The theory of Ab initio calculation of energy constants and equilibrium geometries of multi-atom molecules

Ali Sahandabadi

Kherad High School, Isar town Resalat street second Alley no.16, Urmia, Iran
Ali.Sahandabadi@yahoo.com

Abstract

Consider a HF-LCAO calculation to indicate participated rules in finding analytical gradient equation in which the electron energy is in

$$\varepsilon_e = \mathrm{trace}(Ph_1) + \frac{1}{2}\mathrm{trace}(PG)$$

Matrix P contains HF-LACO coefficients and has components which consists of single-electron integrals (Kinetic energy and nuclear or core magnetism) on basis functions of x_1,---x_n. Matrix G contains of di-electron integrals and Matrix P components. If we want to differentiate parameter "a" which can be a core or nuclear feature or the component of the used electric field, so we must calculate an equation such as

$$\frac{\partial}{\partial_a}\int X_i(r)h(r)X_j(r)d\tau$$

And

$$\frac{\partial}{\partial_a}\int X_i(r_1)X_j(r_1)g(r_1,r_2)X_k(r_2)X_l(r_2)d\tau_1\,d\tau_2$$

And

$$\frac{\partial P_{ij}}{\partial_a}$$

The first two are called derivative integrals. They are the derivations of integral which are well-known in molecular structure theorem and are easily calculated. The third equation resulted in a problem and we must use a series of equations which called Hartree-Fock paired equation to solve them. The Hartree-Fock paired method is different from the new one.

The general equations are determined for energy constants and molecules bipolar derivations. So, the occurred problems are reviewed from scientific applications. The main emphasize is located in using Hartree-Fock function as approximate wave function and the number of its features are discussed and re-emphasized. The main content of this paper is to expand Hartree-Fock disorder theory which makes possible the direct calculation of energy constants and bipolar momentum derivations from SCF-MO wave function. Necessarily, this theory $\partial\varphi_i/\partial R^a_J$ provides a MO derivation considering nuclear or core feature.

The general equation of exact energies on core (the negative derivations of total energy considering core coordinates) is applied for Hartree-Fock wave functions. It is suggested that the energy constants must be calculated by energy numerical differential. This method which called energy method is numerically exact and needs less calculation in compared with popular way of numerical double-differential from energy. It causes quick determination of equilibrium geometry by releasing atomic coordinate as far as the energy disappeared. It is emphasized Hellmann-Feynman energy methods are distrustful. The question that which energy constants are calculated the best Ab initio is still discussed.

References

[1] Fletcher, R. (1981) Practical Methods of Optimization, Wiley, Chichester.
[2] Foresman, J. B., Head-Gordon, M., Pople, J. A. and Frisch, M. J. (1992) J. Phys. Chem. **96**, 135.
[3] Frost, A. A, Rouse, R. A. and Vescelius, L. (1968) Int. J. Quantum Chemistry **IIS**, 43.
[4] Gerratt, J. and Mills, I. M. (1968) J. Chem. Phys. **49**, 1719.
[5] Green, S. (1974) Advances in Chemical Physics **25**, 179.