



# Hückel theory and distinguishing between isospectral molecules: 1,4-divinylbenzene and 2-phenylbutadiene, and tetramethylenemethane and cyclobutadiene + carbon

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## Abstract

Although Hückel molecular orbital theory (HMO) has been generally outdated as a computational method for the energetics of organic molecules, there is still much we can learn from it. This paper explores two compounds, 1,4-divinylbenzene and 2-phenylbutadiene, which, according to Hückel theory, are isospectral, i.e., they have the same eigenvalues and orbital energy levels. However, by using a small, well-defined perturbation, we show it is mathematically possible to distinguish between these two compounds. We suggest that this is a general procedure for distinguishing isospectral pairs of molecules as opposed to the two species being identical.

**Keywords** Hückel Theory · Isospectral · Eigenvalues · Perturbation

## Introduction

Although Hückel molecular orbital theory (HMO) [1–4] has been generally viewed as outdated as a computational method for the energetics of organic molecules [5–11], there is still much we can learn from it [12–14]. Hückel theory, created by Erich Hückel, is a molecular orbital-based theory that states a hydrocarbon with a conjugated  $\pi$  system can be described mathematically using an adjacency matrix, i.e., the eigenvectors of an adjacency matrix are the  $\pi$  orbitals, and the corresponding eigenvalues are the corresponding orbital energies. Take the example of benzene, as shown in Fig. 1. The carbons can be labeled in either formulation but will produce the same result mathematically. There are many ways the carbons can be labeled, 6 (720) in fact, since there are six carbon atoms that may be arbitrarily permuted.

As there are six carbons, a 6-by-6 Hamiltonian matrix can be constructed where an  $\alpha$  is placed on each of the diagonal elements and a  $\beta$  is placed where two carbons are connected. The  $\alpha$ 's represent the energy of a 2p atomic orbital, and the  $\beta$ 's represent the overlap of two such carbon 2p orbitals and, thus, the energy of an electron in a  $\pi$  molecular orbital.  $\alpha$  is typically set equal to 0 for a carbon atom, with some other value to specify a heteroatom as found for the nitrogen in pyridine.  $\beta$  is often set equal to 1 for the energy level of the  $\pi$  orbital as found in ethylene. A modified  $\beta$  is used for bonds involving heteroatoms such as found in pyridine for the two carbon-nitrogen bonds, C<sub>2</sub>-N and C<sub>6</sub>-N. An example of a 6-by-6 Hamiltonian matrix for benzene is shown in Fig. 2 where we have used the first numbering system from Fig. 1. (The Hamiltonian matrix is equivalent to the adjacency matrix since it tells us what atoms are adjacent, hence bonded, to each other.)

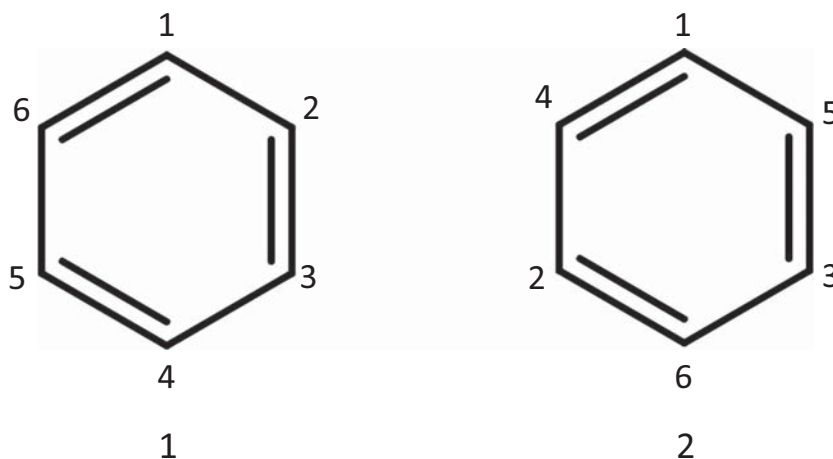
Taking the Hückel Hamiltonian in Fig. 2, with  $\alpha = 0$  and  $\beta = 1$  as mentioned above, and substituting into the matrix equation that follows, one can find the energy levels for the  $\pi$  molecular orbitals of benzene by solving for the eigenvalues and eigenvectors of the so-defined adjacency matrix. The matrix equation,  $(H - E) \psi = 0$ , is equivalent to solving  $H \psi = E \psi$ , the Schrödinger equation as customarily written. Using the “eig” function in MATLAB R2019b [15] and the “Eigenvalues” and “Eigenvectors” functions in Wolfram Mathematica 12.0 [16], we then obtain the eigenvalue spectrum for benzene  $\{2, 1, 1, -1, -1, -2\}$ , along with their

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**Fig. 1** Two of 720 different ways to number the carbons on benzene for use in Hückel theory



corresponding eigenvectors. Both packages shall be used for the remainder of our study for determination of the eigenvalues and eigenvectors of the matrices which may be related to the energy levels and orbitals of the molecules of interest.

Hückel theory has been used for predicting energy levels of conjugated molecules, but not necessarily for distinguishing between molecules in that two different molecules occasionally have the same set of eigenvalues, i.e., they are defined as isospectral [17–20]. This paper explores two different pairs of isospectral compounds; an admittedly commonly cited pair of isospectral molecules, 2-phenylbutadiene and 1,4-divinylbenzene [21–25], as well as the mathematically simplest isospectral pair tetramethylenemethane (neopentane-1,1',1'',1'''-tetrayl), as related to spiro[4, 4]nonane-1,4,6,9-tetrayl [26, 27], and cyclobutadiene with a fifth unconnected carbon (planar methane) [28]. From reference 28, we find the terms isospectral and cospectral are synonyms. Since “cospectral” has generally been used in mathematical settings and “isospectral” has generally been used in chemical settings, we shall use the term isospectral through the remainder of this article. It is confirmed that the two molecules of each isospectral pair are in fact different species. We admit now that a knowledge of undergraduate organic chemistry, even

just the first course, is more than adequate to perceive the difference; we want to do this within the Hückel framework of the current study.

## Results and discussion

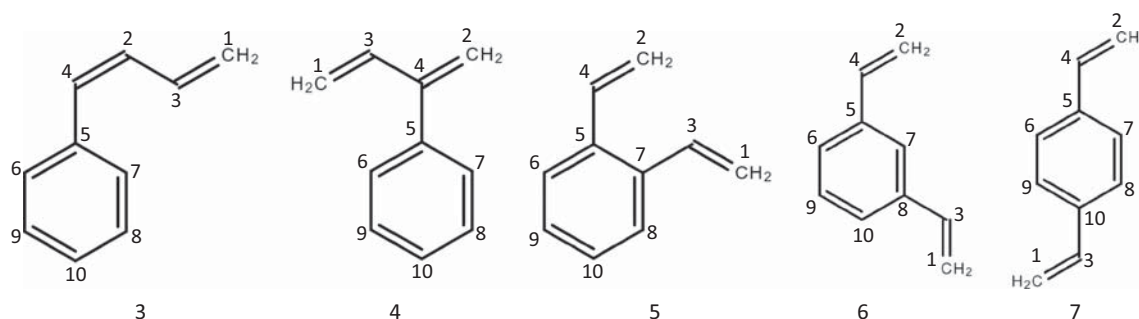
For the first part of the results and discussion, we address the isospectral pair of 2-phenylbutadiene and 1,4-divinylbenzene. It has been shown in previous studies that 2-phenylbutadiene and 1,4-divinylbenzene are isospectral. However, 2-phenylbutadiene and 1-phenylbutadiene are isomeric but not isospectral, and, similarly, 1,4-divinylbenzene, 1,3-divinylbenzene, and 1,2-divinylbenzene are also isomeric but not isospectral. The structures of these molecules are shown in Fig. 3.

Out of simplicity, we are ignoring 1,5-divinylbenzene, 1,6-divinylbenzene, 3-phenylbutadiene, and 4-phenylbutadiene in order to not have any repeat structures; we immediately identify them as identical except for the drawing and numbering of other divinylbenzenes and phenylbutadienes in our list. We are also not distinguishing between the (*Z*)- and (*E*)-isomers of 1-phenylbutadiene, as the numbering of the carbons, and,

**Fig. 2** a The six-by-six Hückel Hamiltonian matrix for benzene. b The Hückel Hamiltonian matrix with  $\alpha$  set equal to 0 and  $\beta$  set equal to 1

$$\begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix} \quad \mathbf{a}$$

$$\begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \quad \mathbf{b}$$



**Fig. 3** The five molecules of the first part of our study. (3) 1-phenylbutadiene, (4) 2-phenylbutadiene, (5) 1,2-divinylbenzene, (6) 1,3-divinylbenzene, and (7) 1,4-divinylbenzene, where we have labeled the carbons 1–10 on reflecting there are ten carbon atoms in each species

therefore, the eigenvalues would be the same. The eigenvalue spectra of the molecules, calculated using both MATLAB R2019a and Mathematica 12.0, are shown in Table 1. We reiterate that the eigenvalue spectra of 2-phenylbutadiene and 1,4-divinylbenzene are identical.

The question then stands: is there any systematic (i.e., not “merely” visual) way to distinguish between the two isospectral molecules? We show that if a small perturbation is applied, it becomes possible to distinguish between these two molecules. Say we have a Hamiltonian  $H_1$  for 2-phenylbutadiene and a Hamiltonian  $H_2$  for 1,4-

divinylbenzene. We then have two matrix equations,  $H_1\psi_1 = E_1\psi_1$ , and  $H_2\psi_2 = E_2\psi_2$ . We can define a matrix  $A$  that we add to each Hamiltonian matrix. When the matrix elements  $A_{ij}$  equals  $A\delta_{ij}$ , the eigenvalues of  $H + A$  equal those of  $H$  to which we add the constant  $A$ . However, say  $A$  is not constant but still diagonal and is dependent on the number of neighboring (i.e., directly bonded) carbons, as shown in Fig. 4. It then becomes possible to differentiate between these two molecules. For example, let  $A_{ii} = 0.01$  when the carbon specified has one carbon neighbor,  $A_{ii} = 0.02$  when the carbon specified has two carbon neighbors,  $A_{ii} = 0.03$  when the carbon speci-

**Table 1** Eigenvalue spectra for the five molecules of the first part of the study

Molecule	Eigenvalues
1-phenylbutadiene (3)	{2.1543, 1.6540, 1.1878, 1.0000, 0.4736, -0.4736, -1.0000, -1.1878, -1.6540, -2.1543}
2-phenylbutadiene (4)	{2.2143, 1.6751, 1.0000, 1.0000, 0.5392, -0.5392, -1.0000, -1.0000, -1.6751, -2.2143}
1,2-divinylbenzene (5)	{2.2470, 1.4142, 1.4142, 0.8019, 0.5550, -0.5550, -0.8019, -1.4142, -1.4142, -2.2470}
1,3-divinylbenzene (6)	{2.2216, 1.6180, 1.2399, 0.7261, 0.6180, -0.6180, -0.7261, -1.2399, -1.6180, -2.2216}
1,4-divinylbenzene (7)	{2.2143, 1.6751, 1.0000, 1.0000, 0.5392, -0.5392, -1.0000, -1.0000, -1.6751, -2.2143}

Notice that the eigenvalue spectra of 2-phenylbutadiene and 1,4-divinylbenzene are identical

**Fig. 4** Matrix entries for the matrix  $A_1$

$$A_1 = \begin{cases} 0, & i \neq j \\ 0.01, & i = j \text{ where carbon specified has one neighbor} \\ 0.02, & i = j \text{ where carbon specified has two neighbors} \\ 0.03, & i = j \text{ where carbon specified has three neighbors} \\ 0.04, & i = j \text{ where carbon specified has four neighbors} \end{cases}$$

**Table 2** New eigenvalue spectra of the molecules of part one using the variable value of  $A_1$ 

Molecule	Eigenvalues
1-phenylbutadiene (3)	{2.1318, 1.6312, 1.1671, 0.9800, 0.4560, -0.4912, -1.0200, -1.2085, -1.6696, -2.1769}
2-phenylbutadiene (4)	{2.1904, 1.6544, 0.9800, 0.9800, 0.5239, -0.5545, -1.0200, -1.0200, -1.6959, -2.2383}
1,2-divinylbenzene (5)	{2.2226, 1.3942, 1.3942, 0.7839, 0.5374, -0.5725, -0.8200, -1.4342, -1.4342, -2.2714}
1,3-divinylbenzene (6)	{2.1980, 1.5958, 1.2208, 0.7088, 0.6003, -0.6358, -0.7433, -1.2590, -1.6403, -2.2452}
1,4-divinylbenzene (7)	{2.1909, 1.6523, 0.9840, 0.9800, 0.5214, -0.5569, -1.0160, -1.0200, -1.6980, -2.2377}

Notice now the difference between the eigenvalue spectra of 2-phenylbutadiene and 1,4-divinylbenzene

fied has three carbon neighbors, and likewise  $A_{ii} = 0.04$  when the carbon specified has four carbon neighbors (multiple bonds are counted as single bonds for this procedure). We call this matrix  $A_1$ . The new eigenvalues for all the molecules of study using this method are shown in Table 2. Notice the difference now between 1,4-divinylbenzene and 2-phenylbutadiene. Notice also that the differences in the values in Tables 1 and 2 are small, but, nevertheless, significant.

Similarly, say  $A$  follows that of Fig. 5 instead of Fig. 4, matrix  $A_2$ . Notice the difference is by one order of magnitude. However, this one order of magnitude produces a greater difference in eigenvalues, as shown in Table 3. In other words, even though  $H_1$  and  $H_2$  have identical sets of eigenvalues,  $H_1 + A$  and  $H_2 + A$  have different sets, so the

species that generated these sets are different. Suppose now that the eigenvalue spectra for  $H_1 + A$  and  $H_2 + A$  are the same, as well as the eigenvalue spectra for the earlier enunciated  $H_1$  and  $H_2$ . Although we have never known this to happen, our immediate suggestion is to try adding an alternative matrix  $B$  to the matrices  $H_1 + A$  and  $H_2 + A$ . Now, are the eigenvalue spectra for  $H_1 + A + B$  and  $H_2 + A + B$  identical? If they are not, then the species that generated  $H_1$  and  $H_2$  are different. It is increasingly unlikely that the new eigenvalue spectra are the same unless the two species are identical, and so we proceed with increasing confidence that they are identical if this is the case.

We now move to the second part of the results and discussion which focus on the isospectral pairs

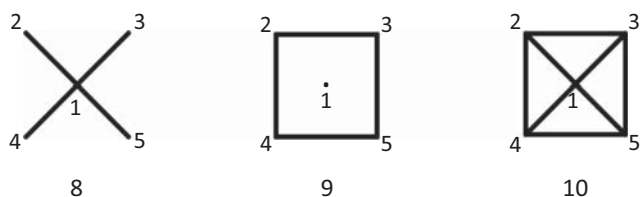
**Fig. 5** Variable matrix entries for the matrix  $A_2$ 

$$A_2 = \begin{cases} 0, & i \neq j \\ 0.1, & i = j \text{ where carbon specified has one neighbor} \\ 0.2, & i = j \text{ where carbon specified has two neighbors} \\ 0.3, & i = j \text{ where carbon specified has three neighbors} \\ 0.4, & i = j \text{ where carbon specified has four neighbors} \end{cases}$$

**Table 3** New eigenvalue spectra of the molecules of part one using the variable value of  $A_2$ 

Molecule	Eigenvalues
1-phenylbutadiene (3)	{1.9298, 1.4595, 0.9817, 0.8000, 0.2975, -0.6495, -1.2000, -1.3954, -1.8428, -2.3809}
2-phenylbutadiene (4)	{1.9768, 1.4690, 0.8021, 0.8000, 0.3859, -0.6929, -1.2000, -1.2019, -1.8835, -2.4555}
1,2-divinylbenzene (5)	{2.0277, 1.2296, 1.2161, 0.6225, 0.3902, -0.7199, -0.9810, -1.6009, -1.6159, -2.4684}
1,3-divinylbenzene (6)	{1.9866, 1.3988, 1.0506, 0.5524, 0.4396, -0.7951, -0.8983, -1.4326, -1.8433, -2.4587}
1,4-divinylbenzene (7)	{1.9812, 1.4500, 0.8413, 0.8000, 0.3606, -0.7160, -1.1613, -1.2000, -1.9064, -2.4493}

Notice the difference between these eigenvalue spectra and those from the previous two tables



**Fig. 6** The three molecules of the second part of our study. (8) Tetramethylenemethane (neopentane-1,1',1'',1'''-tetrayl), (9) cyclobutadiene with a fifth unconnected carbon, (10) cyclobutadiene with the fifth carbon connected to each other carbon, where we have labeled the carbons 1–5 on reflecting there are five carbon atoms in each species

tetramethylenemethane (neopentane-1,1',1'',1'''-tetrayl) and cyclobutadiene with a fifth unconnected carbon (planar methane). For this study, we will also include cyclobutadiene with the fifth carbon connected to each other carbon in the molecule, which is not isospectral to the other molecules. The structures of these molecules are shown in Fig. 6, and the eigenvalue spectra of each molecule are listed in Table 4.

Now say that we take the Hamiltonian of each of the molecules above and add them by a matrix  $A$  such that  $A$  follows that in Fig. 4, matrix  $A_1$ . The new eigenvalues obtained using this method are given in Table 5. Notice, now, just as in the isospectral pair of 2-phenylbutadiene

and 1,4-divinylbenzene above, the eigenvalues of tetramethylenemethane and the cyclobutadiene with an unconnected fifth carbon are slightly different. Similarly, say  $A$  follows that in Fig. 5 and not Fig. 4, matrix  $A_2$ . The eigenvalues of this method are shown in Table 6. Notice the differences in the eigenvalues of Tables 5 and 6 where the  $A_{ii}$  values of each matrix  $A$  used for each differ by just one order of magnitude. It, therefore, follows that the method used in part one is not an isolated incident.

## Conclusion

The study shown can be used to differentiate between varieties of isospectral compounds. Say we have  $i$  number of isospectral compounds such that  $H_0\psi_0 = E_0\psi_0 \dots H_i\psi_i = E_i\psi_i$ . The eigenvalues would be the same by construction, but the number of neighboring carbons most likely would not. Therefore, if one adds each Hamiltonian by a matrix  $A$  such that  $A_{ii}$  differs depending on the number of neighboring carbons, it becomes possible to mathematically distinguish between pairs of isospectral molecules, so long as the Hamiltonian matrices remain distinct.

**Table 4** Eigenvalue spectra for the three molecules of the second part of the study

Molecule	Eigenvalues
Tetramethylenemethane (8)	{2, 0, 0, 0, -2}
Cyclobutadiene with 5th unconnected carbon (9)	{2, 0, 0, 0, -2}
Cyclobutadiene with 5th connected carbon (10)	{3.2361, 0, 0, -1.2361, -2}

**Table 5** New eigenvalue spectra of the molecules of part two using the variable value of  $A_1$

Molecule	Eigenvalues
Tetramethylenemethane (8)	{2.0251, 0.01, 0.01, 0.01, -1.9751}
Cyclobutadiene with 5th unconnected carbon (9)	{2.02, 0.02, 0.02, 0.02, -1.98}
Cyclobutadiene with 5th connected carbon (10)	{3.2688, 0.03, 0.03, -1.1988, -1.97}

**Table 6** New eigenvalue spectra of the molecules of part two using the variable value of  $A_2$

Molecule	Eigenvalues
Tetramethylenemethane (8)	{2.2556, 0.1, 0.1, 0.1, -1.7556}
Cyclobutadiene with 5th unconnected carbon (9)	{2.2, 0.2, 0.2, 0, -1.8}
Cyclobutadiene with 5th connected carbon (10)	{3.5642, 0.3, 0.3, -0.8642, -1.7}

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflicts of interest.

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