ERICH HÜCKEL
(1896–1980)

Erich Hückel was born August 9, 1896 in Berlin, Germany and died in 1980. He began university studies in physics and mathematics shortly before the outbreak of the First World War, and was drafted to perform aerodynamics research. He received his doctorate in physics from the University of Göttingen in 1920 for applications of x-ray diffraction to liquid crystals, supervised by Peter Debye. After his doctorate, Hückel followed Debye to Zürich, and it was there that they developed the Debye-Hückel theory of dilute electrolyte solutions. Following a brief appointment at the Technische Hochschule in Stuttgart, Hückel joined the faculty of Philips University in Marburg. During a visit to Copenhagen in 1929, Niels Bohr suggested investigating the carbon-carbon double bond. This led Hückel to develop the theory of sigma-pi separation in 1930, which he used to explain the restricted rotation of ethene. Hückel's brother, Walter—a chemist—suggested applying this to benzene, and in 1931 Hückel generalized his theory to treat conjugated cyclic hydrocarbons, resulting in the now famous $4n + 2$ rule. During the late 1930s he extended this work to pi-conjugated biradicals and unsaturated hydrocarbons. During the Second World War, Hückel was the sole theoretical physics faculty member at Philips University in Marburg, and was required to teach all of the courses with any assistants. Overwork and health problems prevented him from further research work after the war. The importance of Hückel's pi-electron theory work was unrecognized for nearly 20 years, which many attribute to poor communication skills—in particular, his difficult writing style, publishing only in theoretical physics (instead of chemistry) journals, and reluctance to present at conferences.

CHAPTER 6

Hückel Molecular Orbital Theory

The Hartree-Fock calculations discussed in the previous chapter are surprisingly accurate and relatively easy to perform. Yet neither the underlying conceptual reasons for "why" these answers arise nor the physical interpretation of the results is entirely straightforward. Simplified model chemistries, such as the Hückel (or "tight-binding") theory discussed in this chapter, are one way to make the calculation and its interpretation intelligible. Historically, simplifying the Hamiltonian was a pragmatic way of avoiding numerical calculation before the advent of computers. Today, these types of simplified electronic structure theories remain useful for treating the properties of large nanostructures, and as ways of deriving simple explanations for a variety of chemical phenomena.

6.1 THEORY

Unlike the Hartree-Fock theory discussed in Chapter 5, Hückel theory considers only the pi-electron wavefunction. This section first reviews the formal sigma-pi separability principle that enables one to ignore sigma-bonding contributions, and then introduces the simplifying approximations used to formulate the Hückel model.

6.1.1 Sigma-pi separability

The qualitative model of bonding taught in introductory chemistry courses describes each atom as having a set of atomic orbitals (AOs) that combine to form molecular orbitals (MOs). As discussed in our treatment of the variational principle (Section 4.4.2), this is just a statement that the basis functions (AOs) form linear combinations (MOs) that are variational eigenstates of the molecular Hamiltonian. One also learns that planar molecules with double bonds, such as ethylene, C_2H_2, or benzene, C_6H_6, combine these AO functions to form σ and π MOs. Symmetry considerations separate these two different types of MOs. Suppose that the molecule is oriented in the xy-plane. The σ bonds are symmetrical (even symmetry) with respect to this plane, and thus can only be comprised of AOs having the same symmetry. In this case, these are s-like AOs and the $2p_x$- and $2p_y$-like AOs that are in the plane of the molecule. In contrast the π bond changes sign (odd symmetry) across the plane of the molecule, and thus can only be comprised of AOs with that symmetry, i.e., a $2p_z$ AO whose nodal plane coincides with the plane containing the molecule. The separability of the σ and

π MOs arises from this symmetry difference.[1] Therefore, the electronic structure for each of these sets of MOs can be found independently of each other. The σ-bonding electronic structure is less interesting, since σ MOs are spatially localized and tend to be less reactive. In contrast, the π MOs tend to be spatially delocalized over the molecule (and hence can vary greatly between different types of molecules), and are generally more reactive. The transitions between occupied and unoccupied π molecular orbitals also give rise to ultraviolet and visible (UV/vis) spectroscopic features,[2] in contrast to the transitions between σ orbitals, which are much higher in energy for organic molecules. For these reasons, focusing completely on the π-electron part of the molecular Hamiltonian will shed light on many of the properties, spectroscopy, and reactivity of this class of molecules.

6.1.2 Simplifying assumptions

Conceptually, the π-electron MO, ψ, is a superposition of $2p_z$ (AO) basis functions, ϕ_n, centered on each atom, n. In principle, one could define this basis in terms of Slater- or Gaussian-type functions, and then compute the overlap, one-electron Hamiltonian, Coulomb, exchange, and Fock matrices needed for the Hartree-Fock equations discussed in Chapter 5. Such a *first-principles* or ab initio approach becomes computationally expensive for large molecules, due to the large number of integrals required. Instead, Hückel theory proposes a simple model for constructing these matrices, based on three assumptions.

Assumption 1: Basis function orthonormality

The first assumption is that the basis functions are orthonormal, i.e, $S_{nm} = \int \phi_n^* \phi_m \, d^3\vec{r} = \delta_{nm}$. Although it is straightforward to construct normalized functions, atomic orbitals centered on different nuclei are typically *not* orthogonal (as in previous experiences with the $1s$ atomic orbitals of the hydrogen molecule in Section 5.2). Numerical calculations show that the overlap between adjacent carbon $2p_z$ AOs (i.e., nearest-neighbor atoms "bonded" to each other) in a typical molecule are on the order of 0.1, and this rapidly goes to zero for more distant atoms. This relatively small contribution suggests that they can be approximately set to zero as an assumption in the model. The practical benefit of this assumption is that it eliminates the need to compute the overlap matrix elements, and also reduces the problem to a simple (rather than generalized) eigenvalue problem.

Assumption 2: Ignore the two-electron contributions

The second assumption is that an "effective" one-electron problem—that does not depend on the charge density matrix—can be used instead of the full many-electron Hamiltonian. This assumption may be rationalized in two ways: (i) only the one-electron terms in Eq. (5.46) are necessary because the Coulomb and exchange integral terms are comparatively small; or (ii) the effective one-electron problem is actually just the (mean field) Fock matrix, whose

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[1] This separability is only strictly true for planar molecules. In nonplanar molecules, there is a (relatively) small mixing between π and σ MOs that is often ignored.

[2] i.e., pretty colors

matrix elements may be chosen to contain an average Coulomb and exchange contribution (but without explicitly calculating these). The practical benefit of this assumption is that it obviates both the Coulomb and exchange matrix elements integral calculations, as well as the iterative self-consistent calculation. Two potential negative consequences of this assumption are that (i) the effects of charge redistribution in the molecule no longer appear in the model Hamiltonian, since the charge density matrix does not modify the one-electron effective Hamiltonian; and (ii) there is no difference between the energies of singlet and triplet (or other) spin configurations having the same orbital occupation, due to the lack of exchange terms.

Assumption 3: One-electron Hamiltonian terms are parameterized to bond types

The third assumption is that these one-electron Hamiltonian terms, $H_{nm} = \int \phi_n^* \hat{H} \phi_m \, d^3\vec{r}$, are accurately described by empirical values, obtained by fitting to reproduce experimental spectroscopic or thermodynamic data. In principle, the experimental properties "know" the values of these integrals, so one can rationalize this as a circuitous way of having Nature "compute" these values. The fitting procedure assumes that H_{nm} is only nonzero when n and m are either the same (i.e., an AO interacting with itself) or adjacent to each other (n and m are nearest neighbors connected by a "bond" in a Lewis diagram). This is plausible because the Hamiltonian matrix elements scale roughly as the overlap between AOs, and therefore fall off very quickly beyond nearest neighbors.[3] In practice, this assumption eliminates the need to perform *any* integration; the Hamiltonian matrix elements are determined solely by the connectivity of the atoms. This assumption has the potential negative consequence that the results no longer derive from the first principles of the Schrödinger (or Hartree-Fock) equations, but are instead dependent on parameterization to a limited set of (potentially faulty) experimental data. It would be useless if every molecule needed a unique set of parameters, so a further implicit assumption is that these matrix elements depend only on the types of atoms that are connected, independent of details about their molecular environment, such as local variations in charge or bond length. In other words, the Hückel Hamiltonian matrix element describing the interaction between two adjacent carbon atoms is assumed to be the same, regardless of whether those two carbon atoms are in an ethylene molecule or in a naphthalene molecule.

Summary

To summarize:

- the overlap matrix is now simply the identity matrix
- the Hamiltonian matrix is now solely defined by atom connectivity, without dependence on charge redistribution within the molecule or the precise inter atomic geometry

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[3] The astute reader will note an inconsistency in arguing that the nearest-neighbor Hamiltonian matrix elements are nonzero because the AO overlaps of those atoms are nonzero, while the first assumption took the AOs as orthonormal. Apparently, this did not bother Hückel.

Despite this radical oversimplification of the problem, Hückel theory explains many of the properties of planar aromatic molecules, as discussed in this chapter. We will first perform a few classic small molecule problems to demonstrate how to perform elementary Hückel calculations. This is followed by a discussion of some useful advanced features in Mathematica that will help construct more complicated Hückel calculations and plot your results. Finally, we will discuss and demonstrate how to calculate various chemical properties and reactivity trends using Hückel theory.

6.2 ELEMENTARY EXAMPLES

Three canonical examples are typically used to illustrate Hückel theory calculations. First, the simplest possible π-electron system is the ethylene molecule. Second, the generalization to larger linear molecules is demonstrated using the butadiene molecule. Third, the generalization to cyclic molecules is demonstrated using the benzene molecule.

6.2.1 Ethylene

The simplest example of Hückel molecular orbital theory is the ethylene molecule:

Here the carbons participating in the π-electron system are arbitrarily labeled 1 and 2. Hückel theory treats only the π-electron Hamiltonian, and thus only the $2p_z$ AOs are used as the basis. Each row/column in the Hamiltonian matrix corresponds to the matrix element involving the $2p_z$ AO located on a specific carbon atom.

$$\mathbf{H} = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \tag{6.1}$$

Since each carbon atom has only one $2p_z$ AO, the "which atom" index is identical to a "which AO" (i.e., "which basis function") index. We'll construct the Hamiltonian matrix in this basis, following the approximations discussed above. Because all the atoms are the same, it is convenient to choose $H_{rr} = 0$, i.e., the Hamiltonian matrix element of a carbon $2p_z$ atomic orbital with itself. This choice makes all the diagonal terms equal to zero. Physically, this is equivalent to defining the energy of an isolated carbon $2p_z$ AO as the "zero" of energy; energies that are lower or higher than this zero correspond to net bonding or antibonding relative to the isolated atoms. Because the two carbon atoms are "bonded" to each other, they have a nonzero off-diagonal matrix element, $H_{rs} = t = \langle r|\hat{H}|s\rangle$.

$$\mathbf{H} = \begin{bmatrix} 0 & t \\ t & 0 \end{bmatrix} \tag{6.2}$$

It is easiest to define the connectivity using just ones and zeros,

```
MatrixForm[ hMatr={{0,1},{1,0}} ]  (* ethylene Hamiltonian *)
```

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

and then multiply the entire matrix by the desired value of t before computing the eigenvalues and eigenvectors. A typical value, based on reproducing spectroscopic transitions of small polyaromatic molecules, is $t = -2.7$ eV. The particular numerical value depends on the spectroscopic or thermodynamic parameterization. Although this changes the quantitative eigenvalues, both the eigenvectors and the qualitative ordering of the eigenvalues are independent of the precise value. One way to avoid making an explicit choice for this value is to use `t` as a unit of energy when describing Hückel theory results for polyaromatic hydrocarbons. (Note that t must be negative in order for the "bonding" MO to be lower in energy than the "antibonding" MO.)

Having constructed the Hamiltonian matrix, `hMatr`, its eigenvalues (`evals`) and eigenvectors (`evecs`) are obtained as in previous chapters.

```
t=-2.7;  (*typical π-π Hamiltonian matrix element, in eV*)
{evals,evecs}=Eigensystem[t*hMatr] (*get eigenvalues/vectors*)
```

```
{{-2.7 2.7}, {{-0.707107, -0.707107}, {-0.707107, 0.707107}}}
```

The π MOs are comprised of an equal superposition of the two AO basis functions. The set of eigenvectors, `evecs`, contains the linear variational coefficients for each state.

```
evecs
```

```
{{-0.707107, -0.707107}, {-0.707107, 0.707107}}
```

Note how the low-energy solution (first eigenvector) has both AOs with the same phase (both terms in the eigenvector have the same sign), and the high-energy solution (second eigenvector) has a node between the atoms (the terms have opposite signs, so they must cross through zero). This corresponds to the bonding and antibonding π molecular orbitals that you learned about during introductory chemistry.

The molecular orbitals should be orthonormal. Consequently, the vector representation of the molecular orbitals stored in the `evecs` vector must be orthonormal. Since Hückel theory assumes the overlap matrix is an identity matrix, evaluating $\langle\psi|\psi\rangle$ is equivalent to taking the vector scalar product ("dot product") of the two vectors (as was introduced in Section 4.3.2). Let's test the normalization of the two eigenstates:

```
evecs[[1]].evecs[[1]] (*check normalization for first MO...*)
evecs[[2]].evecs[[2]] (*...and second MO*)
```

```
1.
1.
```

Testing the orthogonality of the two states is left as an exercise for the reader.

Transitions between energy levels occur when the molecule absorbs a photon. Transitions between electronic states are typically in the UV/vis spectrum for π-conjugated molecules. The lowest-energy electronic transition, and thus the lowest-energy photon the molecule can absorb in this spectral region, occurs between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO). The energy difference between these is referred to as the HOMO-LUMO gap. Because Hückel theory considers only the π electrons, each carbon atom contributes one π electron. In the current case of ethylene, the molecule has two π electrons, and hence one doubly occupied molecular orbital. Thus, ethylene's HOMO-LUMO gap is the difference between the second (lowest-unoccupied) and first (highest-occupied) molecular orbital energy, stored in the list of eigenvalues, `evals`:

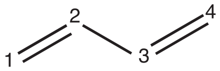
```
evals[[2]]-evals[[1]]    (* in eV, since t is defined in eV units *)
```

```
5.4
```

Since the value of `t`, defined earlier in the calculation, is in electron volts (eV), the HOMO-LUMO gap will also be in electron volts.

6.2.2 Butadiene

The next example is the butadiene molecule:



Once again, the diagram includes (arbitrarily ordered) index labels for each carbon atom in the π-electron system. In this basis, the Hamiltonian matrix has the form

$$\mathbf{H} = \begin{bmatrix} H_{11} & H_{12} & H_{13} & H_{14} \\ H_{21} & H_{22} & H_{23} & H_{24} \\ H_{31} & H_{32} & H_{33} & H_{34} \\ H_{41} & H_{42} & H_{43} & H_{44} \end{bmatrix}. \tag{6.3}$$

Following the simplifying assumptions described in Section 6.1.2, Hückel theory assumes that the off-diagonal matrix elements are nonzero only when the two $2p_z$ atomic orbital basis functions are adjacent to each other. Thus, $H_{12} = t$, but $H_{13} = H_{14} = 0$, using the atomic labeling scheme above. As before, the diagonal matrix elements, $H_{rr} = 0$, defines unbonded carbon atoms as the system's zero of energy. These simplifying assumptions result in a Hamiltonian matrix element of the form

$$\mathbf{H} = \begin{bmatrix} 0 & t & 0 & 0 \\ t & 0 & t & 0 \\ 0 & t & 0 & t \\ 0 & 0 & t & 0 \end{bmatrix}. \tag{6.4}$$

Observe that the Hamiltonian matrix is Hermitian ($H_{rs} = H_{sr}^*$)—or more strictly speaking, real symmetric, since t is real valued ($t = t^*$). This is true regardless of the labeling scheme used to index the $2p_z$ AO basis functions in the molecule. Moreover, so long as the connectivity is the same, any consistent labeling scheme will give equivalent eigensolutions.

To implement this in Mathematica, we first construct the connectivity matrix and then multiply by `t` to scale the energies to experimental units:

```
t=-2.7;
MatrixForm[ hMatr={{0,1,0,0},{1,0,1,0},{0,1,0,1},{0,0,1,0}} ]
{evals,evecs}=Eigensystem[t*hMatr]
```

```
⎛ 0  1  0  0 ⎞
⎜ 1  0  1  0 ⎟
⎜ 0  1  0  1 ⎟
⎝ 0  0  1  0 ⎠
```

```
{{4.36869, -4.36869, 1.66869, -1.66869},
 {{-0.371748, 0.601501, -0.601501, 0.371748}, {0.371748, 0.601501,
   0.601501, 0.371748}, {0.601501, -0.371748, -0.371748, 0.601501},
  {0.601501, 0.371748, -0.371748, -0.601501}}}
```

According to the *Aufbau principle,* the MO occupations are determined by filling in the electrons from lowest energy to highest energy. However, Mathematica returns numerical eigenvalues sorted by magnitude, rather than by value. Simply applying `Sort[]` would only sort the eigenvalues, without also shuffling the eigenvectors in the corresponding order. To sort the corresponding list of eigenvectors, the `Ordering[]` function can be used to generate a list that will correctly shuffle the eigenvalues into lowest-to-highest numerical order. This shuffling list can be applied to both `evals` (the list of eigenvalues) and `evecs` (the list of eigenvectors) to sort them in the same order. More specifically:

```
sortEigen=Ordering[evals];  (*find ascending sorting pattern*)
evals=evals[[sortEigen]]    (*sort eigenvalues*)
evecs=evecs[[sortEigen]]    (*sort eigenvectors*)
```

```
{-4.36869, -1.66869, 1.66869, 4.36869},
{{0.371748, 0.601501, 0.601501, 0.371748},
 {0.601501, 0.371748, -0.371748, -0.601501},
 {0.601501, -0.371748, -0.371748, 0.601501},
 {-0.371748, 0.601501, -0.601501, 0.371748}}
```

To simplify the subsequent calculations, let us define a function, `sortedEigensystem[]`, that returns sorted eigenvalues and eigensystems of an input `hamiltonian`:

```
sortedEigensystem[hamiltonian_]:=Module[{evals,evecs,sortEigen},
  {evals,evecs}=Eigensystem[hamiltonian];
  sortEigen=Ordering[evals]; (*find ascending sorting pattern*)
  evals=evals[[sortEigen]];  (*sort eigenvalues*)
  evecs=evecs[[sortEigen]];  (*sort eigenvectors*)
  {evals,evecs}  (*return list of sorted eigenvalues and eigenvectors*)
]
```

To confirm that it implemented correctly, let's reproduce the last calculation:

```
{evals,evecs}=sortedEigensystem[t*hMatr]
```

```
{{-4.36869, -1.66869, 1.66869, 4.36869},
 {{0.371748, 0.601501, 0.601501, 0.371748}, {0.601501, 0.371748,
   -0.371748, -0.601501}, {0.601501, -0.371748, -0.371748, 0.601501},
  {-0.371748, 0.601501, -0.601501, 0.371748}}}
```

What is the significance of this result? The lowest-energy eigenstate of butadiene has no nodes in the molecular orbital (MO) wavefunction (observe how all the eigenvector coefficients in `evecs[[1]]` are positive), and successively higher-energy states have an increasing number of nodes between the atoms. This is the same type of nodal structure observed in the 1D-PIB wavefunctions. In fact, the free-electron model of polyenes treats the conjugated π system as a 1D-PIB problem. This correspondence is unsurprising given the mathematical similarity of the Hamiltonian matrix here to the 1D finite difference Hamiltonian for the 1D PIB in Chapter 2. In the finite difference calculation, box-shaped basis functions were used to describe the eigenvectors and Hamiltonian. Here the basis of the eigenvectors—and the basis used to construct the Hamiltonian—are the different atom-centered AO basis functions. Despite the different basis functions, the Hamiltonian matrices in both cases are tri-diagonal—they have nonzero entries only on the main diagonal and the first diagonals above and below the main diagonal—and hence the eigenvectors have similar nodal patterns.

Finally, the HOMO-LUMO gap of this 4-π-electron-containing molecule can be calculated by taking the difference between the highest-occupied and lowest-unoccupied molecular orbital energies:

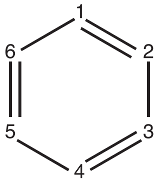
```
evals[[3]]-evals[[2]]  (* HOMO-LUMO gap, in eV *)
```

```
3.33738
```

This is smaller than the ethylene HOMO-LUMO gap, consistent with the predictions of the 1D-PIB free-electron model for conjugated π systems.

6.2.3 Benzene

A third classic example of Hückel theory is the benzene molecule:



Each carbon atom is connected to two nearest neighbors (i.e., "left" and "right"), forming a ring of atoms. Labeling each atom 1, 2, 3, 4, 5, 6 (with each of these corresponding to a particular row or column index in the Hamiltonian matrix), the connection between atoms 1 and 6 closes the ring. Rather than constructing `hMatr` as a list of lists, it is simpler to input this using the graphical editor, accessed by the Insert >Table >Matrix >New . . . menu. As in the previous examples, the eigenvalues and eigenvectors (molecular orbitals, MOs) of the Hamiltonian are obtained by solving the matrix eigenvalue problem numerically:[4]

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[4] Do not be alarmed if your eigenvectors differ by a minus sign from the ones shown here. Here all of the orbital coefficients for the lowest-energy molecular orbital have a negative sign, but in some previous versions of Mathematica these are all positive. Physically and mathematically, the difference in sign is just

```
                           ⎛0 1 0 0 0 1⎞
                           ⎜1 0 1 0 0 0⎟
t = -2.7;   hMatr =        ⎜0 1 0 1 0 0⎟ ;
                           ⎜0 0 1 0 1 0⎟
                           ⎜0 0 0 1 0 1⎟
                           ⎝1 0 0 0 1 0⎠
{evals, evecs} = sortedEigensystem[t * hMatr]
```

```
{{-5.4, -2.7, -2.7, 2.7, 2.7, 5.4},
 {{-0.408248, -0.408248, -0.408248, -0.408248, -0.408248, -0.408248},
  {0.288675, -0.288675, -0.57735, -0.288675, 0.288675, 0.57735},
  {0.5, 0.5, -1.64477 × 10^-16, -0.5, -0.5, 0.},
  {-0.5, 0.5, 1.64477 × 10^-16, -0.5, 0.5, 0.},
  {0.288675, 0.288675, -0.57735, 0.288675, 0.288675, -0.57735},
  {0.408248, -0.408248, 0.408248, -0.408248, 0.408248, -0.408248}}}
```

Benzene has six π electrons (one from each carbon $2p_z$ AO), so the first three molecular orbitals are doubly occupied. The list of eigenvalues, `evals`, indicates that the highest-occupied MO (`evals[[3]]`) and lowest-unoccupied MO (`evals[[4]]`) are both doubly degenerate (with the `evals[[2]]` and `evals[[5]]` levels, respectively).

As in Section 6.2.1, we can check the orthonormalization of the states by taking the dot product of each eigenvector with itself. First, we can test the normalization of the first few molecular orbitals,

```
evecs[[1]].evecs[[1]] (* check normalization *)
evecs[[2]].evecs[[2]]
evecs[[3]].evecs[[3]]
```

```
1.
1.
1.
```

to confirm that the states are properly normalized to one. (Testing the other states is left as an exercise for the reader.) Second, we test the orthogonality of a few of the pairs of states:[5]

```
evecs[[1]].evecs[[2]] (* check orthogonality *)
evecs[[2]].evecs[[3]]
```

```
3.88578 × 10^-16
-2.77556 × 10^-17
```

The result is not precisely zero, but instead is a very small number, due to the finite numerical precision of the eigenvectors. (Indeed, you may get a slightly different small number,

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an irrelevant global phase; only changes between positive and negative signs within a particular molecular orbital are important.

[5] In some older versions of Mathematica, degenerate eigenvectors were not always orthogonal to each other, conflicting with this requirement. However, since any linear combination of degenerate MOs is itself a valid eigensolution, these can be combined to generate a set of orthogonal solutions, by applying the `Orthogonalize[]` function to the set of eigenvectors.

depending on the default settings for the eigenvalue solver in your particular version of Mathematica.) For our scientific purposes, these very tiny values are effectively zero. If you wish to have a simpler output, the `Chop[]` function can be used to replace real numbers such as these that are very close to zero by the exact integer value of zero. However, in this case it is a purely aesthetic decision, and will have no impact on subsequent calculations.

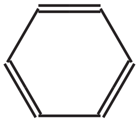
6.3 ADVANCED MATHEMATICA TECHNIQUES

The strategy demonstrated in the previous section—drawing a molecule, numbering the atoms, constructing the corresponding Hamiltonian matrix, and finding the `Eigenvalues[]` and `Eigenvectors[]`—corresponds to the traditional approach for solving Hückel theory problems. This section investigates ways of using Mathematica to streamline the calculations and visualize results. First, we'll demonstrate the use of Mathematica's `ChemicalData[]` functionality to query an online chemical structure database and use the results to construct the Hamiltonian matrix. Then, we'll see how to create `Graphics[]` comprised of basic shapes.

6.3.1 Using ChemicalData[]

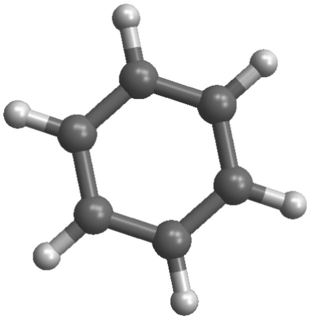
The built-in `ChemicalData[]` function provides access to a number of chemical properties. Among these are the atom connectivities, which can be used to automate construction of the Hückel Hamiltonian matrix, and the atom positions, which can be used to plot the results. `ChemicalData[]` takes two arguments, provided as strings: (1) the name of the molecule and (2) the desired property to return. The property `StructureDiagram` returns a standard two-dimensional organic-chemistry skeletal-formula diagram, excluding hydrogen atoms:

```
struct2d=ChemicalData["Benzene","StructureDiagram"]
```



The property `MoleculePlot` is a 3D diagram that can be rotated interactively (try it!):

```
struct3d=ChemicalData["Benzene","MoleculePlot"]
```



The property `AdjacencyMatrix` returns a matrix containing the connectivity between adjacent atoms in the molecule:

```
MatrixForm[ ChemicalData["Benzene","AdjacencyMatrix"] ]
```

```
0  2  1  0  0  0  1  0  0  0  0  0
2  0  0  1  0  0  0  1  0  0  0  0
1  0  0  0  2  0  0  0  1  0  0  0
0  1  0  0  0  2  0  0  0  1  0  0
0  0  2  0  0  1  0  0  0  0  1  0
0  0  0  2  1  0  0  0  0  0  0  1
1  0  0  0  0  0  0  0  0  0  0  0
0  1  0  0  0  0  0  0  0  0  0  0
0  0  1  0  0  0  0  0  0  0  0  0
0  0  0  1  0  0  0  0  0  0  0  0
0  0  0  0  1  0  0  0  0  0  0  0
0  0  0  0  0  1  0  0  0  0  0  0
```

The entries in this matrix correspond to the Lewis-diagram bond orders 2 indicates a double bond and 1 a single bond. The indexing of this matrix corresponds to the ordering of the atoms in the `StructureDiagram`. For example, in benzene the 12 columns/rows correspond to each of the 12 atoms (6 carbons, 6 hydrogens) in the molecule, and the "single" and "double" bonds correspond to the bond orders shown in the `StructureDiagram` figure. These properties—and many others—are documented in the online help entry for `ChemicalData[]`; take a few minutes to browse some of the examples.

We can use `ChemicalData[]` results to construct the Hückel Hamiltonian. The `AdjacencyMatrix` is almost correct, except that we need to (1) discard the non-π-bonding atoms, and (2) only consider connectivity (rather than the Lewis-theory bond types). First, we need to determine which sites are carbon atoms participating in the π-bonding network. The `VertexTypes` property returns a list of which atoms are at which location,

```
types=ChemicalData["Benzene","VertexTypes"]
```

```
{C, C, C, C, C, C, H, H, H, H, H, H}
```

indicating that the first six atoms are carbon atoms, so the first six rows/columns in the `AdjacencyMatrix` correspond to these carbon atoms. In general, hydrogen atoms are always returned last by `ChemicalData[]`. The `Take[]` function can be used to extract the upper-left corner (rows 1–6 and columns 1–6) of the `AdjacencyMatrix`:

```
MatrixForm[
  hMatr=Normal[
    Take[ChemicalData["Benzene","AdjacencyMatrix"],{1,6},{1,6}] ] ]
```

```
0  2  1  0  0  0
2  0  0  1  0  0
1  0  0  0  2  0
0  1  0  0  0  2
0  0  2  0  0  1
0  0  0  2  1  0
```

Mathematica's internal representation is a sparse matrix, since most of the entries are zero (i.e., most atoms are not connected to each other, so this avoids storing mostly zeros). The `Normal[]` function converts the sparse matrix into a "normal" matrix containing all the zeros, to make it easier for you to visualize. Computationally, this is unnecessary, as the eigenvalue routines will work with the sparse matrix representations.[6] This matrix is still not quite correct, because it still contains Lewis-theory-style "double" and "single" bond information (1 and 2 entries), whereas a Hückel Hamiltonian should only have the connectivity. The `Unitize[]` function converts all nonzero entries to ones, but leaves all the zero entries as they are, yielding a properly formed Hückel Hamiltonian matrix like the ones seen earlier in the chapter:

```
MatrixForm[ hMatrBenzene=Unitize[hMatr] ]
```

$$\begin{pmatrix} 0 & 1 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 1 & 0 \end{pmatrix}$$

Note that this Hamiltonian matrix differs from the one in Section 6.2.3, due to the different row/column ordering of the atoms used by the `ChemicalData[]` result. However, only the connectivity matters for computing physical properties such as eigenvalues, not the specific labels given to each of the atoms. In other words, the matrix here simply corresponds to labeling the atoms in a different order than before, but the connectivity is the same. To confirm that the eigenvalues are the same as in Section 6.2.3:

```
t=-2.7;
{evalsBenzene,evecsBenzene}=sortedEigensystem[t*hMatrBenzene]
```

```
{{-5.4, -2.7, -2.7, 2.7, 2.7, 5.4},
 {{0.408248, 0.408248, 0.408248, 0.408248, 0.408248, 0.408248},
  {0., -0.5, 0.5, -0.5, 0.5, 0.},
  {-0.57735, -0.288675, -0.288675, 0.288675, 0.288675, 0.57735},
  {5.81516 × 10^-17, 0.5, -0.5, -0.5, 0.5, 0.},
  {0.57735, -0.288675, -0.288675, -0.288675, -0.288675, 0.57735},
  {0.408248, -0.408248, -0.408248, 0.408248, 0.408248, -0.408248}}}
```

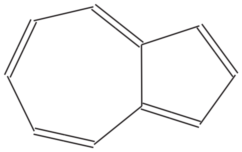
Likewise (after proceeding through the orthogonalization steps, etc.) one would obtain the same eigenvectors, only with a different ordering of the AO basis functions.

---

[6] Moreover, there are numerical efficiency advantages to working with the sparse representation for larger problems, as mentioned in Section 2.2.1. However, none of this is relevant for the small ($< 50 \times 50$) matrices treated in this chapter.

To show how concise this evaluation can be, consider the case of azulene:

```
ChemicalData["Azulene"]
ChemicalData["Azulene","CompoundFormulaDisplay"]
```



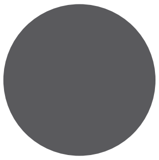
$C_{10}H_8$

```
t=-2.7;
hMatrAzulene=Unitize[Normal[
   Take[ChemicalData["Azulene","AdjacencyMatrix"],{1,10},{1,10}]]];
{evalsAzulene,evecsAzulene}=sortedEigensystem[t*hMatrAzulene];
```

6.3.2 2D graphics in Mathematica

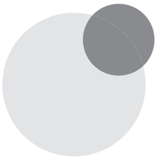
Constructing visual representations of the MOs requires learning the basics of two-dimensional graphics in Mathematica. This is best learned by considering a simple example:

```
Graphics[{Blue,Disk[{1,1},1]}]
```



`Graphics[]` generates an image from a list of attributes. The list of attributes includes color (e.g., `Blue`) and shape. The shape function `Disk[]` requires two arguments: the Cartesian coordinates of the center (e.g., `{1,1}`) and the radius (e.g., `1`). The list of graphic primitives can be arbitrarily long, and can include many objects defined in succession. For example:

```
blueCenter={1.25,1.25}; redCenter={0,0};
Graphics[
  {Blue,Opacity[0.7],Disk[blueCenter,1],
   Red, Opacity[0.2],Disk[redCenter,2]} ]
```



The `Opacity[]` attribute sets the relative opacity (equal to one minus transparency) of the figures. The final graphics object returned by `Graphics[]` shows a visual representation of all the attributes in the list.

We can use `Graphics[]` to draw representations of molecular orbitals on top of chemical structures. The first step is to find out where the atoms are located in the drawing canvas. The

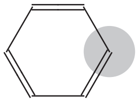
`VertexCoordinates` property of `ChemicalData[]` returns a list of 2D Cartesian coordinates of each element in the diagram, with the same ordering as the `AdjacencyMatrix` and `VertexTypes` lists:

```
xy=ChemicalData["Benzene","VertexCoordinates"] (* atom coords *)
```

```
{{100., 286.6}, {50., 200.}, {50., 373.21}, {-50., 200.},
 {-50., 373.21}, {-100., 286.6}, {162., 286.6}, {81., 146.31},
 {81., 426.9}, {-81., 146.31}, {-81., 426.9}, {-162., 286.6}}
```

These are not the actual positions of the atoms in three dimensions, but rather the positions in the two-dimensional `StructureDiagram` graphic returned by `ChemicalData[]`. Using these coordinates, we can draw `Graphics[]` (such as `Disk[]`) located at each atomic position. The `Show[]` function combines two or more graphical objects and displays the result. We can use `Show[]` to combine the `StructureDiagram` image (stored as `struct2d` in Section 6.3.1) and a new graphic of our own making, such as a `Blue` semitransparent `Disk[]` centered on the xy-coordinates of atom 1:

```
Show[ struct2d, Graphics[{Blue,Opacity[0.3],Disk[xy[[1]],50]}] ]
```



6.3.3 Application: Plotting molecular orbitals

The `Graphics[]` construction techniques of Section 6.3.2 can be used to superimpose MOs on the molecule by drawing a series of `Disk[]`s on top of a `StructureDiagram` image. The area of each `Disk[]` will be scaled to represent the magnitude of the MO coefficients on the particular site.[7] Since `Disk[]` takes the radius as an argument, we'll first write a scaling function to compute the appropriately scaled radius:

```
scaledRadius[referenceArea_,desiredArea_,arbitraryRadius_:50]:=
  Sqrt[desiredArea/referenceArea]*arbitraryRadius;
```

Note that the third argument of this function is defined as `arbitraryRadius_:50`. The colon indicates that this is an *optional* argument for the function, with an assumed value of 50 if it is not specified otherwise. As the name of the argument implies, this is chosen arbitrarily so that it has about the right size on the molecular image, but does not have any physical meaning.

To generate the plot of the molecular orbitals, we'll provide an indication of `whichMO` to plot, a set of atomic coordinates, the entire set of eigenvector coefficients, and the size of the basis. We'll then iterate through each atom position using a `Do[]` loop, and at each position `AppendTo[]` a list of graphics object, `graphicsList`, the desired color, `Opacity[]`, and `Disk[]` position and size that will indicate the magnitude of the molecular orbital coefficient.

---

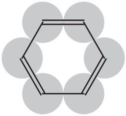
[7] Humans perceive magnitude by area. Using the radius of the circles to indicate magnitude would lead to an exaggerated perception by the typical human viewer of the relative magnitudes.

Positive and negative values of the molecular orbital are typically indicated by `Blue` and `Red`, respectively. One way to do this is with the following function:

```
plotMO[whichMO_,xyCoords_,coeffs_,nBasis_]:=Module[
  {graphicsList={},refArea=1/Sqrt[nBasis]},
  Do[ (*loop over the atoms*)
    If[ coeffs[[whichMO]][[r]]>0, (*check if positive sign*)
      AppendTo[graphicsList,Blue],  (*if true, i.e., >0*)
      AppendTo[graphicsList,Red]    (*if false, i.e., <0*)
    ];
    AppendTo[graphicsList,Opacity[0.3]];
    AppendTo[graphicsList, Disk[xyCoords[[r]],
      N[scaledRadius[refArea,Abs[coeffs[[whichMO]][[r]]]]]] ];
    ,{r,1,nBasis}];
  Graphics[graphicsList] (*return composite graphical object*)
];
```

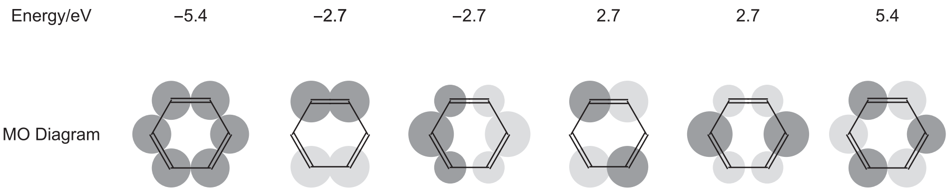
We can test this by plotting the lowest-energy π orbital of benzene,

```
t=-2.7;
struct2d=ChemicalData["Benzene","StructureDiagram"];
xy=ChemicalData["Benzene","VertexCoordinates"];
Show[ struct2d, plotMO[1,xy,evecsBenzene,6] ]
```



The `plotMO[]` function can then be called iteratively to display all of the MOs, as a `Table[]`:

```
GraphicsGrid[
  Transpose[Prepend[
    Table[{evalsBenzene[[i]],
           Show[struct2d,plotMO[i,xy,evecsBenzene,6]]},{i,1,6}],
    {"Energy/eV","MO Diagram"}]]]
```



6.4 HETEROATOMIC AROMATIC MOLECULES IN HÜCKEL THEORY

Different types of atoms have different atomic orbitals, and thus different one-electron, Coulomb, exchange, and Fock-matrix integrals. Consequently, the on-site and nearest-neighbor Hückel Hamiltonian matrix elements describing the π electrons of noncarbon atoms will be different from the ones for carbon atoms. It is simplest to keep the carbon

Element		h_X		k_{XY}
Boron	B(0)	-1.0	B-C	0.7
			B-N	0.8
Nitrogen	N(1)	0.5	C-N(1)	1.0
	N(2)	1.5	C-N(2)	0.8
Oxygen	O(1)	1.0	C=O(1)	1.0
	O(2)	2.0	C-O(2)	0.8
Fluorine	F(2)	3.0	C-F	0.7
Chlorine	Cl(2)	2.0	C-Cl	0.4
Bromine	Br(2)	1.5	C-Br	0.3

Table 6.1. Heteroatomic Hückel parameters, referenced to carbon. The number in parentheses after the symbol for the atom is the number of electrons contributed by that atom to the π-electron system, e.g., pyridine-type nitrogen atoms contribute one π electron and pyrrole-type nitrogen atoms contribute two. Similarly, carbonyl-type oxygen atoms contribute one π electron and phenol/ether-type oxygen atoms contribute two. Halogen atoms always contribute two π electrons. The next column distinguishes types of bonds, e.g., a boron-carbon bond differs from a boron-nitrogen bond. From Streitwieser.

$2p_z$ on-site energy as the zero of energy, and reference everything else with respect to this. Suppose that this value is $\alpha_C = 0$. Similarly, the energy scale is determined by the choice of the off-diagonal matrix elements, $t = -2.7$ eV. Suppose that this value is $\beta_{C-C} = t$. All the other atoms and bonds between them can be defined with reference to this zero and scale (unit system), as follows: the on-site (diagonal) Hamiltonian for a particular atom, X, is given by

$$\alpha_X = \alpha_C + h_x t, \tag{6.5}$$

and the nearest-neighbor coupling (off-diagonal) Hamiltonian matrix element by

$$\beta_{XY} = k_{XY} t. \tag{6.6}$$

Many researchers have compiled values for the h_X and k_{XY} parameters; the values shown in Table 6.1 are the "canonical" values from Streitwieser's book;[8] but many alternate values have been proposed.[9] Qualitatively, they are all roughly the same, and the differences are

---

[8] A. Streitwieser, *Molecular Orbital Theory for Organic Chemists*, (New York: Wiley, 1961), p. 135.

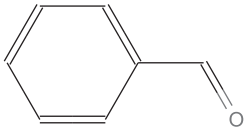
[9] E.g., the set by F. A. Van-Catledge, "A Pariser-Parr-Pople-Based Set of Hueckel Molecular Orbital Parameters," *J. Org. Chem.* **45**, 4801–4802, (1980), http://dx.doi.org/10.1021/jo01311a060.

perhaps less important than the relative inaccuracy of the Hückel method itself. In other words, do not take any particular set of values too seriously.

Qualitatively, the on-site (diagonal) Hamiltonian terms are proportional to the electronegativity of the atom. With the electronegativity of carbon as "zero," species such as oxygen and nitrogen and halogens will be more electronegative, and species such as boron will be less electronegative. How does this correspond to the values of h_X in Table 6.1? (Hint: Recall $t < 0$.) The nearest-neighbor coupling terms indicate the extent to which the AOs can hybridize with each other. For example, it is easier to delocalize across a C-C bond than across a C-F bond. How does this correspond to the values of k_{XY} in Table 6.1?

You can construct the heteroaromatic Hamiltonians entirely by hand (as in Section 6.2) or by using `ChemicalData[]` (as in Section 6.3.1 with some small modifications to the final output). As an example, let's first consider the case of benzaldehyde:

```
ChemicalData["Benzaldehyde"]
ChemicalData["Benzaldehyde","VertexTypes"]
```



```
{O, C, C, C, C, C, C, C, H, H, H, H, H, H}
```

Just as in the benzene example of Section 6.3.1, only the nonhydrogen atoms participating in π bonding should be retained in the `AdjacencyMatrix` and used to build the Hamiltonian. The main difference from Section 6.3.1 is that the noncarbon on-site terms and the non-(carbon-carbon) nearest-neighbor terms must be replaced with values from Table 6.1. The on-site terms must be changed by modifying the corresponding diagonal entry in the Hamiltonian matrix (e.g., `hMatrBenzaldehyde[[1,1]]` and `hMatrAniline[[1,1]]`), and the nearest-neighbor terms can be changed by rescaling the entire row and column containing that element (e.g., `hMatrBenzaldehyde[[1, 1;;8]]` and `hMatrBenzaldehyde[[1, 1;;8]]`), as follows:

```
t=-2.7;
MatrixForm[ hMatrBenzaldehyde=Unitize[Take[Normal[
    ChemicalData["Benzaldehyde","AdjacencyMatrix"]],{1,8},{1,8}]]];
hMatrBenzaldehyde[[1,1;;8]]*=1; (* C=O bond off-diagonal matrix element *)
hMatrBenzaldehyde[[1;;8,1]]*=1;
hMatrBenzaldehyde[[1,1]]=1;      (* oxygen atom on-diagonal matrix element *)
MatrixForm[hMatrBenzaldehyde]
```

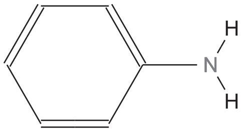
```
⎛ 1  0  0  0  0  0  0  1 ⎞
⎜ 0  0  1  1  0  0  0  1 ⎟
⎜ 0  1  0  0  1  0  0  0 ⎟
⎜ 0  1  0  0  0  1  0  0 ⎟
⎜ 0  0  1  0  0  0  1  0 ⎟
⎜ 0  0  0  1  0  0  1  0 ⎟
⎜ 0  0  0  0  1  1  0  0 ⎟
⎝ 1  1  0  0  0  0  0  0 ⎠
```

After constructing the Hamiltonian matrix, solve for the eigenstates as in previous examples:

```
{evalsBenzaldehyde,evecsBenzaldehyde}=sortedEigensystem[t*hMatrBenzaldehyde];
```

Although the C=O matrix elements are the same as the C=C matrix elements, this is not generally true. Consequently, you'll need to use the appropriate parameters from Table 6.1. For example, let us consider the example of the aniline molecule:

```
ChemicalData["Aminobenzene"] (*i.e., aniline*)
ChemicalData["Aminobenzene","VertexTypes"]
```



```
{N, C, C, C, C, C, C, H, H, H, H, H, H, H}
```

Table 6.1 indicates that amine nitrogens (which contribute two π electrons to the aromatic system) have an on-site matrix element that is $1.5t$, and a C-N nearest-neighbor Hamiltonian matrix element of $0.8t$. Consequently, in constructing the Hamiltonian, the relevant diagonal and off-diagonal matrix elements must be modified as follows:

```
t=-2.7;
hMatrAniline=Unitize[Take[Normal[
   ChemicalData["Aminobenzene","AdjacencyMatrix"]],{1,7},{1,7}]];
hMatrAniline[[1,1;;7]]*=0.8; (*C-N (amine) matrix elements*)
hMatrAniline[[1;;7,1]]*=0.8;
hMatrAniline[[1,1]]=1.5;      (*N (amine) atom matrix element*)
MatrixForm[hMatrAniline]
```

```
( 1.5  0.8  0.   0.   0.   0.   0. )
( 0.8  0    1    1    0    0    0  )
( 0.   1    0    0    1    0    0  )
( 0.   1    0    0    0    1    0  )
( 0.   0    1    0    0    0    1  )
( 0.   0    0    1    0    0    1  )
( 0.   0    0    0    1    1    0  )
```

```
{evalsAniline, evecsAniline} = sortedEigensystem[t * hMatrAniline];
```

Check your strategy for constructing the Hamiltonian matrix by building the Hamiltonians for these two molecules by hand, and comparing your eigenvalues to those computed in these examples.

6.5 INTERPRETING THE CHARGE DENSITY MATRIX

The charge density matrix, P_{tu} (Eq. (5.45)), was introduced in Chapter 5 as a means of computing the two-electron interactions. This section explores its qualitative significance for chemical properties and reactivity.

6.5.1 Construction

Although we originally wrote a function to compute a charge density matrix in Section 5.1.3, we'll generalize it here to allow the basis size and the number of occupied electrons to be specified as arguments of the function, so that these are not limited to a single global setting for either of these properties:

```
chargeDensMatr[coeffs_,nOcc_,nBasis_]:= Table[
   Sum[2*coeffs[[i,r]]*coeffs[[i,s]],{i,1,nOcc}],
   {r,1,nBasis},{s,1,nBasis}]//Chop;
```

As before, the factor of two arises from the implied double occupation of each MO, and no complex conjugation is performed because the eigenvectors are real valued. The `Chop[]` function is applied to the resulting `Table[]` to set very small real-valued entries that arise from finite numerical precision to be exactly zero (for the same reasons as in Section 6.2.3). Let's take a look at the charge density matrix of benzene, using the eigenvectors computed earlier in the chapter:

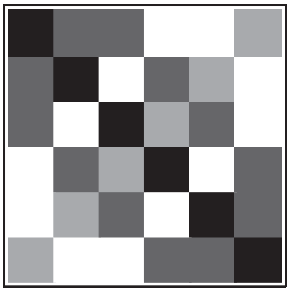
```
MatrixForm[SetPrecision[
  pMatrBenzene=chargeDensMatr[evecsBenzene,3,6] , 2]]
```

```
  1.0    0.67   0.67    0       0     -0.33
 0.67    1.0     0     0.67   -0.33    0
 0.67     0     1.0   -0.33   0.67     0
  0      0.67  -0.33    1.     0      0.67
  0     -0.33   0.67    0      1.     0.67
-0.33     0      0     0.67   0.67    1.0
```

The number of digits displayed on the screen has been altered using the `SetPrecision[]` function; the second argument sets the number of decimal places (in this case two) for the sake of making it fit on the screen.

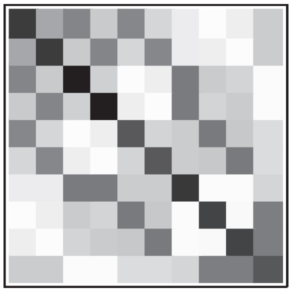
Sometimes looking at a list of numbers is not the most convenient strategy. The `ArrayPlot[]` function depicts the magnitude of each matrix element graphically:

```
ArrayPlot[pMatrBenzene]
```



How does this compare qualitatively to the charge density matrix of azulene (using the eigenvectors computed in Section 6.3.1)?

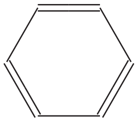
```
ArrayPlot[ pMatrAzulene=chargeDensMatr[evecsAzulene,5,10] ]
```



6.5.2 Electron density

The charge density matrix provides information on the local electron density in the molecule. From the premises of Hückel theory, each AO is centered on an individual atom, and there is no overlap between the AOs on adjacent atoms. Each MO "contains" one electron,[10] and the probability of the electron being at a particular atomic site corresponds to the square of the relevant AO coefficient. It follows that the diagonal terms in the charge density matrix are just $|\psi|^2$ in the AO basis. (Because this Hamiltonian only considers the π electrons, this analysis will only describe the π-electron contributions to the charge density.) The electron density is contained in the diagonal entries of the charge density matrix. Comparing the `ArrayPlot[]` results above, one observes that benzene has an equal number of π electrons on each atom, whereas azulene does not. However, in both cases the sum of the number of electrons on each atom must equal the total number of π electrons in the molecule. To make this more quantitative, we can extract the `Diagonal[]` matrix entries into their own list so as to have a list of only electron densities, and compute the trace (sum of the diagonal entries) of the charge density matrix, using the `Tr[]` function, to get the total number of electrons. For example:

```
ChemicalData["Benzene"]
Diagonal[pMatrBenzene]
Tr[pMatrBenzene]
```



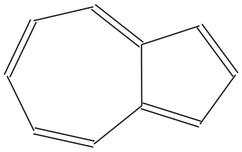
```
{1., 1., 1., 1., 1., 1.}

6.
```

---

[10] We multiply by a factor of two for the doubly occupied MOs.

```
ChemicalData["Azulene"]
Diagonal[pMatrAzulene]
Tr[pMatrAzulene]
```



```
{1.02743, 1.02743, 1.17288, 1.17288,
 0.854946, 0.854946, 1.0466, 0.986447, 0.986447, 0.870001}

10.
```

Indeed, benzene has six π electrons and azulene has ten.

Rather than showing the total number of π electrons on each site (which will always be a positive number), it can be more insightful to see how the number of electrons at a particular atom in the molecule differs from the number of electrons that the atom *would* have if it were in isolation, i.e., the extent to which the atom has acquired a net positive or negative charge by becoming part of the molecule. The charge distribution can be depicted by drawing circles whose areas correspond to the net charge on each carbon atom in the π-electron system. The `plotCharge[]` function follows the same logic as the molecular orbital plotting function (`plotMO[]`) defined earlier in this chapter:

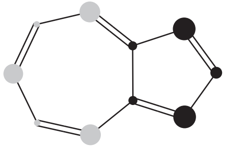
```
plotCharge[netCharges_,xyCoords_,nAtoms_]:=Module[
  {graphicsList={},refArea=1},
  Do[ (* loop over the atoms *)
    If[netCharges[[r]]>0,
      AppendTo[graphicsList,Black],        (* excess electrons *)
      AppendTo[graphicsList,LightGray] ]; (* deficient electrons *)

    AppendTo[graphicsList,Opacity[1]];
    AppendTo[graphicsList,Disk[xyCoords[[r]],
    N[scaledRadius[refArea,Abs[netCharges[[r]]]]]] ];
    ,{r,1,nAtoms} ];

  Graphics[graphicsList]
];
```

Black and gray represent positive and negative values, respectively, and the area of each disk represents the magnitude. A list of net charges is obtained by taking the `Diagonal[]` of the charge density matrix, and then subtracting the number of electrons associated with the (neutral) parent atom. Carbon atoms each have one π electron, so for the case of azulene the net charge is computed by subtracting one (1) from all of these entries before passing it to the `plotCharge[]` function.

```
azuleneChargePlot=Show[
  ChemicalData["Azulene","StructureDiagram"],
  plotCharge[Diagonal[pMatrAzulene]-1,
  ChemicalData["Azulene","VertexCoordinates"], 10 ]
]
```



It is much easier to interpret a plot than a list of numbers. This graphical representation makes it clear that the net charge is asymmetrically distributed across the azulene molecule; the pentagonal portion is enriched in π electrons and the heptagonal portion is depleted in π electrons.

Although the total electron density distribution as a function of position in space is a well-defined physical quantity, partitioning the electron density to particular atoms is somewhat arbitrary. Theoretical chemists have developed many different types of charge analysis methods corresponding to different ways of thinking about the problem. The charge partitioning described above, in which electrons are assigned to the atoms on which the AOs are centered, is known as "Mulliken population analysis. (See also Problem 5-21(d).)" The primary benefit of this method is computational simplicity, but it has two conceptual flaws. First, because the AO basis functions have a finite spatial extent, some portion of the charge density of an electron in that AO actually resides in the spatial location of other atoms in the molecule. This is especially a problem for spatially diffuse AO basis sets used in modern quantum chemistry calculations. Second, basis functions that are not centered on an atom do not contribute charge to any atom in the Mulliken procedure. This is a problem if we include "ghost" basis functions, as in Problem 5-15. Moreover, the Mulliken scheme cannot be applied to the (spatially delocalized) planewave basis sets used for solid-state quantum mechanical calculations, since the basis functions do not belong to any particular atom in the system. However, because of the lack of overlap between the atom-centered AOs assumed when constructing our Hamiltonian, neither of these flaws is relevant to Hückel theory. Despite these limitations, the Mulliken population analysis can be a useful and computationally simple method of studying the qualitative properties of the charge distribution in molecules. We will see how the Mulliken charges can be used to compute the dipole moment in Section 6.5.3, and how they can lend insight into chemical reactivity in Section 6.6.1.

6.5.3 Dipole moment

Given a set of net charges and positions associated with each atom, the dipole moment is calculated by summing over the product of these quantities:

```
calcDipoleVector2D[netCharges_,xyCoords_,nAtoms_]:=
  Sum[ netCharges[[r]]*xyCoords[[r]], {r,1,nAtoms} ];
```

The example here only considers a two-dimensional (xy-plane) set of atom positions, since the $\sigma - \pi$ separability in Hückel theory is only strictly valid for planar molecules, and the positions specified by `VertexCoordinates` are only given in two dimensions.[11] Even with the "correct" positions, the dipole moments calculated within Hückel theory are at best qualitative, since the σ electrons and distortions of the molecule by the uneven charge distribution (both ignored by the underlying assumptions) play an important role. As a concrete example, let us calculate the dipole moment vector and its magnitude for azulene:

```
azuleneDipole=calcDipoleVector2D[ Diagonal[pMatrAzulene]-1,
  ChemicalData["Azulene","VertexCoordinates"], 10 ]

dipoleMoment=Sqrt[azuleneDipole.azuleneDipole]   (* units of charge/pm *)

{95.7645, 0.476481}
95.7657
```

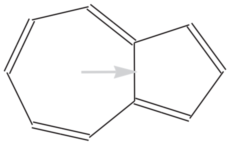
Based on the azulene net charge distribution plot in Section 6.5.2, and the symmetry of the molecule, the `0.47` component of the `azuleneDipole` vector seems suspect; there is no reason to expect any such asymmetry. However, this is less than half a percent of the other value, and arises from numerical round-off of the charges and positions rather than a physically meaningful asymmetry. Nevertheless, it is clear that azulene has a dipole moment. Note that a dipole moment has units of charge/length. The "length" is whatever units `VertexCoordinates` uses, so be careful in your physical interpretation and unit conversion.[12]

The orientation of the dipole moment is more easily interpreted as a picture. For example, to draw a vector as a `Green Arrow[]` centered at the geometric center of the molecule, and pointing along a specified direction, we could define the function

```
plotDipoleVector2D[dipoleVec_,xyCoords_,nAtoms_]:=
  Graphics[ {Thick, Green, Arrowheads[.1],
    Arrow[{Mean[xyCoords]-dipoleVec/2,Mean[xyCoords]+dipoleVec/2}]} ];
```

and combine it with a plot of the azulene molecule `StructureDiagram` using the `Show[]` function:

```
Show[
  ChemicalData["Azulene","StructureDiagram"],
  plotDipoleVector2D[azuleneDipole,
    ChemicalData["Azulene","VertexCoordinates"],10 ]   ]
```



The insignificance of the `0.47` component is clear when plotted in this way.

---

[11] For nonplanar molecules, `VertexCoordinates` corresponds to the 2D organic-chemistry-type diagram returned by `StructureDiagram`, which is an arbitrarily distorted (nonmetric-conserving) projection onto the xy-plane. This is a fancy way of saying that the 2D diagram doesn't correspond to anything particularly physical about the 3D structure of the molecule, aside from preserving the Lewis-bond connectivity. This is just the regular practice of drawing 3D molecules in 2D that you see in every organic chemistry textbook.

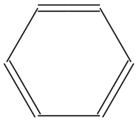
[12] To do this correctly, you should work in 3D and use the `AtomPositions` property in `ChemicalData[]`, which gives the 3D position in units of picometers. But this level of quantitative accuracy is unwarranted given the limitations of Hückel theory and the Mulliken population analysis.

6.5.4 Bond order/length/strength

What about the off-diagonal entries in the charge density matrix? These can be interpreted as the *bond order* between atoms. As you will recall from introductory chemistry, bond order generalizes the idea of "single," "double," and "triple" bonds from Lewis theory to a continuum of possible values. Moreover, bond order serves as a link between the "strength" (bond dissociation energy) and length of the bond: (i) the higher the bond order, the stronger the bond; (ii) the stronger the bond, the shorter the bond. This bond-order/length/strength relationship allows us to gain insight into the relative bond lengths and strengths in the molecule. Since the Hückel Hamiltonian considers only π electrons, these results only describe the π-electron bond order. Though the σ bond order is not described by this Hamiltonian, σ bonds are localized and are only weakly affected by the molecular context in which they occur. To a first approximation, all σ bonds between carbon atoms have about the same energy. In contrast, since the π orbitals are delocalized over the molecule, the π bond order depends on the total molecular environment, and it is precisely this influence that we seek to understand.

The bond order matrix is defined as the elements of the charge density matrix corresponding to the nearest-neighbor bonds between atoms. You could simply read the entries contained in the full charge density matrix, but it also contains lots of terms that do not correspond to "bonds between atoms" as they would be understood relative to Lewis structures. Taking advantage of the fact that the Hückel Hamiltonian has only nonzero entries at exactly these nearest-neighbor bond positions,[13] we will remove these additional terms by performing an element-by-element multiplication of the charge density and Hamiltonian matrices:

```
ChemicalData["Benzene"]
MatrixForm[
  SetPrecision[nnBOMatrBenzene=pMatrBenzene*Unitize[hMatrBenzene], 2] ]
```



```
  0    0.67  0.67   0     0     0
0.67   0     0    0.67    0     0
0.67   0     0     0    0.67    0
  0    0.67  0     0     0    0.67
  0     0   0.67   0     0    0.67
  0     0    0    0.67  0.67    0
```

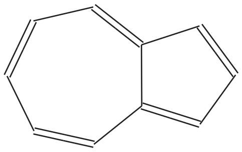
Note that the asterisk operator (*) is *not* matrix-matrix multiplication; rather, it proceeds element by element through the matrices (which are both the same size), and computes a new matrix by multiplying each particular element by the corresponding element in the other matrix.

---

[13] With the exception of on-site terms in heteroatomic aromatic molecules, e.g., those in Section 6.4, where there would also be diagonal elements to be removed.

Similarly, the bond order matrix for azulene can be computed by

```
ChemicalData["Azulene"]
MatrixForm[
  SetPrecision[nnBOMatrAzulene=pMatrAzulene*Unitize[hMatrAzulene], 2] ]
```



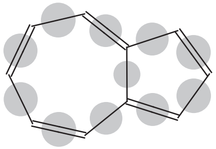
```
⎛  0   0.40 0.60  0   0.59  0    0    0    0    0  ⎞
⎜0.40   0    0   0.60  0   0.59  0    0    0    0  ⎟
⎜0.60   0    0    0    0    0   0.66  0    0    0  ⎟
⎜  0   0.60  0    0    0    0   0.66  0    0    0  ⎟
⎜0.59   0    0    0    0    0    0   0.66  0    0  ⎟
⎜  0   0.59  0    0    0    0    0    0   0.66  0  ⎟
⎜  0    0   0.66 0.66  0    0    0    0    0    0  ⎟
⎜  0    0    0    0   0.66  0    0    0    0   0.64⎟
⎜  0    0    0    0    0   0.66  0    0    0   0.64⎟
⎝  0    0    0    0    0    0    0   0.64 0.64  0  ⎠
```

All of the bonds in benzene have a greater bond order than any of the bonds in azulene, suggesting that the aromatic bonds in benzene are more stable than those in azulene (greater bond order implies greater bond strength). Furthermore, all of the bonds in benzene are the same (equal bond order implies equal bond length), as expected from the molecular symmetry. In contrast, the bonds in azulene seem to vary, suggesting that some of the bonds are shorter or longer than others. A comparison to the bond orders in benzene suggests that the azulene C-C bonds are all about the same or longer than the C-C bond lengths in benzene. As before, it is convenient to plot the results. The strategy is basically the same as in the previous examples of the molecular orbital and charge density plotting functions from Sections 6.5.1 and 6.5.2, except that each `Disc[]` is placed between two atom positions rather than centered on an atom.

```
plotBondOrders[nnBondOrderMatr_,xyCoords_,nAtoms_]:=Module[
  {graphicsList={}},
  Do[
    AppendTo[graphicsList,Orange];
    AppendTo[graphicsList,Opacity[0.5]];
    AppendTo[graphicsList,
      Disk[ Mean[{xyCoords[[r]], xyCoords[[s]]}],
        N[scaledRadius[1.6, Abs[nnBondOrderMatr[[r,s]] ]]]]];
    ,{r,1,nAtoms-1},{s,r+1,nAtoms}];
  Graphics[graphicsList]
];
```

Plotting the bond orders in azulene,

```
Show[
  ChemicalData["Azulene","StructureDiagram"],
  plotBondOrders[nnBOMatrAzulene,
    ChemicalData["Azulene","VertexCoordinates"], 10] ]
```



one sees that the bond lengths tend to alternate slightly longer and shorter than average as one proceeds around the ring, and that the vertical C-C bond shared by the heptagon and pentagon rings has the lowest bond order, and is thus predicted to be the weakest and the longest bond in the molecule. How does this compare to experiment or ab initio (i.e., "first-principles") calculations?

6.6 MOLECULAR REACTIVITY

Within the Born-Oppenheimer approximation, a "molecule" is just a local minimum of the total energy, as a function of the spatial arrangement of a collection of nuclei with a certain number of electrons. The energy of the collection of nuclei and electrons as a function of their relative positions defines the *potential energy surface*. If there are N atoms, each located in a three-dimensional space, then there are roughly $3N$ dimensions in the potential energy hypersurface (a few less, depending on the symmetry of the molecules and removing the center of mass motion of the system). Different electronic states of the molecule have different potential energy surfaces. "Chemical reactions," then, are simply transitions between local minima on these high-dimensional potential energy surfaces. The rates at which transitions occur (i.e., the reaction kinetics) can be computed using the toolbox of chemical dynamics theory—the simplest example being classical transition state theory, but more exact methods that take into account the quantum nature of particles (and factors such as tunneling) are also used. The "reaction coordinate," discussed in the typical introductory chemistry treatment of transition state theory, corresponds to a line between a particular "reactant" and "product" arrangement in this high-dimensional space. Since the lowest-barrier paths are the fastest (and hence contribute most to the rate), this reaction coordinate path is chosen to do the least amount of "hill climbing" along the way from reactants to product. Saddle points along this reaction coordinate correspond to the "transition state" arrangements. Basins (i.e., local minima) along this path correspond to reactive intermediates. In this way, the solution to the electronic Schrödinger equation provides a complete understanding of chemical reactivity.

In practice, this is rather challenging. First, calculating the potential energy surface is computationally expensive. Second, to have physical meaning, the barrier heights must be quite accurate, since these appear in an exponential when computing the Boltzmann factors. Consider the numerical errors seen in previous exercises in this book, relative to $k_B T \approx 10^{-3}\ E_h$ at room temperature. Third, chemical dynamics theory requires a combination of statistical mechanics and quantum mechanics that may be out of the scope of your present coursework. So while this comprehensive theory for computing chemical reaction rates is plausible, the calculations are beyond the scope of this book.

An alternative theory of reactivity is to consider the propensity of certain initial states toward chemical reactions. This is much simpler, since it only requires computing a single point (i.e., just one molecule, in one particular initial "reactant" state) on the potential energy surface. In practice, this tends to accurately identify the relative reactivities of different parts of the molecule, though without the information of the energy along the reaction coordinate it does not give quantitative rate predictions.

Organic reactions may be broadly classified into three types: polar, nonpolar, and pericyclic. In polar reactions, a new bond is formed when a nucleophile provides a pair of electrons to an electrophile. An electrophilic ("electron-loving"[14]) reagent is "attracted" to electrons, and participates in the chemical reaction by accepting an electron pair (i.e., as a Lewis acid). Consequently, electrophiles are expected to attack the most electron-rich part of the target molecule, i.e., the region of the target molecule that is best able to provide electrons. A nucleophilic ("nucleus-loving") reagent donates electrons, and is thus a Lewis base. Consequently, nucleophiles will attack the most electron-poor part of the target molecule, i.e., the region of the target molecule that is best able to accept the electrons that are being donated. As seen earlier in the chapter, the charge distribution can be calculated using Hückel theory, suggesting that the results can be used to predict these reactive sites. Nonpolar reactions occur when both species contribute electrons "equally" to the new bond. The classic example of these are radical reactions, and this property can be described using the *free valence index* introduced in Section 6.6.3. Finally, pericyclic reactions are concerted processes involving cyclic transition states where the electrons simultaneously break and form bonds. The classic examples of pericyclic reactions are electrocyclic reactions and Diels-Alder cycloaddition reactions. These can be understood in terms of the difference between the HOMO and LUMO energies and the relative phases of the π molecular orbitals.

6.6.1 Charge density and polar reactions

As discussed above, electrophilic reagents are expected to attack the most electron-rich regions of the target molecule and nucleophilic reagents are expected to attack the most electron-poor regions of the target molecule. The net charge on each atom (discussed in Section 6.5.2) quantifies how "rich" or "poor" a site is. If a particular atomic site has more electrons located on it (as given by the charge density matrix) than the neutral atom, it has a net negative charge and will be more susceptible to electrophilic attack. If the site is electron poor, it will have a net positive charge.

Consider the napthalene, azulene, aniline, and benzaldehyde molecules. Construct the appropriate molecular Hamiltonians, determine the eigensolutions, and then create the charge density plot. I'll let you do this as an exercise, and just show the result of these plots here:

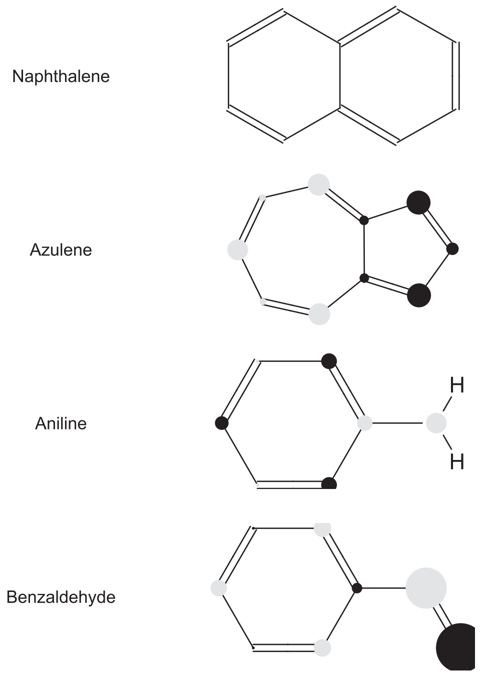
```
(* Generate a charge density matrix and use it to construct a
 benzaldehydeChargePlot on your own before continuing. *)

GraphicsGrid[{
  {"Naphthalene",naphthaleneChargePlot},
  {"Azulene",azuleneChargePlot},
```

---

[14] The sense of "love" in this case is somewhere between the theories presented by Aristophanes, Agathon's concessions to Socrates's questioning, and the theory of Diotima related by Socrates in Plato's *Symposium*.

```
{"Aniline",anilineChargePlot},
{"Benzaldehyde",benzaldehydeChargePlot} }]
```



Notice how naphthalene has a uniform charge density; the charge density–based initial state theory of reactivity does not give any information about reactivity (this is resolved in the next section). Azulene has a clear preference for electrophilic attacks on the pentagon and nucleophilic attacks on certain sites of the heptagon. The amine group in aniline strongly activates the ring toward electrophilic reaction by pushing electron density into the ortho and para sites of the benzene ring. Conversely, the carbonyl group in benzaldehyde is a deactivating group. By withdrawing electron density from the ring, particularly from the ortho and para sites, it makes those sites less susceptible to electrophilic aromatic substitution reactions. Consequently, the meta positions are the *least deactivated* (they still have the full number of electrons that an isolated carbon atom has), and thus carbonyl is described as a meta-directing group. In this way, the patterns of ortho-para-activation by electron-donating groups and meta-direction by electron-withdrawing groups are a simple consequence of the π electronic structure. While it is easy to memorize these types of rules for single rings, Hückel theory allows us to calculate how these directing groups behave in polycyclic aromatics. Organic chemists tend to enjoy these types of calculations.

6.6.2 Frontier molecular orbitals and polar reactions

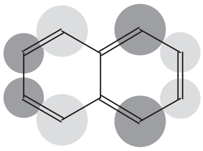
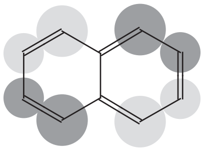
Contrary to the charge-density analysis predictions of the previous section, experiment indicates that the positions in naphthalene are not equally reactive. This is a general problem for most unsubstituted aromatic hydrocarbon molecules,[15] resolved by the Nobel Prize–winning insights of Kenichi Fukui that one must also consider the role of the highest-occupied and lowest-unoccupied molecular orbitals in the bonding process.[16] These molecular orbitals are referred to as the "frontier" molecular orbitals, since they are at the boundary of the occupied and unoccupied molecular orbital states. If the electron density is uniform in all sites (i.e., all else being equal), then taking the electron from the highest-occupied molecular orbital (HOMO) changes the total energy by the least amount. The sites where the HOMO density (i.e., $|\psi|^2$) is largest indicate locations with the highest relative propensities for this reaction. Similarly, when extra electrons are added to the molecule, they will be placed into the lowest-unoccupied molecular orbital (LUMO). Regions where the LUMO density is lowest thus correspond to addition sites that induce the least total energy change.

Returning to the specific case of naphthalene, although the charge density is predicted to be uniform for all the sites, the HOMO and LUMO orbitals are not:

```
evalsNaphthalene

GraphicsGrid[
  Prepend[
    Table[
      {evalsNaphthalene[[i]], Show[
         ChemicalData["Naphthalene","StructureDiagram"],
         plotMO[i,ChemicalData["Naphthalene","VertexCoordinates"],
           evecsNaphthalene,10] ]},
      {i,6,5,-1}],
    {"Energy/eV","MO Diagram"}] ]
```

```
{-6.21749, -4.36869, -3.51749, -2.7,
 -1.66869, 1.66869, 2.7, 3.51749, 4.36869, 6.21749}
```

Energy/eV	MO Diagram
1.66869	
–1.66869	

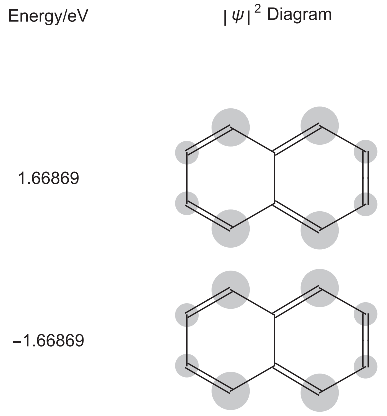
---

[15] Specifically, *alternant hydrocarbons* all have uniform charge density in Hückel theory. An alternant hydrocarbon is one in which neighboring sites can be labeled as "a" or "b" in alternating sequence, without ever having an "aa" or "bb" nearest neighbor. You can see this yourself by trying to label naphthalene or benzene (both alternant hydrocarbons) versus azulene (a nonalternant hydrocarbon).

[16] K. Fukui, T. Yonezawa, H. Shingu, "A Molecular Orbital Theory of Reactivity in Aromatic Hydrocarbons," *J. Chem. Phys.* **20**, 722–725 (1952), http://dx.doi.org/10.1063/1.1700523.

The nodes on the bridging carbons indicate that these will be the least reactive. Since the reagent only cares about the magnitude of the wavefunction coefficient and not the sign, it is clearer to represent $|\psi|^2$ for these frontier MOs:

```
GraphicsGrid[
  Prepend[
    Table[
      {evalsNaphthalene[[i]],
       Show[
         ChemicalData["Naphthalene","StructureDiagram"],
         plotMO[i,ChemicalData["Naphthalene","VertexCoordinates"],
           evecsNaphthalene^2,10] ]},
      {i,6,5,-1}],
    {"Energy/eV","|ψ|²" Diagram}] ]
```



This plot shows that the reactivity pattern of naphthalene toward electrophilic and nucleophilic reagents is spatially the same. The α carbons (closer to the middle) are predicted to have higher reactivity than the β carbons (furthest from center), and the bridging carbons are predicted to be unreactive. Thus, despite the uniform electron density, the spatial distribution of the molecular orbitals determines the reactivity patterns of molecules.

6.6.3 Free valence index and radical attack

The free valence index measures the degree that atoms in a molecule are bonded to adjacent atoms relative to a maximum theoretical bonding power. The free valence index for a particular atom, r, is defined as

$$F_r = N_{max} - \sum_{s \in n.n.(r)} P_{rs}, \tag{6.7}$$

where the sum is performed over other atoms, s, that are nearest neighbors (connected by a "bond") of atom r. The maximum π bond order for a carbon atom is $N_{max} = \sqrt{3}$.[17] The carbon atom with the largest free valence index has the greatest propensity to radical attack. We can rationalize this in the following way: To bond with the radical, the atom must "give up" one electron. If the adjacent bonds already have a claim on the electron, it will not be available for the new bond with the radical. The free valence index thus measures the amount of that atom's electron that is not already participating in chemical bonding (as measured by the bond order entries, P_{rs}).

The free valence index can be easily computed using the bond order matrices calculated in Section 6.5.4. In constructing the bond order matrix, only the nearest-neighbor terms remain. Thus, summing over a particular row (or column) corresponding to atom r will give the sum needed for Eq. (6.7). F_r (Eq. (6.7)) is evaluated for each atomic site, `r`, using a `Table[]` function that loops over the atom indices. For example, using the bond order matrix of benzene (`nnBOMatrBenzene`) defined in Section 6.5.4,

```
benzeneFreeValence=Table[
  Sqrt[3]-Sum[nnBOMatrBenzene[[r,s]],{s,1,6}]
  ,{r,1,6}]
```

```
{0.398717, 0.398717, 0.398717, 0.398717, 0.398717, 0.398717}
```

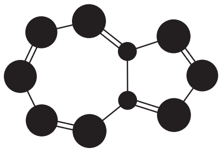
all of the F_r values are identical, in contrast to azulene,

```
azuleneFreeValence = Table[
  Sqrt[3]-Sum[nnBOMatrAzulene[[r,s]],{s,1,10}]
  ,{r,1,10}]
```

```
{0.149677, 0.149677, 0.48038, 0.48038,
 0.482214, 0.482214, 0.419972, 0.429112, 0.429112, 0.454253}
```

in which the atoms have different values of F_r and hence different propensities to radical attack. The positions with greater values of F_r can be visualized by utilizing the `plotCharge[]` function, previously defined in Section 6.5.2, to overlay the list of F_r values contained in `azuleneFreeValence` on top of the structure of the azulene molecule:

```
Show[
  ChemicalData["Azulene","StructureDiagram"],
  plotCharge[azuleneFreeValence,
    ChemicalData["Azulene","VertexCoordinates"],10] ]
```



---

[17] An alternative definition uses the total bond order, i.e., for a π-bonded carbon atom this would consist of three σ bonds plus the π bond for a total of $N_{max} = 3 + \sqrt{3}$. Similarly, then, the bond order sum would be expanded to include each of the σ bonds, which would nominally be 3 (one for each of the σ bonds).

6.6.4 Orbital symmetry conservation in pericyclic reactions

The Woodward-Hoffmann rules and Diels-Alder reactions rely on the conserved symmetry of the various ring-opening and ring-closing reactions. The basic principle in these pericyclic reactions is phase (sign of the wavefunction) matching of the various components. The required phase matching then enforces a constraint on whether the rotation will occur in a conrotatory or disrotatory fashion, ultimately leading to different stereochemical consequences.[18] The techniques described in Section 6.3.3 can be used to make diagrams for your own molecules. Although the π-electron theory discussed in this chapter is often a good start, rotations of the bonds induce σ–π mixing, breaking the assumed neglect of these AOs. We will not discuss pericyclic reactions in depth here, but for further reference see the following sources:

- R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry* (Weinheim/Bergstr.: Verlag Chemie, 1970)
- Keith Yates, *Hückel Molecular Orbital Theory* (New York: Academic Press, 1978)

6.6.5 Limitations of Hückel theory for chemical reactivity

Although Hückel theory is convenient for illustrating basic quantum theories of chemical reactivity, many other factors contribute to the outcome of reactions. For example, the calculations discussed above do not account for steric contributions that alter the likelihood of specific reactions occurring. Using only the initial molecular states ignores the details of the potential energy landscape; thus it cannot account for cases where the outcome of reactions is determined by kinetic factors. Restricting ourselves to the π-electron Hamiltonian, effects of σ-π mixing are ignored. Moreover, the extremely simplified Hamiltonian—particularly the complete neglect of electron-electron interactions—precludes incorporating many other factors, such as the effects of solvent polarity. Yet despite these limitations, Hückel theory makes surprisingly accurate predictions for aromatic hydrocarbon reactivity, and thus can still provide a conceptual framework for understanding chemical reactions. This is valuable for explaining your work to others (and yourself!), and can be substantiated with more quantitatively accurate ab initio calculations.

6.7 LOOKING FORWARD

Hückel theory's underlying approximations (described in Section 6.1.2) limit the types of molecules and properties that can be described and the accuracy of those predictions. Removing these simplifying approximations—by including electron-electron interactions and σ electrons—provides a path toward predicting molecular structure, spectroscopy, and reactivity for all molecules. We'll conclude the chapter with a brief discussion of semiempirical electronic structure theories that implement intermediate approximations, followed by an

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[18] R. B. Woodward and R. Hoffmann, "Orbital Symmetries and endo-exo Relationships in Concerted Cycloaddition Reactions," *J. Am. Chem. Soc.* **87**, 395–397 (1965), http://dx.doi.org/10.1021/ja00947a033.

overview of the role of electronic structure calculations in the theory of molecular property prediction.

6.7.1 Beyond pi-electron theory

Neglecting the Coulomb and exchange interactions is an extreme approximation, with the consequence of removing the difference between singlet and triplet electronic states. In addition, there is more to chemistry than planar aromatic hydrocarbons. How can we go beyond these limitations without going back to the full Hartree-Fock theory discussed in Chapter 5?

One way is to include the Coulomb and exchange interactions in an approximate way. One class of theories (e.g., the Parr-Parriser-Pople theory, the Hubbard model) extend the π-electron theory for planar hydrocarbons by adding Coulomb and exchange integrals (described as parameterized functions). The parameters of the Coulomb and exchange integral functions are derived from spectroscopic or thermodynamic experiments, like the one-electron integrals used here, and the functions represent the average behavior of the integral between the various carbon $2p_z$ orbitals. By including the Coulomb and exchange integrals, one can carry out a semiempirical Hartree-Fock calculation, analogous to the hydrogen molecule calculations in Section 5.2. Because the integrals are approximated as simple functions of distance, they can be calculated rapidly. Inclusion of the Coulomb and exchange terms allows for a more accurate description of the charge distribution, and allows for different spin states. Unfortunately, though, this requires an iterative SCF calculation rather than the simple "one-shot" calculations performed in this chapter. Another benefit is that the two-electron integrals can be used to perform configuration-interaction calculations that go beyond the mean field Hartree-Fock scheme. That being said, these theories are still limited to the π-electronic structure of planar aromatic molecules.

Another strategy for improving Hückel theory is by including the other valence electron orbitals, while still assuming that the core electrons do not participate in bonding. One example is the "extended" Hückel theory (EHT), which includes not only the $2p_z$ orbitals on the carbons, but all the other valence atomic orbitals on all the atoms (including hydrogens). The Hamiltonian is constructed in a similar way as above, but with the use of certain distance-dependent rules to compute the Hamiltonian matrix elements, e.g., scaling them by a function of the overlap between the valence atomic orbital functions. Conceptually, this only adds the complications of dealing with 3D geometries and the additional parameters describing the integrals between the many basis functions on each atom. The principal advantage over Hückel theory is that geometric effects such as bond-length changes and nonplanarity are now included in the Hamiltonian. Like Hückel theory, there are no Coulomb or exchange integrals in EHT, so it shares the same limitations with respect to the self-consistency of the charge distribution, lack of distinction between singlet and triplet states with the same molecular orbital occupation, etc. The natural next step is to account for the interactions by including Coulomb and exchange terms (again, in the form of semiempirical functions fitted to reproduce experimental data), yielding the various families of semiempirical Hartree-Fock methods—e.g., CNDO, ZINDO, AM1, MNDO, PM3, PM6, PM7. With some clever matrix manipulations and numerical tricks, these semiempirical methods can be scaled up to perform quantum calculations on small proteins.

Historically, the development of these semiempirical techniques was motivated by the high computational cost of performing full ab initio Hartree-Fock calculations using large basis sets. However, improvements in computer hardware and algorithms have made ab initio Hartree-Fock and even post-Hartree-Fock corrections computationally unremarkable for even somewhat large (50–100 atom) systems. Of course, "feasible" depends on your definition of what a "large" molecule is, what a "good enough" basis set is, how "fast" you want your results, and how "fast" your computer is. Semiempirical molecular orbital theories might still be the only appropriate tool for treating large nanostructures containing more than 10^3 atoms, or computing the many thousands of points needed for the potential energy surface (indeed, if our calculations are fast enough, we might consider computing the potential energy surface "on the fly"). From a conceptual point of view, the simpler theories let us "turn off" certain interactions in predictable ways, and perhaps give us insight into the properties of molecules.

6.7.2 Understanding molecular spectroscopy and reactivity from electronic structure

The choice of model chemistry provides an approximate solution to the electronic structure problem, with varying trade-offs between computational feasibility and accuracy. The Hückel model used in this chapter provides a simple means of performing electronic structure calculations that are amenable to a quick, pedagogical examination. In principle, Hartree-Fock calculations (Chapter 5), post-Hartree-Fock methods (Section 5.3.1), density functional theory methods (Chapter 8), or quantum Monte Carlo methods (Chapter 9) could all be used instead for more accurate (but more time-consuming) predictions. The same type of analysis of molecular properties and reactivity can be undertaken with these more sophisticated methods. For example, going beyond the π-electron theory allows the role of sigma-bonding electrons in molecular properties and reactivity to be calculated. The total energy of the system can be minimized by moving the atoms around (similar to Section 5.2.7, although now with $3N$ possible choices rather than just a single internuclear distance). If you want to determine the energy change as you move a particular atom, reach in to your simulation and move it! This gives us a new way to study chemical reaction mechanisms by explicitly computing various hypothetical reaction paths. For an overview of this field, see Bachrach's textbook.[19]

The reader with a background in statistical mechanics will realize that this provides a toolbox for calculating all the possible vibrational, rotational, and electronic states, which may then be used to construct a partition function for computation of all the thermodynamic properties for noninteracting systems. (See also Appendix D.) For interacting (nonideal gas systems or condensed phases), the intermolecular interactions[20] can be calculated and used

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[19] Steven M. Bachrach, *Computational Organic Chemistry*, 2nd ed., (Hoboken: Wiley-Interscience, 2014).

[20] At least the simple electrostatic ones like dipole-dipole interactions, and hydrogen bonding. The dispersion forces arise from electron correlation, necessitating a post-Hartree-Fock theory.

to approximate the partition function by Metropolis Monte Carlo sampling (discussed in Chapter 11). In this way, electronic structure calculations provide a formal basis for molecular spectroscopy, reactivity, and thermodynamics.

PROBLEMS

6-1. Which is more stable, phenanthrene or anthracene? Both have the same number of σ bonds, so the difference is due to aromatic stabilization. Because the electrons are non-interacting, the total π contribution to the total energy is simply the sum of the occupied eigenstates,

$$E^{\pi}_{\text{total}} = 2\sum_{i=1}^{N_{\text{occ}}} E^{\pi}_{i}, \tag{6.8}$$

where E^{π}_{i} is the energy of the ith MO. (The factor of two comes from each state being doubly occupied.) Use this equation to determine which molecule has the lowest total energy, i.e., is the most thermodynamically stable.

6-2. An alternative expression for the π contribution to the total energy is

$$E^{\pi}_{\text{total}} = \sum_{r=1}^{N_{\text{basis}}} P_{rr}\alpha_r + 2\sum_{r=1}^{N_{\text{basis}}}\sum_{s>r}^{N_{\text{basis}}} P_{rs}\beta_{rs}, \tag{6.9}$$

where P_{rs} are the elements in the charge density matrix from Section 6.5, α_r is the on-site Hamiltonian matrix element for atom r, and β_{rs} is the nearest-neighbor coupling Hamiltonian matrix between atoms r and s. Calculate the total energies of phenanthrene and anthracene and compare to the values you found in the previous problem. (This is one way to double-check your calculations.)

6-3. Biphenyl consists of two connected phenyl rings that are rotated relative to each other by an angle θ. While Hückel theory does not account for steric energy contributions, the effect of this twist on the π molecular orbital structure can be modeled by setting the nearest-neighbor Hamiltonian matrix element for the bond between the two rings to $t\cos\theta$, where t is the usual carbon-carbon interaction introduced in Section 6.2. Plot E^{π}_{total} (Eq. (6.8)) as a function of θ. Given that the experimental equilibrium torsional angle is $\theta = 44.4°$, comment on the relative roles of steric interactions and π conjugation on the total energy (and hence the geometry).

6-4. Terphenyl (also known as diphenylbenzene or triphenyl) consists of a central benzene ring with two phenyl substituents. Using Hückel theory, compare the total π energy of ortho-, meta-, and para-terphenyl and predict the relative abundance of the three isomers. (For simplicity, assume that these are planar.) Calculate the lowest-energy π transitions for each species, and comment on how they might be distinguished by UV/vis spectroscopy.

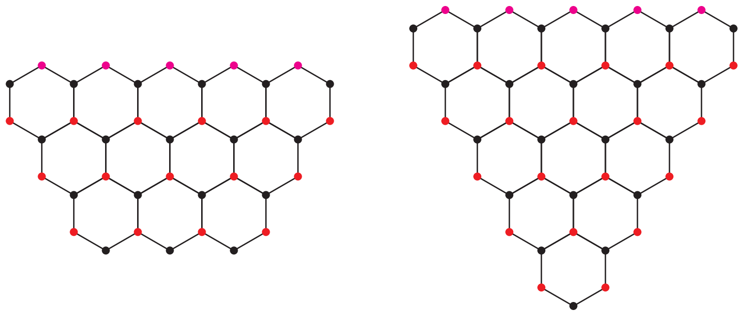

Figure 6.1. "Trapezoid" and "triangle" graphene nanoparticles with nonbonding MOs.

6-5. Nonbonding molecular orbitals. In the text, we have seen examples of bonding MOs (with energies lower than the parent AOs) and antibonding MOs (with energies higher than the parent AOs). However, it is also possible to have "nonbonding" MOs, which are linear combinations with the same energy as the parent AOs. The "triangle" and "trapezoid" polyaromatic hydrocarbons shown in Figure 6.1 are two examples of molecules with nonbonding π MOs.[21] Using Hückel calculations, determine the number of nonbonding MOs for these two molecules. You will have to build the Hückel matrix by hand since these molecules aren't in the `ChemicalData[]` database. (Hint 1: It is easy to make mistakes; one sanity check is to verify that your matrix is Hermitian. Hint 2: Use `Chop[]` to turn numerical values that are very close to zero (in this case on the order of 10^{-16}) into "zeros" when counting them.)

6-6. Lycopene is a carotenoid pigment found in many foods, such as tomatoes and watermelon. Perform a Hückel calculation for lycopene ($C_{40}H_{56}$), and calculate the HOMO-LUMO gap. What color does Hückel theory predict? (Hint 1: Not all the carbons are part of the π-electron system; only carbons that are part of the π system should be described in your Hückel Hamiltonian. Hint 2: Use a color wheel to identify complementary colors.)

6-7. Acidity and basicity. Adding a proton to a base can be considered as a chemical reaction that converts the molecule from X to XH^+. The change in energy, $\Delta E = E_{XH^+} - E_X$, is thus proportional to the equilibrium constant for the reaction, as measured by the pK_a.

(a) Protonation of a nitrogen atom in a heterocyclic base changes the nitrogen atom types from pyridine-like ($\dot{N}$) to pyrrole-like (N^+), requiring changes in the on-site and off-diagonal Hamiltonian matrix elements. Calculate the change in the π energy and rank the following molecules from lowest pK_a to highest: acridine, isoquinoline, pyridine, quinoline.

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[21] P. Potasz, A. D. Gluclu, P. Hawrylak, "Zero-Energy States in Triangular and Trapezoidal Graphene Structures," *Phys. Rev.* B **81**, 033403 (2010), http://dx.doi.org/10.1103/PhysRevB.81.033403.

(b) A “rule of thumb” that can be derived from Hückel theory[22] is that the change in energy—and hence the pK_a—is proportional to the charge on the nitrogen atom. Using the charge density matrix for the molecules in the previous part, rank them from lowest pK_a to highest. How does this compare to your previous result?

6-8. Experimentally, 6,6-diphenyl-fulvene has a larger dipole moment than 6,6-bis-(p-chlorophenyl)fulvene.[23] Using Hückel calculations, calculate the dipole moments of these species. (Hint: The former is available as `ChemicalData["Diphenylfulvene"]`; you’ll have to build the latter yourself, being sure to incorporate the correct chlorine matrix elements from Table 6.1.)

6-9. The infrared N-H stretching frequency for primary aromatic amines is proportional to the electron density on the nitrogen atom.[24] Rank the following molecules in terms of their predicted N-H stretching frequencies: aniline, *ortho*-chloroaniline, *meta*-chloroaniline, *para*-chloroaniline.

6-10. The infrared C-H stretching frequency correlates with the free valence index on the carbon atom.[25] Rank the different C-H stretching frequencies for the unique sites in the styrene molecule.

6-11. Using the bond-order/length/strength relationship, predict the relative bond lengths for all of the (unique) C-C bonds in biphenylene.

6-12. The infrared C=O stretching frequency can be predicted by using the bond-order/length/strength relationships in Section 6.5.4. Higher C=O bond order corresponds to “stiffer” bonds with higher C=O vibrational frequency, and lower C=O bond order corresponds to “looser” bonds with lower C=O vibrational frequency.

(a) Using the C=O bond order, rank these molecules for increasing carbonyl stretching frequency: acrolein, benzaldehyde, benzophenone, formaldehyde.

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[22] H. C. Longuet-Higgins, “Some Studies in Molecular Orbital Theory II. Ionization Constants in Heteroaromatic Amines and Related Compounds,” *J. Chem. Phys.*, **18**, 275–282 (1950), http://dx.doi.org/10.1063/1.1747619; in fact, this paper takes it one step further and relates the basicity to the charge on the corresponding nonheteroatomic aromatic hydrocarbon. Back when all these calculations needed to be done by hand, there was a strong motivation not to perform new calculations! However, the relationship between increasing nitrogen charge and increasing pK_a is more rigorous, and holds even for more sophisticated all-electron Hartree-Fock and density functional theory calculations, e.g., S. R. A. Leite, “Basicities of Primary Arylamines and Calculated Amine Nitrogen Electronic Charges,” *Ecl. Quím. (São Paulo)* **23**, 71–80 (1998), http://dx.doi.org/10.1590/S0100-46701998000100006.

[23] G. W. Wheland and D. E. Mann, “The Dipole Moments of Fulvene and Azulene,” *J. Chem. Phys.* **17**, 264–268 (1949), http://dx.doi.org/10.1063/1.1747237.

[24] S. F. Mason, “The Frequencies and Intensities of the N–H Stretching Vibrations in Primary Amines,” *J. Chem. Soc.* 3619–3627 (1958), http://dx.doi.org/10.1039/JR9580003619.

[25] G. M. Badger and A. G. Moritz, “The C-H Stretching Bands of Methyl Groups Attached to Polycyclic Aromatic Hydrocarbons,” *Spectrochim. Acta* **15**, 672–678 (1959), http://dx.doi.org/10.1016/S0371-1951(59)80363-5.

(b) Is it possible to distinguish between 1-naphthaldehyde and 2-naphthaldehyde based solely on the C=O stretching frequency?

(c) Modify the benzaldehyde Hamiltonian to investigate the effect of substituting a chlorine atom in the ortho, meta, and para positions relative to the carbonyl group. Order your predicted carbonyl stretching frequencies, and compare to experiment.

(d) Put a carbonyl group on the end of a pi-conjugated chain of carbon atoms (e.g., ethylene, butadiene, hexatriene, octatetraene). How does the carbonyl stretching frequency change as a function of the length of the pi-conjugated chain?

6-13. At what positions would you expect nucleophilic, electrophilic, and radical attacks to occur in phenanthrene?

6-14. At what positions would you expect nucleophilic, electrophilic, and radical attacks to occur in acetophenone?

6-15. Resveratrol is a polyphenol found in grape skins and seeds; it is nearly planar, so assume that Hückel theory is valid. Where would you expect nucleophilic, electrophilic, and radical attacks to occur? (Hint: Modify your Hamiltonian to account for the different on-site and nearest-neighbor matrix elements involving the oxygen atoms, as discussed in Section 6.4. Also, be sure to count the π electrons correctly.)

6-16. The relative rates of reaction of a trichloromethyl radical toward aromatic hydrocarbons correlates with the highest free valence index, F_r, of the hydrocarbon—i.e., larger maximum F_r corresponds to a faster reaction rate.[26] Using this principle, rank the following hydrocarbons from slowest to fastest reaction with a trichloromethyl radical by using the highest F_r at any site in the molecule: anthracene, benzene, chrysene, naphthalene, stilbene, phenanthrene.

6-17. Polychlorinated biphenyls (PCBs) are now known as persistent organic pollutants, but until the 1970s they were widely used in a number of applications due to their high dielectric constant, thermal conductivity, flashpoint, and relative inertness. PCBs were typically produced by electrophilic halogenation of biphenyl, resulting in the addition of many chlorines in many different sites. Use Hückel theory to predict the properties of the PCB mixtures.

(a) Run calculations for planar biphenyl, and biphenyl with a 44.4° twist between the rings (see Problem 6-3). Obtain the charges and frontier molecular orbitals in the two cases.

(b) Where do you predict the electrophilic addition of the first chlorine atom to occur on biphenyl, based on your calculations from the previous part? Does the planarity make a difference? Are there multiple equivalent sites?

(c) Perform Hückel calculations for the monochlorinated biphenyl you predicted in the previous calculation (again, for both the planar and nonplanar forms). Based on

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[26] E. C. Kooyman and E. Farenhost, "The Relative Reactivities of Polycyclic Aromatics towards Trichloromethyl Radicals," *Trans. Faraday Soc.* **49**, 58–67 (1953), http://dx.doi.org/10.1039/TF9534900058.

the charges and/or frontier MOs, predict the site for the second chlorination. Again, identify equivalent or nearly equivalent sites, and characterize any differences between the planar and nonplanar models.

(d) In principle you can continue adding chlorine atoms.[27] Repeat the calculations from the previous steps to determine the most likely positions of the third chlorine atom.

6-18. Hydrocarbon reduction by alkali metals (Birch reduction). When aromatic hydrocarbons are put in solution with alkali metals, the dianion of the hydrocarbon is formed. Addition of a proton source (e.g., an alcohol) results in the addition of two hydrogens. The position of these additions can be predicted using Hückel theory. For a concrete example, consider the case of naphthalene.

(a) Naphthalene first gains an electron from the alkali metal. Calculate the charge density of the molecular anion. (Hint: Be sure to include the singly occupied state when computing the charges.)

(b) The first proton attacks at the site of the highest electron density of the anion. Identify this site. (If there are multiple equivalent sites, one is chosen at random.)

(c) After addition of the first proton, the π conjugation of the molecule is disrupted—the carbon atom to which the first proton was attached now no longer participates in π bonding. Recalculate the Hückel solution, omitting this carbon atom from your calculation. This new molecule gains an electron from the alkali metal. Calculate the charge density of this second molecular anion.

(d) The second proton attacks at the site of the highest electron density of the second molecular anion (which you calculated in the previous step). Identify this site.

6-19. Carry out the same calculation as in the previous problem, but for reduction of phenanthrene.

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[27] In fact, one of the most common PCBs in the United States was Aroclor 1016, a mixture of congeners consisting of approximately half $C_{12}H_7Cl_3$.