

Study the effect of the atomic number on the atomic properties of He- like ions

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Abstract:

In this research we studied the effect of the atomic number on some atomic properties for systems have two electrons but different in atomic numbers like He-atom ($Z=2$) , H^- -ion ($Z=1$) and Li^+ -ion ($Z=3$) .

We observed that the correlation energy increasing with increased atomic number , where the results are (-0.48793, -2.85316 and -7.23632) .The comparison with the experimental results we found good agreement .

All properties studied in this research were checked according to the normalization condition and we the atomic unit were used .

دراسة تأثير العدد الذري على الخواص الذرية للهليوم والايونات الشبيهة

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الخلاصة :

في هذا البحث درسنا تأثير العدد الذري على بعض الخواص الذرية لنظام يمتلك الكترونين ولكن يختلف في العدد الذري مثل ذرة (He) حيث ($Z=2$) , ايون (H^-) ($Z=1$) وايون (Li^+) ($Z=3$) . حيث تم ملاحظة زيادة طاقة الترابط بزيادة العدد الذري , حيث كانت النتائج (-0.48793,-2.85316,-7.23632) وعند المقارنة مع النتائج العملية وجدنا تقارب كبير . لابد من الإشارة إلى أن كل الخواص المدروسة ضبطت بالاعتماد على شرط العيارية مستخدمين الوحدات الذرية.

Introduction:

The Hartree-Fock (HF) atomic wavefunctions are independent particle-model approximations to non-relativistic Schrödinger equation for stationary states. For any system is mathematical expression which describes the system properties as position, momentum, energy and etc. given by the wave function

$$[1]. \Psi(r_1, r_2, r_3, \dots, r_n)$$

In the uncorrelated wave function approximation, each particle is assumed to move in only the average field of all the other particles of the system.

This kind of calculation uses approximation, that is called Hartree-Fock approximation (HF). [2]

For atoms with more than one electron, Schrödinger equation cannot be solved exactly. However, for heavy atom or molecule, the problem become more complicated by the presence of potential energy terms, which arise from the mutual repulsion between any two electrons. In practice the exact solution to Schrödinger equation for many-electron system is unobtainable. [3]

The correlation problem is still a field of active research and many methods of analysing and studying the best correlation have been proposed for the last years, such as Sinanoğlu method. [4]

Theory:

The Hamiltonian operator for many electron systems [3]:

$$\hat{H} = -\sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i=1}^N \frac{Ze^2}{r_i} + \sum_{j>i}^N \sum_{i=1}^N \frac{e^2}{r_{ij}}$$

where the first term represents the kinetic energy operator., the second term is the potential energy for the attractions between the electrons and

the nucleus of charge Z and the last term is the potential energy of the interelectronic repulsions.

The single determinant can be written as the antisymmetrized of all occupied HF spin-orbital for atoms

$$\Psi_{HF}(123\dots N) = A \Pi(123\dots N) \dots (2)$$

Where A is the antisymmetrized operator given by [5]:

$$A = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P \dots (3)$$

$(-1)^P$ takes the values +1 and -1 for even and odd permutation, P is any permutation of the electron, and the factor $\frac{1}{\sqrt{N!}}$ introduced to ensure that the wavefunction is normalized.

For our purpose the wavefunction can be written as

$$\Psi_{HF}(123\dots N) = \sum_{i<j}^N A_{ij}^{mn} (-1)^P A \Pi_{ij} \dots (4)$$

where the pair function A_{ij}^{mn} can be defined as [5]:

$$A_{ij}^{mn} = \phi_i(m) \phi_j(n) - \phi_j(m) \phi_i(n) \dots (5)$$

and Π_{ij} represents the product of all occupied HF-spin orbital except $\phi_i(m)$ and $\phi_j(n)$. i and j represent spin orbital labels, also m and n refer to electron labels.

The product $\Pi(123\dots N)$ in equation (5) can be defined as:

$$\Pi(123\dots N) = \left| \phi_1(1) \phi_2(2) \phi_3(3) \dots \phi_N(N) \right| \dots (6)$$

The Hartree-Fock spin-orbital ϕ are designated by the numerals 1,2,3...N starting with the lowest orbital with spin. Consequently all odd

integers for α spin and all even ones for β spin.

Equation(5) can be expressed in terms of Slater determinant as follows:

$$\Psi_{\text{HF}}(123\dots N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1)\phi_1(2) & \dots & \phi_1(N) \\ \phi_2(1)\phi_2(2) & \dots & \phi_2(N) \\ \dots & \dots & \dots \\ \phi_N(1)\phi_N(2) & \dots & \phi_N(N) \end{vmatrix} \quad \dots(7)$$

The HF or analytic self-consistent field atomic wavefunction provides the un-correlated description of each atom.

For any atom or ion, the Hartree -fock spatial orbital may be written as [6]:

$$\phi = \sum_{i=1}^j c_i \chi_i \quad \dots(8)$$

represents the constant coefficient yield from the SCF method is the c_i basis function as a standard normalized Slater-type orbital χ_i (STO's), which is given by [6]:

$$\chi_{n\ell m_\ell}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell m_\ell}(\theta, \phi) \dots (9)$$

represented the radial part of $R_{n\ell}(r)$ the wavefunction and it given as

$$R_{n\ell}(r) = N_{n\ell m_\ell} S_{n\ell}(r) \quad \dots(10)$$

the normalization constant given $N_{n\ell m}$ by[3]:

$$N_{n\ell m} = \frac{(2\zeta)^{n+\frac{1}{2}}}{[(2n)!]^{\frac{1}{2}}} \quad \dots(11)$$

$$S_{n\ell}(r) = r^{n-1} e^{-(\zeta r)} \dots(12)$$

is called slater type $S_{n\ell}(r)$ Where $Y_{\ell m}(\theta, \phi)$ orbital(STO's) and represents the angular part of the wavefunction.

Atomic properties:

The atomic properties are studied in this research are :

1-One-particle radial densitydistrib - -ution function $D(r_1)$:

The radial density distribution function $D_{ij}(r_1)$ is a measure of the probability of finding an electron in each shell and it is defined as [7]:

$$D_{ij}(r_1) = \int_0^\infty D_{ij}(r_1, r_2) dr_2 \quad \dots(13)$$

In each individual electronic shell, the two-particle radial density distribution function $D(r_1 r_2)$ is defined by [7]

$$D(r_1, r_2) = \iint \Gamma(r_1, r_2) r_1^2 r_2^2 d\Omega_1 d\Omega_2 \quad \dots (14)$$

2- The inter-particle distribution function $f(r_{12})$:

The inter-particle distribution function associated with the spin-orbital pair (i, j) is given by [8]:

$$f_{ij}(r_{12}) dr_{12} = \int \Gamma_{ij}(r_1, r_2) dr_1 dr_2 \dots(15)$$

is the inter-particle distance r_{12} where

3- One-particle expectation and inter-particle values:

The one-particle expectation value can be calculated from [9]:

$$\langle r_1^n \rangle = \int D_{ij}(r_1) r_1^n dr_1 \quad \dots(16)$$

In case (n=0), one can calculate the Normalization condition

The inter-particle expectation values can be calculated from [10]:

$$\langle r_{12}^n \rangle = \int f_{ij}(r_{12}) r_{12}^n dr_{12} \dots(17)$$

The standard deviation of the distance of the test electron from the nucleus r_1 , is defined as [11]:

$$\Delta r_1 = \sqrt{\langle r_1^2 \rangle - \langle r_1 \rangle^2} \quad \dots(18)$$

while the standard deviation of the inter electronic distance of the two electrons, is defined as [12]:

$$\Delta r_{12} = \sqrt{\langle r_{12}^2 \rangle - \langle r_{12} \rangle^2} \quad \dots (19)$$

4- Energy expectation value $\langle E \rangle$:

The energy expectation value associated with the Hamiltonian operator can be written as follows :[13]

$$E = \langle \hat{H} \rangle = \int \psi^* \hat{H} \psi d\tau \quad \dots(20)$$

for the N – electron system is given

by : \hat{H} and

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_{i < j} \frac{1}{r_{ij}} \quad \dots(21)$$

Since $E = T + V_{en} + V_{ee}$, equation (21) is used to find the expectation values of the kinetic and potential energies ,and is given by :

$$\langle T \rangle = -\frac{1}{2} \int \psi^* \left[\sum_i \nabla_i^2 \right] \psi d\tau \quad \dots(22)$$

$$\dots(23) \langle V \rangle = \int \psi^* \left[\sum_i -\frac{Z}{r_i} + \sum_{i < j} \frac{1}{r_{ij}} \right] \psi d\tau$$

Results and Discussion:

Table (1): Data of Hartree-Fock function for He ion-electronic series

Part A: Data for H⁻ ion (Z=1)[13].

n	ζ	C
1	0.30	0.2733433
1	0.70	0.5340164
2	0.70	0.0988397
1	1.30	0.2288345
2	1.30	-0.042995

Part B: Data for He atom (Z=2)[14].

n	ζ	C
1	1.45286	0.82958
1	2.77954	0.18334
1	4.34600	0.00824

Part C: Data for Li⁺ ion (Z=3)[14].

n	ζ	C
1	2.46376	0.89459
1	4.70359	0.11839
1	6.46694	-0.00232
1	1.35790	0.00445

We calculated One-particle radial density distribution function $D(r_1)$ for two electron systems in the K-shell by using equation (13) and the results indicated in table (2) and fig. (1) . From these results we noted that the

maximum values of $D(r)$ increases as atomic number increases also positions of these values are contract toward the nucleus as atomic number increases because the nuclear charge effect increases , In addition to these, when ($r=0$) , $D(r_1)=0$, that means that the electron is not found in the nucleus ,when $r_1 = \infty$ then $D(r_1)=0$,that means the electron is not found out the atom .

Table(2): Values of positions and maximum values of One-particle radial density distribution function

Atom or ion	$D(r_1)$	r_1
H ⁻	0.326	1.3
He	0.861	0.6
Li ⁺	1.395	0.4

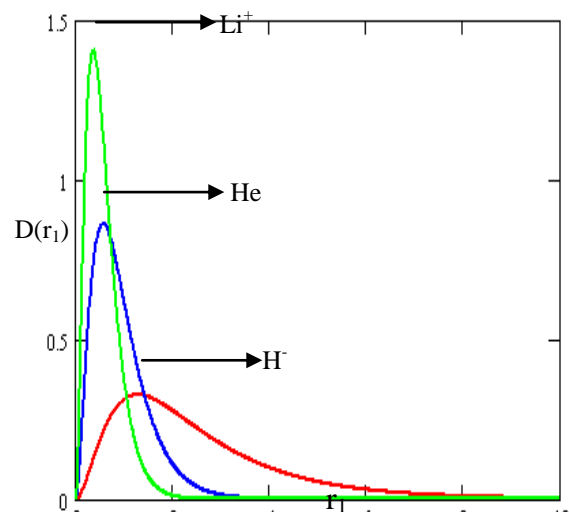


Fig. (1) :The One-particle radial density distribution function for He iso-electronic series.

Tables (3) and (4) represented The one-particle expectation and the inter-particle expectation values for different values of n (-2,-1,0,1,2) are calculated by using equations (16) and (17) respectively , Also we calculated the standard deviation of the distance of the test electron from the nucleus r_1 and the standard deviation of the inter

electronic distance of the two electrons by using equations (17) and (18) respectively .From these results we observed that as atomic number increases the values of $\langle r_1^n \rangle$, $\langle r_{12}^n \rangle$ increase for n negative values and

inverse for n positive values. Also for all systems the standard deviation values Δr_1 and Δr_{12} decrease as atomic number increases because the attraction force are increased .

Table(3) : Values of one-particle expectation and standard deviation .

Atom or ion	$\langle r^{-2} \rangle$	$\langle r^{-1} \rangle$	$\langle r^0 \rangle$	$\langle r^1 \rangle$	$\langle r^2 \rangle$	Δr
H ⁻	1.081494	0.685788	1.001596	2.52609	9.712252	1.82513
He	5.981103	1.680607	0.994066	0.919112	1.1695111	0.56986
Li ⁺	14.91063	2.68734	0.99999	0.57237	0.44531	0.34308

Table(4) : Values of inter-particle expectation and standard deviation.

Atom or ion	$\langle r_{12}^{-2} \rangle$	$\langle r_{12}^{-1} \rangle$	$\langle r_{12}^0 \rangle$	$\langle r_{12}^1 \rangle$	$\langle r_{12}^2 \rangle$	Δr_{12}
H ⁻	0.29025	0.39570	1.00319	3.78425	19.45550	2.26604
He	1.82812	1.01609	0.98817	1.34185	2.32514	0.72427
Li ⁺	4.72609	1.65160	0.99997	0.83830	0.89060	0.43341

Fig (2) represented the relation between inter – particle distribution function and the inter distance for electrons , From this we observed that the maximum values of inter – particle distribution function increases as atomic number increases also The positions of these values approach to the nucleus as Z increases because the nuclear charge effect is increased

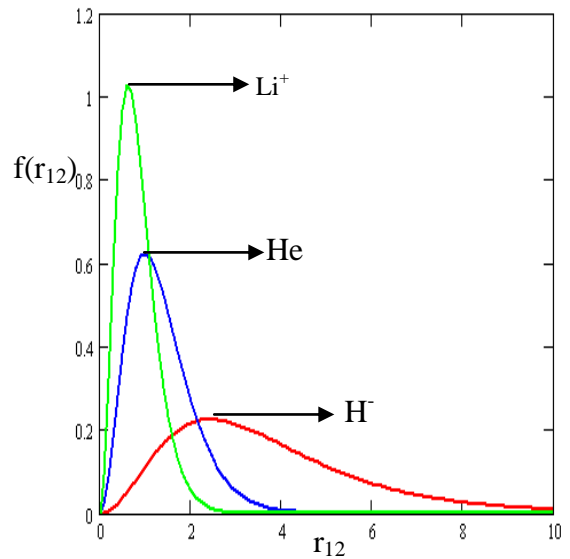


Fig. (2) :The inter-particle density distribution function for He iso-electronic series

Energy expectation is calculated by using equation (20). In addition to calculate the kinetic and

potential energies by using the equations (22)and (23) respectively.

These values are tabulated in table (5) for two – electrons system also we compared the energy expectation value results with the experimental results .

Table(5):Expectation values of the Potential energy <V >, Kinetic energy < T >and Total energy <E> .

Atom or ion		< V >	< T >	< E >
H ⁻	Present work	-0.97588	0.48793	-0.48793
	Ref.[13]	–	–	-0.4880
He	Present work	-5.70638	2.85316	-2.85316
	Ref.[14]	-5.7233	2.86168	-2.86168
Li ⁺	Present work	-14.47264	7.23632	-7.23632
	Ref.[14]	-14.47263	7.23621	-7.23621

Conclusions :

1-As Z increases the maximum values of inter – particle distribution function $f(r_{12})$ and the one – particle radial density distribution function $D(r)$ are increased .

2-When $n=0$, $\langle r_1^n \rangle \cong \langle r_{12}^n \rangle \cong 1$

represents the normalization condition

3-The positions of these maximum values decreases as Z increases .

As Z increases the values of $\langle r_1^n \rangle$ and $\langle r_{12}^n \rangle$ increases for n negative values and decreases for n positive values .

4-For all systems the standard deviation values Δr_1 decrease[as Z increases .

5- As Z increases , all the energies are increased for all systems .

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