

Koopmans' Theorem

Koopmans' theorem states that the first ionization energy of a molecule is equal to the negative of the energy of the highest occupied molecular orbital (HOMO).

Introduction

Koopmans' theorem uses the Hartree-Fock method for approximation of orbital energy ϵ_i which is derived from the wavefunction of the spin orbital and the kinetic and nuclear attraction energies. This theorem applies when an electron is removed from a molecular orbital in order to form a positive ion. It was originally only used for ionization energies in a closed-shell system, but has been generalized to be used to calculate energy changes when electrons are added to or removed from a system. Based on this generalization, it is possible to use the same method to approximate the electron affinity. In this case, the molecular orbital energy would be the one associated with the orbital to which the electron is being added. Koopmans' theorem is useful because the use of this approximation means that it is not necessary to calculate the two separate energies of the original molecule and its ion in order to find the ionization energy and electron affinity.

Basic Description

In order to understand Koopmans' theorem, we must first understand its background, which is based in Hartree-Fock method. Hartree-Fock method is used to approximate the wave function and energy of a multi-electron system. This method starts by expressing the wave function of the system as a Slater determinant of the wave function of each single-particle orbital. The Slater determinant for a system with N electrons is

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} \equiv |\chi_1 \ \chi_2 \ \cdots \ \chi_N|, \quad (1)$$

By breaking up the electrons into individual wave functions, we can create single-particle Hartree-Fock equations, which can be used as an operator whose eigenvalue is the energy of a particle in a particular orbital.

$$\hat{F}|\varphi_i\rangle = \epsilon_i|\varphi_i\rangle \quad (2)$$

Where $\hat{F}$ is the Fock operator corresponding to the Hartree-Fock equation, ϵ_i is the energy of the particle in the orbital, and φ_i is the wave function of the particle. Using Koopmans' theorem, the equation from above and the wave function of the HOMO, we can approximate the first order ionization energy of a molecule.

Advanced Description

The Hartree-Fock equation for a particle takes the form

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r}) + V_{nucleus}(\mathbf{r})\psi_i(\mathbf{r}) + V_{electron}(\mathbf{r})\psi_i(\mathbf{r}) - \sum_j \int d\mathbf{r}' \frac{\psi_j^*(\mathbf{r}')\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} = \epsilon_i\psi_i(\mathbf{r}) \quad (3)$$

So, the Fock operator derived from this is

$$\hat{F} = \hat{H}^0 + \sum_{j=1}^N (2\hat{J}_j - \hat{K}_j) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + \sum_{j=1}^N (2\hat{J}_j - \hat{K}_j) \quad (4)$$

This is the operator that is applied to the wave function, and gives the eigenvalues that describe the energy of a given orbital. Notice that the first two terms in this equation are the same as the operator which corresponds to the energy of a hydrogen atom. The third term accounts for the potential energy applied by the other electrons in the molecule. This method of calculating the potential energy assumes that the electron only interacts with the average charge of the electron cloud.

Ionization energies and electron affinities are equal to the negative of the energy of the orbital which is added or removed, i.e.

$$E_{N-1} - E_N = -\epsilon_k \quad (5)$$

for ionization, and

$$E_N - E_{N+1} = -\epsilon_k. \quad (6)$$

for electron affinity.

✓ Example 1: Calculating Ionization Energy

Koopmans' theorem also applies to the calculation of electron affinity. We will use Hartree-Fock equations to calculate the energy change when an electron is added to the N+1 orbital. The energy of the N-electron determinant with spin-orbitals ϕ_i through ϕ_N occupied is

$$E_N = \sum_{i=1}^N \langle \phi_i | T + V | \phi_i \rangle + \sum_{i=1}^N [J_{i,i} - K_{i,i}]$$

or

$$E_N = \sum_{i=1}^N \langle \phi_i | T + V | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^N [J_{i,j} - K_{i,j}].$$

And the energy of the N+1 electron determinant is

$$E_{N+1} = \sum_{i=1}^{N+1} \langle \phi_i | T + V | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^{N+1} [J_{i,j} - K_{i,j}] = \epsilon_{N+1}.$$

Since we are adding the N+1 orbital the electron affinity is equal to the negative of the energy of the N+1 electron determinant.

$$EA = -\epsilon_{N+1}.$$

However, we must remember that Koopmans' theorem is merely an approximation of ionization energies and electron affinities. The more accurate method would be to calculate the separate energies of the parent and daughter molecules and subtract them to calculate the difference. This is because Koopmans' theorem does not account for orbital relaxation; it uses the orbitals of only one of the molecules to describe both of the species, which is not necessarily true.

Contributors and Attributions

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