

Why Does Resonance Take Place?

Conjugation and/or resonance are the most important and useful concepts in organic chemistry. But have you ever considered the cause? The cause of resonance is not written in the textbooks of organic chemistry at all and I think that it is a most complain for organic chemists that they are unable to understand what is written in the books of quantum chemistry. I would like to explain this problem here as plainly as possible. But there is no telling whether it is more intelligible to read it since I (tanuki¹⁾) myself think that it is freely intelligible. If are unable to understand, please ask tanuki by e-mail.

Although it may not be necessary to explain anew, resonance or conjugation is the following phenomenon.

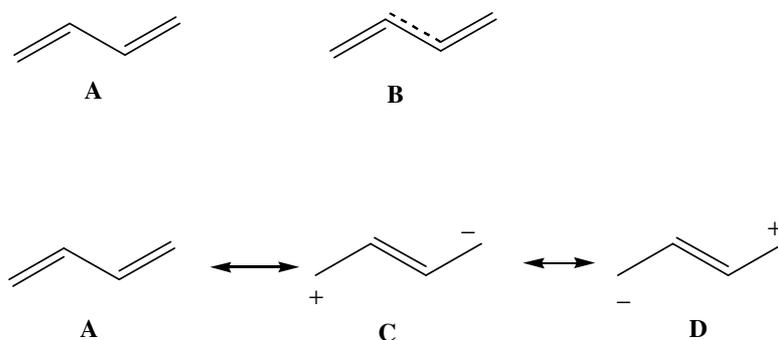
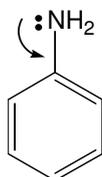


Fig. 1. An example of resonance.

For example, in butadiene (A), resonance is a phenomenon in which a part of π electrons of the double bonds flows into single bond (B). The textbook of organic chemistry explains it as the state where the electronic structures of A, B, and C are put together. Although this explanation borrows the results of the valence bond method (valence bond theory: VB), one theory of the quantum chemistry. A simple question is the reason why such a phenomenon necessarily needs to happen. The textbooks of quantum chemistry explain it in the way merely that the energy is lowered and do not mention why it falls.



A part of lone-pair electrons of N in aniline flows into the benzene ring (thus, the basicity of the amino group is decreased). Look, the electrons move from N with a large electronegativity to small C. It is clear inconsistency of the theory of organic chemistry. Although there is explanation by conjugated structures, since the problem here is why conjugation happens, then, this is not an answer.

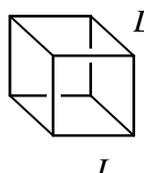
If a conclusion is said previously, the cause of resonance and/or conjugation originates in the most fundamental expression of nature called the Heisenberg's uncertainty relation. Only now, since you probably do not understand, the route which results in this conclusion is explained systematically.

1. When an electron is shut up in a narrow space, the electron has big energy.

It is a fact of nature although one may think what that is at all. If things are considered classically (in macroscopic way), such a fact is a very unacceptable phenomenon. In our world (macroscopic world), even if an object is put into a big box or put into a small box, the energy which the object has is same. However, these well-known ideas in the macroscopic world sometimes completely differ in the microscopic world. An electron confined in a narrow space has big kinetic energy. In other words, it would be said that the electron moves violently. On the contrary, if restriction of movement is not added, the kinetic energy of the electronic is 0. Such an electron does not move. This surprising phenomenon is known by the following discussion.

When an electron is shut up in the cube of L , the behavior of the electron follows Eq.1 (Schrödinger equation). (How to solve this equation is not explained here.) In Eq.1, ∇^2 are an operator called Laplacian and m is the rest mass of electron and h is a constant called Planck's constant. E is kinetic energy and ψ is the wavefunction which determines the behavior of the electron.

If you have the knowledge the first grade of scientific course of university, you may solve the Eq. 1. (See <http://www.aromaticity.net/Qorg/Tutorial/QOC/Prt1/1-4Wd.pdf> [particles in a box] for knowing how to solve.) The kinetic energy of the electron shut up in the box (cube) is given by Eq. 2.



$$E\psi(x, y, z) = \frac{-h^2}{8\pi^2 m} \nabla^2 \psi(x, y, z) \quad 1$$

$$E(n_x, n_y, n_z) = (n_x^2 + n_y^2 + n_z^2) \frac{h^2}{8mV^{2/3}} \quad 2$$

Fig. 2. Schrödinger equation and its solution of an electron in a box.

In Eq. 2 V is the volume (L^3) of the box. And, n_x , n_y , and n_z are called quantum numbers, are values automatically introduced in the solving process, and take independently the natural number as 1, 2, 3, and ... Now, let's consider only the case of $n_x=n_y=n_z=1$.

Equation 2 shows that E becomes large, if volume V of the box is made small. Conversely, if V is enlarged and is made infinite, the kinetic energy of the electron will approach 0. Since any system tends to decrease its energy as low as possible, it can be said that an electron has the character of spreading. Therefore, as for the case between the adjacent π bonds, the π electrons tend to spread rather than staying in one double bond. Similarly, as for the amino group of aniline, the lone-pair electrons tend to enter into the benzene ring rather than staying on N. This happens because the fall

of the kinetic energy exceeds the rise due to opposing electronegativity.

Let us actually calculate how much the energy is, when an electron is confined in the box of 1\AA^3 . Into Eq.2, the constants, $n_x=n_y=n_z=1$, $h=6.626 \times 10^{-34}\text{J}\cdot\text{s}$, $m=9.1091 \times 10^{-31}\text{kg}$, $V=1\text{\AA}^3$ are put and the result is multiplied by the Avogadro's number ($6.022 \times 10^{23}\text{mol}^{-1}$) to give about 10^4kJ/mol . In order to shut up an electron into the box of 1\AA^3 , more than 10^4kJ/mol of energy is needed. Conversely, it may be said that the electron shut up in the box of 1\AA^3 has the kinetic energy of more than 10^4kJ/mol .

Solving the Schrödinger equation makes us know that resonance and conjugation originate in the character that an electron tends to spread. However, even if the factor which determines the behavior of the electron is found, it will not be the perfect explanation why it becomes so. Namely, why does an electron have kinetic the energy, if restriction is added to the range of movement?

2. Concerning the Relationship Between Kinetic Energy and the Uncertainty Relation.

The uncertainty relation (principle) is expressed by the following formula.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \quad \left(\hbar = \frac{h}{2\pi} \right) \quad 3$$

Here, Δp and Δx are the ambiguities of momentum and location of the particle. The uncertainty relation was called "uncertainty principle", but "uncertainty relation" seems to be recommended to use, since this is not a principle but a relationship.

Let us consider the relationship between the uncertainty relation and the kinetic energy quantitatively. In order to simplify the story, let us consider one-dimensional coordinate. The position of the electron confined in the range of length L on x is examined. Since the electron exists somewhere between 0 and L , the ambiguity of position is set to L ($L=\Delta x$). Since the momentum ($p: p=mv$; m , electronic mass and v , its velocity) has directivity, the average (\bar{p}) of the momentum by observation becomes 0 (the probability of rightward movement and leftward movement is the same and when the average is taken it will be offset mutually). The crossbar attached upwards shows the average value. The ambiguity of momentum (Δp) is the gap from the average value of momentum, $p - \bar{p}$. Therefore,

$$(\Delta p)^2 = \overline{(p - \bar{p})^2} = \overline{p^2} \quad 4$$

Using the uncertainty relationship, $\Delta p \geq \frac{\hbar}{2L}$, one may get $(\Delta p)^2 = \overline{p^2} \geq \left(\frac{\hbar}{2L} \right)^2$ and thus the

average of observable kinetic energy (\bar{E}) is expressed by,

$$\bar{E} = \frac{\overline{p^2}}{2m} \geq \frac{\hbar^2}{8mL^2} \quad 5$$

Equation 5 is very similar to Eq. 2. In Eq. 5, since one dimension is considered, $V^{2/3}$ of Eq. 2 is replaced by L^2 .

Look at Eq. 5. It is easily understood that \bar{E} becomes infinitive at L approaching 0. That is, the more the electronic position is made to decide small in its ambiguity (this means L is made small), the more the average energy is large. In other words, an electron has a large kinetic energy when it is packed in a small area. It originates in the uncertainty relation, i. e., a fundamental expression of quantum theory. If it is right, what will be the true character of the uncertainty relation? In advance, let us make a close look at wave.

3. Motion of Electron Is That of Wave Packet.

Particles are objects with mass. Since an electron has mass, it is a particle. If we think a particle macroscopically, since one can determine the speed of a particle at a certain time, it is easy to determine the momentum and the location of the particle at the same time as definite values. But when it comes to a microscopic object like an electron, such measurement is impossible.

Next, let us consider the situation of wave. There are many kinds of wave as sonic wave, the wave that moves on the surface of water, light, and so on. A common character of wave is that centering a point, something vibrates up and down or forth and back. (Remember the shape of a sine wave.) The cases are that this “something” has mass like water wave or has not like light. And that “something” is not wave but a medium. What wave is characterized are the distance (wavelength: λ) of the peaks of vibration, the strength (amplitude: A) and the wave velocity (u) of propagation. The number of times of vibrating in 1 second at a fixed position (frequency: ν) is also added.

(The feature of a wave is denoted by mathematical function (for example, $\Psi = A \sin 2\pi \left(\frac{x - ut}{\lambda} \right)$) using A , x , u , t , and Ψ is called a wavefunction.)

Thus, a wave is abstract while a particle is concrete and they are conflicting. But they are united in the microscopic world in the form of a wave with mass. What I emphasize here is that a particle is a wave.

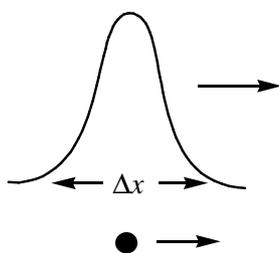


Fig. 3. The motion of a particle is that of a wave packet.

Since it is confirmed by experiments that a substance is a wave, this fact cannot be denied.

It is natural to think that the wave of a particle naturally does not exist in the place where the

particle does not exist. The wave of a particle locally exists near the position where the particle exists. This local wave is called wave packet. If the concept of a wave is used, movement of a particle is interpreted as that of a wave packet.

By the way, a pure wave is determined with a definite wavelength, speed and amplitude, and does not change with time. A wave which is decreased with time is not a pure wave but that of some kinds of waves being overlapped. Likewise, a wave packet is a bunch of waves with various wavelengths. That is, the wave packet is made of superposition of many waves, and in order to express the wave function of a wave packet, many wave functions are needed so that Δx becomes small. The example which made the wave packet by the technique of the Fourier transformation using ten sine functions is shown in Fig. 4.

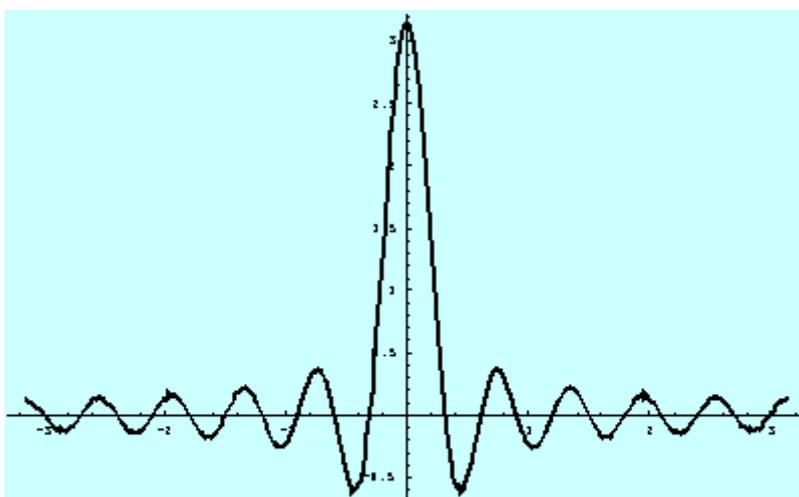


Fig. 4. A wave packet consists of many kinds of waves

4. What the Uncertainty Relation Means.

Now we have sufficient knowledge to understand the reason why the uncertainty relation exists. We know that the wave packet (Ψ^{packet}) corresponding to restricted movement of an electron is expressed by superposition of many kinds of wavefunctions. Here without losing generality, we can assume that the amplitude of each wavefunction (ψ_i) is standardized as,

$$\int_{-\infty}^{+\infty} \psi_i^2 dx = 1 \quad 6$$

This procedure is called normalization. A general promise is that unless mentioned in particular, a wavefunction is normalized since if not, discussions became very complicated.

Using normalized wavefunctions, the wavefunction of a wave packet (Ψ^{packet}) is expressed in terms of ψ_i and its rate of contribution (C_i).

$$\Psi^{packet} = C_1\psi_1 + C_2\psi_2 + C_3\psi_3 + \quad 7$$

In the above equation, ψ_1, ψ_2, \dots are the wavefunctions with the frequencies of ν_1, ν_2, \dots or with the momenta of p_1, p_2, \dots .

The square of the wavefunction is interpreted as the probability of its existence. So, Eq. 7 is squared.

$$(\Psi^{packet})^2 = (C_1\psi_1 + C_2\psi_2 + C_3\psi_3 + \dots)(C_1\psi_1 + C_2\psi_2 + C_3\psi_3 + \dots) = \sum_i \sum_j C_i C_j \psi_i \psi_j \quad 8$$

Since the electron must exist somewhere in space, summation of $(\Psi^{packet})^2 dx$ with respect to x becomes unity. If it is expressed by mathematically,

$$\int_{-\infty}^{+\infty} (\Psi^{packet})^2 dx = \int_{-\infty}^{+\infty} \sum_i \sum_j C_i C_j \psi_i \psi_j dx = 1 \quad 9$$

is obtained. And every wavefunction can be assumed without losing generality as the value of $\int_{-\infty}^{+\infty} \psi_i \psi_j dx$ is 1 (being normalized) when $i=j$, otherwise 0 (being orthogonalized). Equation 9 turns out to be,

$$\int_{-\infty}^{+\infty} (\Psi^{packet})^2 dx = \sum_i C_i^2 = 1 \quad 10$$

C_i^2 is interpreted as the actual rate of contribution of ψ_i to the observable quantity of the wave packet (Ψ^{packet}) . So, the average momentum of the wave packet is,

$$\bar{p} = C_1^2 p_1 + C_2^2 p_2 + C_3^2 p_3 + \dots \quad 11$$

Equation 11 means that the average probability of the wave packet takes the probability of p_1 is C_1^2 , and that of p_2 is C_2^2 and so on. And, Δp is the difference between the maximum p_{max} and minimum p_{min} among p_1, p_2, \dots, p_n .

If one expresses the average kinetic energy in terms of frequency ν using the relationships of $u=\lambda\nu$ and $\epsilon=h\nu$, the following equation is derived.

$$\bar{\epsilon} = h(C_1^2 \nu_1 + C_2^2 \nu_2 + C_3^2 \nu_3 + \dots) \quad 12$$

In order to decide the position of an electron's existence correctly, many kinds of waves are needed, and the average value of momentum becomes large. This equals to the phenomenon that the average value of kinetic energy becomes large. On the contrary, if the position of an electron is not decided at all, the wave of such an electron is denoted by a single wavefunction of a single wavelength. Since the wavelength is constant, the momentum and therefore the kinetic energy are also constant, i.e., $\Delta p=0$. This is the essence of the uncertainty relation.

Since a particle is wave, it has a certain width around the position of the particles' existence. If the width is made small, the waves of various wavelengths (or frequencies) must be added in. This

equals to taking many waves in. This means that the possibility of taking various momenta increases so much, i.e., the momentum becomes uncertain.

5. Summary

An answer to the question why resonance and conjugation take place is that an electron has the spreading character. Why it spreads is because an electron has big kinetic energy when it is packed in a narrow area. The reason for having big kinetic energy is due to a fundamental law of nature called the Heisenberg's uncertainty relation (principle). The reason why the uncertainty relation exists is that a substance is a wave. Don't you feel something uneasy was cleared up?

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1. A "tanuki" is a raccoon-like mountain dog living near-by human area in Japan. He is clever enough but he sometimes jokes human-beings. Be aware!