

Revisiting Woodward–Hoffmann Rules

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Physical chemists are missing a wonderful opportunity to explore Hückel theory in a nontraditional environment. The Woodward–Hoffmann rules (1) for electrocyclization reactions, a standard part of current organic chemistry curriculums, provide a marvelous example of Hückel-type computations that are only slightly more complicated than those discussed in typical first-year physical chemistry courses. Renewed interest in these kinds of reactions makes understanding this discussion even more germane (2).

Following Woodward and Hoffmann's example we employ the electrocyclic reaction of forming a single bond between termini of a system containing four carbon atoms, each sp^2 hybridized, with their σ bond skeleton essentially "frozen", and each contributing a p-electron (i.e., the example concerns the conversion of butadiene to cyclobutene [see Fig. 1]).

We remove the protons (these protons are often used as markers to distinguish conrotatory and disrotatory motions in qualitative discussions) for clarity and focus entirely on the π , p , and p_z orbital structure. We define the molecule's plane as containing the x and z axes, with the y -axis perpendicular to that plane; carbons 1 and 4 define the z -axis, and the x - y plane bisects the 1–4 line. This means that we are dealing with p_y orbitals when we do normal Hückel computations (see Fig. 1).

Defining the Conrotatory and Disrotatory Processes

To proceed, we define the twist angles (θ 's) (see Fig. 2) required to follow the reaction in order to define a reaction coordinate (ω). The difference between disrotatory and conrotatory motions is seen in the relationship between the concerted changes in these angles; that is, $\theta_{1-2} = \theta_{3-4}$ for conrotatory, and $\theta_{1-2} = -\theta_{3-4}$ for disrotatory. Finally, we define an enlarged basis set using p_z for "horizontal" and p_y for

"vertical" normalized p-orbitals. A generalized orbital (for atoms 1 and/or 4) then is

$$p = p_z \sin \theta + p_y \cos \theta \quad (1)$$

Since the Hückel scheme is intimately tied to the overlap between orbitals on different carbon atoms, we next compute the relevant overlap integrals.

Overlap Integrals

The overlap between the orbital on atom 2 and the orbital on atom 1 is

$$S_{1-2} = S_{2-1} = \int p_2(p_z \sin \theta_{1-2} + p_y \cos \theta_{1-2})_1 dt \quad (2)$$

Because p_2 is a p_y orbital orthogonal to p_z , we know that the first term vanishes. Thus

$$S_{1-2} = \langle p_{y1} | p_{y1} \rangle \cos \theta_{1-2} \quad (3)$$

since p_2 and p_y are identical (but relatively displaced) normalized p orbitals, parallel to each other (i.e., the standard Hückel assumption).

Normally, the exchange integrals are declared proportional to the overlap integrals, so we now turn our attention to these exchange integrals.

The Exchange Integral (between Carbons 1–2 and 3–4)

The matrix element of the Hamiltonian connecting these two orbitals would be

$$\mathcal{H}_{1-2} = \mathcal{H}_{2-1} = \int p_1 \mathcal{H} p_2 dt = \int ((p_z \sin \theta_{1-2} + p_y \cos \theta_{1-2})_1) \mathcal{H} p_2 dt \quad (4)$$

which gives

$$\mathcal{H}_{1-2} = \int (p_z \sin \theta_{1-2} \mathcal{H} p_z + p_y \cos \theta_{1-2} \mathcal{H} p_y) dt \quad (5)$$

Since p_2 is a p_y orbital (and is "perpendicular" [orthogonal]

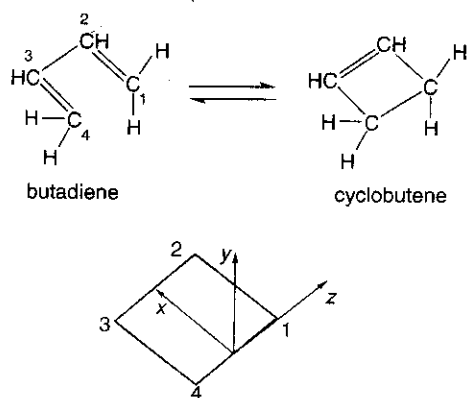


Figure 1. Butadiene interconverting to cyclobutene. The coordinate system shown defines "vertical" orbitals as p_y , and the making/breaking bond as being formed from p_z .

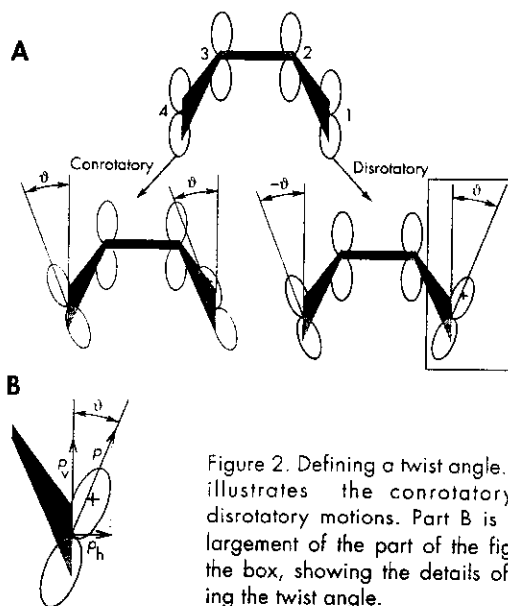


Figure 2. Defining a twist angle. Part A illustrates the conrotatory and disrotatory motions. Part B is an enlargement of the part of the figure in the box, showing the details of defining the twist angle.

to p_z), according to normal usage, we have

$$\mathcal{H}_{1-2} = \int p_x \mathcal{H} p_z \cos \theta_{1-2} d\tau \equiv \beta \cos \theta_{1-2} \quad (6)$$

β is the standard Hückel value assigned for parallel p-orbitals (here p_x) having a preexisting σ bond. Equation 6 often leads one to declare the exchange integral proportional to the overlap integral (eq 3).

The Exchange Integral (between Carbons 1-4)

We artificially constrain the carbon geometry to a square, so that the forming 1-4 bond will not be canted relative to the emerging bond line. (Had we left the sp^2 hybridization of atoms 2 and 3, the 1-2-3 and 2-3-4 bond angles would be 120° , which would have forced the p-orbitals on atoms 1 and 4 to approach each other in canted fashion. Instead, we force the 1-2-3 and 2-3-4 bond angles to 90° so that the forming bond [p_σ or p_σ^*] is optimally aligned. This substitutes for the 109.471° expected if atoms 1 and 4 rehybridized into sp^3 .) The 1-4 Hamiltonian matrix element then is

$$\mathcal{H}_{1-4} = \int (p_{h1} \sin \theta_{1-2} + p_{y1} \cos \theta_{1-2}) \mathcal{H} (p_{h4} \sin \theta_{3-4} + p_{y4} \cos \theta_{3-4}) d\tau \quad (7)$$

that is,

$$\begin{aligned} \mathcal{H}_{1-4} = & \int p_{h1} \sin \theta_{1-2} \mathcal{H} p_{h4} \sin \theta_{3-4} d\tau + \\ & \int p_{h1} \sin \theta_{1-2} \mathcal{H} p_{y4} \cos \theta_{3-4} d\tau + \int p_{y1} \cos \theta_{1-2} \mathcal{H} p_{h4} \sin \theta_{3-4} d\tau + \\ & \int p_{y1} \cos \theta_{1-2} \mathcal{H} p_{y4} \cos \theta_{3-4} d\tau \end{aligned} \quad (8)$$

Since p_y is orthogonal to p_x , half of these integrals vanish. We obtain

$$\mathcal{H}_{1-4} = \beta^h \sin \theta_{1-2} \sin \theta_{3-4} + \beta \cos \theta_{1-2} \cos \theta_{3-4} \quad (9)$$

where we are defining a "horizontal" β^h in analogy with the "parallel" one normally used in these kinds of calculations. Since there is no σ_{1-4} bond (from prehybridized sp^2 orbitals), the normal Hückel rules tell us that the second term in eq 9 vanishes:

$$\mathcal{H}_{1-4} = \beta^h \sin \theta_{1-2} \sin \theta_{3-4} \quad (10)$$

The One-Electron Hamiltonian Matrix

The one-electron Hückel Hamiltonian is

$$\begin{pmatrix} \alpha & \beta \cos \theta_{1-2} & 0 & \mathcal{H}_{1-4} \\ \beta \cos \theta_{2-1} & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \cos \theta_{3-4} \\ \mathcal{H}_{4-1} & 0 & \beta \cos \theta_{4-3} & \alpha \end{pmatrix} \quad (11)$$

where, when $\theta_{3-4} = \theta_{1-2} = 0$, we have maximum overlap. α is the standard Hückel $\langle i | \mathcal{H} | i \rangle$ matrix element. Notice that as θ_{1-2} approaches 90° , the overlap between orbitals on atoms 1 and 4 increases to a maximum, and the overlap between orbitals on atoms 1 and 2 as well as between 3 and 4 decreases to zero. Notice further that we need the β^h (previously defined) to distinguish between the nascent σ bond forming (1-4) and the destroyed π bonds (1-2 and 3-4; there is no twist angle for 2-3).

Theoretically we can now plot the energy as a function of the reaction coordinate ω . The conrotatory and disrotatory aspects are obtained by choosing the previously noted relation between the relevant angles, i.e., $\theta_{1-2} = \theta_{3-4} \equiv \omega$ or $\theta_{1-2} = -\theta_{3-4} \equiv \omega$. (In the original Woodward and Hoffmann book,

the example is predicated on the transformation of the sp^2 terminal hybrids to sp^3 hybrids, so that σ bonds could be formed between atoms 1 and 4. We choose instead to leave the hybridization alone and allow these terminal carbon atoms to bond using p_σ orbitals. Only the symmetry considerations matter, so our approach is good enough.) In both cases, the 1-2 and the 3-4 " π " bonds are broken, a 2-3 " π " bond forms, and a 1-4 σ bond forms.

Defining the Reaction Path

Conrotatory Hamiltonian

For conrotatory motions, defining the twist angle $\theta_{1-2} = \theta_{3-4} \equiv \omega$, we have (using eq 10)

$$\begin{pmatrix} \alpha & \beta \cos \omega & 0 & \beta^h \sin^2 \omega \\ \beta \cos \omega & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \cos \omega \\ \beta^h \sin^2 \omega & 0 & \beta \cos \omega & \alpha \end{pmatrix} \quad (12)$$

At $\omega = 0$ we have

$$\begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix} \quad (13)$$

and at $\omega = \pi/2$ we have

$$\begin{pmatrix} \alpha & 0 & 0 & \beta^h \\ 0 & \alpha & \beta & 0 \\ 0 & \beta & \alpha & 0 \\ \beta^h & 0 & 0 & \alpha \end{pmatrix} \quad (14)$$

Disrotatory Hamiltonian

For disrotatory motions, defining the twist angle $\theta_{1-2} = -\theta_{3-4} \equiv \omega$, we therefore have

$$\begin{pmatrix} \alpha & \beta \cos \omega & 0 & -\beta^h \sin^2 \omega \\ \beta \cos \omega & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \cos \omega \\ -\beta^h \sin^2 \omega & 0 & \beta \cos \omega & \alpha \end{pmatrix} \quad (15)$$

At $\omega = 0$ we have (again)

$$\begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix} \quad (16)$$

and at $\omega = \pi/2$ we have

$$\begin{pmatrix} \alpha & 0 & 0 & -\beta^h \\ 0 & \alpha & \beta & 0 \\ 0 & \beta & \alpha & 0 \\ -\beta^h & 0 & 0 & \alpha \end{pmatrix} \quad (17)$$

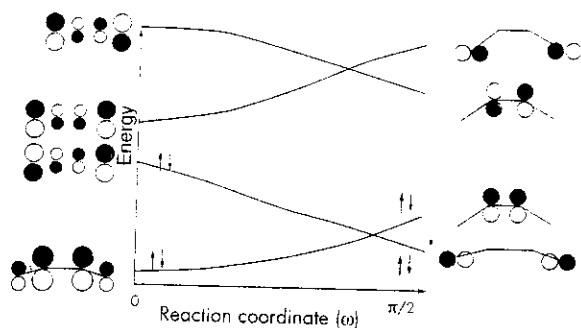


Figure 3. Disrotatory ring closure with $\beta^h < 0$ and conrotatory ring closure with $\beta^h > 0$. The latter corresponds to the thermally allowed ring closure predicted by Woodward and Hoffmann.

The difference between the two reaction paths shows up in the \mathcal{H}_{1-4} term, where the product of sines reflects the difference in signs between the two angles.

What Is the Sign of the "Horizontal" β^h ?

We need to establish a value for β^h . Technically, β^h corresponds to evaluating an integral (3) such as

$$\beta^h = \int (z - R/2)e^{-\alpha r_1} \mathcal{H}(z + R/2)e^{-\alpha r_2} dt \quad (18)$$

where r_1 and r_2 are the distances from nucleus 1 and 4, respectively, to the electron, and R is the distance between carbon atoms one and four.

Solving the Schrödinger Equation

Rather than evaluate such an integral, since everything now hinges on the sign of β^h , it is reasonable to do the computations twice, based first on one sign, and then on the other.

Assume the "Horizontal" β^h Is Negative

If one follows the adiabatic paths during conrotatory and disrotatory ring closure, starting at the ground state, one has the following. For disrotatory ring closure, when one adiabatically follows the energy levels as the twist angle changes from zero to $\pi/2$ the four ground state electrons remain in the ground state, switching identity, but no more (see Fig. 3). For the conrotatory ring closure, one sees that the ground state electrons find themselves in an excited state of the cyclic product (see Fig. 4).

Assume the "Horizontal" β^h Is Positive

We start with disrotatory ring closure and adiabatically follow the energy levels as the twist angle changes from zero to $\pi/2$. The ground state electrons find themselves promoted to an excited state (see Fig. 4).

For the conrotatory ring closure, we find that the ground state electrons adiabatically remain in a ground state configuration (see Fig. 3). Clearly, given these diagrams, it is very important what the sign of β^h is! Contrary to expectations about β , which is negative, β^h turns out to be positive. This behavior is reminiscent of the behavior of p_z orbitals in the discussion of p_σ bond formation in H_2^+ .

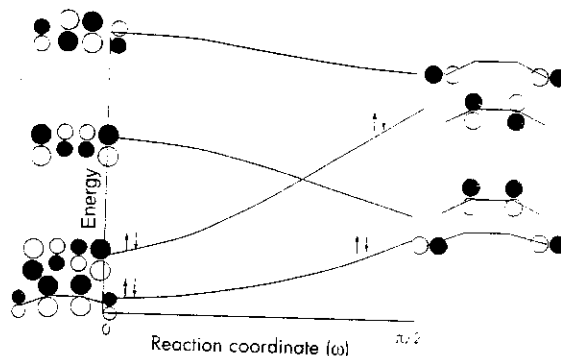


Figure 4. Conrotatory ring closure with $\beta^h < 0$ and disrotatory ring closure with $\beta^h > 0$.

Discussion

In these days, symbolic mathematical manipulation programs (Maple, Mathematica, Macsyma, etc.) make it extremely simple for students to assign numerical values to the various constants, assemble the Hamiltonian matrix, diagonalize it, and inspect both the eigenvectors and the eigenvalues emerging from the calculation. Repeating the calculation as ω changes allows students to track the reaction coordinate and watch changes in both eigenvectors and eigenvalues as they occur.

Discussing the Woodward–Hoffmann rules from the point of view articulated here shows in manifest detail how many and what kind of assumptions are being made, even in simplified models for electrons and bonding.

Since the idea of a "reaction coordinate" occurs also in elementary kinetics, it seems valuable to follow this calculation from that point of view also.

It is interesting to note that a slightly different approach based on Möbius strips (5) can be seen here in the plots in Figures 3 and 4, where, midway between the end points—that is, at the "crossing points" (6) ($\omega = 45^\circ$)—the pattern of energy levels is Möbius-like.

Acknowledgment

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