23

Perturbation Theory for Degenerate Levels

A Diagonalization of $H^{(1)}$: Transformation to Proper Zeroth-Order Basis

Assume the eigenvector for the energy state with eigenvalue E_n is degenerate; i.e., assume g_n independent eigenvectors exist such that

$$H^{(0)}|nr^{(0)}\rangle = E_n^{(0)}|nr^{(0)}\rangle, \qquad \text{with} \quad r = 1, 2, \dots, g_n, \tag{1}$$

where the label r may just be an ordinal label identifying the different eigenvectors, or it may be a shorthand notation for additional quantum numbers. Clearly, our previous method might lead to difficulties, because now zeros could be in the energy denominators $(E_n^{(0)} - E_k^{(0)})$. A state $|k^{(0)}\rangle$ different from $|nr^{(0)}\rangle$ could now include a state with the same zeroth-order energy. Note, however, if $H^{(1)}$ is made diagonal within the g_n-dimensional subspace, $|nr^{(0)}\rangle$, with $r = 1, 2, \dots, g_n$, this difficulty will never arise. Therefore, the first step of the perturbation expansion will involve a transformation from the subbasis $|nr^{(0)}\rangle$ to the new subbasis $|nr'^{(0)}\rangle$, with

$$|nr'^{(0)}\rangle = \sum_{r=1}^{g_n} |nr^{(0)}\rangle\langle nr^{(0)}|nr'^{(0)}\rangle = \sum_{r=1}^{g_n} |nr^{(0)}\rangle c_r, \tag{2}$$

such that

$$\langle ns'^{(0)}|H^{(1)}|nr'^{(0)}\rangle = \delta_{rs} E_{nr'}^{(1)}. \tag{3}$$

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Rewriting the first-order equation of the perturbation expansion for the transformed state $|nr'^{(0)}\rangle$ yields

$$(E_n^{(0)} - H^{(0)})|nr'^{(1)}\rangle = (H^{(1)} - E_n^{(1)})|nr'^{(0)}\rangle. \tag{4}$$

Left-multiplying by $\langle nr^{(0)}|$ leads to a zero for the left-hand side of this equation, so

$$\langle nr^{(0)}|H^{(1)}|nr'^{(0)}\rangle - E_n^{(1)}\langle nr^{(0)}|nr'^{(0)}\rangle = 0. \tag{5}$$

Introducing the unit operator $\sum_s |ns^{(0)}\rangle\langle ns^{(0)}|$ for the subspace in question, we can transform this equation into

$$\sum_{s=1}^{g_n}\langle nr^{(0)}|H^{(1)}|ns^{(0)}\rangle\langle ns^{(0)}|nr'^{(0)}\rangle = E_n^{(1)}\sum_{s=1}^{g_n}\delta_{rs}\langle ns^{(0)}|nr'^{(0)}\rangle, \tag{6}$$

or, in shorthand form, with $\langle ns^{(0)}|nr'^{(0)}\rangle \equiv c_s$,

$$\sum_s^{g_n}(H_{rs}^{(1)} - E_n^{(1)}\delta_{rs})c_s = 0, \qquad \text{with} \quad r = 1, \ldots, g_n. \tag{7}$$

This system of g_n linear equations will have a solution for the c_s if and only if the determinant of the coefficients is equal to zero

$$|H_{rs}^{(1)} - E_n^{(1)}\delta_{rs}| = 0. \tag{8}$$

This equation leads to an equation of degree g_n in the unknown $E_n^{(1)}$ with g_n solutions $E_{nr'}^{(1)}$, such that

$$H^{(1)}|nr'^{(0)}\rangle = E_{nr'}^{(1)}|nr'^{(0)}\rangle, \qquad \text{with} \quad |nr'^{(0)}\rangle = \sum_s |ns^{(0)}\rangle c_s. \tag{9}$$

The first task in the case of degenerate-level perturbation theory then is to find those linear combinations of the zeroth-order eigenvectors $|ns^{(0)}\rangle$ that diagonalize $H^{(1)}$. These so-called *proper* or *stabilized* zeroth-order eigenvectors will be the basis for the subsequent steps in the perturbation expansion. Three possibilities need to be considered.

B Three Cases of Degenerate Levels

Case (1): The initial basis $|nr^{(0)}\rangle$ may already be such that $H^{(1)}$ is diagonal in this basis. (If higher order terms exist, such as $H^{(2)}$, we assume they are also diagonal in this basis.) This may not be such a fortuitous accident. Often, we choose the initial basis to be adapted to the symmetry of the problem. Both $H^{(0)}$ and $H^{(1)}$ may have symmetries that naturally lead to a *proper* choice of basis. The choice of this *proper* or *symmetry-adapted* basis may obviate the first step in degenerate-level perturbation theory, the diagonalization of $H^{(1)}$ in the initial zeroth-order basis. Effectively, therefore, such a case can be treated by nondegenerate perturbation theory.

Other cases now exist in which the nondegenerate perturbation theory formulae of Chapter 21 are sufficient to some order in the parameter of smallness, λ. For example, suppose two (or more) degenerate states $|nr^{(0)}\rangle$ and $|ns^{(0)}\rangle$ are not connected with each other through second order. Assume they are connected with each other only in third order, either through the action of $H^{(1)}$ three times, or through terms such as

$$\langle ns^{(0)}|H^{(1)}|n''u^{(0)}\rangle\langle n''u^{(0)}|H^{(1)}|n't^{(0)}\rangle\langle n't^{(0)}|H^{(1)}|nr^{0)}\rangle$$

in the perturbation expansion (or similar terms combining a single action of both $H^{(1)}$ and $H^{(2)}$). In that case, if we are interested only in second-order corrections to the energy, the degenerate states $|nr^{(0)}\rangle$ and $|ns^{(0)}\rangle$ are effectively unconnected in second order and the nondegenerate perturbation theory formulae of Chapter 21 apply.

Case (2): The diagonalization of $H^{(1)}$ in the initial zeroth-order basis may lead to a set of g_n-distinct eigenvalues $E^{(1)}_{nr'}$, with $E^{(1)}_{nr'} \neq E^{(1)}_{ns'}$, for $r \neq s$. In this case, the subsequent steps in the perturbation expansion closely parallel those for nondegenerate-level perturbation theory.

Case (3): The diagonalization of $H^{(1)}$ may not remove the zeroth-order degeneracy completely. In this case, a special treatment is necessary. This treatment is similar to that discussed in a next chapter for two (or several) nearly (or precisely) degenerate levels, the toughest of all cases. Again, this case is not as uncommon as might have been thought. For example, the symmetries of $H^{(0)}$ and $H^{(1)}$ could be such that all matrix elements of $H^{(1)}$ are zero in the $|nr^{(0)}\rangle$ sub-basis. Perhaps the $|nr^{(0)}\rangle$ all have the same parity and $H^{(1)}$ has the opposite parity. In this case, we cannot diagonalize $H^{(1)}$ to find the *proper* zeroth-order basis.

C Higher Order Corrections with Proper Zeroth-Order Basis

Let us consider case (2). In this case, the first-order equation

$$(E^{(0)}_n - H^{(0)})|nr'^{(1)}\rangle = (H^{(1)} - E^{(1)}_{nr'})|nr'^{(0)}\rangle \tag{10}$$

leads to

$$\begin{aligned} Q^{(0)}_n|nr'^{(1)}\rangle &= Q^{(0)}_n\frac{1}{E^{(0)}_n - H^{(0)}}Q^{(0)}_n H^{(1)}|nr'^{(0)}\rangle \\ &= \sum_{k\neq n}\sum_{s}|ks^{(0)}\rangle\frac{\langle ks^{(0)}|H^{(1)}|nr'^{(0)}\rangle}{(E^{(0)}_n - E^{(0)}_k)}. \end{aligned} \tag{11}$$

Upon left-multiplication with $\langle nr'^{(0)}|$, the second-order equation

$$(E^{(0)}_n - H^{(0)})|nr'^{(0)}\rangle = (H^{(1)} - E^{(1)}_{nr'})|nr'^{(1)}\rangle + (H^{(2)} - E^{(2)}_{nr'})|nr'^{(0)}\rangle \tag{12}$$

leads to

$$0 = \sum_{k\neq n}\sum_{s} \frac{\langle nr'^{(0)}|H^{(1)}|ks^{(0)}\rangle\langle ks^{(0)}|H^{(1)}|nr'^{(0)}\rangle}{(E_n^{(0)} - E_k^{(0)})} + \langle nr'^{(0)}|H^{(2)}|nr'\rangle - E_{nr'}^{(2)}, \tag{13}$$

so

$$E_{nr'}^{(2)} = \langle nr'^{(0)}|H^{(2)}|nr'^{(0)}\rangle + \sum_{k\neq n}\sum_{s} \frac{|\langle ks^{(0)}|H^{(1)}|nr'^{(0)}\rangle|^2}{(E_n^{(0)} - E_k^{(0)})}. \tag{14}$$

All steps in this and subsequent steps in the perturbation formalism parallel the earlier nondegenerate-state perturbation theory, except state vectors $|n^{(0)}\rangle$ or their conjugate bras must be replaced by $|nr'^{(0)}\rangle$ and the projection operators $Q_n^{(0)}$ will have to include besides the sum over $k \neq n$ a sum over the degeneracy label s. Note, in particular, that the states $|ks^{(0)}\rangle$ need *not* be transformed to primed form.

D Application 1: Stark Effect in the Diatomic Molecule Rigid Rotator

Let us consider a nonhomonuclear diatomic molecule, with a permanent electric dipole moment, which is perturbed by an external electric field, $\vec{\mathcal{E}}$. Let us consider only the lowest energies of this system, so the molecule can be considered as a rigid rotator, with zeroth-order energy eigenvalues and eigenfunctions (or eigenvectors)

$$E_l^{(0)} = \frac{\hbar^2}{2I_e} l(l+1), \qquad Y_{lm}(\theta,\phi) = \langle\theta,\phi|lm\rangle, \tag{15}$$

with $I_e = \mu r_e^2$ and

$$H^{(0)}|lm^{(0)}\rangle = E_l^{(0)}|lm^{(0)}\rangle, \qquad \text{with} \quad m = +l, \dots, -l. \tag{16}$$

The l^{th} level, thus, has a $(2l+1)$-fold degeneracy, the general degeneracy associated with rotationally invariant sytems. In the presence of an external electric field, $\vec{\mathcal{E}}$, we must add a term

$$H^{(1)} = -\vec{\mu}^{(el.)} \cdot \vec{\mathcal{E}} = -\mu_e \cos\theta \mathcal{E}, \tag{17}$$

where we have assumed the electric field $\vec{\mathcal{E}}$ is in the space-fixed z direction and the symmetry axis of the molecule makes a polar angle θ with this z direction. This Stark perturbation (Stark effect) is often used to identify the l values of initial states in purely rotational transitions. To show $H^{(1)}$ is a weak perturbation, assume the electric field is 1,000 Volts/cm, a strong field. The permanent electric dipole moments, μ_e, of diatomic molecules are of order $e \times 10^{-8}$ cm. Thus, even in this strong field, $H^{(1)}$ can be expected to be of order 10^{-5}eV. Take the HCl molecule as a specific example, so $\mu \approx m_{\text{proton}}$, with $\mu c^2 \approx 10^9 eV$. Take $r_e \approx 10^{-8}$cm (the precise value is known from the rotational spectrum to be 1.2746 × 10^{-8}cm). Then,

$$\frac{\hbar^2}{2\mu r_e^2} = \frac{(\hbar c)^2}{2(\mu c^2) r_e^2} \approx \frac{(1.973 \times 10^{-5} eVcm)^2}{2 \times 10^9 eV \times 10^{-16} cm^2} \approx 2 \times 10^{-3} eV, \tag{18}$$

showing the Stark term, $H^{(1)}$, can indeed be treated as a perturbation. To calculate the matrix elements of $H^{(1)}$, recall (Chapter 9)

$$\cos\theta\, Y_{lm} = \sqrt{\frac{[(l+1)^2 - m^2]}{(2l+1)(2l+3)}}\, Y_{(l+1)m} + \sqrt{\frac{[l^2 - m^2]}{(2l+1)(2l-1)}}\, Y_{(l-1)m}, \tag{19}$$

so

$$\begin{aligned} \langle (l+1)m|\cos\theta|lm\rangle &= \sqrt{\frac{[(l+1)^2 - m^2]}{(2l+1)(2l+3)}}, \\ \langle (l-1)m|\cos\theta|lm\rangle &= \sqrt{\frac{[l^2 - m^2]}{(2l+1)(2l-1)}}. \end{aligned} \tag{20}$$

Our $H^{(1)}$ does not have matrix elements diagonal in the quantum number, l. No first-order contribution to the Stark energy shift occurs. At first, it appears this belongs to case (3) of section B of this chapter and might require further treatment. All matrix elements of the perturbing Hamiltonian, however, are diagonal in m. States of a particular m are therefore completely unconnected from states of different m. We can therefore treat states of a particular m by themselves, as if they were unconnected from the rest, hence, by nondegenerate perturbation theory. This is of course connected to the symmetry of our Hamiltonian, even, including the full perturbation, our Hamiltonian has axial symmetry. Our zeroth-order state vectors, of good eigenvalue m, are automatically the *proper symmetry-adapted* zeroth-order state vectors. (If we had chosen to call the direction of the $\vec{\mathcal{E}}$ field the x rather than the z direction, our $H^{(1)}$ would have been $-\mu_e \sin\theta\cos\phi\mathcal{E}$. If we had diagonalized this $H^{(1)}$, we would essentially have effected a rotation from our original x direction to a new z direction. By choosing our z rather than our x direction along the direction of the outside $\vec{\mathcal{E}}$, our zeroth-order state vectors have automatically become the *proper* ones for the perturbation calculation.

The second-order contributions to the energy are then simply

$$\begin{aligned} \lambda^2 E_{lm}^{(2)} &= \sum_{l'=l\pm 1} \frac{|\langle l'm^{(0)}|H^{(1)}|lm^{(0)}\rangle|^2}{E_l^{(0)} - E_{l'}^{(0)}} = \frac{\mu_e^2\mathcal{E}^2}{\hbar^2/2I_e} \\ &\times \left(\frac{[l^2 - m^2]/(2l+1)(2l-1)}{[l(l+1) - (l-1)l]} + \frac{[(l+1)^2 - m^2]/(2l+3)(2l+1)}{[l(l+1) - (l+1)(l+2)]}\right) \\ &= \frac{2I_e\mu_e^2\mathcal{E}^2}{\hbar^2}\left(\frac{[l^2 - m^2]}{2l(2l+1)(2l-1)} - \frac{[(l+1)^2 - m^2]}{2(l+1)(2l+1)(2l+3)}\right) \\ &= \frac{2I_e\mu_e^2\mathcal{E}^2}{\hbar^2}\frac{[l(l+1) - 3m^2]}{2l(l+1)(2l-1)(2l+3)}. \end{aligned} \tag{21}$$

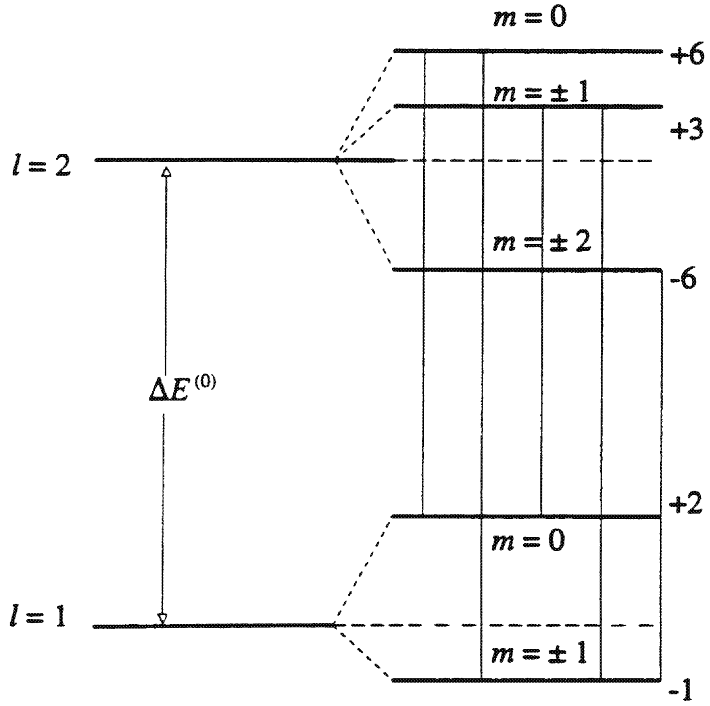

FIGURE 23.1. Second order Stark splitting of the $l = 2$ and $l = 1$ states of the diatomic molecule rigid rotator. The energy shifts are in units of $[I_e \mu_e^2 \mathcal{E}^2/\hbar^2 l(l+1)(2l-1)(2l+3)]$. $\Delta E^{(0)} = 2\hbar^2/I_e$.

The Stark splitting of the $l = 2$ and $l = 1$ levels is shown in Fig. 23.1., where energy shifts are shown in units of $(I_e \mu_e^2 \mathcal{E}^2/\hbar^2 l(l+1)(2l-1)(2l+3)$. Note that the l^{th} rotational level is split into only $(l+1)$ levels since the second order energy shift depends only on m^2. The transition probabilities for the $l = 2 \rightarrow l = 1$ transitions are now given by the matrix elements of

$$\mu_x^{(el.)} = \mu_e \sin\theta \cos\phi; \qquad \mu_y^{(el.)} = \mu_e \sin\theta \sin\phi; \qquad \mu_z^{(el.)} = \mu_e \cos\theta. \quad (22)$$

These lead to the selection rules, $\Delta m = \pm 1$ for the x and y components, and $\Delta m = 0$ for the z component. Thus the $l = 2 \rightarrow l = 1$ transition is split into five components, corresponding to the transitions $m = 2 \rightarrow 1, 1 \rightarrow 0, 1 \rightarrow 1, 0 \rightarrow 1, 0 \rightarrow 0$. (Actually, the transition would be observed through an induced absorption process). The line pattern, including relative intensities, is shown in Fig. 23.2, where the shifts in frequency from the unperturbed frequency, $(h/2\pi^2 I_e)$, are given in units of $\Delta = (I_e \mu_e^2 \mathcal{E}^2/2\pi\hbar^3 210)$.

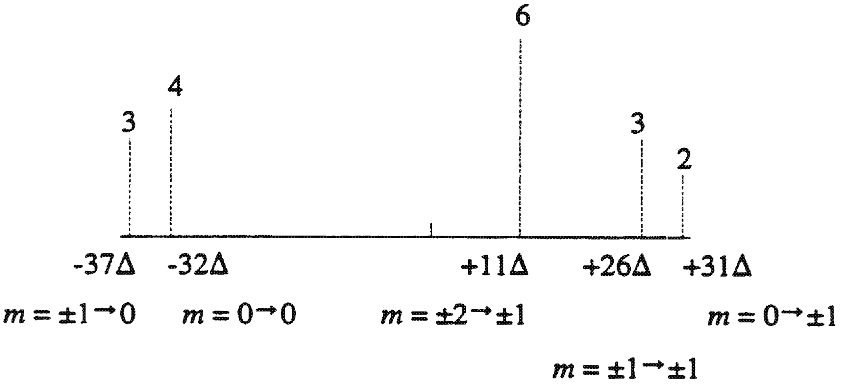

FIGURE 23.2. The Stark splitting of the $l = 2 \rightarrow l = 1$ transition. The numbers above the lines give the relative intensities. Frequency shifts from the zeroth-order frequency are given in units of $\Delta = (I_e \mu_e^2 \mathcal{E}^2 / 2\pi\hbar^3 210)$.

E Application 2: Stark Effect in the Hydrogen Atom

In an external electric field, $\vec{\mathcal{E}}$, the perturbing Hamiltonian is now

$$H^{(1)} = -(-e\vec{r}_1 + e\vec{r}_2) \cdot \vec{\mathcal{E}} = e(\vec{r}_1 - \vec{r}_2) \cdot \vec{\mathcal{E}} = ea_0 r \cos\theta \mathcal{E}, \tag{23}$$

where a_0 is the Bohr radius and we have again introduced a dimensionless r via $|\vec{r}_{\text{relative}}| = a_0 r$. For an electric field $\mathcal{E}$ of 1,000 Volts/cm, $H^{(1)}$ is again of order 10^{-5}eV, but now the zeroth-order energy is the Bohr energy $\mu e^4/\hbar^2 = 27$eV, so $|H^{(1)}/H^{(0)}| \ll 1$, the ratio now being of order 10^{-6}. Although the m quantum number is again a good quantum number to all orders, because the perturbation can not change m, several l values now exist for a given m [with the exception of the states with $m = \pm(n-1)$]. Let us take the four-fold degenerate state with $n = 2$ as a special example. Now, a nonzero $H^{(1)}$ matrix element connecting the $m = 0$ states with $l = 0$ and $l = 1$ exists,

$$\begin{aligned} \langle nlm = 210|\lambda H^{(1)}|nlm = 200\rangle &= ea_0\mathcal{E}\langle 210|r\cos\theta|200\rangle \\ &= ea_0\mathcal{E} I^{\text{rad.}}_{21,20}\frac{1}{\sqrt{3}}, \end{aligned} \tag{24}$$

where the angular part of the matrix element, with value $1/\sqrt{3}$, follows from eq. (19) and the radial part is given by

$$\begin{aligned} I^{\text{rad.}}_{21,20} &= \int_0^\infty dr r^2 R_{n=2,l=1}(r) r R_{n=2,l=0}(r) \\ &= \frac{1}{4\sqrt{3}}\int_0^\infty dr r^4 (1 - \frac{r}{2}) e^{-r} \\ &= \frac{1}{4\sqrt{3}}(4! - \frac{5!}{2}) = -3\sqrt{3}, \end{aligned} \tag{25}$$

leading to the 4 × 4 matrix

$$\langle 2l'm|\lambda(H^{(1)} - E^{(1)}_{n=2})|2lm\rangle =$$

$$\begin{array}{c|cccc} & 200 & 210 & 21+1 & 21-1 \\ \hline 200 & -\lambda E_2^{(1)} & -3ea_0\mathcal{E} & 0 & 0 \\ 210 & -3ea_0\mathcal{E} & -\lambda E_2^{(1)} & 0 & 0 \\ 21+1 & 0 & 0 & -\lambda E_2^{(1)} & 0 \\ 21-1 & 0 & 0 & 0 & -\lambda E_2^{(1)} \end{array}.$$

The energy determinant leads to the values $\lambda E_2^{(1)} = +3ea_0\mathcal{E}, -3ea_0\mathcal{E}, 0$, and 0. The corresponding *proper* zeroth-order eigenvectors are

$$\begin{aligned} &\text{For} \quad +3ea_0\mathcal{E}: && \frac{1}{\sqrt{2}}(|200\rangle - |210\rangle) \\ &\text{For} \quad -3ea_0\mathcal{E}: && \frac{1}{\sqrt{2}}(|200\rangle + |210\rangle) \\ &\text{For} \quad 0: && |21+1\rangle \\ &\text{For} \quad 0: && |21-1\rangle. \end{aligned} \tag{26}$$

Because the first-order Stark effect in atomic hydrogen is very small, these first-order results may be sufficient. Because we have determined the *proper* zeroth-order eigenvectors, we could now use eq. (14) to calculate the Stark energy corrections to second order. The sum over states with $k \neq n$, however, is now a sum over an infinite number of discrete states and in fact includes a continuum sum (i.e., an integral) over the hydrogenic continuum states, because the operator $r\cos\theta$ has nonzero matrix elements connecting a state nlm to states $n'(l \pm 1)m$, with *all* possible values of $n' \neq n$. (We shall find the stretched parabolic coordinates of problems 6 and 26 will give us an elegant way out of this computational difficulty; see problem 37.)