A toplogical view of a molecule along free electrons trajectories

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Abstract

Understanding how an organic molecule works like a mechanical device is an ultimate goal for biological scientists. To achieve the goal, we suggest a novel way to see the molecule.

A organic molecule such as enzymes, proteins is just a compound consisting of carbon, nitrogen, hydrogen or oxigen etc. The chemicals carry electrons, naturally every molecule forms a cloud of electrons bound to atoms and more there are 'free electrons'[1] moving around the cloud. For molecular structure study, people have been working on X-ray scattering and developed methods of getting an electron density map of the electron cloud.

In this note[2], under the hypothesis that free electrons are responsible for molecular behavior[3], we look at possible trajectories of the free electrons for a given electron density function and associate a topological space with a molecule. We hope this novel view leads to understand how the molecular motors work.

1 Brief review on structure factor, electron density related by Fourier transform[4]

In this section, we will give rough description about how an electron density function of a molecule is obtained. X-ray crystallography is a technique used for determining the atomic and molecular structure of a crystal, in which the crystalline structure cause a beam of incident X-rays to diffract into many specific directions, related to integer Miller indices (h, k, l). The diffracted rays make an image. As an example, see the image below, which is R. Franklin's X-ray DNA picture [5]

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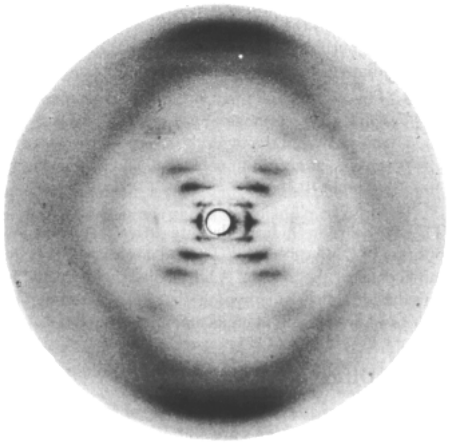
[1] They are also called by free radicals.

[2] Created on 2018.10.3, last modified on 2018.10.5

[3] Binding, dissociation etc are due to change of distribution of free electrons.

[4] This topic was brought to the author's attention by Prof. Hyunkyu Song at Korea University who replied kindly to some questions.

[5] https://www.mun.ca/biology/scarr/Franklins_crystallograph.html



By the theory of quantum mechanics, a wave like X-ray is represented by a complex function $A\exp(2\pi i(\mathbf{k}\cdot\mathbf{x}))$ and the square of its absolute value is the intensity[6]. Since each spot corresponding a Miller index(h,k,l) is made by the sum of all waves diffracted by electrons all over, i.e.

$$\int \rho(x,y,z)\exp(2\pi i(h,k,l)\cdot(x,y,z))dv \tag{1}$$

The integral is carried out over volume elements dv, over the unit cell of the crystal, $\rho(x,y,z)$ is the electron density at (x,y,z). The summation (1) is called structure factor and denoted by

$$\mathbf{F}(h,k,l) = F(h,k,l)\exp(2\pi i\alpha(h,k,l)) \tag{2}$$

where $F(h,k,l)$ is the absolute value and $\alpha(h,k,l)$ is a phase depending on Miller indices. The intensities$(=F(h,k,l)^2)$ of black spots are only things we can measure from the images, methods of calculating phases are developed[7] and ready to apply inverse operation, namely inverse Fourier transform. Spots are centered at specific places related to Miller indices which means integration will be Dirac delta functional on those Miller indices, and we get the electron density function,

$$\rho(x,y,z) = \frac{1}{V}\sum_{h,k,l} F(h,k,l)\exp(-2\pi i(h,k,l)\cdot(x,y,z) + 2\pi i\alpha(h,k,l)) \tag{3}$$

where V is the volume of the unit cell. Since ρ is real,

$$\rho(x,y,z) = \frac{1}{V}\sum_{h,k,l} F(h,k,l)\cos(2\pi((h,k,l)\cdot(x,y,z) - \alpha(h,k,l))) \tag{4}$$

[6]It will be expressed density or probability depending on situations.

[7][Yang2016] H Yang, E Peisach, JD Westbrook, J Young, HM Berman and SK Burley. DCC: a Swiss army knife for structure factor analysis and validation (2016) Journal of Applied Crystallography 93:569-575 doi:10.1107/S1600576716004428

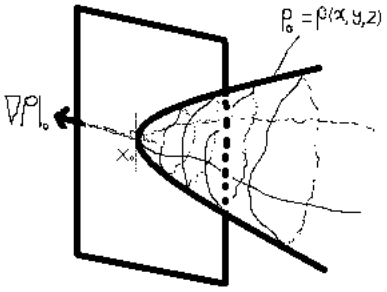
Well, this approximation method of calculating electron densities turns out to be good enough to identify the atoms and get molecular structures. So for a topological view of a molecule, we start with the electron density function ρ.

2 Free electron trajectories make holes through a cloud of electrons

From this ρ, how a molecule can be viewed as a topological space will be explained intuitively.

Before going into some mathematical calculation, for a quick grasp of a picture, let's imagine about rains falling on a mountain. By graviational force the rains become water flowing along the valleys in the 2-dimensional surface of mountain. Extend this picture to our molecule wrapped around electrons, then instead of rains and gravitation we have corresponding free electrons, the repelling force between electrons. Free electrons will be moving towards less denser places and, in the 3-dimensional cloud of electrons we expect curves corresponding to valleys(* more precisely, bottom of valleys). We call the curve by 'duct' and are going to compute some necessary conditions for the 1-dimensional duct.[8]

LetX_0=$(x_0,\ y_0,\ z_0)$ be a generic point on a duct. Denote the Hessian of ρ=$\begin{pmatrix} \frac{\partial^2\rho}{\partial x^2} & \frac{\partial^2\rho}{\partial x\partial y} & \frac{\partial^2\rho}{\partial x\partial z} \\ \frac{\partial^2\rho}{\partial x\partial y} & \frac{\partial^2\rho}{\partial y^2} & \frac{\partial^2\rho}{\partial y\partial z} \\ \frac{\partial^2\rho}{\partial z\partial x} & \frac{\partial^2\rho}{\partial z\partial y} & \frac{\partial^2\rho}{\partial z^2} \end{pmatrix}$ by $H(\rho)$, $H(\rho)_0$ at X_0 the gradient, $\nabla\rho$=$\begin{pmatrix} \frac{\partial\rho}{\partial x} \\ \frac{\partial\rho}{\partial y} \\ \frac{\partial\rho}{\partial z} \end{pmatrix}$ at X_0 by$\nabla\rho|_0$ and $\rho(x_0, y_0, z_0)$ by ρ_0 respectively. Then near X_0, ρ should look like this:



[8]Remind how accurately molecules work, it seems natural to think free electrons move under some rules such as moving along these ducts. This argument might be applicable to MRI research since MRI images are obtained by the same mathematical principle.

From the picture, we can draw two conclusions.

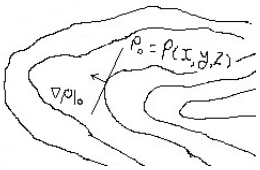
First, on the surface ρ_0=$\rho(x,y,z)$, $\nabla\rho\cdot\nabla\rho$ has a minimum at X_0. So if we let $\gamma(t)$ be a curve on ρ_0=$\rho(x,y,z)$ with $\gamma(0)=X_0$ and $g(t)=\nabla\rho|_{\gamma(t)}\cdot\nabla\rho|_{\gamma(t)}$ has zero derviative at $t=0$, we get

$$g'(0)=(\nabla\rho|_0)^T H(\rho)_0\gamma'(0)=0$$

and

$$(\nabla\rho|_0)^T H(\rho)_0 v_i=0\, for\, i=1,\,2,\,3 \tag{5}$$

, where $v_1=\begin{pmatrix} -\frac{\partial\rho}{\partial y}|_0 \\ \frac{\partial\rho}{\partial x}|_0 \\ 0 \end{pmatrix}$, $v_2=\begin{pmatrix} -\frac{\partial\rho}{\partial z}|_0 \\ 0 \\ \frac{\partial\rho}{\partial x}|_0 \end{pmatrix}$, v_3=$\begin{pmatrix} 0 \\ -\frac{\partial\rho}{\partial z}|_0 \\ \frac{\partial\rho}{\partial y}|_0 \end{pmatrix}$ which are perpendicular to $\nabla\rho|_0$. For intuition, refer to the cross section containing the $\nabla\rho|_0$ below.



Second, the surface ρ_0=$\rho(x,y,z)$ is concave near X_0. So by choosing a proper coordinate without changing the geometric shape, we can make X_0 a critical point and apply the Morse lemma(p6, [1]). Which implies, for a proper coordinate system, $H(\rho)_0$ is $\begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & -2 \end{pmatrix}$and on the surface ρ_0=$\rho(x,y,z)$, we have the positive definite conditions at X_0,

$${v_i}^T H(\rho)v_i>0\, for\, i=1,\,2,\,3 \tag{6}$$

So if the set of points satifying equations (5) and (6)(i.e. ducts) is removed, then the domain which the electron density function is defined will be a cloud with thin holes like a cheese having holes, which represent a molecule as a topological object.

References

[1] http://www-structmed.cimr.cam.ac.uk/Course/Fourier/Fourier.html

[2] J. Milnor, Morse theory, Princeton Univ. Press, 1963