lambda^2 \frac{(\hbar\omega_c)^2}{\hbar\omega_1}\left(\frac{25}{8} + \frac{3\omega_1}{2(\omega_1 + 2\omega_2)}\right), \end{aligned}$$

$$+ \lambda^2 \tfrac{1}{4}(3\hbar\omega_d + 39\hbar\omega_e + 5\hbar\omega_f). \tag{16}$$

In particular, in this special example, $H^{(1)}$ does not contribute a second-order term to H'_{nm}, but it does contribute to the two diagonal terms, via

$$\begin{aligned}
&\sum_{k_1k_2 \neq 10,02} \frac{|\langle k_1k_2|H^{(1)}|10\rangle|^2}{(E_{10}^{(0)} - E_{k_1k_2}^{(0)})} = \\
&\frac{|\langle 20|H^{(1)}|10\rangle|^2}{-\hbar\omega_1} + \frac{|\langle 22|H^{(1)}|10\rangle|^2}{(-\hbar\omega_1 - 2\hbar\omega_2)} + \frac{|\langle 00|H^{(1)}|10\rangle|^2}{\hbar\omega_1} \\
&= \frac{(\hbar\omega_c)^2}{\hbar\omega_1}\left(\frac{1}{4}\frac{1}{(-1)} + \frac{1}{8}\frac{1}{(+1)} + \frac{1}{2}\frac{\omega_1}{(-(\omega_1 + 2\omega_2))}\right)
\end{aligned} \tag{17}$$

and

$$\begin{aligned}
&\sum_{k_1k_2 \neq 10,02} \frac{|\langle k_1k_2|H^{(1)}|02\rangle|^2}{(E_{02}^{(0)} - E_{k_1k_2}^{(0)})} = \frac{|\langle 12|H^{(1)}|02\rangle|^2}{-\hbar\omega_1} + \frac{|\langle 14|H^{(1)}|02\rangle|^2}{(-\hbar\omega_1 - 2\hbar\omega_2)} \\
&= \frac{(\hbar\omega_c)^2}{\hbar\omega_1}\left(\frac{25}{8}\frac{1}{(-1)} + \frac{3}{2}\frac{\omega_1}{(-(\omega_1 + 2\omega_2))}\right).
\end{aligned} \tag{18}$$

This example has been chosen as a simplified model for a real near degeneracy. The linear symmetrical CO_2 molecule, with an O-C-O configuration, has three vibrational frequencies, an in-phase and an out-of-phase stretching of the two CO bonds with frequencies, named ω_1 and ω_3, and a two-fold degenerate oscillation in which the C atom moves in a direction perpendicular to the equilibrium line relative to the O–O group, where this two-fold degenerate frequency has been named ω_2. For CO_2, the three observed frequencies are

$$\frac{\hbar\omega_1}{hc} = 1351.2cm^{-1}, \qquad \frac{\hbar\omega_2}{hc} = 672.2cm^{-1}, \qquad \frac{\hbar\omega_3}{hc} = 2396.4cm^{-1}.$$

(In molecular spectroscopy, “frequencies” are usually given in “wavenumbers,” i.e., in cm^{-1}, in waves per centimeter.) Note that $\hbar\omega_1 - 2\hbar\omega_2 = 6.8cm^{-1}$. This difference is much less than the experimentally deduced coupling term $\frac{1}{2}\hbar\omega_c = 50cm^{-1}$. The problem of this near degeneracy was first solved by Fermi. The near degeneracy in CO_2 is known as the Fermi resonance. (Finally, we have made our simplified Hamiltonian such that $V(y) = +V(-y)$, so it mimicks the real potential of CO_2.)

Finally, we need to have a more explicit expression for the perturbed state vectors $|n\rangle$ and $|m\rangle$. We have converted $H|n\rangle$ and $H|m\rangle$ into $UH|n\rangle = UHU^{\dagger}(U|n\rangle)$ and $UH|m\rangle = UHU^{\dagger}(U|m\rangle)$, where we now have $H' = UHU^{\dagger}$ acting on $|n^{(0)}\rangle = U|n\rangle$ (similar for $U|m\rangle$). Thus, we have

$$|n\rangle = U^{-1}|n^{(0)}\rangle = (1 - i\lambda G - \frac{\lambda^2}{2}G^2)|n^{(0)}\rangle, \tag{19}$$

leading to

$$|n\rangle = |n^{(0)}\rangle - i\lambda \sum_{k \neq n,m} |k^{(0)}\rangle\langle k^{(0)}|G|n^{(0)}\rangle$$

$$
\begin{aligned}
&-\frac{\lambda^2}{2}\sum_{k\neq n,m}\Big(|n^{(0)}\rangle\langle n^{(0)}|G|k^{(0)}\rangle\langle k^{(0)}|G|n^{(0)}\rangle \\
&\qquad + |m^{(0)}\rangle\langle m^{(0)}|G|k^{(0)}\rangle\langle k^{(0)}|G|n^{(0)}\rangle\Big) \\
&= |n^{(0)}\rangle\left(1-\frac{\lambda^2}{2}\sum_{k\neq n,m}\frac{|\langle k^{(0)}|H^{(1)}|n^{(0)}\rangle|^2}{(E_n^{(0)}-E_k^{(0)})^2}\right) \\
&+ |m^{(0)}\rangle\left(-\frac{\lambda^2}{2}\sum_{k\neq n,m}\frac{\langle m^{(0)}|H^{(1)}|k^{(0)}\rangle\langle k^{(0)}|H^{(1)}|n^{(0)}\rangle}{(E_n^{(0)}-E_k^{(0)})(E_m^{(0)}-E_k^{(0)})}\right) \\
&+ \lambda\sum_{k\neq n,m}|k^{(0)}\rangle\frac{\langle k^{(0)}|H^{(1)}|n^{(0)}\rangle}{(E_n^{(0)}-E_k^{(0)})},
\end{aligned}
\tag{20}
$$

with a similar expression for $|m\rangle$. The final expression for the eigenvectors associated with the energy eigenstates $|E_{\pm}\rangle$ of eq. (13) will be

$$
\begin{aligned}
|E_+\rangle &= c|n\rangle + s|m\rangle, \\
|E_-\rangle &= -s|n\rangle + c|m\rangle,
\end{aligned}
\tag{21}
$$

$$
\text{with}\quad \frac{c}{s} = \frac{H'_{nm}}{(E_+ - H'_{nn})}, \qquad\qquad \text{with}\quad c^2+s^2=1. \tag{22}
$$