

Should We Use Force instead of Energy in the Analysis of Chemical Phenomena?

-2 Electrostatic Theorem

As a method of searching for the force committed in the nucleus in a molecule, we know the Hellmann-Feynmann or electrostatic theorem. However, this method is unable to elucidate the cause of a phenomenon. Let's consider this affair. First, since this theorem is based on adiabatic approximation, the concept of adiabatic approximation is affirmed.

In a molecular system, adiabatic approximation is equivalent to the Born-Oppenheimer approximation. That is, in a molecule, since nuclear movement is far slow compared with an electron, the approximation says that nuclei stand still against each moment of electrons, in obtaining electronic state of a system. The energy which is settled as a function of the position of the nuclei by this method is called "adiabatic potential" to nuclear movement. The point is that electronic energy serves as the eigenfunction of the Hamiltonian of the system ($E^{el}\Psi=H\Psi$).

The Hellmann-Feynmann Theorem

The Hellmann-Feynmann theorem tells that concerning a parameter, ω , if $E(\omega)\Psi(\omega) = H(\omega)\Psi(\omega)$ holds, then,

$$\frac{\partial E}{\partial \omega} = \int \Psi^* \left(\frac{\partial H}{\partial \omega} \right) \Psi d\tau \quad 1$$

holds. It is a natural consequence since H is Hermitian. This will be mentioned in the next section.

Concerning the Fact that Electrostatic Force is Composite One

Since Eq. 1 holds concerning any ω if H being Hermitian, so does it with respect to position parameter, R . That is, if one differentiates the total electronic energy (E^{el}) with respect to R ,

$$\frac{\partial E^{el}}{\partial R} = \int \Psi^* \left(\frac{\partial H}{\partial R} \right) \Psi d\tau + E^{el} \left(\int \frac{\partial \Psi^*}{\partial R} \Psi d\tau + \int \Psi^* \frac{\partial \Psi}{\partial R} d\tau \right) \quad 2$$

is obtained. Here, the second term of Eq. 2 becomes null because of H being Hermitian and E^{el} being the eigenvalue of Ψ . The reason why the bracketed term in Eq. 2 becomes 0 is as follows.

$$\left(\int \frac{\partial \Psi^*}{\partial R} \Psi d\tau + \int \Psi^* \frac{\partial \Psi}{\partial R} d\tau \right) = \int \frac{\partial}{\partial R} (\Psi^* \Psi) d\tau = 0$$

H in Eq.2 consists of the operators of the kinetic energy of electrons (\tilde{T}), one-electron potential energy (\tilde{V}_{eN}), and two-electron potential energy (\tilde{V}_{ee}). So, Eq. 2 becomes,

$$\begin{aligned} \frac{\partial E^{el}}{\partial R} &= \int \Psi^* \left(\frac{\partial H}{\partial R} \right) \Psi d\tau = \int \Psi^* \left(\frac{\partial(\tilde{T} + \tilde{V}_{eN} + \tilde{V}_{ee})}{\partial R} \right) \Psi d\tau = \int \Psi^* \left(\frac{\partial \tilde{T}}{\partial R} \right) \Psi d\tau \\ &+ \int \Psi^* \left(\frac{\partial \tilde{V}_{eN}}{\partial R} \right) \Psi d\tau + \int \Psi^* \left(\frac{\partial \tilde{V}_{ee}}{\partial R} \right) \Psi d\tau = \int \Psi^* \left(\frac{\partial \tilde{V}}{\partial R} \right) \Psi d\tau \end{aligned} \quad 3$$

$\int \Psi^* \left(\frac{\partial \tilde{T}}{\partial R} \right) \Psi d\tau$ and $\int \Psi^* \left(\frac{\partial \tilde{V}_{ee}}{\partial R} \right) \Psi d\tau$ are both zero since \tilde{T} and \tilde{V}_{ee} are the functions of position of electrons only and do not contain R . However, one should notice that they are true only if Ψ is the true wavefunction. In the case that the wavefunction is expanded by another series of functions (e.g. LCAO), the parameter that adjust the size of the basis functions (scale parameter) is a function of R and the scale parameter must be optimized to obtain the 0 value. This will be further mentioned in series 3. Meanwhile we suppose the Ψ is the true wavefunction.

Equation 3 means that the partial differential of E^{el} with respect to R equals the expectation value of the partial differential operator of V with respect to R . This relationship is called the electrostatic theorem.

What happens if the relationship like Eq.2 holds for a component of E^{el} , for example, the kinetic energy ($\langle T \rangle$)?

$$\frac{\partial \langle T \rangle}{\partial R} = \int \Psi^* \frac{\partial \tilde{T}}{\partial R} \Psi d\tau + \int \frac{\partial \Psi^*}{\partial R} \tilde{T} \Psi d\tau + \int \Psi^* \tilde{T} \frac{\partial \Psi}{\partial R} d\tau \quad 4$$

Since the kinetic energy operator (\tilde{T}) does not contain R , the first term of Eq.3 becomes 0. However, the sum of the second and third terms of Eq. 3 is not zero, since $\langle T \rangle$ is not the eigenvalue or Ψ is not the eigenfunction of \tilde{T} .

As you may well know, the electronic energy (E^{el}) is the sum of the kinetic energy of electron ($\langle T \rangle$), one-electron potential energy ($\langle V_{eN} \rangle$), and the two-electron potential energy ($\langle V_{ee} \rangle$). That is, $E^{el} = \langle T \rangle + \langle V_{eN} \rangle + \langle V_{ee} \rangle$. This is partial-differentiated with respect to R and equalized to Eq. 3 to give a very interesting relationship.

$$\frac{\partial E^{el}}{\partial R} = \left\langle \frac{\partial V_{eN}}{\partial R} \right\rangle = \frac{\partial \langle T \rangle}{\partial R} + \frac{\partial \langle V_{eN} \rangle}{\partial R} + \frac{\partial \langle V_{ee} \rangle}{\partial R} \quad 5$$

This means that the force by the electrostatic theorem is a composite one that consists of the fundamental forces like $\frac{\partial \langle T \rangle}{\partial R}$ etc. Therefore, in order to seek the causes of a chemical phenomenon, we need to get the partial differentials of each component. The detail is shown the literature below. H. Tokiwa, Y. Osamura, and H. Ichikawa, "Energy-component analysis along zero virial path," Chem. Phys., 181, 97-105 (1994).

The electrostatic theorem is used to obtain the region map of bonding and antibonding areas. But it is “resultant” map. The map does not tell the reason why the areas become so.

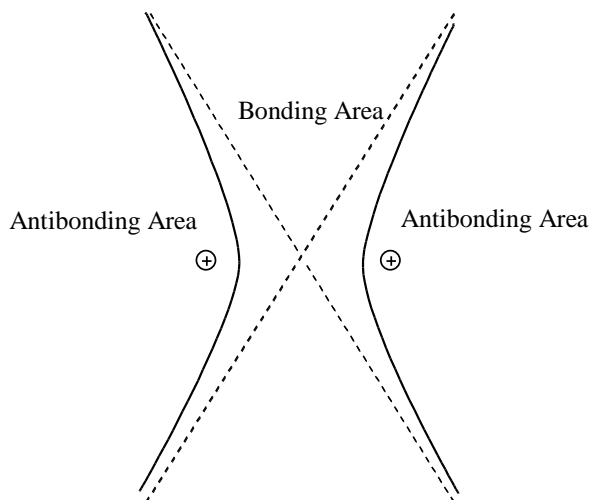


Fig. 1. Berlin diagram of two like nuclei

Now, we understand that the electrostatic theorem is not usable to seek the cause of a phenomenon. In the next article I will introduce the way how to obtain the partial differentials of the kinetic energy ($\langle T \rangle$), one-electron potential energy ($\langle V_{eN} \rangle$), and two-electron potential energy ($\langle V_{ee} \rangle$) with respect to R .