The use of groups and their subgroups is of much importance when *perturbation theory* is employed in understanding molecular orbital theory and spectroscopy. Perturbation theory begins with the premise that one knows the solutions (energies, $E_1^{(0)}$, $E_2^{(0)}$, $E_3^{(0)}$, … and eigenfunctions, $\psi_1^{(0)}$, $\psi_2^{(0)}$, $\psi_3^{(0)}$, …) for some *unperturbed* problem for which the Hamiltonian is $\mathcal{H}^{(0)}$. (The superscript "(0)" refers to the unperturbed problem as the "zeroth-order" problem.) Consider the introduction of an additional "perturbation" – contained in an additional term in the Hamiltonian, $\mathcal{H}'$, that is added to the zeroth-order Hamiltonian to give a (more) complete Hamiltonian for the system: $\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}'$. Standard quantum mechanics texts derive formulas the corrections to the energies and wavefunctions that result from this new term in the Hamiltonian:

$$E_i = E_i^{(0)} + E_i^{(1)} + E_i^{(2)} + \cdots = E_i^{(0)} + H'_{ii} + \sum_{j \neq i} \frac{\left|H'_{ij}\right|^2}{E_i^{(0)} - E_j^{(0)}} + \cdots \qquad \text{where } H'_{ij} \equiv \int \psi_i^{(0)} \mathcal{H}' \psi_j^{(0)} d\tau$$

$$\psi_i = \psi_i^{(0)} + \psi_i^{(1)} + \cdots = \psi_i^{(0)} + \sum_{j \neq i} \frac{H'_{ij}}{E_i^{(0)} - E_j^{(0)}} \psi_j^{(0)} + \cdots$$

The terms in these formulas can be interpreted as follows: each of the *first*-order corrections to the energies, $E_i^{(1)}$, involve the expectation value of the perturbed part of the Hamiltonian, $\mathcal{H}'$, and the corresponding *zeroth*-order wavefunction, $\psi_i^{(0)}$. In other words, we look at the wavefunctions as they exist in zeroth-order and first consider what the perturbation does to the energies of those wavefunctions without considering changes to the wavefunctions. The *first*-order corrections to the wavefunctions, $\psi_i^{(1)}$, involve the *mixing* of each the *other* wavefunctions, $\psi_j^{(0)}$ ($j=1,2,3,\ldots \neq i$) into $\psi_i^{(0)}$ to the extent that $\mathcal{H}'$ "couples" $\psi_i^{(0)}$ and $\psi_j^{(0)}$ together. The *second*-order corrections to the energies, $E_i^{(2)}$, reflect the energetic corrections due to the mixing we see in the first-order wavefunctions. We will not consider higher-order corrections in perturbation theory here.
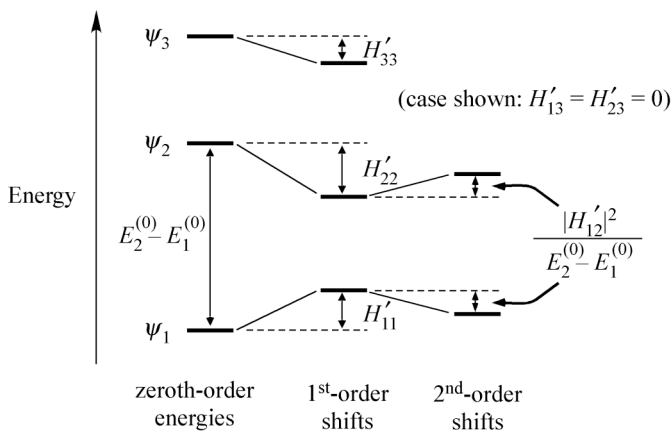
Schematic results of applying perturbation theory in which the perturbation "mixes" the lower two levels.

Two examples based on Hückel theory will illustrate how perturbation theory works and the role that group theory plays in its application. These examples are discussed in some detail in an effort to put across some general features of perturbation theory in practice.

I. A simple example of a perturbational MO analysis is provided by treating the π-bonding in $H_2B=NH_2$ as a perturbed example of ethylene, as illustrated here:
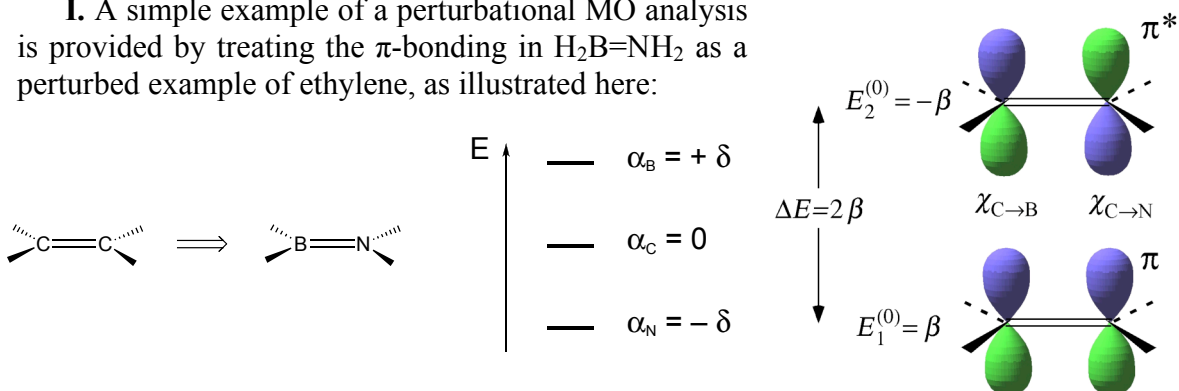
We begin with the Hückel π orbitals and energies for ethylene (the atomic orbitals are labeled according to how they are to be 'transformed' on moving from $H_2C=CH_2$ to $H_2B=NH_2$):

$$E_1^{(0)} = \beta \quad \psi_1^{(0)} = \frac{1}{\sqrt{2}}\left(\chi_{C\to B} + \chi_{C\to N}\right) \Bigg\} \quad \text{(recall, } \beta < 0\text{)}$$
$$E_2^{(0)} = -\beta \quad \psi_2^{(0)} = \frac{1}{\sqrt{2}}\left(\chi_{C\to B} - \chi_{C\to N}\right)$$

The perturbation of the system is reflected in the changed values of α for the two pπ orbitals, which we will assume to be as illustrated above: the nitrogen atom pπ orbital is *lower* in energy than the carbon atom pπ orbital by δ, the boron atom pπ orbital is *higher* in energy than the carbon atom pπ orbital by δ. In order to use perturbation theory, we need to know the matrix elements of $\mathcal{H}'$ using the zeroth-order wavefunctions, $\psi_1^{(0)}$ and $\psi_2^{(0)}$, as a basis. The matrix for $\mathcal{H}'$ in this basis can be obtained by taking the difference between the matrices for $\mathcal{H}$ and $\mathcal{H}^{(0)}$:

$$\mathbf{H}^{(0)} = \begin{bmatrix} \int \psi_1^{(0)}\mathcal{H}^{(0)}\psi_1^{(0)}d\tau & \int \psi_1^{(0)}\mathcal{H}^{(0)}\psi_2^{(0)}d\tau \\ \int \psi_2^{(0)}\mathcal{H}^{(0)}\psi_1^{(0)}d\tau & \int \psi_2^{(0)}\mathcal{H}^{(0)}\psi_2^{(0)}d\tau \end{bmatrix} = \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} = \begin{bmatrix} \beta & 0 \\ 0 & -\beta \end{bmatrix}$$

$$\mathbf{H} = \begin{bmatrix} \int \psi_1^{(0)}\mathcal{H}\psi_1^{(0)}d\tau & \int \psi_1^{(0)}\mathcal{H}\psi_2^{(0)}d\tau \\ \int \psi_2^{(0)}\mathcal{H}\psi_1^{(0)}d\tau & \int \psi_2^{(0)}\mathcal{H}\psi_2^{(0)}d\tau \end{bmatrix} ; \text{ Let's take each matrix element in turn,}$$

$$\int \psi_1^{(0)}\mathcal{H}\psi_1^{(0)}d\tau = \tfrac{1}{2}\int (\chi_{C\to B} + \chi_{C\to N})\mathcal{H}(\chi_{C\to B} + \chi_{C\to N})d\tau =$$

$$\tfrac{1}{2}\left[\int \chi_{C\to B}\mathcal{H}\chi_{C\to B}d\tau + \int \chi_{C\to N}\mathcal{H}\chi_{C\to N}d\tau + 2\int \chi_{C\to B}\mathcal{H}\chi_{C\to N}d\tau\right]$$

$$\therefore \int \psi_1^{(0)}\mathcal{H}\psi_1^{(0)}d\tau = \tfrac{1}{2}\left[\delta - \delta + 2\beta\right] = \beta$$

$$\int \psi_2^{(0)}\mathcal{H}\psi_2^{(0)}d\tau = \tfrac{1}{2}\int (\chi_{C\to B} - \chi_{C\to N})\mathcal{H}(\chi_{C\to B} - \chi_{C\to N})d\tau =$$

$$\tfrac{1}{2}\left[\int \chi_{C\to B}\mathcal{H}\chi_{C\to B}d\tau + \int \chi_{C\to N}\mathcal{H}\chi_{C\to N}d\tau - 2\int \chi_{C\to B}\mathcal{H}\chi_{C\to N}d\tau\right]$$

$$\therefore \int \psi_2^{(0)}\mathcal{H}\psi_2^{(0)}d\tau = \tfrac{1}{2}\left[\delta - \delta - 2\beta\right] = -\beta$$

$$\int \psi_1^{(0)} \mathcal{H} \psi_2^{(0)} d\tau = \tfrac{1}{2} \int (\chi_{C\to B} + \chi_{C\to N}) \mathcal{H} (\chi_{C\to B} - \chi_{C\to N}) d\tau =$$

$$\tfrac{1}{2}\left[\int \chi_{C\to B} \mathcal{H} \chi_{C\to B} d\tau - \int \chi_{C\to N} \mathcal{H} \chi_{C\to N} d\tau \right]$$

$$\therefore \int \psi_1^{(0)} \mathcal{H} \psi_2^{(0)} d\tau = \int \psi_2^{(0)} \mathcal{H} \psi_1^{(0)} d\tau = \tfrac{1}{2}\left[\delta + \delta \right] = \delta$$

$$\therefore \mathbf{H} = \begin{bmatrix} \beta & \delta \\ \delta & -\beta \end{bmatrix} \; ; \text{ So, finally we use the relationship } \mathbf{H}' = \mathbf{H} - \mathbf{H}^{(0)}$$

$$\mathbf{H}' = \begin{bmatrix} \beta & \delta \\ \delta & -\beta \end{bmatrix} - \begin{bmatrix} \beta & 0 \\ 0 & -\beta \end{bmatrix} = \begin{bmatrix} 0 & \delta \\ \delta & 0 \end{bmatrix}$$

We should point out a few things at this point. First, readers may be asking themselves, "If we have the matrix $\mathbf{H}$, then why not solve the secular equation *exactly* (within the very crude Hückel approximation)?" We will do just that below – our purpose here is to show how perturbation theory works by applying it to a problem where we can compare to the "exact" solution. Second, we should note that the way we found $\mathbf{H}'$ is not usual, but since Hückel theory never really involves calculation of integrals containing differential operators, $\mathcal{H}'$ is only *defined* in terms of the matrix elements of $\mathbf{H}'$. Finally, we note that the elements of $\mathbf{H}'$ are actually rather easy to understand: H'_{11} and H'_{22} are both zero because both the bonding and antibonding π orbitals are equally spread over both atoms. If we raise the energy of one atomic orbital by 'converting' a carbon into a boron and lower the energy of the other atomic orbital by the same amount upon 'converting' a carbon into a nitrogen, then there should be no *first-order* shift in energy of the MOs, since the *first-order* energy shifts are computed using the initial, zeroth-order orbitals. On the other hand, H'_{12} $(= H'_{21})$ are not zero because the π MOs that were appropriate for ethylene are *not* appropriate for $H_2B=NH_2$ and these matrix elements ensure that there will be mixing of these two MOs to when we 'convert' $H_2C=CH_2$ to $H_2B=NH_2$. We can now summarize the results of applying perturbation theory:

$$E_1 \simeq E_1^{(0)} + E_1^{(1)} + E_1^{(2)} = \beta + 0 + \frac{|\delta|^2}{\beta - (-\beta)} = \beta + \frac{\delta^2}{2\beta} \quad ; \quad \psi_1 \simeq \psi_1^{(0)} - \frac{\delta}{2|\beta|} \psi_2^{(0)}$$

$$E_2 \simeq E_2^{(0)} + E_2^{(1)} + E_2^{(2)} = \beta + 0 + \frac{|\delta|^2}{-\beta - (\beta)} = \beta + \frac{\delta^2}{-2\beta} \quad ; \quad \psi_2 \simeq \psi_2^{(0)} + \frac{\delta}{2|\beta|} \psi_2^{(0)}$$

(again, remember that $\beta < 0$)

Which is shown pictorially on the next page.

We can compare the perturbation theory results with exact results (within Hückel theory) by finding the eigenvalues and eigenvectors of $\mathbf{H}$. In the basis of the eigenfunctions of the unperturbed problem, $\mathbf{H} = \begin{bmatrix} \beta & \delta \\ \delta & -\beta \end{bmatrix}$, but when expressed in the atomic orbital basis, $\{\chi_B, \chi_N\}$, $\mathbf{H} = \begin{bmatrix} \delta & \beta \\ \beta & -\delta \end{bmatrix}$. The eigenvalues of both matrices are the same, since one obtains the *exact* orbital energies for $H_2B=NH_2$ no matter which basis one begins with. That is, the choice of initial basis doesn't affect the energies or orbitals finally obtained if the basis functions in one basis are just linear combinations of basis
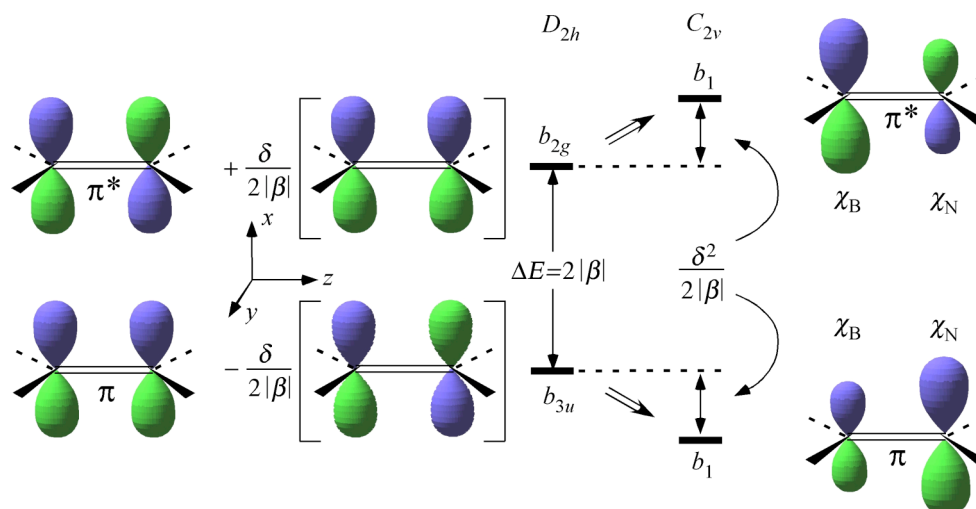
functions in the other. To find the exact energies, we solve the secular equation in either

basis: $\begin{vmatrix} \beta - E & \delta \\ \delta & -\beta - E \end{vmatrix} = \begin{vmatrix} \delta - E & \beta \\ \beta & -\delta - E \end{vmatrix} = 0$ to obtain $E = \pm\sqrt{\beta^2 + \delta^2}$.

Perturbation theory provides an approximate approach to solving quantum mechanical problems, and works best when the perturbation is 'small'. In the present context, a 'small' perturbation is one in which $\delta \ll |\beta|$. In this case, we can expand the square-root and see how perturbation theory give the first two terms in the expansion:

$$E = \pm\sqrt{\beta^2 + \delta^2} = \pm|\beta|\sqrt{1 + \left(\delta/\beta\right)^2} = \pm|\beta|\left(1 + \frac{1}{2}\left(\frac{\delta}{\beta}\right)^2 - \frac{1}{8}\left(\frac{\delta}{\beta}\right)^4 + \cdots\right) \simeq \pm\left(|\beta| + \frac{\delta^2}{2|\beta|}\right)$$

It is left to the reader to find that the wavefunctions also come into correspondence in the limit that $\delta \ll |\beta|$. Before leaving this example, let's summarize the main features and emphasize a point about symmetry we have not yet mentioned:
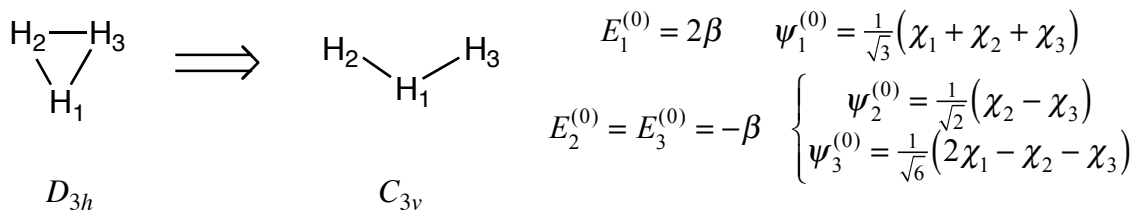
• Besides the points already emphasized, note that when a perturbation is introduced, the lower energy of the two states (orbitals, in this case) is pushed lower by mixing with the upper state (orbital) and the upper state (orbital) is pushed higher. This *must always occur* in the second-order term of perturbation theory because the energy difference in the denominator is negative in the first case and positive in the second case – the numerator must be positive. (Note that this does not mean that the first-order shifts, which were zero in this example, can't generally be either positive or negative.)

• Even when perturbation theory is problematic because the 'perturbation' isn't very small, the signs and trends in the analysis are still useful – perturbation theory is a valuable *qualitative* tool.

• Finally, note that the perturbation in this example lowers the symmetry of the system from D_{2h} to C_{2v}. The π (b_{3u}) and π^* (b_{2g}) orbitals, which belonged to different irreducible representations in D_{2h}, belong to the same representation (b_1) in C_{2v}. This must be the case if they are to mix. Conversely, if *even after applying a perturbation*, two states (levels, in this case) *still* belong to different irreducible representations in the

perturbed system, then they cannot mix. We can see this algebraically by noting that if $\psi_i^{(0)}$ and $\psi_j^{(0)}$ belong to different irreducible representations, H'_{ij} must be zero.

II. Our second example is nearly as simple as the first, but shows how to handle degeneracies using perturbation theory and the role that symmetry plays in this process. We'll examine the molecular orbitals of the H_3 molecule, first assuming it to have D_{3h} symmetry, and then we'll consider the opening of one of the bonds to generate a C_{2v}-symmetry bent structure. We'll again use Hückel theory and the perturbation will come in the form of a lost interaction (β) between H_2 and H_3. The unperturbed (D_{3h}) energies and wavefunctions are easily found:

$$E_1^{(0)} = 2\beta \qquad \psi_1^{(0)} = \tfrac{1}{\sqrt{3}}\left(\chi_1 + \chi_2 + \chi_3\right)$$

$$E_2^{(0)} = E_3^{(0)} = -\beta \quad \begin{cases} \psi_2^{(0)} = \tfrac{1}{\sqrt{2}}\left(\chi_2 - \chi_3\right) \\ \psi_3^{(0)} = \tfrac{1}{\sqrt{6}}\left(2\chi_1 - \chi_2 - \chi_3\right) \end{cases}$$

D_{3h} $\qquad\qquad\qquad$ C_{3v}

Energies and wavefunctions for the bent (C_{2v}) molecule are also easily found,

$$E_1 = \sqrt{2}\beta \qquad \psi_1 = \tfrac{1}{\sqrt{2}}\chi_1 + \tfrac{1}{2}\left(\chi_2 + \chi_3\right)$$

$$E_2 = 0 \qquad \psi_2 = \tfrac{1}{\sqrt{2}}\left(\chi_2 - \chi_3\right)$$

$$E_3 = -\sqrt{2}\beta \qquad \psi_3 = \tfrac{1}{\sqrt{2}}\chi_1 - \tfrac{1}{2}\left(\chi_2 + \chi_3\right)$$

and, when viewed pictorially, the correlation from D_{3h} MOs to C_{2v} MOs is intuitively obvious:
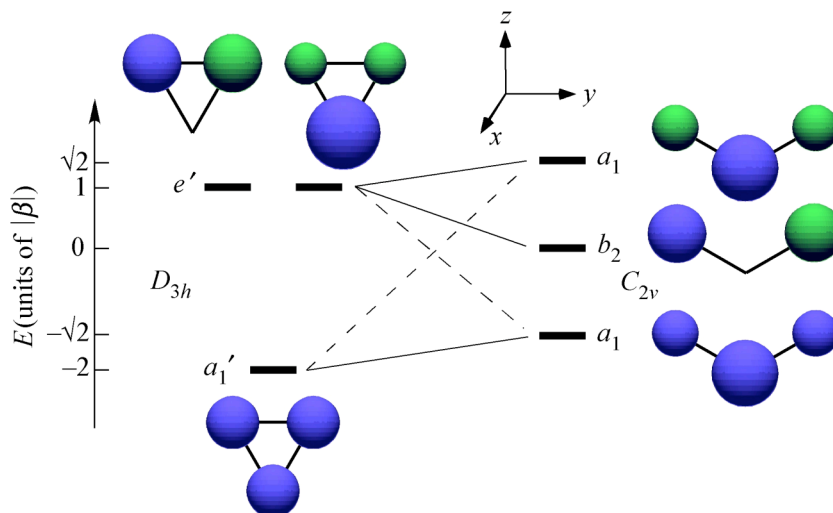
Now let's analyze this problem using perturbation theory. Expressed in terms of inter*atomic* interactions, the perturbation can be stated as $\int \chi_2 \mathcal{H} \chi_3 d\tau \to 0$. Keeping this in mind we can write the matrices $\mathbf{H}^{(0)}$ and $\mathbf{H}$ easily, and again get $\mathbf{H}'$ by difference (once again, we use the zeroth-order eigenfunctions as the basis for all three):

$$\mathbf{H}^{(0)} = \begin{bmatrix} E_1 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 \end{bmatrix} = \begin{bmatrix} 2\beta & 0 & 0 \\ 0 & -\beta & 0 \\ 0 & 0 & -\beta \end{bmatrix}$$

$$\mathbf{H} = \begin{bmatrix} \int \psi_1^{(0)} \mathcal{H} \psi_1^{(0)} d\tau & \int \psi_1^{(0)} \mathcal{H} \psi_2^{(0)} d\tau & \int \psi_1^{(0)} \mathcal{H} \psi_3^{(0)} d\tau \\ \int \psi_2^{(0)} \mathcal{H} \psi_1^{(0)} d\tau & \int \psi_2^{(0)} \mathcal{H} \psi_2^{(0)} d\tau & \int \psi_2^{(0)} \mathcal{H} \psi_3^{(0)} d\tau \\ \int \psi_3^{(0)} \mathcal{H} \psi_1^{(0)} d\tau & \int \psi_3^{(0)} \mathcal{H} \psi_2^{(0)} d\tau & \int \psi_3^{(0)} \mathcal{H} \psi_3^{(0)} d\tau \end{bmatrix}$$

Let's take each matrix element in turn,

$$\int \psi_1^{(0)} \mathcal{H} \psi_1^{(0)} d\tau = \tfrac{1}{3} \int (\chi_1 + \chi_2 + \chi_3) \mathcal{H} (\chi_1 + \chi_2 + \chi_3) d\tau =$$

$$\tfrac{1}{3} \left[\int \chi_1 \mathcal{H} \chi_1 d\tau + \int \chi_2 \mathcal{H} \chi_2 d\tau + \int \chi_3 \mathcal{H} \chi_3 d\tau + 2\int \chi_1 \mathcal{H} \chi_2 d\tau + 2\int \chi_1 \mathcal{H} \chi_3 d\tau + 2\int \chi_2 \mathcal{H} \chi_3 d\tau \right]$$

$$\therefore \int \psi_1^{(0)} \mathcal{H} \psi_1^{(0)} d\tau = \tfrac{1}{3} \left[3\alpha + 2\beta + 2\beta + 0 \right] = \alpha + \tfrac{4}{3}\beta \quad \text{(we'll take } \alpha = 0 \text{, as usual)}$$

$$\int \psi_2^{(0)} \mathcal{H} \psi_2^{(0)} d\tau = \tfrac{1}{2} \int (\chi_2 - \chi_3) \mathcal{H} (\chi_2 - \chi_3) d\tau = 0$$

$$\int \psi_3^{(0)} \mathcal{H} \psi_3^{(0)} d\tau = \tfrac{1}{6} \int (2\chi_1 - \chi_2 - \chi_3) \mathcal{H} (2\chi_1 - \chi_2 - \chi_3) d\tau = -\tfrac{4}{3}\beta$$

$$\int \psi_2^{(0)} \mathcal{H} \psi_1^{(0)} d\tau = \tfrac{1}{\sqrt{6}} \int (\chi_2 - \chi_3) \mathcal{H} (\chi_1 + \chi_2 + \chi_3) d\tau = 0$$

$$\int \psi_3^{(0)} \mathcal{H} \psi_1^{(0)} d\tau = \tfrac{1}{\sqrt{18}} \int (2\chi_1 - \chi_2 - \chi_3) \mathcal{H} (\chi_1 + \chi_2 + \chi_3) d\tau = \tfrac{\sqrt{2}}{3}\beta$$

$$\int \psi_3^{(0)} \mathcal{H} \psi_2^{(0)} d\tau = \tfrac{1}{\sqrt{12}} \int (2\chi_1 - \chi_2 - \chi_3) \mathcal{H} (\chi_2 - \chi_3) d\tau = 0$$

$$\therefore \mathbf{H} = \begin{bmatrix} \tfrac{4}{3}\beta & 0 & \tfrac{\sqrt{2}}{3}\beta \\ 0 & 0 & 0 \\ \tfrac{\sqrt{2}}{3}\beta & 0 & -\tfrac{4}{3}\beta \end{bmatrix} \quad \text{; So, finally we use the relationship } \mathbf{H}' = \mathbf{H} - \mathbf{H}^{(0)}$$

$$\mathbf{H}' = \begin{bmatrix} \tfrac{4}{3}\beta & 0 & \tfrac{\sqrt{2}}{3}\beta \\ 0 & 0 & 0 \\ \tfrac{\sqrt{2}}{3}\beta & 0 & -\tfrac{4}{3}\beta \end{bmatrix} - \begin{bmatrix} 2\beta & 0 & 0 \\ 0 & -\beta & 0 \\ 0 & 0 & -\beta \end{bmatrix} = \begin{bmatrix} -\tfrac{2}{3}\beta & 0 & \tfrac{\sqrt{2}}{3}\beta \\ 0 & \beta & 0 \\ \tfrac{\sqrt{2}}{3}\beta & 0 & -\tfrac{1}{3}\beta \end{bmatrix}$$

The diagonal elements of $\mathbf{H}'$ are easily understood: the most bonding orbital $\psi_1^{(0)}$ and the antibonding orbital $\psi_3^{(0)}$ are both destabilized by loss of overlap between χ_2 and χ_1. Since the product of the coefficients of these two AOs is twice as large for $\psi_1^{(0)}$ as for $\psi_3^{(0)}$, the destabilization of $\psi_1^{(0)}$ twice as large ($H'_{11} = 2H'_{33}$). On the other hand, the antibonding orbital $\psi_2^{(0)}$ is *stabilized* by loss of overlap between χ_2 and χ_1, and the magnitude of the product of the coefficients of these two AOs is three times as large for $\psi_1^{(0)}$ as for $\psi_3^{(0)}$ ($H'_{22} = -3H'_{33}$).

The off-diagonal elements of $\mathbf{H}'$ are important to understand – indeed, they are the key to understanding how degenerate perturbation theory should be applied. The only unique nonzero off-diagonal matrix element is $H'_{13}(= H'_{31})$. However, had the e' orbitals been chosen differently, both H'_{23} and H'_{13} could have been nonzero. Remember, any orthogonal pair of orbitals constructed from the two e' orbitals is a legitimate alternative choice as long as the molecule has D_{3h} symmetry. Thus, if we constructed combinations,

$\psi_{2p}^{(0)} = a\psi_2^{(0)} + b\psi_3^{(0)}$, $\psi_{3q}^{(0)} = b\psi_2^{(0)} - a\psi_3^{(0)}$, $(a^2 + b^2 = 1)$, $\psi_{2p}^{(0)}$ and $\psi_{3q}^{(0)}$ form a basis for the e' representation. But *only* the combination of e' orbitals chosen here are *correct zeroth-order wavefunctions* for the perturbed system. This is so because in the C_{2v} subgroup appropriate for the perturbed problem, $\psi_2^{(0)}$ belongs to the b_2 representation and $\psi_3^{(0)}$ belongs to the a_1 representation – any other choice would require mixing orbitals of different symmetry in the perturbed system. The essential requirement of the e' orbital combination that must be used in this case is that orbitals must be chosen such that they are (anti)symmetric with respect to the C_2 or $\sigma(xz)$ plane – which amounts to the same thing since both e' orbitals must be symmetric with respect to $\sigma(yz)$. An exactly analogous choice of degenerate orbitals (or states) must be always be chosen in any perturbation theory application where the perturbation lowers the symmetry of the system:
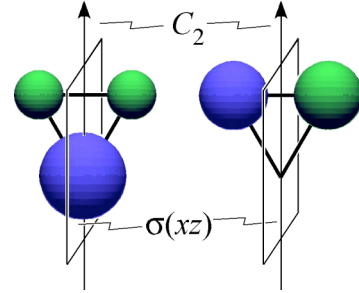
> *Correct zeroth-order wavefunctions must be chosen for degenerate states such that each of the higher-symmetry wavefunctions belongs to particular irreducible representations of the subgroup of the perturbed system.*

Now we can proceed to write down the perturbed energies and wavefunctions:

$$E_1 \simeq E_1^{(0)} + E_1^{(1)} + E_1^{(2)} = 2\beta - \tfrac{2}{3}\beta + \frac{\left|\frac{\sqrt{2}}{3}\beta\right|^2}{2\beta - (-\beta)} = \tfrac{38}{27}\beta \quad ; \quad \psi_1 \simeq \psi_1^{(0)} + \frac{\sqrt{2}}{9}\psi_3^{(0)}$$

$$E_2 \simeq E_2^{(0)} + E_2^{(1)} + E_2^{(2)} = -\beta + \beta + 0 = 0 \quad ; \quad \psi_2 \simeq \psi_2^{(0)}$$

$$E_3 \simeq E_3^{(0)} + E_3^{(1)} + E_3^{(2)} = -\beta - \tfrac{1}{3}\beta + \frac{\left|\frac{\sqrt{2}}{3}\beta\right|^2}{-\beta - (2\beta)} = -\tfrac{38}{27}\beta \quad ; \quad \psi_3 \simeq \psi_3^{(0)} - \frac{\sqrt{2}}{9}\psi_1^{(0)}$$
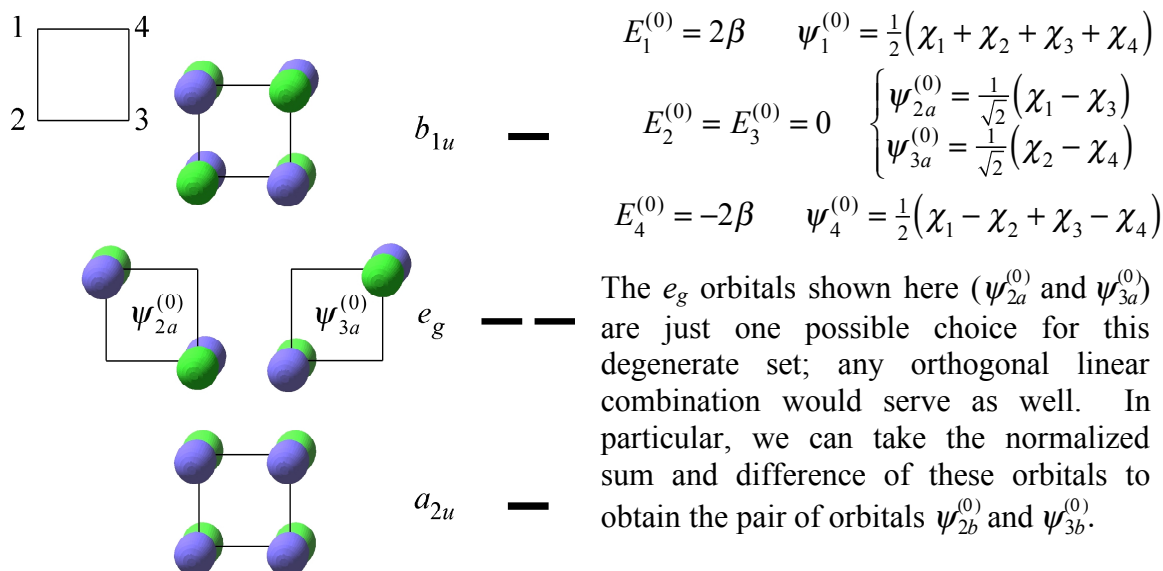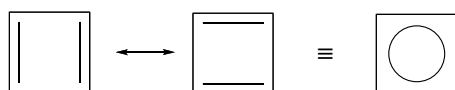
(again, remember that $\beta < 0$)

The first order energy shifts have been discussed; the second order effects are seen only in the a_1 energy levels and wavefunctions because only levels of the same symmetry (in the perturbed system) can be mixed by the perturbation. The second-order effect on the lower a_1 level *must* push it down in energy and we should expect that it modifies the wavefunction by increasing the contribution of center hydrogen atom (which is still bonded to two neighbors) and decreasing the contribution of the two outer hydrogen atoms (which have each lost a bonding neighbor). Correspondingly, the upper a_1 level *must* be pushed up in energy in second-order and in the wavefunction is modified by increasing the contribution of outer hydrogen atoms which were formerly 'in phase' within the upper a_1 orbital.

A comparison of the *exact* and perturbed results shows perturbation theory to yield a remarkably good approximation, especially since the magnitude of the perturbation is not small:

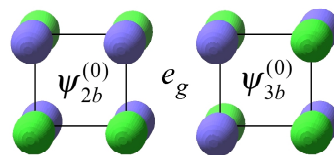|	Exact (units of $|\beta|$)	*Perturbation Theory	Zeroth-Order
E_1	$-\sqrt{2} = -1.414\ldots$	$-1.407\ldots$	-2
E_2	0	0	1
E_3	$\sqrt{2} = 1.414\ldots$	$1.407\ldots$	1
ψ_1	$\frac{1}{\sqrt{2}}\chi_1 + \frac{1}{2}(\chi_2 + \chi_3)$	$0.6971\chi_1 + 0.5070(\chi_2 + \chi_3)$	$\frac{1}{\sqrt{3}}\chi_1 + \frac{1}{\sqrt{3}}(\chi_2 + \chi_3)$
ψ_2	$\frac{1}{\sqrt{2}}(\chi_2 - \chi_3)$	$\frac{1}{\sqrt{2}}(\chi_2 - \chi_3)$	$\frac{1}{\sqrt{2}}(\chi_2 - \chi_3)$
ψ_3	$\frac{1}{\sqrt{2}}\chi_1 - \frac{1}{2}(\chi_2 + \chi_3)$	$0.7169\chi_1 - 0.4929(\chi_2 + \chi_3)$	$\frac{2}{\sqrt{6}}\chi_1 - \frac{1}{\sqrt{6}}(\chi_2 + \chi_3)$

*The perturbed wavefunctions have been renormalized.

III.   Let's look at a final pair of examples to more fully illustrate the manner in which symmetry affects the application of perturbation theory in practice. Consider the cyclobutadiene molecule, for which the π orbital energies and wavefunctions are given below.
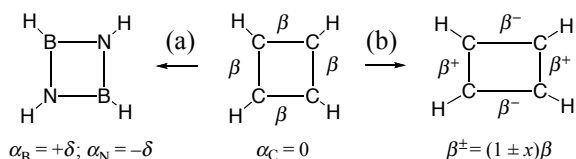

$E_1^{(0)} = 2\beta \qquad \psi_1^{(0)} = \frac{1}{2}(\chi_1 + \chi_2 + \chi_3 + \chi_4)$

b_{1u} —

$E_2^{(0)} = E_3^{(0)} = 0 \qquad \begin{cases} \psi_{2a}^{(0)} = \frac{1}{\sqrt{2}}(\chi_1 - \chi_3) \\ \psi_{3a}^{(0)} = \frac{1}{\sqrt{2}}(\chi_2 - \chi_4) \end{cases}$

$E_4^{(0)} = -2\beta \qquad \psi_4^{(0)} = \frac{1}{2}(\chi_1 - \chi_2 + \chi_3 - \chi_4)$

e_g – –

The e_g orbitals shown here ($\psi_{2a}^{(0)}$ and $\psi_{3a}^{(0)}$) are just one possible choice for this degenerate set; any orthogonal linear combination would serve as well. In particular, we can take the normalized sum and difference of these orbitals to obtain the pair of orbitals $\psi_{2b}^{(0)}$ and $\psi_{3b}^{(0)}$.

a_{2u} —

$\psi_{2b}^{(0)} = \frac{1}{\sqrt{2}}\left(\psi_{2a}^{(0)} - \psi_{3a}^{(0)}\right) = \frac{1}{2}(\chi_1 - \chi_2 - \chi_3 + \chi_4)$

$\psi_{3b}^{(0)} = \frac{1}{\sqrt{2}}\left(\psi_{2a}^{(0)} + \psi_{3a}^{(0)}\right) = \frac{1}{2}(\chi_1 + \chi_2 - \chi_3 - \chi_4)$

We will examine the effect on these orbitals exerted by two different 'perturbations', (a) the transformation of the C_4H_4 ring into an alternating $B_2N_2H_4$ ring of D_{2h} symmetry; (b) the distortion of the square D_{4h} symmetry C_4H_4 ring into a rectangular D_{2h} symmetry C_4H_4 ring in which

the magnitude of the π orbital interactions increase (β^+) for the shorter C-C bonds and decrease (β^-) for the longer C-C bonds. For case (a), the perturbation expressed in terms of AOs is $\int \chi_1 \mathcal{H} \chi_1 d\tau = \int \chi_3 \mathcal{H} \chi_3 d\tau$; $0 \rightarrow +\delta$ and $\int \chi_2 \mathcal{H} \chi_2 d\tau = \int \chi_4 \mathcal{H} \chi_4 d\tau$; $0 \rightarrow -\delta$, since the boron positions are atoms 1 and 3 and the nitrogen positions are atoms 2 and 4. For case (b), the 1–2 and 3–4 interactions increase and the 2–3 and 1–4 interactions are weakened: $\int \chi_1 \mathcal{H} \chi_2 d\tau = \int \chi_3 \mathcal{H} \chi_4 d\tau$; $\beta \rightarrow \beta^+$ and $\int \chi_2 \mathcal{H} \chi_3 d\tau = \int \chi_1 \mathcal{H} \chi_4 d\tau$; $\beta \rightarrow \beta^-$.

Before applying perturbation theory, one should evaluate the correlations between the irreducible representations (IRs) of the original system (D_{4h}) and the IRs of the perturbed system, which have D_{2h} symmetry in both case (a) and (b) – though the symmetry elements retained are different in the cases. In case (a), the $D_{4h} \rightarrow D_{2h}$ correlations for the π orbitals are $a_{2u} \rightarrow b_{1u}$, $e_g \rightarrow b_{2g} \oplus b_{3g}$, and $b_{1u} \rightarrow b_{1u}$; in case (b), the $D_{4h} \rightarrow D_{2h}$ correlations for the π orbitals are $a_{2u} \rightarrow b_{1u}$, $e_g \rightarrow b_{2g} \oplus b_{3g}$, and $b_{1u} \rightarrow a_u$. For treating case (a), the correct zeroth-order e_g orbitals are $\psi_{2a}^{(0)}$ and $\psi_{3a}^{(0)}$, which respectively belong to the b_{3g} and b_{2g} representations in the D_{2h} subgroup appropriate for the $B_2N_2H_4$ system. For case (b), the correct zeroth-order combination of e_g orbitals are $\psi_{2b}^{(0)}$ and $\psi_{3b}^{(0)}$, which respectively belong to the b_{2g} and b_{3g} representations in the D_{2h} subgroup appropriate for the rectangular cyclobutadiene system.

The group-subgroup correlations greatly simplify the application of perturbation theory because the only second-order orbital mixings that can occur involve orbitals with the same symmetry in the subgroup. In case (a), only the upper and lower bonding and antibonding orbitals, both having b_{1u} symmetry in the perturbed system, will be mixed by the perturbation. In case (b), *no second-order mixing occurs* at all, because all the orbitals belong to different irreducible representations in the appropriate D_{2h} subgroup.

We calculate the matrix elements for each case: (a) $H'_{11} = 0$, $H'_{22} = \delta$, $H'_{33} = -\delta$, $H'_{44} = 0$, $H'_{14} = \frac{1}{4}(2\alpha_B - 2\alpha_N) = \delta$; (b) $H'_{11} = 0$, $H'_{22} = \frac{1}{4}(4\beta^+ - 4\beta^-) = 2x\beta$, $H'_{33} = -2x\beta$, $H'_{44} = 0$; and calculation of the both the first and second-order energy shifts is a simple matter. The figure summarizes the results.