Wavefunction Stability Determination

INQUIRY

In quantum mechanics, a wavefunction refers to the mathematical function used to describe the state of the particle system. When the wavefunction of a system is completely determined, all the properties of the system can be calculated. For any specific molecular configuration, a wavefunction can be obtained by solving the self-consistent field equation to describe the state of the molecular configuration. However, an appropriate wavefunction can not always be obtained through this process. When a wavefunction can describe the molecular state appropriately, then it is considered to be stable. An appropriate wavefunction means that there is no wavefunction with lower energy than it. If there is a wave function with lower energy, a recalculation is required until a stable wavefunction is obtained. Wavefunction determines all the properties of the particle system. Therefore, an appropriate wavefunction for the particle system is crucial for accurately describing the properties of the system.

Types of Unstable Wavefunctions

- Instability from the closed-shell to the open-shell

This type of instability only appears when the initial assumption is that the wavefunction is a closed-shell system. This kind of instability means there is an open-shell electronic configuration with lower energy than the closed-shell system. It is necessary to further determine whether this lower electronic configuration is a triplet state or a singlet double radical when determining the stability.

- Internal instability

  This type of instability can appear in the wavefunction that is initially assumed to be a closed shell system, and it can also appear in the wavefunction that is initially assumed to be an open shell system. This instability means that the wavefunction is optimized to the saddle point in the wave function space, rather than the minimum point.

Workflow

In order to obtain a stable electronic configuration form when dealing with an unknown system, we use the following process to obtain a stable wavefunction, and the stable wavefunction is used as the initial configuration for the subsequent optimization.

- Firstly, we assume that the molecule is a closed-shell system (the premise is that it is an even-numbered electronic system), and we

optimize the structure of the molecule to obtain a stable configuration.

- Then, we carry out a stability test using the above-mentioned stable configuration as the initial structure.

  If the result shows that the wavefunction has closed-shell to open-shell instability, it indicates that the stable wavefunction is in the open-shell electronic configuration. We then use the triplet and singlet double radical wavefunctions to determine their stability.

  If the result shows that the wave function has internal instability, it means that the stable wavefunction is in the closed-shell electronic configuration, and has not been optimized to a minimum point. The wavefunction is at the saddle point, which leads to instability. it is necessary to re-assume the initial wavefunction until a stable wave function is determined.

- After the stable wavefunction under different electronic configurations is obtained, we compare the energy levels to take the low-energy electronic configuration as the ground state wavefunction.
- Finally, we use the obtained electronic configuration of the stable wavefunction to optimize the structure in order to obtain more reliable calculation results.

Source: https://wavefunction.alfa-chemistry.com/services/wavefunction-stability-determination.html