

Testing Mulliken approximation using hydrogen atom

E. O. Aiyohuyin and Amen A. Oni-Ojo

Department of Physics, University of Benin, Benin City, Nigeria

Abstract

We computed the ground state energy of the hydrogen atom within the semi-empirical method prescribed by Mulliken. The one-particle basis functions used are Slater-type-orbitals (STO). The exponential parameters terminated at 25. The more the basis set used in the calculation, the better the result, in agreement with standard electronic-structure calculations. The density matrix for the free electron gas at zero temperature was adopted (Xiaoding Zhang and D. A. Drabold. Phys. Rev. B63, 233109 (2001) [10]).

1.0 Introduction

Ab initio quantum chemical methods are limited in their practical applicability because of their heavy demands of CPU-time and storage space on disk or in the computer memory where such facilities are even available. At the Hartree-Fock level, the problem is seen to be in the large number of 2-electron integrals that need to be evaluated.

Semi empirical methods provide workers with a way to study larger systems. The results usually obtained are typically less accurate than that of ab initio methods, but they are generated more quickly.

As the name suggests, semi-empirical methods are a combination of ab initio methods coupled with the use of data from empirical (experimental) studies. It is the search for a good semi-empirical method that informed the trial of the Mulliken approximation in this work.

A self-consistent field (SCF) calculation done within a set of L basis functions requires the computation of L^4 matrix elements V_{ijkl} . One form of approximation usually used is called the semi empirical SCF method. There are variants of this.

In this approach, the Coulomb and exchange integrals are neglected. Only the matrix elements containing the effect of the inner core electrons through the potential $v(r)$ are retained. These matrix elements are approximated using the prescription of Mulliken. Peter Fulde (1995 [4]).

$$t_{ij} = \frac{1}{2}(t_{ii} + t_{jj})S_{ij}$$

The indices i, j refer to the orbital on different atoms and s_{ij} is the overlap matrix.

2.0 Ground State Energy E.

$$E = \frac{1}{2} \sum_{ij}^L (t_{ij} + f_{ij}) P_{ij}$$

where

$$f_{ij} = t_{ij} + \sum_{kl} \left(V_{ijkl} - \frac{1}{2} V_{ijkl} \right) P_{kl}$$

are the SCF equations for a finite basis set. $p_{ij} = \sum_{\sigma} \langle a_{i\sigma}^+ a_{j\sigma} \rangle$ is called the bond-order matrix. σ_i s the spin index $a_{i\sigma}^+ a_{j\sigma}$ are a set of electron creation and annihilation operators.

$$t_{ij} = \int d^3 r f_i(\vec{r}) \left(\frac{\Delta^2}{2} + V(\vec{r}) \right) f_j(\vec{r})$$

$$V_{ijkl} = \int d^3 r d^3 r' f_i(\vec{r}) f_j^*(\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} f_k^*(\vec{r}') f_l(\vec{r}')$$

Atomic unit is used through out. In this unit $m = \hbar = e = 1$. Bohr radius 0.52917\AA is the unit of length. The unit of Energy is the hartree which is 2 Ryd. and 1 Ryd = 13.61 eV.

L is the number of basis function f used. These functions are centered generally at different atoms.

S_{ij} is the overlap matrix.

$$S_{ij} = \int d^3 r f_i^*(\vec{r}) f_j(\vec{r})$$

3.0 Basis functions

The one particles basis functions are Slater type Orbitals (STO)

$$(n, l, m) = N r^{n-1} e^{-\zeta r} Y_{l,m}(\theta, \phi)$$

where $N = (2\zeta)^{n+1/2} [(2n)!]^{1/2}$. The value of ζ is determined from empirical rules formulated by Slater and Burns, Clementi and Raimondi and it is $\zeta = \frac{(z - \sigma)}{n^*}$ where σ is the screening constant, n^* is the effective principal quantum number and z is the nuclear charge. However, from the complete hydrogen atom wave functions given in standard textbooks

$$\zeta = \frac{2z}{na}, \text{ where } Z(-e)$$

is the nuclear charge, n is the principal quantum number and a is the Bohr radius.

4.0 One -particle density matrix

The bond order matrix, without the σ summation is called the one -particle density matrix. The one particle density matrix for the free electron gas at zero temperature is given as

$$\rho(\vec{X}, \vec{X}') = 3n [\sin \theta - \theta \cos \theta] / \theta^3$$

$\theta = k_f \left(\vec{X} - \vec{X}' \right)$, k_f is the Fermi wave vector and n is density of the electrons gas. The behaviour of the one particle density matrix is similar to that of electrons pair distribution function. For a Fermi-liquid, the one particle density matrix described the distribution of the quasi particles.

$$n_{p\sigma} = \left(e^{(\epsilon(p)\sigma - \mu) / K_B T} + 1 \right)^{-1}$$

Fulde (1995 [4]) and Akira Isihara (1993 [1]) where $\epsilon(p)$ is the energy of a quasiparticle arising from the interaction of an electron with the field of all the other electrons.

5.0 Calculations

In this paper we use the Mulliken approximation Fulde (1995 [4]) for the ground state energy.

$$\begin{aligned}
E &= \frac{1}{2} \sum_{ij=1}^L (t_{ij} + f_{ij}) p_{ij} \\
E &\approx \frac{1}{2} \left(t_{11} + \frac{1}{2} (t_{11} + t_{22}) S_{12} \right) P_{12} \\
&+ \frac{1}{2} \left(t_{22} + \frac{1}{2} (t_{22} + t_{11}) S_{21} \right) P_{21} \quad \text{for } L = 2 \\
E &\approx \frac{1}{2} \left(t_{12} + \frac{1}{2} (t_{11} + t_{22}) S_{12} \right) P_{12} \\
&+ \frac{1}{2} \left(t_{13} + \frac{1}{2} (t_{11} + t_{33}) S_{13} \right) P_{13} \\
&+ \frac{1}{2} \left(t_{21} + \frac{1}{2} (t_{22} + t_{11}) S_{21} \right) P_{21} \\
&+ \frac{1}{2} \left(t_{21} + \frac{1}{2} (t_{22} + t_{11}) S_{21} \right) P_{21} \\
&+ \frac{1}{2} \left(t_{31} + \frac{1}{2} (t_{33} + t_{11}) S_{31} \right) P_{31} \\
&+ \frac{1}{2} \left(t_{32} + \frac{1}{2} (t_{33} + t_{22}) S_{32} \right) P_{32}, \text{ for } L = 3
\end{aligned}$$

The quality of the result depends on the quality of the wave function more than the semi empirical method used. The result is enhanced by using an enhanced value for the exponential parameter. The value of the bond order matrix is obtained from the one particle density matrix.

The factor 2 is used to take care of the summation. The results obtained are as follows

Table 1

Exponential parameter ζ	Normalisation constant for wave function N	Energy of hydrogen atom E(Ryd)
2	5.66	-0.02
10	89.44	-0.18
15	116.19	-0.30
25	250.00	-0.50

Comparing these results to the acceptable literature value of the energy of hydrogen atom which is -1Ryd; the Mulliken approximation depends a lot on the exponential parameter. And until the determination of the exponential parameter is enhanced, the Mulliken, approximately will remain weak.

6.0 Conclusion

The Mulliken's approximation is found to be weak. The orbitals neglected are obviously important. The matrix elements t_{ij} contain the effect of the inner core electrons through the potential $v(r)$. The Mulliken's approximation does not work very well at this level unless the parameter ζ is increased to beyond 25. This is the only way to get some agreement with standard electronic structure calculations.

References

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