5.80 Small-Molecule Spectroscopy and Dynamics
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THE VAN VLECK TRANSFORMATION IN PERTURBATION THEORY[1]

Although frequently it is desirable to carry a perturbation treatment to second or third order for a degenerate state, the required calculations often become very complicated. A simple procedure due to Van Vleck makes this task considerably easier.

I. Perturbation Theory and the Problem of Degeneracy[?, ?, ?]

In many quantum mechanical problems, the Hamiltonian may be written

$$\mathbf{H} = \mathbf{H}^\circ + \mathbf{H}' \tag{1}$$

where the solution for the unperturbed Hamiltonian $\mathbf{H}^\circ$ is known, and $\mathbf{H}'$ is a small perturbation. Perturbation theory may be used to find the small changes in the energy levels and wave functions introduced by $\mathbf{H}'$.

If the matrix elements of $\mathbf{H}$ are evaluated in the $\mathbf{H}^\circ$ representation, i.e., calculated with the unperturbed wave functions, the $\mathbf{H}^\circ$ matrix is diagonal,

$$\mathbf{H}^\circ_{kj} = E^\circ_k \delta_{kj}.$$

Several quantum numbers may be needed to label the states of $\mathbf{H}^\circ$; here k represents the entire set. Some of the unperturbed states may be degenerate and k must then include an index to distinguish the members of the degenerate set.

The perturbation matrix $\mathbf{H}'$ will have off-diagonal terms which couple the various unperturbed states as well as diagonal terms which directly shift the energy levels.

In the usual perturbation theory, the shift of a particular unperturbed energy level E°_k and its wave function ψ°_k is evaluated by expanding the Hamiltonian in powers of a parameter λ,

$$\mathbf{H} = \mathbf{H}^\circ + \lambda \mathbf{H}' + \lambda^2 \mathbf{H}'' + \ldots \tag{2}$$

The solution of the Schrödinger equation,

$$\mathbf{H}\lambda = E\lambda \tag{3}$$

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[1]These notes were written by Professor Dudley Herschbach.

is sought, where

$$E_k = E_k^\circ + \lambda E_k' + \lambda^2 E_k'' + \dots$$
$$\lambda_k = \lambda_k^\circ + \lambda \psi_k' + \lambda^2 \psi_k'' + \dots \tag{4}$$

which reduces to the unperturbed solution as $\lambda \to 0$. On substituting (4) into (3) and equating the coefficients of like powers of λ, the perturbed energy levels are found to be

$$E_k = E_k^\circ + \lambda \mathbf{H}_{kk}' + \lambda^2 \mathbf{H}_{kk}'' + \lambda^2 \sum_{j \neq k} \frac{\mathbf{H}_{kj}' \mathbf{H}_{jk}'}{E_k - E_j} + \dots \tag{5}$$

to second order. The first contributions are merely the perturbation averaged with the unperturbed wave function of state k. In the second order approximation, there is a sum over the influence of the other states. The energy level is displaced upward by the states of lower energy and downward by those of higher energy; the displacements are proportional to the square of the coupling term as given by the matrix elements of $\mathbf{H}'$ and inversely proportional to the corresponding energy differences.

However, if some states are degenerate with state k, the treatment must be modified because of the vanishing energy denominators which make (5) infinite (except, of course, in the special case that the offending terms have zero matrix elements, e.g., due to symmetry considerations).

If the unperturbed E_k° belongs to a group of g_k degenerate levels, its wave function ψ_k° is not completely determined, but may be arbitrarily chosen to be any linear combination of a set of g_k orthonormal functions associated with the degenerate level. The perturbation will in general cause energy splittings which at least remove the degeneracy to some extent. However, as $\lambda \to 0$, the perturbed wave function ψ_k will not, in general, reduce to the arbitrarily chosen initial ψ_k°, as in (5), but will become a linear combination of the initial set of g_k degenerate functions, the particular combination depending on the perturbation. To apply perturbation theory, one must then first determine this correct limiting linear combination and make the functions for the other unperturbed states that are degenerate with state k be orthogonal to state k. This requirement means that the transformation of matrix elements accompanying the transformation to these correct zero-order wave functions should uncouple the degenerate states in $\mathbf{H}'$. Thus $\mathbf{H}'$ becomes diagonal for the block of states that are degenerate with state k, and all the terms with vanishing denominators in (5) disappear. The determination of the zeroth-order wave functions therefore requires solving the secular equation,

$$|\mathbf{H}'(k) - \xi \mathbb{1}| = 0 \tag{6}$$

which corresponds to diagonalizing $\mathbf{H}'(k)$, which is the $g_k \times g_k$ block of $\mathbf{H}'$ that corresponds to the g_k degenerate unperturbed states of energy E_k°. The solution immediately provides the diagonal term ξ_k in the transformed $\mathbf{H}'$ which is needed for the first approximation in (5). However, if it is desired to evaluate the

second or higher order terms, then the off-diagonal matrix elements $\mathbf{H}'_{kj}$ coupling state k to all other states j must be transformed to correspond to the transformation to the correct zero-order wave function for state k. Moreover, in case the first order perturbation did not remove completely the degeneracy present in the unperturbed problem, as would happen if part of the $\mathbf{H}'$ matrix were diagonal and itself degenerate, then for the second order treatment it would be necessary to initially diagonalize the submatrix of the entire Hamiltonian that includes not only all second order terms $\mathbf{H}''_{kk'}$, coupling state k to each state k' degenerate with it, but also terms of the form $\mathbf{H}'_{kj}$ and $\mathbf{H}'_{k'j}$ which couple the degenerate states in second order through other states j (see reference [**?**]).

The program of the usual degenerate perturbation theory outlined above is often difficult or impossible to apply. The difficulty is the more serious because the upper, continuous portion of the energy spectrum can be handled only by introduction of an awkward box normalization or some equivalent. We shall now consider the Van Vleck procedure which brings great simplification because it allows any block of interest to be uncoupled (to third order) from the rest of the $\mathbf{H}'$ matrix and afterwards diagonalized. This minimizes the size of the secular equations that must be solved, and there is ordinarily no difficulty in diagonalizing those blocks of $\mathbf{H}'$ associated with the lower unperturbed energy levels in which there is greatest physical interest.

II.   The Van Vleck Transformation

Although the Van Vleck method has been applied to a variety of problems, it is seldom described in the literature. Only the discussion by Kemble[**?**] is more than two or three paragraphs. The method was first used by Van Vleck in his classic paper on sigma type doubling and electron spin.[**?**] One of his students, Jordahl, in a paper on paramagnetic susceptibility,[**?**] carried the method to third order but omitted the derivation; also his formula has two minor but misleading errors. Other papers include applications to rotation-vibration interactions,[**?**, **?**] hindered internal rotation,[**?**] and the Stark effect.[**?**]

Van Vleck introduced a canonical transformation, $\mathbf{T}(\lambda)$, which eliminates the terms of first order in λ from the matrix elements of $\mathbf{H}'$ connecting any particular unperturbed energy E_k° with the other distinct unperturbed levels. The remaining coupling terms are then of second order or higher, and since they are off-diagonal, they cannot contribute to the energy until fourth order. Therefore, they may be neglected immediately if the theory is taken only to second or third order, which is usually adequate in practice. This uncoupling of the blocks of $\mathbf{H}'$ permits the separate treatment of each block, up to third order.

For convenience, we shall label the states in the $\mathbf{H}'$ block of interest by m or m', and states outside this block by n or n'. We need not be confined to the case in which the unperturbed states corresponding to the m block are degenerate; often the unperturbed energy levels may be grouped into widely spaced

sets given by one quantum number (q, say), each set consisting of fine structure levels distinguished by other quantum numbers, and the Van Vleck transformation may be used to approximately diagonalize the Hamiltonian in q. In this case m is identified with the principal quantum number q, so it has the same value for all states of the m block and the formulas are simplified. After the transformation, the block is then diagonalized in the other quantum numbers to obtain the fine structure.

The Van Vleck transformation may be derived by replacing ψ_m° in the expansion of ψ_m in (4) by a linear combination of the g_m degenerate unperturbed functions with arbitrary coefficients which are to be determined from the Schrödinger equation and the condition of orthonormality, as in the derivation of the usual perturbation theory formulas (see Ref. 5, §4; ref. 2, p. 154). This essentially amounts to carrying out the diagonalization required to remove the degeneracy only up to the order in λ of interest rather than exactly. The derivation we shall present here, however, is shorter and deals directly with the matrix transformation.

The transformation $\mathbf{T}(\lambda)$ is to be unitary, and may be conveniently written in terms of a Hermitian matrix $\mathbf{S}$ as

$$\mathbf{T} = e^{i\lambda\mathbf{S}} = 1 + i\lambda\mathbf{S} - \frac{\lambda^2}{2}\mathbf{S}^2 + \ldots \tag{7}$$

We wish to construct $\mathbf{T}$ so that the first order term in the Hamiltonian,

$$\mathbf{T}^\dagger\mathbf{H}\mathbf{T} = \mathbf{G}(\lambda) = \mathbf{G}^\circ + \lambda\mathbf{G}' + \lambda^2\mathbf{G}'' + \ldots \tag{8}$$

has vanishing matrix elements between the m and n blocks, or $G'_{mn} = 0$.

Schematically,

$$\mathbf{T}^\dagger \left[\begin{array}{c|c} mm' & mn \\ \hline nm & nn' \end{array} \right] \mathbf{T} = \left[\begin{array}{c|c} mm' & 0(\lambda^2) \\ \hline 0(\lambda^2) & nn' \end{array} \right].$$

On expanding (8)

$\mathbf{G}^\circ + \lambda\mathbf{G}' + \lambda^2\mathbf{G}'' + \ldots$

$$= \left(1 - i\lambda\mathbf{S} - \frac{\lambda^2}{2}\mathbf{S}^2 + \ldots\right)[\mathbf{H}^\circ + \lambda\mathbf{H}' + \lambda^2\mathbf{H}'' + \ldots]\left(1 + i\lambda\mathbf{S} - \frac{\lambda^2}{2}\mathbf{S}^2 + \ldots\right) \tag{9}$$

and equating coefficients of like powers of λ, one obtains

$$\mathbf{G}^\circ = \mathbf{H}^\circ$$

$$\mathbf{G}' = \mathbf{H}' + i(\mathbf{H}^\circ\mathbf{S} - \mathbf{S}\mathbf{H}^\circ)$$

$$\mathbf{G}'' = \mathbf{H}'' + i(\mathbf{H}'\mathbf{S} - \mathbf{S}\mathbf{H}') + \mathbf{S}\mathbf{H}^\circ\mathbf{S} - \frac{1}{2}(\mathbf{H}^\circ\mathbf{S}^2 + \mathbf{S}^2\mathbf{H}^\circ)$$

$$\mathbf{G}''' = \mathbf{H}''' + i(\mathbf{H}''\mathbf{S} - \mathbf{S}\mathbf{H}'') + \mathbf{S}\mathbf{H}'\mathbf{S} - \frac{1}{2}[\mathbf{H}'\mathbf{S}^2 + \mathbf{S}^2\mathbf{H}'] + \frac{i}{2}(\mathbf{S}\mathbf{H}^\circ\mathbf{S}^2 - \mathbf{S}^2\mathbf{H}^\circ\mathbf{S}) - \frac{i}{6}(\mathbf{H}^\circ\mathbf{S}^3 - \mathbf{S}^3\mathbf{H}^\circ)$$

$$\ldots \tag{10}$$

If we choose,

$$S_{mm'} = 0, S_{nn'} = 0 \tag{11}$$

then **T** does not directly affect the m or n blocks. To make $G'_{mn} = 0$, we require from (10)

$$S_{mn} = \frac{i\mathbf{H}'_{mn}}{E_m - E_n}. \tag{12}$$

Thus the desired transformation has been constructed; it is seen to depend on the particular unperturbed level to be dealt with.

On using (11) and (12) in (10), we obtain the formula for the transformed matrix elements of the mm' block, without the necessity of carrying out an exact diagonalization to obtain the proper zero-order wave function. By straightforward algebra, the result is to third order,

$$G_{mm'} = E_m^\circ \delta_{mm'} + \lambda \mathbf{H}'_{mm'} + \lambda^2 \mathbf{H}''_{mm'} + \frac{\lambda^2}{2} \sum_n \left[\frac{\mathbf{H}'_{mn}\mathbf{H}'_{nm'}}{E_m - E_n} + \frac{\mathbf{H}'_{mn}\mathbf{H}'_{nm'}}{E_{m'} - E_n} \right] + \lambda^3 \mathbf{H}'''_{mm'}$$

$$+ \frac{\lambda^3}{2} \sum_n \left[\frac{\mathbf{H}'_{mn}\mathbf{H}''_{nm'}}{E_m - E_n} + \frac{\mathbf{H}''_{mn}\mathbf{H}'_{nm'}}{E_{m'} - E_n} \right] - \frac{\lambda^3}{2} \sum_n \sum_{m''} \left[\frac{\mathbf{H}'_{mm''}\mathbf{H}'_{m''n}\mathbf{H}'_{nm'}}{(E_{m''} - E_n)(E'_m - E_n)} + \frac{\mathbf{H}'_{mn}\mathbf{H}'_{nm''}\mathbf{H}'_{m''n'}}{(E_m - E_n)(E_{m''} - E_n)} \right]$$

$$+ \lambda^3 \sum_n \sum_{n'} \left[\frac{\mathbf{H}'_{mn}\mathbf{H}'_{nn'}\mathbf{H}'_{n'm'}}{(E_m - E_n)(E_{m'} - E_{n'})} \right] \tag{13}$$

Here the superscript zero is omitted in denominators, for simplicity. This block of the **G** matrix may now be treated independently of the rest; on diagonalization by exact or approximate methods (e.g., perturbation methods might be applied within the block), the associated energy levels can be obtained to third order.

As mentioned above, the special case in which m has only one value is often useful, and the corresponding simplification of (13) is included in (14), below.

To extend the theory to fourth order, Eq. (10) is continued. The off-diagonal elements G_{mn}, which are $0(\lambda^2)$ by construction, are evaluated from (10), (11), and (12), and the Van Vleck transformation is applied to remove the coupling terms in λ^2 from the G_{mn}, thus adding an additional term in λ^4 to the $G_{mm'}$. We give the result only for the case in which m takes just one value and $\mathbf{H} = \mathbf{H}^\circ + \lambda\mathbf{H}'$, since the fourth order contribution would seldom be desired for the more general case.

$$G_{mm} = E_m^\circ + \lambda\mathbf{H}'_{mm} + \lambda^2 \sum_n \frac{\mathbf{H}'_{mn}\mathbf{H}'_{nm}}{E_m - E_n} + \lambda^3 \sum_n \sum_{n'} \frac{\mathbf{H}'_{mn}\mathbf{H}'_{nn'}\mathbf{H}'_{n'm}}{(E_m - E_n)(E_m - E_{n'})} - \lambda^3 \mathbf{H}'_{mm} \sum_n \frac{\mathbf{H}'_{mn}\mathbf{H}'_{nm}}{(E_m - E_n)^2}$$

$$+ \lambda^4 \sum_n \sum_{n'} \sum_{n''} \frac{\mathbf{H}'_{mn}\mathbf{H}'_{nn'}\mathbf{H}'_{n'n''}\mathbf{H}'_{n''m}}{(E_m - E_n)(E_m - E_{n'})(E_m - E_{n''})} + \lambda^4 [\mathbf{H}'_{mm}]^2 \sum_n \frac{\mathbf{H}'_{mn}\mathbf{H}'_{nm}}{(E_m - E_n)^3}$$

$$- \lambda^4 \sum_n \left[\frac{\mathbf{H}'_{mn}\mathbf{H}'_{nm}}{E_m - E_n} \right] \left[\sum_n \frac{\mathbf{H}'_{mn}\mathbf{H}'_{nm}}{(E_m - E_n)^2} \right] - \lambda^4 \mathbf{H}'_{mm} \sum_n \sum_{n'} \left[\frac{\mathbf{H}'_{mn}\mathbf{H}'_{nn'}\mathbf{H}'_{n'm}}{(E_m - E_n)^2(E_m - E_{n'})} + \frac{\mathbf{H}'_{mn}\mathbf{H}'_{nn'}\mathbf{H}'_{n'm}}{(E_m - E_n)(E_m - E_{n'})} \right]$$

$$\tag{14}$$

III.   A Favorite Example: Coupled Harmonic Oscillators

As a simple example, we treat the ground and first excited state of two coupled linear harmonic oscillators to second order by both the usual perturbation theory and the Van Vleck transformation. The Hamiltonian is

$$\mathbf{H}^\circ = \mathbf{H}_x^\circ + \mathbf{H}_y^\circ = -\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + x^2 + y^2$$

$$\lambda\mathbf{H}' = \lambda xy \tag{15}$$

where appropriate units have been chosen to eliminate the constant factors. In these units, the unperturbed energy levels for a single oscillator are just the odd integers,

$$E_n^\circ = 1, 3, 5, \ldots 2n + 1 \tag{16}$$

and the coordinate matrix elements are

$$x_{mn} = \sqrt{\frac{m}{2}}\delta_{m,n+1} + \sqrt{\frac{n}{2}}\delta_{m+1,n}. \tag{17}$$

The unperturbed energy levels,

$$E_{nn'}^\circ = 2(n + n' + 1), \tag{18}$$

may be conveniently labeled by the quantum numbers n and n' for the individual oscillators. Except for the lowest level, they are degenerate with the weight,

$$g_{nn'} = n + n' + 1. \tag{19}$$

The unperturbed wave functions are just products of those for the separate oscillators,

$$\psi_{nn'}^\circ(x, y) = \psi_n^\circ(x)\psi_{n'}^\circ(y). \tag{20}$$

The matrix elements of the perturbation are found from (17),

$$\mathbf{H}'_{mn,m'n'} = x_{mm'}y_{nn'} \tag{21}$$

thus the Hamiltonian matrix is

	00	01	10	20	11	02	30	21	12	03
00	2				$\frac{\lambda}{2}$					
01		4	$\frac{\lambda}{2}$						$\frac{\lambda}{\sqrt{2}}$	
10		$\frac{\lambda}{2}$	4					$\frac{\lambda}{\sqrt{2}}$		
20				6	$\frac{\lambda}{\sqrt{2}}$					
11	$\frac{\lambda}{2}$			$\frac{\lambda}{\sqrt{2}}$	6	$\frac{\lambda}{\sqrt{2}}$				
02					$\frac{\lambda}{\sqrt{2}}$	6				
30							8	$\frac{\sqrt{3}\lambda}{2}$		
21			$\frac{\lambda}{\sqrt{2}}$				$\frac{\sqrt{3}\lambda}{2}$	8	λ	
12		$\frac{\lambda}{\sqrt{2}}$						λ	8	$\frac{\sqrt{3}\lambda}{2}$
03									$\frac{\sqrt{3}\lambda}{2}$	8

$$(22)$$

where only the non-zero elements are given.

For the ground state, the non-degenerate perturbation formula (5) may be applied (the Van Vleck formula (14) is the same in this case),

$$E_{00} = 2 + 0 + \frac{\left(\frac{\lambda}{2}\right)^2}{2 - 6} = 2 - \frac{\lambda^2}{16}. \tag{23}$$

To treat the degenerate first excited state, the corresponding 2×2 block in $\mathbf{H}'$ must first be diagonalized to obtain the zero order wave functions.

The secular equation (6) is

$$
\begin{array}{c c}
 & \begin{array}{cc} 01 & 10 \end{array} \\
\begin{array}{c} 01 \\ 10 \end{array} &
\left| \begin{array}{cc} +\xi & \frac{\lambda}{2} \\ \frac{\lambda}{2} & \xi \end{array} \right| = 0
\end{array}
\qquad \text{or } \xi = \pm \frac{\lambda}{2} \tag{24a}
$$

Therefore the degeneracy is split in first order and the first order perturbation energies are,

$$E'_{+01} = \frac{\lambda}{2}, \quad E'_{-01} = -\frac{\lambda}{2}. \tag{24b}$$

The eigenvectors of (24b) are $\frac{1}{\sqrt{2}}(1, 1)$ and $\frac{1}{\sqrt{2}}(1, -1)$, so the correct zero-order combinations of the degenerate unperturbed wave functions are

$$
\psi^{\circ}_{+01} = \frac{1}{\sqrt{2}} \left[\psi^{\circ}_0(x)\psi^{\circ}_1(y) + \psi^{\circ}_1(x)\psi^{\circ}_0(y) \right]
$$

$$
\psi^{\circ}_{-01} = \frac{1}{\sqrt{2}} \left[\psi^{\circ}_0(x)\psi^{\circ}_1(y) - \psi^{\circ}_1(x)\psi^{\circ}_0(y) \right] \tag{24c}
$$

In order to apply the usual perturbation theory in second order, the off-diagonal matrix elements coupling the first excited state block to others in (22) must first be transformed in accordance with the transformation (24c) to the correct zero-order first excited state wave functions. Due to the "next–door–neighbor"

selection rule in (17), the +01 and −01 levels are coupled only to the 21 and 12 levels and on recomputing the matrix elements (21) by (17) and (24c), the relevant part of the matrix (22) becomes,

$$
\begin{array}{c|ccccc}
 & +01 & -01 & \ldots & 21 & 12 \\
\hline
+01 & \frac{\lambda}{2} & & & \frac{\lambda}{2} & \frac{\lambda}{2} \\
-01 & & -\frac{\lambda}{2} & & -\frac{\lambda}{2} & \frac{\lambda}{2} \\
\vdots & & & & & \\
\hline
21 & \frac{\lambda}{2} & -\frac{\lambda}{2} & & & \\
12 & \frac{\lambda}{2} & \frac{\lambda}{2} & & &
\end{array}
\tag{24d}
$$

Thus the second order perturbation energies are

$$
E''_{+01} = E''_{-01} = 2\frac{\left(\frac{\lambda}{2}\right)^2}{4-8} = -\frac{\lambda^2}{8}.
\tag{24e}
$$

The series of steps in Eqs. (24) may now be contrasted with the Van Vleck transformation. On applying (13) directly to (22), the block of interest is uncoupled and its secular equation may be set up as

$$
\begin{vmatrix}
\dfrac{\left(\frac{\lambda}{\sqrt{2}}\right)^2}{4-8} - E' & \dfrac{\lambda}{2} \\[2ex]
\dfrac{\lambda}{2} & \dfrac{\left(\frac{\lambda}{\sqrt{2}}\right)^2}{4-8} - E'
\end{vmatrix} = 0
\tag{25}
$$

with $E = 4 + E'$. Thus we have

$$
\left(\frac{\lambda^2}{-8} - E'\right)^2 - \left(\frac{\lambda}{2}\right)^2 = 0
$$

from which the perturbation energy is found to be

$$
E' = \pm\frac{\lambda}{2} - \frac{\lambda^2}{8}.
$$

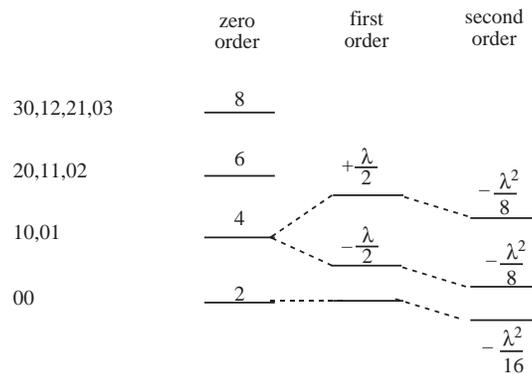

Figure 1: Energy levels for coupled oscillators.

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