Dipole Moment Calculation to Small Diatomic Molecules: Implementation on a Two-Electron Self-Consistent-Field *ab initio* Program

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Abstract

The knowledge of the dipole moment is one way to charge distribution analysis in the molecules and to chemists arguments of the electronegativity comparison.

This work present an implementation of the dipole moment calculation to small diatomic molecules into a simple two-electron self-consistent-field program using *1s* minimal STO-3G functions basis set. Although using the minimal basis set, all quantum mechanical principles are take account leading an *ab initio* calculations. The molecules HeH+ and LiH++ are used to testing the routine and results obtained are compared with others theoretical and experimental values.

Keywords: Dipole moment, Small molecules, Diatomic molecules, HeH+, LiH++.

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Cálculo do Momento de Dipolo para Moléculas Diatômicas pequenas: Implementação em um Programa ab initio de Campo Auto-Consistente para dois elétrons

Resumo

     Este trabalho apresenta uma implementação do cálculo do momento de dipolo para pequenas moléculas de dois elétrons em um programa simples de campo auto-consistente usando um conjunto mínimo de funções de base *1s* do tipo STO-3G. Embora usando um conjunto mínimo de funções de base, todos os princípios quanto-mecânicos foram levados em conta, conduzindo a um cálculo a partir dos primeiros princípios. As moléculas HeH+ e LiH++ são usadas para o teste da rotina e os resultados obtidos são comparados com outros resultados teóricos e experimentais.

Palavaras-Chave: Momento de dipolo, Pequenas moléculas, Moléculas diatômicas, HeH+, LiH++.

Introduction

SZABO, A. and OSTLUND, N. S.(1982) presents a two-electron self-consistent-field program to STO-nG (n=1,2,3) wave functions calculations, for any two-electrons diatomic molecules. This program is a simple implementation of the *ab initio* Hartree-Fock method for two-electron diatomic molecules. Only two *1s* STO (Slater Type Orbital) functions are used. This STO functions are expanded into *1s* GTO (Gaussian Type Orbital) functions and 1, 2 or 3 Gaussians functions can be selected by the input parameters. The final results obtained with this program are the total energy of molecule in atomic units and Mulliken orbital populations. This program was edited in Fortran IV language.

The first step were the conversion of the original program to Turbo Pascal 7 language for microcomputers Windows 95/98 based, compilation and test with original example presented.

Following, the theoretical formalization and implementation of a routine to dipole moment calculation were included. A routine to a Lowdin Populations analysis were included too.

Two-electron HeH+ and LiH++ diatomic molecules was calculated and results used to comparison with others theoretical and experimental values.

1. Dipole Moment Formalization

It is well known that quantum mechanical dipole moment for a molecule is (SZABO, A. and OSTLUND, N. S., 1982),

$$\vec{\mu} = \langle \Psi_0 | - \sum_i \vec{r}_i | \Psi_0 \rangle + \sum_A Z_A \vec{R}_A , \quad (1)$$

where the first term represents the matrix elements of the dipole moment operator and second term the nuclear contributions.

Using a general form to expand Ψ_0 wave functions, $\Psi_0 = \sum_\mu c_{\mu i} \Phi_\mu(\vec{r})$ in a set $\{\Phi_\mu\}$ of basis functions and using general rules to matrix elements, we can obtain that

$$\vec{\mu} = -\sum_a \sum_b P_{ab} \langle a|\vec{r}_i|b\rangle + \sum_A Z_A \vec{R}_A \quad , \quad (2)$$

where P_{ab} are the density matrix elements.

How the heteronuclear diatomic molecules are linear molecules, the dipole moment is not null on the z-axial molecular direction. From equation (2), we can to obtain that z-component of the dipole moment is

$$\mu_z = -\sum_a \sum_b P_{ab} \langle a|z|b\rangle + \sum_A Z_A R_A \quad (3)$$

Then, we need only evaluate the on-electron integrals $\langle a|z|b\rangle$, called dipole moment integrals, to dipole moment μ_z calculate, since that density matrix elements are obtained into original program.

2. Dipole Moment Evaluation

The dipole moment evaluation will be performed using *1s* STO functions expanded on a *1s* GTO set of a basis functions. How the product of two *1s* Gaussian functions, in atomic centers A and B is, apart from a constant, a *1s* GTO function another center P, or

$$\tilde{g}_{1s}(\vec{r}_1 - \vec{R}_A)\tilde{g}_{1s}(\vec{r}_1 - \vec{R}_B) = \tilde{k}\,\tilde{g}_{1s}(\vec{r}_1 - \vec{R}_P), \quad (4)$$

where,

$$\tilde{k} = e^{-p|\vec{R}_A - \vec{R}_B|^2},$$

$$p = \alpha + \beta,$$

$$R_P = (\alpha R_A + \beta R_B)/(\alpha + \beta) \text{ and} \quad (5)$$

$$\tilde{g}_{1s}(\vec{r}_1 - \vec{R}_P) = e^{-p|\vec{r}_1 - \vec{R}_P|^2},$$

the integrals evaluation will relatively easy. Here, $\tilde{g}_{1s}$ represents a *1s* unnormalized Gaussian function.

It is well known that with the GTO functions, the one and two-electron integrals can be evaluate rapidly, but are not optimum basis functions like the STO functions. Therefore, a linear combination of the GTO functions with specific coefficients and exponents, called *contractions*, lead a good approximation to STO functions. This contractions are provided into original program.

Thus,

$$\langle a|z|b\rangle = \tilde{k}\int d\vec{r}_1\ z e^{-p|\vec{r}_1-\vec{R}_P|^2} \quad (6)$$

By transformations of the coordinates to center *P*, shown in the figure 1,

$$\vec{r} = \vec{r}_1 - \vec{R}_P$$
$$d\vec{r} = d\vec{r}_1 \quad (7)$$
$$z = r_1\cos\gamma = R_P - r\cos\theta$$

we obtain that,

$$\langle a\,|\,z\,|\,b\rangle = \tilde{k}\int d\vec{r}(R_P - r\cos\theta)e^{-pr^2} \quad (8)$$

and proceding the integration, results

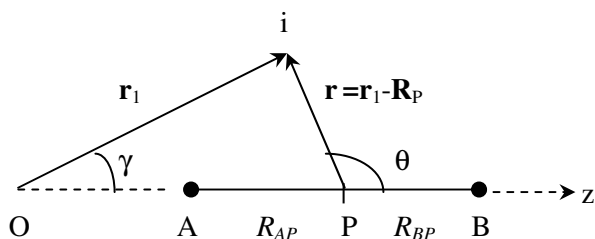$$\langle a|z|b\rangle = \tilde{k}R_P(\pi/p)^{3/2} \quad (9)$$

Figure 1. Schematic representation of diatomic molecule
with A and B atomic centers and P center.

The dipole moments at nucleus A or B, are obtained localizing the center in A or B points and using distance parameters R_{AP} and R_{BP}.

To atom A, $R_P=R_{AP}$, $R_A=0$ and $R_B=R$. To atom B, $R_P=-R_{BP}$, $R_A=R$ and $R_B=0$.

3. Calculations Reports

After routine implementation to obtain the sums on equation (3), using the results of the integrals of the equation (9) into new version of the HF1s program, the calculations for the HeH+ and LiH++ two-electrons diatomic molecules was performed.

3.1 HeH+ molecule

The calculations with GAMESS (M. W. Schmidt et alli., 1993) *ab initio* package performed by input the *1s* STO-3G minimal basis with the same contractions coefficients used into HF1s program, as suggested by SZABO, A. and OSTLUND, N. S.(1982), results the same values obtained by the HF1s program. All intermediate values as overlap integrals, dipole moment integrals, kinetic energy integrals, eigenvalues, etc., are identical. However, the calculations with STO-3G basis as implemented into GAMESS package, leads to different results. It is because the *1s* function to He atom in STO-3G basis implemented into GAMESS package uses different contractions coefficients that the suggest by SZABO, A. and OSTLUND, N. S. (1982).

The Table 1, sums up the results obtained and others to comparison.

Table 1. Sums up of the calculation results. Values of dipole moments μ_z are related to A nuclei. Here, R is the interatomic separation and E_t is the total energy of molecule.

Molecule		R (a.u.)	E_t (a.u.)	μ_z (Debye)
HeH+	HF1s[a]	1.4632	-2.86066	2.2596
	GAMESS[b]		-2.86066	2.2596
	GAMESS[c]		-2.84184	2.8381
	Experimental[d]		-2.97867	
LiH++	HF1s[a]	3.015	-6.80093	7.6549
	GAMESS[c]		-6.80405	7.6457
	HF1s[a]	2.75	-6.76962	6.9750
	GAMESS[c]		-6.77223	6.9694

[a] This work (HF1s *ab initio* program) with *1s* minimal basis.
[b] GAMESS *ab initio* program with *1s* minimal basis (M. W. Schmidt, et all., 1993).
[c] GAMESS *ab initio* program with STO-3G basis (M. W. Schmidt, et all., 1993).
[d] Exact value (L. Wolniewicz, 1965).

We can look that results obtained with HF1s program are in good agreement with others theoretical and experimental ones, considering a minimal *1s* STO-3G basis functions used.

The dipole moment sign for HeH+ (A- B+) molecule indicates that H atom is more positive that He. It is in agreement with eletronegativity arguments. The results from Mulliken populations shown that the charge on He atom is +0.47 and on H atom is +0.53. The value of dipole moment is in good agreement with GAMESS theoretical results for a STO-3G basis functions.

3.2 LiH++ molecule

To LiH++ molecule, the total energy and dipole moment for two interatomic separations considerates, are in good agreement with GAMESS theoretical values, although into GAMESS STO-3G basis implementation, atomic *p* functions are used in basis set for Li atom, better reflecting the polarization effects of the charge distributions. These results shown that the charge on Li atom is +0.999929 and on H atom is + 1.000071, by Mulliken analysis at 3.015 a.u. separation case.

Concluding, we can talk that it is a good exercise to the understanding of the quantum mechanical fundaments for a structure description of the matter, with educational subjects in physical science.

4. References

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