Calculation of potential energy of molecules and kinetic energy of electrons on Slater functions basis

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Abstract

In this work, common analytical expression for potential energies of molecules (interaction energy between electrons and nuclear, and between electrons), and kinetic energies of electrons have been obtained. As basis functions Slater **,** Atomic Orbitals have been used. By applying Hartree-Fock-Roothaan method, calculations for some two atomic molecules with closed and open electronic shells have been carried out. The accuracy of the calculations have been checked by virial theorem.

Keywords: atomic orbital, molecular orbital, Slater functions, potential energy

Introduction and Theoretical Methodology

Various parameters of molecules are calculated by HFR method, based on theorem of calculation of matrix elements of symmetric –scalar operator in comparison with electrons' displacement via determinant wave functions [1]. State of molecule is described by determinant wave function, according to distinguishability principle. Each element of determinant wave function is called molecular spin orbital, and being one electronic wave function. If spin-orbital interaction is not considered, molecular spin orbitals are represented as multiplication of u_i – molecular orbitals and $u_{m_s}(\sigma)$ spin functions of electron. i- molecular quantum numbers. In HFR method u_i molecular orbitals are represented linear by combination of certain atomic orbitals of atoms of molecule:

$$u_i = \sum_{q=1}^{m} c_{qi}\, \mathcal{X}_q \qquad (1)$$

As atomic orbitals, $\mathcal{X}_q \equiv \mathcal{X}_{nlm}$ real Slater atomic orbitals have been used [5]:

$$\mathcal{X}_{nlm}(\xi, \vec{r}) = \frac{(2\xi)^{n+\frac{1}{2}}}{\sqrt{(2n)!}} \cdot r^{n-1} e^{-\xi r} S_{lm}(\theta, \varphi) \qquad (2)$$

$S_{lm}(\theta, \varphi)$ – real spherical functions, the value of exponential parameter-ξ has been calculated by Besis's formula. Values of unknown coefficients – c_{qi} are found by the solution of HFR equations.

Calculation and computer calculation:

Interaction operators between electrons and nuclear, between electrons in molecules, and kinetic energy operators of electrons are represented with atomic units as following:

$$\hat{V}_{e-n} = -\sum_{\mu=1}^{N} \sum_{a=1}^{n} \frac{z_a}{r_{a\mu}} \qquad (3)$$

$$\hat{V}_{e-e} = -\sum_{\mu<v}^{N} \frac{1}{r_{\mu v}} \qquad (4)$$

$$\hat{T} = -\frac{1}{2}\sum_{\mu=1}^{N} \nabla_{\mu}^2 \qquad (5)$$

All the three operators are symmetric- scalar operators in comparison with electrons'displacement. $\hat{V}_{e-n}$, and $\hat{T}$ – are one electron operators, $\hat{V}_{e-e}$ - is two electron operator. By using the mentioned theorem, for interaction energy between electrons and nuclear, between electrons, and kinetic energies of electrons, the following analytic expressions are obtained:

a) Molecules with closed electronic shells:

$$\bar{V}_{e-n} = 2 \sum_i \sum_{pq} c_{pi}^* c_{qi} \int X_p^*(\vec{r}_1) \left[-\sum_{a=1}^n \frac{z_a}{r_{a_1}} \right] X_q(\vec{r}_1) dV_1 \qquad (6)$$

$$\bar{V}_{e-e} = \sum_{ij} \sum_{prqs} c_{pi}^* c_{rj}^* c_{qi} c_{sj} \left(2J_{prqs} - J_{prsq} \right) \qquad (7)$$

$$\bar{T} = 2 \sum_i \sum_{pq} c_{pi}^* c_{qi} \int X_p^*(\vec{r}_1) \left[-\frac{1}{2}\nabla_1^2 \right] X_q(\vec{r}_1) dV_1 \qquad (8)$$

b) Molecules with open electronic shells:

$$\bar{V}_{e-n} = 2 \sum_i f_i \sum_{pq} c_{pi}^* c_{qi} \int X_p^*(\vec{r}_1) \left[-\sum_{a=1}^n \frac{z_a}{r_{a_1}} \right] X_q(\vec{r}_1) dV_1 \qquad (9)$$

$$\bar{V}_{e-e} = \sum_{ijkl} \sum_{prqs} c_{pi}^* c_{rk}^* c_{qj} c_{sl} \left(2A_{ij,kl} J_{prqs} - B_{ij,kl} J_{prsq} \right) \qquad (10)$$

$$\bar{T} = 2 \sum_i f_i \sum_{pq} c_{pi}^* c_{qi} \int X_p^*(\vec{r}_1) \left[-\frac{1}{2}\nabla_1^2 \right] X_q(\vec{r}_1) dV_1 \qquad (11)$$

In these expressions, sums for i, j, k, l are carried out by molecular orbitals occupied by electrons, and sums for p, r, q, and s are carried out by atomic orbitals. In case of open electronic shells molecules, $f_i, A_{ij,kl}$, and $B_{ij,kl}$ quantities are calculated individually for each molecule.

The expressions of $\bar{V}_{e-n}$, and $\bar{T}$ quantities, include one- and two-center nuclear attraction integrals, and one- and two-center kinetic energy integrals accordingly. By calculating $\frac{1}{r}X_{nlm}$ and $\nabla^2 X_{nlm}$ expressions, these integrals are expressed with one- and two-center overlap integrals over Slater type atomic orbitals. At work, analytical expressions of overlap integrals obtained from [6, 2] are used. J_{pqrs} quantities included in $\bar{V}_{e-e}$ are one-center, and two-center two-electronics Coulomb, hybrid, and exchange integrals with Slater atomic orbitals, In order to calculate two-center, two-electronic integrals, translation formula [3] of Slater atomic orbitals are used. Translation formula allows to express two-center two-electronic integrals as one-center two-electronic series of integrals. Coefficients of the series are presented with overlap integrals. The analytical expressions of one-center two-electronic integrals , known from scientific literature , are used.

The values of coefficients c_{qi} have been found by solving HFR equations for selected molecules. And by solving HFR equations, the integrals above mentioned are obtained. These integrals are calculated once, saved, and used for all calculation processes. In order to make calculations based on (6) – (11) formulas Delphi Studio Object Pascal computer program have been designed. The following data have been entered into the computer program for making calculations:

- Number of atomic and molecular orbitals;
- Values of principal, angular, and magnetic quantum numbers of atomic orbitals;
- Values of exponential parameters of atomic orbitals;

- X, Y, and Z Cartesian coordinates of atomic nuclears (heavy atom is located at the origin, light atom is located on Z axis);
- Charge of atomic nuclears;
- Values of $f_i, A_{ij,kl}$, and $B_{ij,kl}$ quantities (in case of molecules with open electronic shells);
- Values of "type of center" parameter, indicates to which atom atomic orbitals relates to;

Calculations have been carried out for BH, NH, AlH, PH, ClH molecules with closed electronic shells, and LiH$^+$, BeH and CH molecules with open electronic shells. For calculations, 1s- Slater atomic orbitals of H atoms, 1s-, 2s-, 2p$_z$- Slater atomic orbitals of Li atoms, 1s-, 2s-, 2p$_x$-, 2p$_y$-, 2p$_z$- Slater atomic orbitals of B, N, C atoms, 1s-, 2s-, 2p$_x$-, 2p$_y$-, 2p$_z$-, 3s-, 3p$_x$-, 3p$_y$-, 3p$_z$- Slater atomic orbitals of Al, P and Cl atoms have been used. The values of inter nuclears distance have been obtained from [6].

The following values of coefficients $f_i, A_{ij,kl}$, and $B_{ij,kl}$ different from zero have been used for LiH$^+$, BeH, and CH molecules:

LiH$^+$:
f(1)=1; f(2)=0,5; f(3)=0; f(4)=0
A(1,1,1,1) =1; A(1,1,2,2) =0,5; A(2,2,1,1) =0,5; A(2,2,2,2) =0,25
B(1,1,1,1) =1; B(1,1,2,2) =0,5; B(2,2,1,1) =0,5; B(2,2,2,2) =0,25

BeH:
f(1)=1; f(2)=1; f(3)=0,5; f(4)=0; f(5)=0
A(1,1,1,1) =1; A(1,1,2,2) =1; A(1,1,3,3) =0,5; A(2,2,1,1) =1; A(2,2,2,2) =0,25; A(2,2,3,3) =0,5;
A(3,3,1,1) =0,5; A(3,3,2,2) =0,5; A(3,3,3,3)=0,25
B(1,1,1,1) =1; B(1,1,2,2) =1; B(1,1,3,3) =0,5; B(2,2,1,1) =1; B(2,2,2,2) =1; B(2,2,3,3) =0,5;
B(3,3,1,1) =0,5; B(3,3,2,2) =0,5; B(3,3,3,3)=0,5

CH:
f(1)=1; f(2)=1; f(3)=1; f(4)=0,5; f(5)=0; f(6)=0
A(1,1,1,1) =1; A(1,1,2,2) =1; A(1,1,3,3) =1; A(1,1,4,4) =0,5; A(2,2,1,1) =1; A(2,2,2,2) =1;
A(2,2,3,3) =1; A(2,2,4,4) =0,5; A(3,3,1,1)=1; A(3,3,2,2) =1; A(3,3,3,3) =1; A(3,3,4,4) =0,5;
A(4,4,1,1) =0,5; A(4,4,2,2) =0,5; A(4,4,3,3) =0,5; A(4,4,4,4) =0,25
B(1,1,1,1) =1; B(1,1,2,2) =1; B(1,1,3,3) =1; B(1,1,4,4) =0,5; B(2,2,1,1) =1; B(2,2,2,2) =1;
B(2,2,3,3) =1; B(2,2,4,4) =0,5; B(3,3,1,1)=1; B(3,3,2,2) =1; B(3,3,3,3) =1; B(3,3,4,4) =0,5;
B(4,4,1,1) =0,5; B(4,4,2,2) =0,5; B(4,4,3,3) =0,5; B(4,4,4,4) =0,5

Result and Discussion

Samples of some molecules with closed electronic shells has been taken also, computer calculations for data have been carried out based on (HFR) theorem. after that, slater Atomic orbitals have been used as exponential functions for the study of (P) phosphor orbitals .

(P) : 1s-, 2s-, 2p$_x$-, 2p$_y$-, 2p$_z$-, 3s-, 3p$_x$-, 3p$_y$-, 3p$_z$.

And Hydrogen orbitals : 1s-,

Also , we have calculated the value of exponential Parameters of atomic orbitals .

By using Besis's formula , we have obtained the following results:

$$\xi_{1s}(P) = 14.46779$$

$$\xi_{2s}(P) = 4.86148$$

$$\xi_{2p_x}(P) = \xi_{2p_y}(P) = \xi_{2p_z}(P) = 5.35627$$

$$\xi_{3s}(P) = 1.67460$$

$$\xi_{3p_x}(P) = \xi_{3p_y}(P) = \xi_{3p_z}(P) = 1.81341$$

$$\xi_{1s}(H) = 1.0$$

Besides , the common analysis for slater Atomic orbitals for (PH) molecule has been found then used as exponential functions based on this parameter .

We have obtained the following results :

$$\chi_{1s}(P) = \chi_{100}(\xi, \vec{r}) = \chi_{100}(14.46779, \vec{r}) = \frac{55.03048}{\sqrt{\pi}} e^{-14.46779r}$$

$$\chi_{2s}(P) = \chi_{200}(\xi, \vec{r}) = \chi_{200}(4.86148, \vec{r}) = \frac{30.08574}{\sqrt{\pi}} r e^{-4.86148r}$$

$$\chi_{2p_x}(P) = \chi_{211}(\xi, \vec{r}) = \chi_{211}(5.35627, \vec{r}) = \frac{66.39818}{\sqrt{\pi}} r e^{-5.35627r} \sin\theta\cos\varphi$$

$$\chi_{2p_y}(P) = \chi_{21-1}(\xi, \vec{r}) = \chi_{21-1}(5.35627, \vec{r}) = \frac{66.39818}{\sqrt{\pi}} r e^{-5.35627r} \sin\theta\sin\varphi$$

$$\chi_{2p_z}(P) = \chi_{210}(\xi, \vec{r}) = \chi_{210}(5.35627, \vec{r}) = \frac{66.39818}{\sqrt{\pi}} r e^{-5.35627r} \cos\theta$$

$$\chi_{3s}(P) = \chi_{300}(\xi, \vec{r}) = \chi_{300}(1.67460, \vec{r}) = \frac{1.28114}{\sqrt{\pi}} r^2 e^{-1.67460r}$$

$$\chi_{3p_x}(P) = \chi_{311}(\xi, \vec{r}) = \chi_{311}(1.81341, \vec{r}) = \frac{2.93228}{\sqrt{\pi}} r^2 e^{-1.81341r} \sin\theta\cos\varphi$$

$$\chi_{3p_y}(P) = \chi_{31-1}(\xi, \vec{r}) = \chi_{31-1}(1.81341, \vec{r}) = \frac{2.93228}{\sqrt{\pi}} r^2 e^{-1.81341r} \sin\theta\sin\varphi$$

$$\chi_{3p_z}(P) = \chi_{310}(\xi, \vec{r}) = \chi_{310}(1.81341, \vec{r}) = \frac{2.93228}{\sqrt{\pi}} r^2 e^{-1.81341r} \cos\theta$$

$$\chi_{1s}(H) = \chi_{100}(\xi, \vec{r}) = \chi_{100}(1.0, \vec{r}) = \frac{1}{\sqrt{\pi}} e^{-r}$$

The values of orbitals energy of (PH) molecule have been found by solving of (HFR) equation, and we have obtained the following results that have been given in Table (1) :

ε_1= -80.306510 ε_6= -0.695569
ε_2= -7.457756 ε_7= -0.416307
ε_3= -5.328264 ε_8= -0.112228
ε_4= -5.328264 ε_9= -0.112228
ε_5= -5.327784 ε_{10}= -0.272841

By solving HFR equations for each molecule, the values of coefficients c_{qi} and ε_i orbital energies have been calculated. According to Koopmans' theorem, the value of ionization potential of each molecule has been defined:

$$I_p = -\varepsilon_0$$
(12)

ε_0 - is energy according to the highest molecular orbital occupied by electrons. The results have been given in Table 1.

On the basis of (6)-(11) formulas, interaction energies between nuclears and electrons, between electrons in molecules, and kinetic energies of electrons have been calculated.

$$\bar{V} = \bar{V}_{e-n} + \bar{V}_{e-e} + \frac{z_a z_b}{R_{ab}}$$
(13)

On the basis of (13), potential energy of molecules have been defined. The accuracy of the calculations have been checked by Virial theorem [6]: $\frac{\bar{V}}{\bar{T}} = -2$. The results have been given in Table 2.

Table 1.
Equilibrium inter nuclear distance R(a.u.), values of ε_i (a.u.) orbital energies, and I_p(eV) ionization potential energies of BH, NH, AlH, PH, ClH, LiH+, BeH and CH molecules

Molecul	R	ε_1	ε_2	ε_3	ε_4	ε_5	ε_6	ε_7	ε_8	ε_9	ε_{10}	I_p
BH	2,74	-7,795	-0,304	-0,369	0,112	0,112	0,345					10,042
NH	2,25	-15,294	-0,781	-0,190	-0,190	-0,038	0,455					5,182
AlH	2,98	-58,856	-4,893	-3,187	-3,187	-3,184	-0,500	-0,286	0,096	0,096	0,353	7,806
PH	2,90	-80,306	-7,457	-5,328	-5,328	-5,327	-0,695	-0,416	-0,112	-0,112	0,272	3,053
ClH	2,39	-105,081	-10,389	-7,853	-7,847	-7,847	-0,985	-0,527	-0,388	-0,388	0,344	10,581
LiH+	3,01	-2,962	-0,141	0,000	0,002							3,850
BeH	2,75	-4,825	-0,441	-0,112	0,000	0,000						3,058
CH	2,47	-11,415	-0,761	-0,435	-0,213	0,000	0,000					5,796

Table 2.
The calculated values (a.u) of $\bar{V}_{e-n}, \bar{V}_{e-e}, \bar{V}_{n-n}, \bar{V}, \bar{T}, \bar{V}/\bar{T}$ quantities for BH, NH, AlH, PH, ClH, LiH+ , BeH, and CH molecules by HFR method

Molecul	V_{e-n}	V_{e-e}	V_{n-n}	V	T	V/T
BH	-60,628545	9,945744	1,823074	-48,859727	23,799447	-2,052849
NH	-135,058644	24,279100	3,111075	-107,668469	53,51057	-2,012113
AlH	-578,181342	97,805194	4,361084	-476,015024	234,334182	-2,031351
PH	-813,077771	135,195570	5,168582	-672,713619	332,517432	-2,023093
ClH	-1101,003569	183,318834	7,096512	-910,588223	451,747620	-2,015701
LiH+	-18,867665	2,696821	0,995025	-15,175819	7,472160	-2,030982
BeH	-36,558349	5,784973	1,454546	-29,318830	14,340832	-2,044430
CH	-92,091567	15,118435	2,429150	-74,543982	36,417360	-2,046935

Conclusion

In this research the value of potential energy of molecules and kinetic energy of electrons have been obtained according to slater functions .

Also , Slater Atomic orbitals are used as exponential functions . calculations for some molecules with closed and open electronic shells have been carried out by computer program, based on (HFR) Hartree – fock – roothan Method .

So, the common analytical expression for potential energy of molecules and kinetic energy of electrons have been obtained . The accuracy of valculations have been checked by virial theorem.

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حساب طاقة الجهد للجزيئات والطاقة الحركية للإلكترونات استناداً إلى دوال سلاتر

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الملخص

في هذه الورقة البحثية تم الحصول على تعبير عام لتحليل طاقات الجهد للجزيئات (طاقات التفاعل بين الالكترونات والنواه، وطاقات التفاعل بين الالكترونات مع بعضها البعض)، وتم الحصول على تعبير عام لتحليل الطاقات الحركية للإلكترونات، وباستخدام دوال سلاتر الأساسية للمدارات الذرية وتطبيق طريقة هارتري – فوك – روتان، أجريت حسابات لبعض الجزيئات الذرية ذات القشرة الإلكترونية المغلقة والمفتوحة وقد تم التحقق من دقة الحسابات من خلال نظرية فيريال.

الكلمات المفتاحية : المدار الذري، المدار الجزيئي، دوال سلاتر، طاقة الجهد.