

Time-Dependent Schrödinger Equation Approximation for Chemical Dynamics

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Abstract

In this paper is represented a method for chemical dynamics by the approximation of the time-dependent Schrödinger equation. The approximation is obtained by substitutions of Newton binomial formula. The analytical solution of the equation is changed by the linear combination solution. The approximation has a correlate in the idea of the molecular orbital method.

Introduction

The time-dependent Schrödinger equation is the best method for theoretical exploration of electron-electron interactions of molecules. This is the so called chemical dynamics of molecules. There is a well known mathematical problem about the analytical solution of the time dependent Schrödinger equation. I represent a simple mathematical approximation of the equation which is correlated with the molecularly orbital method.

Model approximation

The time-dependent Schrödinger equation is:

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi .$$

Solving for $\psi(t)$ gives:

$$\psi(t) = \exp\left(-\frac{i\hat{H}t}{\hbar}\right) \psi(q) \equiv \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{i\hat{H}t}{\hbar}\right)^n \psi(q) .$$

Let us compare this solution with Newton binomial formula:

$$\binom{\alpha}{k} = \frac{\alpha(\alpha-1)\dots(\alpha-k+1)}{k!}, k \in N$$

Let us substitute:

$$-\frac{i\hat{H}t}{\hbar} = \alpha, \text{ and } n=k$$

It can be made a simple mathematical approximation:

$$\sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{i\hat{H}t}{\hbar} \right)^n \approx \frac{\alpha(\alpha-1)\dots(\alpha-k+1)}{k!} \approx \frac{\partial \alpha^k}{\partial k!} \approx k \frac{\partial \alpha}{\partial k!},$$

where k means the number of electrons. Let us assume $k! = k$, it is good approximation for a small number of electrons. So we obtain a simple approximation:

$$\exp\left(-\frac{i\hat{H}t}{\hbar}\right) \approx k \frac{\partial \left(-\frac{i\hat{H}t}{\hbar}\right)}{\partial k} \approx k \sum_{k=1}^s -\frac{i\hat{H}_k t}{\hbar}.$$

The approximation of the time-dependent Schrödinger equation solution is:

$$\psi(t) = k \sum_{k=1}^s -\frac{i\hat{H}_k t}{\hbar} \psi_k(q)$$

In this approximation we can conclude that the number of electrons is equal to the number of $\psi(q)$ functions, so we can say one electron is on one atomic orbital. The time-dependent ψ - function is equal to the linear combination of k-times the Hamiltonian operations on k $\psi(q)$ wave functions, multiplied by the number of electrons k. The conclusion can be made that the time-dependent ψ - function is genetically connected with $\psi(q)$. Let us compare with the general formula that describes $\psi(t)$ as a function of $\psi(q)$:

$$\psi(t) = \sum_n a_n \exp\left(\frac{iE_n t}{\hbar} \psi_n(q)\right) [1].$$

The probabilities a_n and the exponential function in my approximation are compared with the number of electrons and linear combinations. So we can write:

$$\psi(t) = \binom{\alpha}{k} \psi_k(q) = \left(\frac{i\hat{H}t}{\hbar} \right) \psi_k(q) \approx k \sum_{k=1}^s -\frac{i\hat{H}_k t}{\hbar} \psi_k(q),$$

and for computing we have:

$$\psi(t) = \binom{\alpha}{k} \psi_k(q) = \left(\frac{iEt}{\hbar} \right) \psi_k(q) \approx k \sum_{k=1}^s -\frac{iE_k t}{\hbar} \psi_k(q).$$

Let $k=2$ for H_2 and we have a derivate by t:

$$\frac{\partial}{\partial t} \psi(t) \approx 2 \frac{i}{\hbar} [\hat{H}t - \hat{H}] \psi(q)$$

It is a simple equation comparable with the Heisenberg representation of the time dependent operators[1.]:

$$\frac{\partial}{\partial t} \hat{f}(t) = \frac{i}{\hbar} [\hat{H}\hat{f}(t) - \hat{f}(t)\hat{H}]$$

In conclusion we can say that the time derivative on $\psi(t)$ is equal to the linear combination of the ψ functions of the electrons.

Reference:

1. Landau L., Lifshitz E., "Quantum Mechanics Non relativistic Theory", Theoretical Physics Vol. 3.