

Why is benzene stable? - The cause of aromaticity: A conceptual explanation

Organic chemists tend to place more importance on concepts than on formulas. This seems to be true. Any theory cannot be called a true theory unless it can be explained in words. The essence of both the theory of relativity and quantum mechanics can be explained in words (of course, detailed phenomena and quantitative explanations require the help of formulas, but the mathematics used is at high school level). So, I tried to explain the cause of aromaticity in simple terms. It was easier than I thought, so let me introduce it. The original paper is:

Ichikawa, H.; Sakata, K. "Aromaticity/Antiaromaticity in Cyclic Conjugated Hydrocarbons," *Int. J. Quantum Chem.*, 2002, **87**, 135-144.

What is aromaticity?

Most chemists are familiar with the concept of aromaticity. A typical compound with aromaticity is benzene. Benzene is a compound with double bonds, but it is very stable. Stable has two meanings. One is that it is not easily changed chemically, and the other is that it has a low heat of formation.¹ In the case of benzene, it is not easily changed chemically and is thermodynamically stable at the same time. The object of comparison is a hydrocarbon (hexatriene) that has the same number of double bonds.

The characteristic of the chemical phenomenon of aromaticity is that it resists attack by reagents, and no addition reaction occurs, but a substitution reaction occurs instead. This substitution reaction can be understood as an addition reaction to the double bond, but then immediately restores aromaticity with the elimination of H. This represents the phenomenon that the cyclic π electron system consisting of six electrons in the benzene skeleton is stable.

What is antiaromaticity?

On the other hand, what about cyclobutadiene, which is also a cyclic conjugated hydrocarbon? It is extremely unstable. Cyclobutadiene polymerizes immediately after it is produced. Its lifetime (half-life) under normal conditions is said to be less than 10^{-6} seconds. Why is it unstable?

Consequently, the phenomenon of aromaticity and antiaromaticity can be adequately explained by the uncertainty relation and Hund's rule. First, we will explain the uncertainty relation and Hund's rule in words (some simple mathematical expressions will be used).

¹ Heat of formation: The amount of heat (usually the amount of heat per mole of compound) generated or absorbed when a substance (benzene) is produced from existing elements under standard conditions. It is also called enthalpy. In the case of benzene, it is the amount of heat of the product system - the original system when liquid benzene is produced from carbon element (graphite) and hydrogen gas under standard conditions.

Uncertainty Relationship

The uncertainty relation, also known as the Heisenberg uncertainty principle, is a formula that states that the product of the “ambiguity” of position (Δx) and the ambiguity of momentum (Δp) cannot be smaller than a certain value ($\hbar/2$) related to Planck’s constant (h) (Equation 1).

$$\Delta p \Delta x \geq \frac{\hbar}{2} \quad \left(\hbar = \frac{h}{2\pi} \right) \quad 1$$

In Newtonian mechanics (classical mechanics), momentum (p) is mass (m) \times velocity (u), but the concept is different in quantum mechanics. Momentum also applies to waves such as light. Light has no mass, but it has momentum. Think of momentum as the cause of the force that acts on an object. When light is shone on an object, the object is subjected to a force. The momentum (p) of electromagnetic waves such as light can be expressed as $p=h/\lambda$, where λ is the wavelength. This is called the de Broglie formula.

"Ambiguous" is as follows. Let's take the ambiguity of position (x) as an example. Let's say the correct position of an object is x_0 . Ambiguity is the average of the "absolute value" of $x - x_0$ when the object's position x is measured multiple times. For example, let's say the correct position of an object is 3.0. When the position is measured five times, the results are 2.5, 3.2, 2.8, 1.8, and 4.0. The absolute values of the errors are 0.5, 0.2, 0.2, 1.2, and 1.0, respectively. The ambiguity is the average of these, which is $(0.5+0.2+0.2+1.2+1.0) \div 5=0.62$. Reducing the ambiguity is equivalent to narrowing the range of the object's position.

In general, the correct position (x_0) cannot be known, so we will use the average value of the measurements (\bar{x}). In the above example, \bar{x} is $(2.5 + 3.2 + 2.8 + 1.8 + 4.0) \div 5 = 2.86$. Since the probability of shifting to the + side is the same as the probability of shifting to the - side, if you measure it an infinite number of times, $x_0=\bar{x}$.

The uncertainty relation is deeply related to organic chemical phenomena

I'll go off topic for a bit, but the title cannot be emphasized too much, so I'll explain it in a little more detail.

The variables that appear in the uncertainty relation are position (x) and momentum (p) (which can be easily converted into the relationship between time and energy). These are vector quantities because they have directionality. x is a position in three-dimensional space, but it is easier to understand if you limit it to one dimension.

The momentum (p) of a particle (*e.g.* electron) confined in a certain range L ($= \Delta x$) is measured.² If the right direction along the coordinate axis is positive and the left direction is negative, positive and negative values will be observed in equal proportions, so the average momentum (\bar{p}) is 0. The

² Since the particles exists between 0 and L , the ambiguity of the particle's position is L itself.

uncertainty of momentum (Δp) is the deviation $p - \bar{p}$ from the average momentum. Therefore, if we take the square of the uncertainty (Δp),

$$(\Delta p)^2 = \overline{(p - \bar{p})^2} = \overline{p^2} \quad 2$$

Using the uncertainty relation $\Delta pL \geq \hbar/2$, we get $(\Delta p)^2 = \overline{p^2} \geq \left(\frac{\hbar}{2L}\right)^2$.

Here, we use classical physics to estimate the particle's kinetic energy.

$$E = \frac{u^2}{2} = \frac{p^2}{2m} \quad \left(\because u = \frac{p}{m}\right)$$

Using the above formula, the observed kinetic energy (\bar{E}) is,

$$\bar{E} = \frac{\overline{p^2}}{2m} \geq \frac{\hbar^2}{2mL} \quad 3$$

Actually, we solve the Schrödinger equation for an electron trapped in a box³. We get a result that is very similar to equation 3.)

Looking at equation 3, when $L \rightarrow 0$, $\bar{E} \rightarrow \infty$. This means that the smaller L is made, that is, the more precisely the electron's position is determined (making L smaller, in other words, the more the range of electron movement is limited), the greater the average electron's kinetic energy. In other words, the phenomenon of electrons moving around violently (in the classical sense) when they are in a small range originates from the uncertainty relation, a basic equation in quantum theory.

The lowest energy level of the circular motion of an electron has an energy value of 0

Circular motion has no beginning or end. This means that $L = \infty$. Then, from equation 3, $\bar{E} = 0$. In other words, the kinetic energy of the electron in the lowest energy level of the circular motion is 0 (the electron is not moving!). (At energy levels other than the lowest, phase inversion always occurs in the wave function (L is no longer ∞), so $\bar{E} = 0$ does not hold.)

In actual compounds, such as benzene, the potential energy received from the atomic nucleus of the π electron is different on the atom and between atoms, and is not constant, so kinetic energy is generated, but it is predicted that there is an orbital with extremely low energy compared to the orbitals of other levels, and the existence of such a π orbital has actually been confirmed (the reference shown at the beginning is a paper that confirmed this fact).

Next, consider orbitals other than the lowest energy level. Since the kinetic energy is not 0, classically speaking, it is moving (circular motion). Moreover, since there are two degrees of freedom, right and left rotation, two orbitals with the same energy level should overlap (called degeneracy). In fact, there

³ This website → Tutorial → Fundamentals of organic chemistry → Part 1 → Atomic nuclei, uncertainty principle → 1220

are two π orbitals other than the lowest energy level. In other words, in the molecular orbitals of the pi electrons of cyclic conjugated compounds, there is only one orbital at the lowest energy level, and two orbitals at other levels.

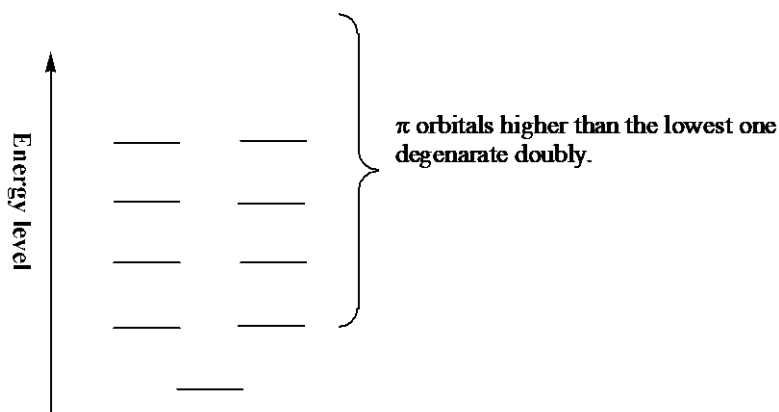


Figure 1. The molecular orbitals of the π electrons in a cyclic conjugated system are doubly degenerate except for the lowest energy level.

How electrons enter the $4n/4n+2$ system

Cyclic conjugated systems are classified as $4n+2$ or $4n$ systems according to the number of electrons entering the system. n can take the values 0, 1, 2, etc. Specifically, $4n+2$ systems have values of 2, 6, 10, 14, etc., with benzene being 6. $4n$ systems have values of 4, 8, 12, etc., with cyclobutadiene being a representative example of 4.

When $4n+2$ electrons enter a π molecular orbital as shown in Figure 1, the pattern shown in Figure 2 will result.

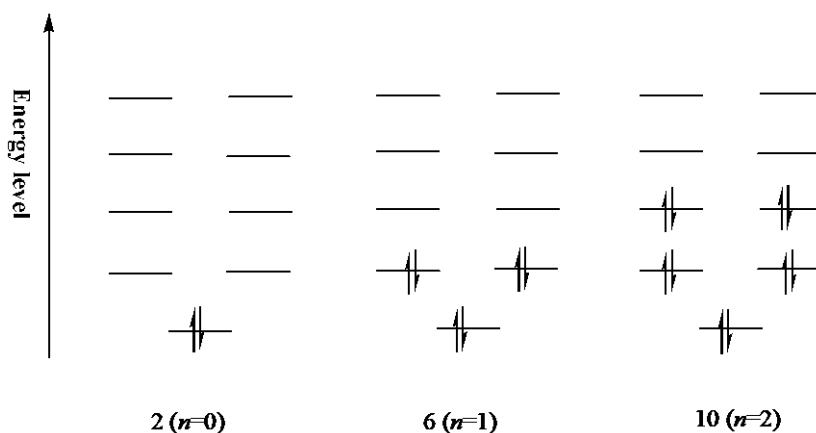


Figure 2. Pattern in which $4n+2$ electrons enter a π molecular orbital.

When electrons pair up ($\uparrow\downarrow$) in a molecular orbital, it means that they are chemically bonded (Note: non-bonding electron pairs (lone pairs) are also electron pairs, but we will not consider them here). The lowest level orbital is (in principle) an orbital with 0 kinetic energy. Electrons that enter this orbital have the lowest energy. Electrons in other orbitals have kinetic energy, but because they are chemically bonded, they are low-energy orbitals. This is why the π electrons in benzene are extremely stable.

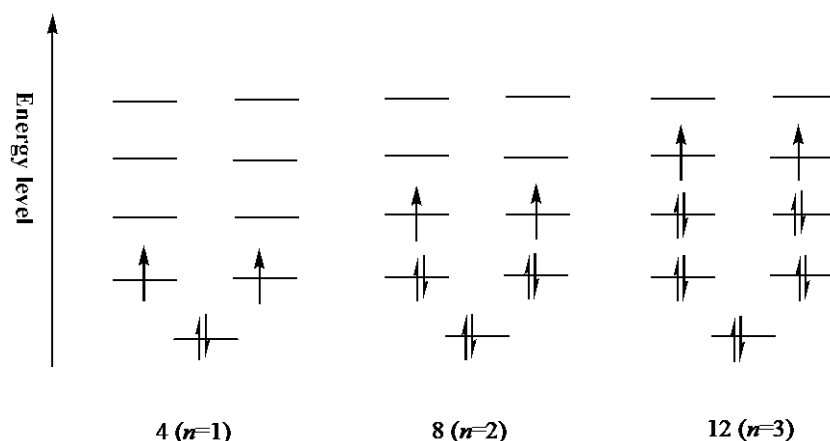


Figure 3. Electron entry pattern for the $4n$ system.

On the other hand, let us look at the case of the $4n$ system. A very unfavorable situation occurs in terms of stability. Two electrons inevitably enter the doubly degenerate highest occupied molecular orbital. According to Hund's rule (the meaning of this rule will be explained later), when an electron enters a degenerate molecular orbital, the spin quantum number of the electron entering must be maximized (because this results in a lower energy).

α spin has an intrinsic spin value (unit: \hbar) of $+1/2$, and β spin has an intrinsic spin value of $-1/2$, and the absolute value of the sum of the individual spin quantum numbers of multiple electrons is called the total spin quantum number (S). In addition, $2S+1$ is called multiplicity, and it is possible to take as many spin states as $2S+1$ electrons. In a normal compound, for example, as shown in Figure 2, the number of α electrons and β electrons in the electronic configuration is the same, so when $S=0$, $2S+1$ is 1. This is called a singlet electronic state. In contrast, the electron arrangement shown in Figure 3 is $S=1$, where $2S+1$ is 3, and this is called the triplet state.

The electronic state shown in Figure 3 is missing one chemical bond because the spins of the two electrons are not paired. Therefore, it can be said to be less stable (has a higher energy state) than the electronic state in Figure 1, at least by the amount of that chemical bond.

The triplet electronic state has two unpaired electrons. In other words, one molecule has two radicals.

In principle, radical reactions do not have an activation state (a high-energy state associated with a reaction), so they react with other molecules or radicals and disappear. It can be said to be chemically very unstable. The reasons for the manifestation of aromaticity and antiaromaticity are summarized below.

Aromaticity

The reason for the aromaticity of benzene and other compounds is that "Because it is a cyclic conjugated system, there is an orbital level where the kinetic energy of the π electrons is, in principle, 0." In a chain-like conjugated system, there is no such orbital.

Antiaromaticity

The reason for the anti-aromaticity of cyclobutadiene and other compounds is that, although there is an orbital level where the kinetic energy of the π electrons in a cyclic conjugated system is, in principle, 0, "two equilibrium spin electrons appear, so no chemical bonds are formed within the molecule, and the molecule takes on a high-energy state, and because it has two radicals, it is highly reactive and chemically unstable."

Supplementary information

The manifestation of reactive aromaticity is related to two factors: Hund's rule and the high reactivity of radicals. As a supplementary explanation, we will explain the reason for the manifestation of Hund's rule and the cause of the instability of radicals.

1. Hund's rule

This is a quote from the tutorial (1320) on this website. If we consider electrons as simple particles in classical mechanics, it seems possible to pack many electrons into one state (atomic orbitals being one of them), but this is not necessarily the case in the microscopic world. It is known that there are two types of microscopic particles.

Bose particles and fermions

Microscopically (quantum mechanically), there are two types of particles. One type is a type of particle in which multiple particles can occupy the same state and is called a boson. Examples of bosons are photons, π mesons, and helium atoms (helium atoms are bosons, and superfluidity occurs in liquid state).

The other type is a type of particle in which more than one of the same particles (or two with different spins) cannot exist in the same state, and is called a fermion. Bosons and fermions are properties inherent to particles. Electrons belong to fermions and are particles that avoid the existence of more than two with different spins in the same state (we do not know why electrons are fermions). The state

here includes not only the spatial state (the orbital occupied by the electron) but also the state of the electron itself (called the internal state). In addition to electrons, protons and neutrons are also fermions. We don't know why fermions and bosons exist, but we only need to acknowledge this fact to understand chemical phenomena.

Electron spin and spin quantum number

It is known that there are two types of internal states of electrons. In the classical model, this corresponds to the rotation of the electron, so it is called spin. We will explain it using the classical model because it is easy to understand the concept.

Let's assume that the electron is a "sphere" (Figure 4). The magnitude of the rotational moment has been measured and is known to have values of $+\hbar/2$ and $-\hbar/2$. One of these is called an α spin electron, and the other is called a β spin electron. \hbar is the value obtained by dividing Planck's constant by 2π , and has a quantity of 1.054572×10^{-34} J·s. The coefficients $1/2$ and $-1/2$ attached to \hbar are called the spin quantum number.

Pauli's principle

When including the spin state, electrons, which are fermions, can have up to two electrons with different spins in one orbital. This is called Pauli's exclusion principle.

An atomic orbital ψ have spatial coordinates (x, y, z in Cartesian coordinate representation; r, θ, φ in polar coordinate representation), and spin has spin coordinates that represent the spin state of the electron. The spatial state defined by the atomic orbital and the internal state of the electron defined by the spin are independent phenomena, so the state of the electron as a whole can be expressed as the product of their functions. For example, when electron 1 has an α spin and occupies ψ , it is expressed as $\psi(1)\alpha(1)$, and when electron 2 has a β spin and occupies ψ , it is expressed as $\psi(2)\beta(2)$.

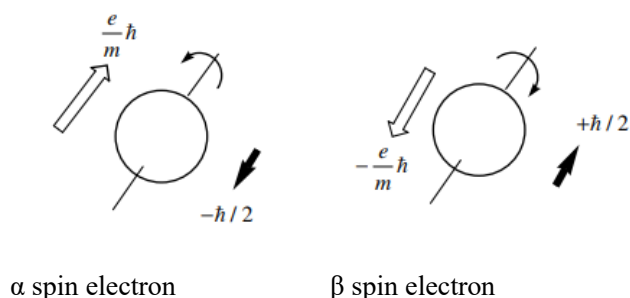


Figure 4. Direction of the electron's rotational angular momentum (black arrow) and magnetic moment (white arrow). e is the elementary charge (1.6022×10^{-19} C), and m is the mass of the electron (9.109×10^{-31} kg).

Magnetic moment of electron spin

As shown in Figure 4, a charged sphere generates magnetic field lines (magnetic momentum) as it rotates. Therefore, when a magnetic field is applied, an energy difference occurs due to the spin.

Hund's rule

Let's consider the configuration of multiple electrons in a degenerate (degeneration: multiple states with the same energy level) atomic orbital. Figure 5 shows the possible combinations of two electrons in two degenerate orbitals (χ_a , χ_b) taking into account Pauli's principle.

The energies of states A, A' and B, B' are all considered to be equal. Similarly, the energies of C and D are equal.

E and F have the same energy as long as no magnetic field is applied to these systems. When there is no magnetic field, the question is which of states A, C, and E has the lowest energy.

It is easy to guess that state A has the highest energy. This is because two electrons occupy the same orbital, so the probability that electrons 1 and 2 are close to each other is higher than in the other cases, and the repulsive energy (positive value) between the electrons is larger than in the other cases.

Comparing C and E, the only difference between them is the spin of the electron. The shape and size of the orbit are not clearly defined, and strictly speaking, the size of the orbit is infinite. For this reason, some of the electrons in orbital χ_a are close to orbital χ_b . If an electron in an χ_a orbital and an electron in χ_b orbital are close to each other, the repulsion between the electrons will naturally be greater, and the energy will be higher accordingly.

This possibility is greater in state C, but less in state E. This is because the two electrons have the same spin, and Pauli's principle makes it more difficult for electrons to move from χ_a to χ_b , or from χ_b to χ_a . This reduces the repulsion between electrons, and the energy of the orbital becomes lower. Therefore, the electron configuration of E (or F) has the lowest energy.

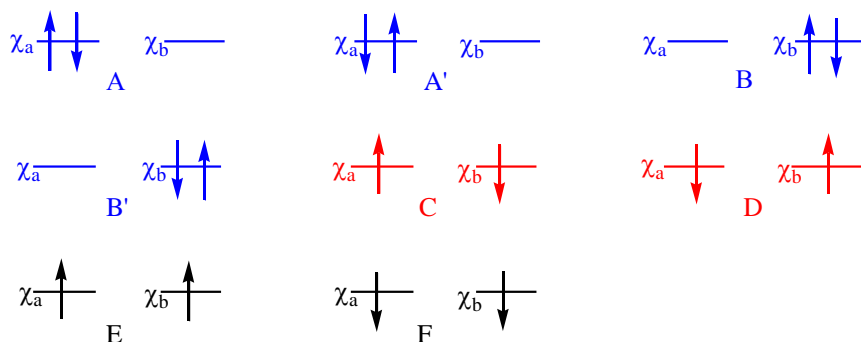


Figure 5. Possibilities when two electrons enter two degenerate orbitals.

[Total spin quantum number]

As already mentioned, an electron has a quantum number of +1/2 or -1/2. Consider the sum of the

spin quantum numbers of each electron. If both electrons have α spin, $1/2 + 1/2 = 1$. If one is α and the other is β spin, $1/2 - 1/2 = 0$. If both have β spin, $-1/2 - 1/2 = -1$. The absolute value of the sum of the spin quantum numbers of each electron is called the total spin quantum number.

$$S = |s_1 + s_2 + \dots + s_n| \equiv \left| \sum_{i=1}^n s_i \right|$$

The way in which the electron with the lowest energy enters a degenerate orbital is the electronic configuration that maximizes the total spin quantum number. This is called the Hund rule. The Hund rule applies not only to atomic orbitals but also to molecular orbitals.

[Spin multiplicity]

There are $2S+1$ magnetic states for the total spin quantum number S (when a magnetic field is applied, it separates into $2S+1$ different energy states). This number is called the spin multiplicity. The numbers 1, 2, 3, ... are called the singlet state, doublet state, triplet state, ... respectively. For example, a hydrogen atom has one electron, so $S=1/2$, and the spin multiplicity is $2 \times (1/2) + 1 = 2$, which is a doublet state. In the lowest energy state (called the ground state), He has two electrons with the spin reversed, so $S=-1/2+1/2=0$, and $2S+1$ is 1, so it is in the singlet state. Most ordinary organic compounds are in the singlet state, with $S=0$. It is easy to imagine that radicals have doublet states, and biradicals have singlet and triplet states.

Reactivity of radicals

Reactions involving radicals involve only the transfer of electrons, which have a small mass, so they are generally more reactive and have a faster reaction rate than ionic reactions. They also react with other molecules to generate new radicals. This makes chain reactions more likely to occur. The rate-determining step in radical reactions is the transfer of unpaired electrons, so there is less influence of steric hindrance compared to ionic reactions, and in many cases, there is no transition state. (Note: Transition states in chemical reactions exist because of steric hindrance between the reacting chemical species.)

Unpaired electrons can easily bond not only with unpaired electrons, but also with bonding electron pairs. In the reaction in which $A\cdot$ radical reacts with B molecule to give $B\cdot$ (Figure 6), there is no transition state in between, so if the energy of the system $A + B\cdot$ after the reaction is lower than that of the initial system, the reaction will proceed in that way. If the energy of the system $A + B\cdot$ is higher, the reaction will not proceed.

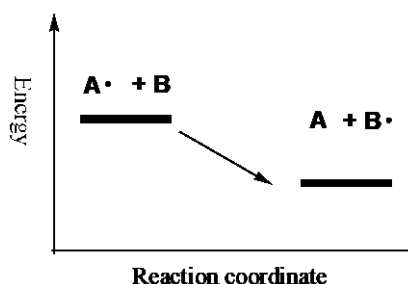


Figure 6. Radical reactions are determined solely by the energy difference before and after the reaction.

Figure 7 shows the reaction that occurs when light is shone on a mixture of chlorine and methane gas. A mixture of chlorine gas and methane does not react in the dark, but when light is shone on it, it reacts explosively, going through the process shown in Figure 7: When chlorine molecules are irradiated with light, chlorine radicals ($\text{Cl}\cdot$) are generated. The chlorine radicals react with nearby methane molecules to form methyl radicals ($\text{CH}_3\cdot$). The methyl radicals react with chlorine molecules to become chlorine radicals, and this chain reaction is repeated.

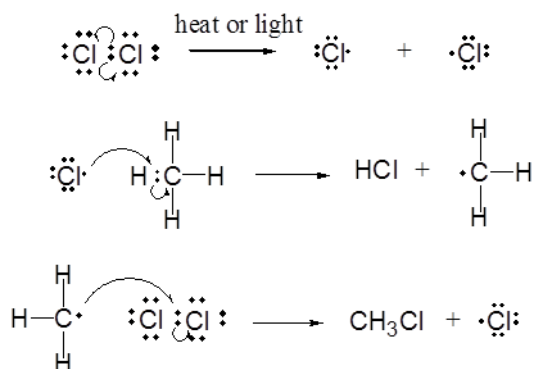


Figure 7. Examples of radical reactions.

Contents of “Aromaticity/Antiaromaticity in Cyclic Conjugated Hydrocarbons” by H. Ichikawa and K. Sakata (Int. J. Quantum Chem, 87, 135-144 (2002))

Historically, the Hückel molecular orbital method has been used to understand aromaticity. This method has been used to understand π electrons in conjugated systems and has been used successfully not only to qualitatively explain aromaticity, but also to quantitatively evaluate it. The Hückel molecular orbital method replaces important parts of the Hamiltonian in the Schrodinger equation with constants to simplify calculations. This raises the question of what the results obtained by the Hückel molecular orbital method represent. In this paper, the authors first contrast the Hückel molecular orbital method with a strict quantum mechanical problem of a particle in a one-dimensional box and

show that the Hückel molecular orbital method calculates the wave function of π electrons and their kinetic energy.

Focusing on the number of π electrons in cyclic conjugated compounds, n can be classified into a series of $4n$ and $4n+2$, where n is a natural number including zero. For example, when $n=1$, $4n$ is cyclobutadiene and $4n+2$ is benzene. It is generally said that $4n$ is unstable and antiaromatic, while $4n+2$ is stable and aromatic ($4n/4n+2$ rule). This fact can be seen to have the same result when using the Hückel molecular orbital method. Hobe demonstrated the mathematical inevitability of this phenomenon by comparing the energies of problems involving electrons in linear and ring-shaped one-dimensional boxes. Ichikawa et al. have shown that the problem of a particle in a box is equivalent to the Hückel molecular orbital, so that the enormous amount of calculation results obtained by the Hückel method could be mathematically justified.

In addition, it was shown that the kinetic energy of the lowest level orbital obtained in the problem of a particle in a ring-shaped box is 0. A kinetic energy of 0 indicates that the electron is not bound. In equation 3, this means that $L=\infty$ (it was thought to be self-evident that this is equivalent to the uncertainty relation and $\Delta p=\infty$, so it was not clearly shown in the paper).

Finally, to investigate whether the electrons that enter the lowest level π molecular orbital in benzene have 0 kinetic energy, the authors placed the center of the benzene structure at the origin of the x, y plane, expressed each atom by the distance from the origin (r), the angle (φ) between the x axis and r , and the z axis, and calculated the energy of the angle (φ) component of the π molecular orbital. As a result, they found that the energy of the lowest level orbital of π electrons is particularly low (small), as expected. (It will not be 0 due to the potential of the atom.)

The Appendix describes the calculation method.