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A linear relation to calculate one particle expectation value <r-1> for 1S2 configuration for 2< Z <100

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ABSTRACT

One particle expectation value <r-1> for 1S2 configuration for Z =2 to 10 are evaluated by using Hartree-Fock-Roothaan (HFR) wavefunction. A linear relation are determined to describe these results, and this relation have tested to check its ability to calculate one particle expectation value <r-1> for atoms with higher atomic numbers (Z = 2 to 100). Results are in good agreement with calculations given by [S.L. Saito Atomic Data and Nuclear Data Tables95, (2009) ,836-870] for Z<20.

Introduction:

The $1S^2$ configuration plays an important role in the quantum mechanical calculations for its simplicity and applicability as a system to calculate some of its atomic properties like the evaluation of the one particle expectation value with power n=-1 $< r_1^{-1} >$, the subject of this research. It's very important to calculate $< r_1^{-1} >$ because of its direct relation with the evaluation of the total energy for the system under studying. Different methods were used in quantum mechanical calculations but Hartree–Fock (HF) equations were first proposed by Fock in 1930 has taken a central role in studies of atomic and molecular electronic structure. Atomic HF equations give physical properties of various atomic systems in the non-relativistic independent particle approximation. These data are also important for molecular calculation, for it is impossible to develop basis sets and pseudo -potentials for use in molecular calculations without them [1][2].

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But these methods still needs many sophisticated mathematical and programming techniques to evaluate an atomic property. In this research a simple linear relation was determined to evaluate one particle expectation value with power n=-1 for $1S^2$ configuration without any need to use the traditional procedures to calculate this property. This relation may help as a fast tool to check published atomic data and may be to guess an approximate values for $< r_1^{-1} >$.

Theory:

One particle expectation value for n= -1 given by the following equation:

$$< r_1^{-1} >= \int_0^{\infty} D(r_1) r_1^{-1} dr_1 ,$$

Where

$D(r)$: is the radial electronic density distribution for an electronic system and given by:

$$D(r_1) = \int_0^{\pi} \int_0^{2\pi} r_1^{\,2} \rho(r_1) d\Omega ,$$

$$\rho(r_1) = N \int \psi^*(x_1, x_2, .., x_N) \times \psi(x_1, x_2, .., x_N) ds_1 dx_2 \ldots ds_N dx_N$$

The standard notation $d\Omega = \sin(\theta) d\theta d\phi$ is employed, x_i denotes a combined spatial and spin coordinate and $\psi(x_1, x_2, .., x_N)$ is normalized [3].

The HF wave function ψ_{HF} are used to perform calculations in this research.

The HF wave function for two electron system is:

$$\psi_{HF}(1,2) = \frac{1}{\sqrt{2}}[\Phi_1(1)\Phi_2(2) - \Phi_1(2)\Phi_2(1)] ,$$

Where

$$\Phi_j(r,\theta,\phi) = R(r)Y(\theta,\phi) ,$$

$R(r)$ is one particle radial wavefunction and $Y(\theta,\phi)$ is the one particle angular wavefunction of the total wavefunction $\psi_{HF}(1,2)$.

Slater-Type Orbital's (STO's) [4] are used within HF wavefunction in equation (4), the radial part of STO's given by the following equation:

$$\mathrm{R(r)} = \sum_{k=1}^{M} C_k N_k r^{n_i-1} e^{-(\xi_k)r_k} , \qquad (5)$$

M : Number of basis sets
n_k : Principle quantum number
ξ_k: Orbital exponent
C_k: Expansion coefficient.
N_k: Normalization constant and given by:

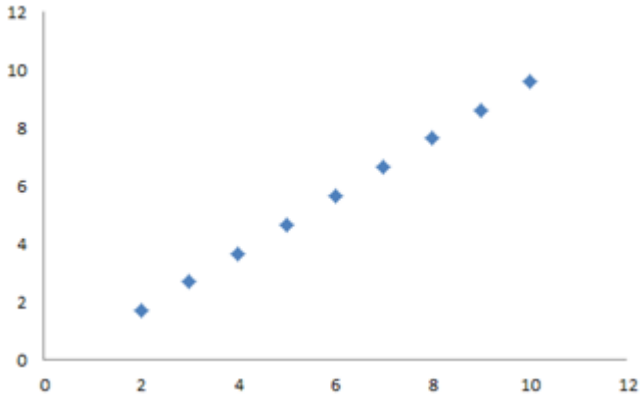
$$N_k = \sqrt{\frac{(2\xi_k)^{2n_k+1}}{(2n_k)!}}$$

The final equation that used to calculate the expectation value by using data give by [5] as follow:

$$< r_1{}^{-1} > = \sum_{k=j}^{M} C_k C_j N_k N_j \frac{(2n_k-1)!}{(2\zeta_k)^{2n_k}} + 2\sum_{j<k}^{M} C_k C_j N_k N_j \frac{(n_k+n_j-1)!}{(\zeta_k+\zeta_j)^{n_i+n_j}} \qquad (6)$$

The one particle expectation value with power n= -1 increases linearly throughout the series as shown in figure(1), so that, the difference between any two values in the series given by:

$$< \mathrm{r_1}^{-1} > \quad \Delta_{i,i+1} = < r_1{}^{-1} >_{i+1} - < r_1{}^{-1} >_i$$



Figure(1): Liner increasing of $< \mathrm{r_1}^{-1} >$ with Z , all results in atomic units (a.u.).

So that, the expectation value $< r_1{}^{-1} >_{i+1}$ for any atom throughout the 2 electron like system for $1S^2$ configuration produced by an additive process, and this phenomenon are used in this work to calculate $< r_1{}^{-1} >$ for Z = 2 to 100 by using the following equation:

$$< r_1{}^{-1} >_{i+1} = < r_1{}^{-1} >_i + \Delta_{i,i+1} .$$

The value of $\Delta_{i,i+1}$ was taken as the average for 10 atoms and equal to 0.99128.

Results and Conclusions:

Tables (1) and figure (2) shows the results of one particle expectation value with n=-1 that calculated by using data from Ref.[5] within equation (6), for atoms of Z= 2 to 10 in addition to the results from equation (7) that represents the new approach in this research for Z=2-100, all results was compared with results of Ref.[2]. All these calculations have made by using MathCad14.

The values of $< r_1{}^{-1} >$ as shown in figure (1) can be divided into three zones, the first for the interval of 2<Z <8 and the second is for the interval 8<Z<16 and the third is for the interval 16<Z<100. The first zone has a very small differences with respect to results given by the traditional method that given by equation (6) and listed within [2], but the best results of the new approach of this research that given in equation (7) appears

clearly in the second zone where the differences are very small with respect to published work. The third zone shows that the differences between the results given by equation (7) and that given by [2] increases linearly with the increasing of Z within this zone and this may be happened because the roots of the linear relation in equation (7) that emerged from HF calculations with its well-known limitations for Z>20 because of the neglecting of relativistic effects [7]. so that the main conclusion in this research is that the linear relation in this research can be used to calculate the one particle expectation value for power n=-1 for Z=2-20 to give a results in good agreement with the published data for $1S^2$ configuration.

Table(1): Expectation values for Z=2-10 by using HFR, expectation value for Z=2-100 by using the common difference approach $\Delta_{i,i+1}$,all results in atomic units (a.u.).

Z	$< r_1^{-1} >^a_{HFR}$	$\Delta_{i,i+1}$	$< r_1^{-1} >^a$	$< r_1^{-1} >^b$	δ^c
2	1.68729		1.687290	1.687282	0.00001
3	2.68386	0.996570	2.678574	2.685034	0.00646
4	3.676414	0.992554	3.669857	3.681877	0.01202
5	4.668731	0.992317	4.661141	4.674339	0.01320
6	5.660406	0.991675	5.652425	5.664439	0.01201
7	6.65196	0.991554	6.643708	6.653236	0.00953
8	7.637847	0.985887	7.634992	7.642171	0.00718
9	8.629412	0.991565	8.626275	8.630362	0.00409
10	9.617559	0.988147	9.617559	9.618054	0.00050
11	10.60884		10.60738	10.60738	0.00146
12	11.60013		11.59795	11.59795	0.00217
13	12.59141		12.58925	12.58925	0.00216
14	13.58269		13.58115	13.58115	0.00154
15	14.57398		14.57355	14.57355	0.00042
16	15.56526		15.56645	15.56645	0.00119
17	16.55654		16.55969	16.55969	0.00315
18	17.54783		17.55323	17.55323	0.00540
19	18.53911		18.54736	18.54736	0.00825
20	19.53040		19.54193	19.54193	0.01154
21	20.52168		20.53754	20.53754	0.01586
22	21.51296		21.53364	21.53364	0.02068
23	22.50425		22.53012	22.53012	0.02587
24	23.49553		23.52726	23.52726	0.03173
25	24.48681		24.52397	24.52397	0.03716
26	25.4781		25.52120	25.52120	0.04310
27	26.46938		26.51866	26.51866	0.04928
28	27.46066		27.51630	27.51630	0.05563
29	28.45195		28.51438	28.51438	0.06244
30	29.44323		29.51205	29.51205	0.06882
31	30.43452		30.50972	30.50972	0.07521
32	31.42580		31.50738	31.50738	0.08158

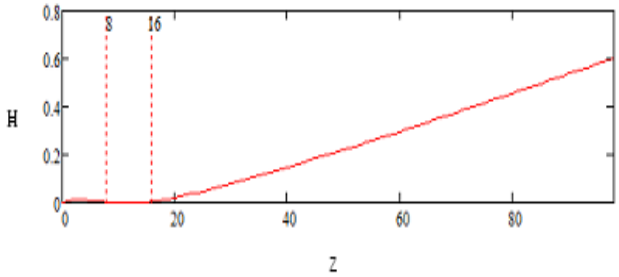
33	**32.41708**	**32.50504**	**0.08796**	**55**	**54.22532**	**54.46797**	**0.24265**
34	**33.40837**	**33.50273**	**0.09436**	**56**	**55.21661**	**55.46669**	**0.25008**
35	**34.39965**	**34.50043**	**0.10078**	**57**	**56.20789**	**56.46547**	**0.25758**
36	**35.39093**	**35.49815**	**0.10722**	**58**	**57.19917**	**57.46444**	**0.26526**
37	**36.38222**	**36.49597**	**0.11375**	**59**	**58.19046**	**58.46358**	**0.27312**
38	**37.37350**	**37.49385**	**0.12035**	**60**	**59.18174**	**59.46262**	**0.28088**
39	**38.36478**	**38.49189**	**0.12711**	**61**	**60.17302**	**60.46169**	**0.28867**
40	**39.35607**	**39.49003**	**0.13396**	**62**	**61.16431**	**61.46080**	**0.29649**
41	**40.34735**	**40.48833**	**0.14098**	**63**	**62.15559**	**62.45994**	**0.30434**
42	**41.33864**	**41.48663**	**0.14800**	**64**	**63.14688**	**63.45898**	**0.31211**
43	**42.32992**	**42.48493**	**0.15501**	**65**	**64.13816**	**64.45827**	**0.32011**
44	**43.32120**	**43.48343**	**0.16222**	**66**	**65.12944**	**65.45748**	**0.32804**
45	**44.31249**	**44.48192**	**0.16943**	**67**	**66.12073**	**66.45671**	**0.33599**
46	**45.30377**	**45.48052**	**0.17675**	**68**	**67.11201**	**67.45597**	**0.34396**
47	**46.29505**	**46.47906**	**0.18401**	**69**	**68.10329**	**68.45525**	**0.35195**
48	**47.28634**	**47.47763**	**0.19129**	**70**	**69.09458**	**69.45455**	**0.35997**
49	**48.27762**	**48.47620**	**0.19858**	**71**	**70.08586**	**70.45377**	**0.36791**
50	**49.26890**	**49.47479**	**0.20589**	**72**	**71.07714**	**71.4530**	**0.37586**
51	**50.26019**	**50.47339**	**0.21320**	**73**	**72.06843**	**72.45225**	**0.38382**
52	**51.25147**	**51.47201**	**0.22054**	**74**	**73.05971**	**73.45151**	**0.39180**
53	**52.24276**	**52.47064**	**0.22789**	**75**	**74.05100**	**74.45078**	**0.39979**
54	**53.23404**	**53.46929**	**0.23525**	**76**	**75.04228**	**75.45007**	**0.40779**

77	**76.03356**	**76.44936**	**0.4158**
78	**77.02485**	**77.44869**	**0.42385**
79	**78.01613**	**78.44802**	**0.43189**
80	**79.00741**	**79.44733**	**0.43991**
81	**79.99870**	**80.44664**	**0.44794**
82	**80.98998**	**81.44595**	**0.45597**
83	**81.98126**	**82.44526**	**0.46400**
84	**82.97255**	**83.44458**	**0.47203**
85	**83.96383**	**84.44390**	**0.48007**
86	**84.95511**	**85.44322**	**0.48811**
87	**85.94640**	**86.44256**	**0.49616**
88	**86.93768**	**87.44190**	**0.50422**
89	**87.92897**	**88.44127**	**0.51230**
90	**88.92025**	**89.44064**	**0.520390**
91	**89.91153**	**90.44011**	**0.52858**
92	**90.90282**	**91.43955**	**0.53674**
93	**91.89410**	**92.43901**	**0.54491**
94	**92.88538**	**93.43851**	**0.55313**
95	**93.87667**	**94.43799**	**0.56132**
96	**94.86795**	**95.43744**	**0.56949**
97	**95.85923**	**96.43694**	**0.57770**
98	**96.85052**	**97.43648**	**0.58597**
99	**97.84180**	**98.4360**	**0.59420**
100	**98.83309**	**99.43553**	**0.60244**

a: Present work

b: Ref.[2]

c: $\delta = \left| < r^{-1} >^{a} - < r^{-1} >^{b} \right|$



Figure(2): The relative difference δ between the results of linear equation and HFR one for $2 \le Z \le 100$.
Where $\delta = |< \boldsymbol{r^{-1}} >^{a} - < \boldsymbol{r^{-1}} >^{b}|$, all results in this figure are in atomic units (a.u.).

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علاقة خطية لحساب القيمة المتوقعة لبعد الالكترون عن النواة <r-1> للغلاف 1S2 للأعداد الذرية 2<Z<100

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الخلاصة

تم حساب القيمة المتوقعة لجسم واحد <r-1> للغلاف 1S2 للذرات ذات اللأعداد الذرية Z من 2 الى 10 باستخدام دالة هارتري–فوك–روثان ، ومن ثم تم ايجاد علاقة خطية تصف هذه البيانات، وقد تم اختبار هذه العلاقة لمعرفة امكانية استخدامها لحساب ذرات ذات اعداد ذرية اكبر (Z من 2 الى 100) وقد اعطت نتائج جيده مقارنة مع [S.L. Saito Atomic Data and Nuclear Data Tables95, (2009) 836-870] ، عندما تكون Z<20 .