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Calculation of the correlation energy of three electron systems of 20 to 25 electrons

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ABSTRACT

In this research the Hartree- Fock energies were calculated for three-electron systems (Ca^{+17} , Sc^{+18}, Ti^{+19}, V^{+20} , Cr^{+21} and Mn^{+22}) have (Z=20-25) are obtained by an account the atomic properties by using the Hartree- Fock method and Mathcad 14 program, the total expectation value energy $\langle E_{HF}\rangle$ and the correlation energy are important property account in this research and when comparing the result with published results. It was found that there is a good agreement.

1.Introduction

Fock applied the Slater determinant to the Hartree method and proposed the Hartree–Fock method, which is one of the core theories in quantum chemistry .The Hartree –Fock (HF) approximation were first proposed by Fock in 1930 .Since then, the HF method has taken a central role in studying the atomic and molecular electronic properties [1].the Hartree –Fock (HF) method enables calculation not only of the ground state but also excited states of atoms and ions.

2. Theory

the Hartree-Fock method is the main idea of to solve the Schrodinger equation for a many-electron system can by choosing an appropriate wave function. As the exact solution for one-electron systems (like the Hydrogen-atom) are known, a first way for an approximate many-electron wave function is the Hartree-product. The total wave function Φ is then the simple product of one-electron hydrogen wave functions φ (orbitals)[2]

$$\Phi(\vec{x}1,\vec{x}2, ..., \vec{x}n) = \varphi_1(\vec{x}1)\cdot\varphi_2(\vec{x}2)\cdot...\cdot\varphi_n(\vec{x}n) \qquad (1)$$

As electrons never only vary in the three spatial coordinates $\vec{r}$ but also have an intrinsic spin variable ω, which is either α or β, a special space-spin coordinate $\vec{x}=\{\vec{r},\omega\}$ is used for the description of the spin orbitals $\varphi(\vec{x})$. These orbitals consist of a spacial orbital φ(ω) and a spin function $\sigma(\vec{r})$[3]

$$\Phi(\vec{x}) = \sigma(\vec{r})\cdot\varphi(\omega) \qquad (2)$$

whereas electrons are fermions ,so the wave function must be antisymmetric (change sign) under exchange of two electrons. The simple Hartree-product wave function (Eqn. 1) do not check the anti-symmetry principle (example with 2 electrons) in general

$$\Phi(\vec{x}1,\vec{x}2) = -\Phi(\vec{x}2,\vec{x}1) \qquad (3)$$

$\varphi 1(\vec{x}1)\cdot\varphi 2(\vec{x}2) \neq -\varphi 1(\vec{x}2)\cdot\varphi 2(\vec{x}1)$

To fulfill the anti-symmetry principle a linear combination of the two products can be chosen

$$\Phi(\vec{x}1,\vec{x}2) = \frac{1}{\sqrt{2}}\,[\varphi 1(\vec{x}1)\cdot\varphi 2(\vec{x}2) - \varphi 1(\vec{x}2)\cdot\varphi 2(\vec{x}1)] \qquad (4)$$

The one-electron radial density function *D(r₁)* represents the probability density function of finding an electron at a distance between r_1 and $r_1 + dr_1$ from the coordinate origin defined as [4]:

$$D(r_1) = \int_0^\infty D(r_1, r_2)dr_2 \qquad (5)$$

The radial electron-electron distribution function $f(r_{12})$, which describes the probability of locating two electrons separated by distance r_{12} from each other, [5,6].

The pair distribution function can be written as [8]:

$$f(r_{12}) = 8\pi^2 r_{12}\left[\int_0^{r_{12}} r_1 d\,r_1 \int_{r_1-r_{12}}^{r_1+r_{12}} \Gamma(r_1, r_2)r_2 dr_2 + \int_{r_{12}}^{\infty} r_1 dr_1 \int_{r_{12}-r_1}^{r_{12}+r_1} \Gamma(r_1, r_2)r_2 dr_2\right] \qquad (6)$$

The one-electron expectation value $\langle r_1{}^n\rangle$ is determined by the expression [8]:

$$\langle r_1^n\rangle = \int_0^\infty D(r_1)r_1^n\, dr_1 \qquad (7)$$

The inter-electron expectation values $\langle r_{12}^n\rangle$ is given by the relation [9]:

$$\langle r_{12}^n\rangle = \int_0^\infty f(r_{12})r_{12}^n\, dr_{12} \qquad (8)$$

The virial theorem is a necessary condition for any stationary state. From the theorem, one is led to [10]:

$$\langle E\rangle = \langle T\rangle + \langle V\rangle \qquad (9)$$

$$\langle E\rangle = -\langle T\rangle = {}^{\langle V\rangle}/_{2} \qquad (10)$$

The expectation value of potential energy is proportional to the expectation values of $\langle r_1^{-1}\rangle$ and $\langle r_{12}^{-1}\rangle$ respectively, where [11]:

$$\langle V_{en}\rangle = -Z.\langle r_1^{-1}\rangle \qquad (11)$$

$$\langle V_{ee}\rangle = \langle r_{12}^{-1}\rangle \qquad (12)$$

The correlation energy E_{corr} is given by the relation [12]:

$$E_{corr} = E_{exact} - E_{HF} \qquad (13)$$

Where E_{exact} is the ground state energy and E_{HF} is the obtained by Hartree–Fock method.

3. Results and Discussion

Table 1. the maximum values of the D(r1) versus corresponding positions values for three - electron systems

Ion	□□□shell		$K_\alpha L_\alpha$ -shell ≡ $K_\beta L_\alpha$- shell			
	r_1	**$D_{max}(r_1)$**	**First peak**		Second peak	
			r_1	**$D_{max}(r_1)$**	**r_2**	$D_{max}(r_2)$
Ca^{+17}	0.0505	10.601	0.0491	5.7094	0.272	1.8083
Sc^{+18}	0.0482	11.142	0.0467	6.0033	0.2582	1.9056
Ti^{+19}	0.0461	11.684	0.446	6.2977	0.2447	2.0029
V^{+20}	0.044	12.225	0.043	6.5909	0.234	2.1001
Cr^{+21}	0.042	12.765	0.041	6.8848	0.224	2.1973
Mn^{+22}	0.04	13.306	0.039	7.1795	0.215	2.2947

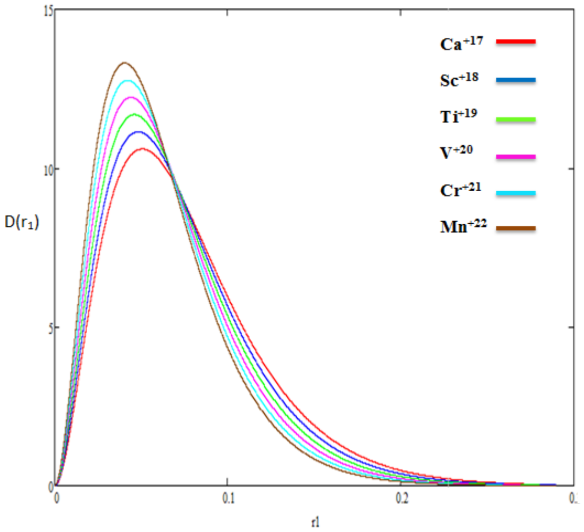

Figure 1. The relation between one electron radial density function $D(r_1)$ with the position(r_1) for K – shell (Three-electron systems).

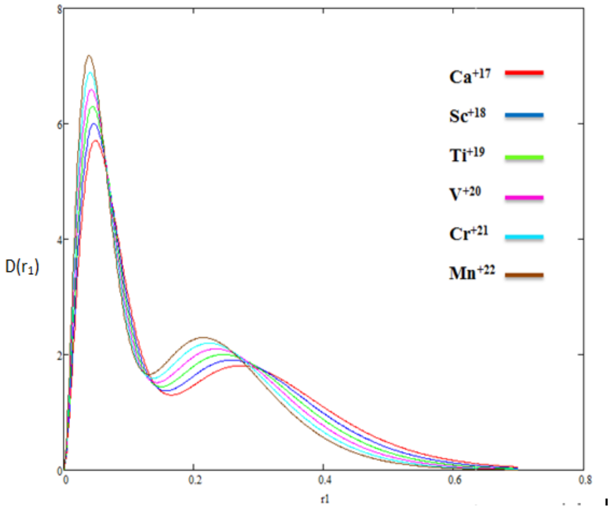

Figure 2. The relation between one electron radial density function $D(r_1)$ with the position(r_1) for ($K_\alpha L_\alpha \equiv K_\beta L_\alpha$) shells.

Table 2. Expectation values $\langle r_1^n \rangle$ of one particle position for different values of n $\{-2 \leq n \leq 2\}$ and standard Δr_1 for three-electron systems.

ion	Shell	$<r_1^{-2}>$	$<r_1^{-1}>$	$<r_1^{+1}>$	$<r_1^{+2}>$	Δr_1
Ca^{+17}	K	777.66342	19.67396	0.07651	0.00782747	0.04443
	$K_\alpha L_\alpha \equiv K_\beta L_\alpha$	431.92921	12.15124	0.19831	0.06367	0.15602
	Average	547.173946	14.6588133	0.15771	0.0450558	0.1188233
Sc^{+18}	K	858.52424	20.67377	0.0728	0.00708516	0.04226
	$K_\alpha L_\alpha \equiv K_\beta L_\alpha$	477.12741	12.77612	0.18834	0.05739	0.14806
	Average	604.25968	15.40867	0.149826	0.04062172	0.112793
Ti^{+19}	K	943.4292	21.67439	0.06943	0.00644381	0.04029
	$K_\alpha L_\alpha \equiv K_\beta L_\alpha$	524.61306	13.4018	0.17933	0.05201	0.14087
	Average	664.21844	16.15933	0.142696	0.0368212	0.107343
V^{+20}	K	1032.26	22.67368	0.06636	0.00588553	0.0385
	$K_\alpha L_\alpha \equiv K_\beta L_\alpha$	574.29741	14.02633	0.17114	0.04734	0.13435
	Average	726.951606	16.90878	0.136213	0.0335218	0.1024
Cr^{+21}	K	1125.04	23.67176	0.06354	0.00539655	0.03687
	$K_\alpha L_\alpha \equiv K_\beta L_\alpha$	626.20474	14.65018	0.16365	0.04327	0.12841
	Average	792.48316	17.657373	0.13028	0.030645	0.097896
Mn^{+22}	K	1222	24.67367	0.06096	0.00496672	0.03536
	$K_\alpha L_\alpha \equiv K_\beta L_\alpha$	680.45649	15.27632	0.15681	0.03971	0.12297
	Average	860.97099	18.40877	0.12486	0.028128	0.093766

Table 3. The maximum values of the inter-particle distribution function $f(r_{12})$ versus corresponding values of the positions for three-electron systems

Ions	K – shell		$K_\alpha L_\alpha$-shell		$K_\beta L_\alpha$ –shell			
					first Peak		second Peak	
	r_{12}	$f_{max}(r_{12})$	r_{12}	$f_{max}(r_{12})$	r_{12}	$f_{max}(r_{12})$	r_{12}	$f_{max}(r_{12})$
Ca^{+17}	0.085	7.7926	0.285	3.3169	0.094	0.53558	0.293	3.2914
Sc^{+18}	0.081	8.1905	0.27	3.4939	0.08	0.56246	0.28	3.4661
Ti^{+19}	0.077	8.5893	0.258	3.6712	0.07	0.59024	0.265	3.6417
V^{+20}	0.073	8.986	0.246	3.8482	0.06	0.60915	0.253	3.8166
Cr^{+21}	0.071	9.383	0.235	4.0249	0.057	0.63759	0.242	3.9912
Mn^{+22}	0.068	9.783	0.225	4.2023	0.05	0.64628	0.232	4.1665

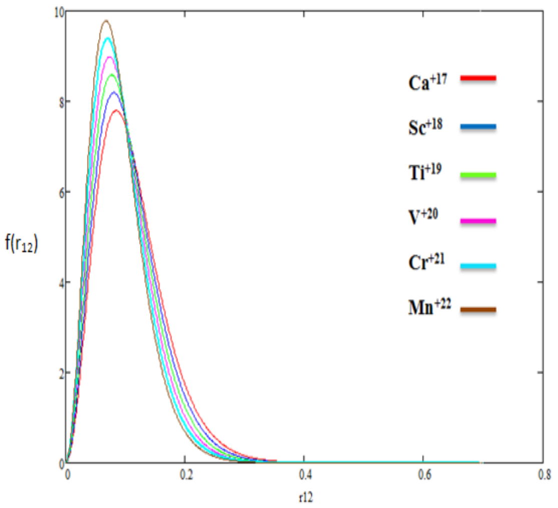

Figure 3. The inter-electron distribution with r_{12} for K- shell of three- electron systems.

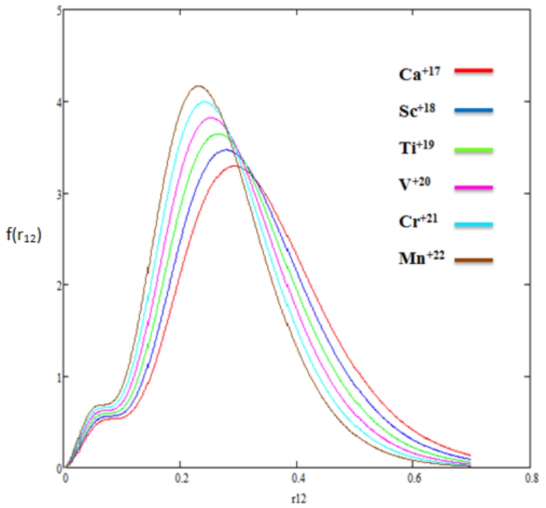

Figure 4. The relation between $f(r_{12})$ with r_{12} for $K_\beta L_\alpha$ -shell of three- electron systems.

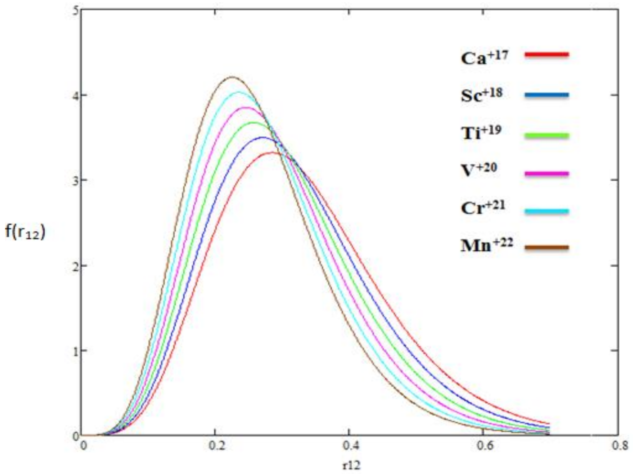

Figure 5. The relation between inter-electron distribution with r_{12} for $K_\alpha L_\alpha$-shell of three-electron systems.

Table 4. Expectation values $\langle r_{12}^{n} \rangle$ where $-2 \leq n \leq 2$ and standard deviation Δ r_{12} for three- electron systems.

Ion	**Shell**	$\langle r_{12}^{-2} \rangle$	$\langle r_{12}^{-1} \rangle$	$\langle r_{12}^{+1} \rangle$	$\langle r_{12}^{+2} \rangle$	Δr_{12}
Ca^{+17}	K	257.3631	12.26731	0.11165	0.01565	0.05648
	$K_\beta L_\alpha$	31.52105	3.93050	0.33064	0.12734	0.13421
	$K_\alpha L_\alpha$	15.39159	3.54225	0.33279	0.12734	0.12881
	Average	101.425246	6.58002	0.25836	0.09011	0.1065
Sc^{+18}	K	284.22207	12.89211	0.10622	0.01417	0.05373
	$K_\beta L_\alpha$	34.98389	4.14051	0.31393	0.1479	0.12743
	$K_\alpha L_\alpha$	17.06800	3.73032	0.31597	0.11479	0.12226
	Average	112.09132	6.92098	0.24537	0.09228	0.10114
Ti^{+19}	K	312.43645	13.5178	0.10131	0.01289	0.05123
	KβLα	38.63035	4.35076	0.29883	0.10401	0.12128
	KαLα	18.83189	3.91859	0.30079	0.10401	0.11633
	Average	123.29956	7.2623833	0.23364	0.07363	0.09628
V^{+20}	K	341.94635	14.14199	0.09682	0.01177	0.04896
	KβLα	42.45414	4.56066	0.28510	0.09468	0.11572
	KαLα	20.68079	4.10653	0.28698	0.09468	0.11098
	Average	135.027093	7.60306	0.22296666	0.06704	0.09188
Cr^{+21}	K	372.74902	14.76464	0.09270	0.01079	0.04689
	KβLα	46.45570	4.77032	0.27257	0.08654	0.11067
	KαLα	22.61503	4.29425	0.27438	0.08654	0.10611
	Average	147.27325	7.94307	0.21321666	0.06129	0.08789
Mn^{+22}	K	405.00641	15.39206	0.08895	0.00993336	0.04496
	KβLα	50.64571	4.98072	0.26113	0.07942	0.10599
	KαLα	24.63910	4.48261	0.26287	0.07942	0.10161
	Average	160.097073	8.28513	0.20431666	0.05625778	0.08418

Table 5 . The expectation values for all attraction, repulsion, kinetic and Hartree-Fock energies for three-electron systems.

Ion	Shell	$-<V_{en}>$	$<V_{ee}>$	$-<V>$	$<T>$	$-<E_{HF}>$	$-<E>eV$
Ca^{+17}	K	393.479	12.26731	381.21189	190.60594	190.60594	5186.387627
	$K_\beta L_\alpha$	243.025	3.93050	239.0943	119.54715	119.54715	3252.877952
	$K_\alpha L_\alpha$	243.025	3.54225	239.48235	119.74117	119.74117	3258.157236
	total	879.529	19.74006	859.7885	429.89426	429.89427	11697.42309
	Ref.[13]	---------	---------	859.79857	429.89798	429.9006	---------
Sc^{+18}	K	434.149	12.89211	421.25706	210.62853	210.62853	5731.202301
	$K_\beta L_\alpha$	268.299	4.14051	264.15801	132.079	132.079	3593.86959
	$K_\alpha L_\alpha$	268.299	3.73032	264.56862	132.28431	132.28431	3599.456075
	total	970.747	20.76294	949.98369	474.99184	474.99184	12924.52797
	Ref.[13]	---------	---------	950.00281	475.00013	475.00268	---------
Ti^{+19}	K	476.837	13.5178	463.31878	231.65939	231.65939	6303.452002
	$K_\beta L_\alpha$	294.84	4.35076	290.48884	145.24442	145.24442	3952.100668
	$K_\alpha L_\alpha$	294.84	3.91859	290.92167	145.46084	145.46084	3957.989456
	total	1066.517	21.78715	1044.7292	522.36465	522.36465	14213.54213
	Ref.[13]	---------	---------	1044.7069	522.35212	522.35478	---------
V^{+20}	K	521.49464	14.14199	507.35265	253.676325	253.676325	6902.532803
	$K_\beta L_\alpha$	322.606	4.56066	318.04493	159.02247	159.02247	4327.001409
	$K_\alpha L_\alpha$	322.606	4.10653	318.49952	159.24976	159.24976	4333.18597
	total	1166.7066	22.80918	1143.8971	571.948555	571.948555	15562.72018
	Ref.[13]	---------	---------	1143.9111	571.95421	571.95688	---------
Cr^{+21}	K	568.1222	14.76464	553.35760	276.67880	276.67880	7528.430148
	$K_\beta L_\alpha$	351.6043	4.77032	346.83400	173.41700	173.41700	4718.67657
	$K_\alpha L_\alpha$	351.60528	4.29425	347.31103	173.65552	173.65552	4725.166699
	total	1271.3317	23.82921	1247.502	623.75132	623.75132	16972.27342
	Ref.[13]	---------	---------	1247.615	623.80601	623.80.900	---------
Mn^{+22}	K	616.84175	15.39206	601.44969	300.72485	300.72485	8182.723169
	$K_\beta L_\alpha$	381.908	4.98072	376.92728	188.46364	188.46364	5128.095644
	$K_\alpha L_\alpha$	381.90675	4.48261	377.42414	188.71207	188.71207	5134.855425
	total	1380.6565	24.85539	1355.8011	677.90056	677.90056	18445.67424
	Ref.[13]	---------	---------	1355.8195	677.90839	677.91111	---------

Table 6 . the correlation energy in (eV) and (H) unit for three-electron system.

ion	**$-E_{exact}$[14]**	**$-E_{(eV)}$**	**$-E_{corr\ (eV)}$**	**$-E_{corr}$ (H)**
Ca^{+17}	11756.5	11697.42309	59.1369133	2.173352198
Sc^{+18}	12996.6	12924.52797	72.0717	2.648721058
Ti^{+19}	14300.3	14213.54213	86.7580	3.188460125
V^{+20}	15667.1	15562.72018	104.379954	3.836087982
Cr^{+21}	17098.1	16972.27342	125.82682	4.624285924
Mn^{+22}	18592.6	18445.67424	146.92603	5.399707093

From allabove figures It is observed that the maximum values of $D(r_1)$ and $f(r_{12})$ increases as Z increases, while the locations of these peaks are contracted toward the nucleus where It is noted that the maximum values of $D(r_1)$ and $f(r_{12})$ for Mn^{+22} is closer to the nucleus from $D(r_1)$ and $f(r_{12})$ for Ca^{+17} .This difference occurs because the Mn^{+22} nucleus Z=25 exerts a much stronger attractive force on electrons than does the Ca^{+17} nucleus (Z=20), also found that the probability of finding an electron in the K-shell is larger than another shells because K- shell is the nearest to nucleus, so that the attraction force between the nucleus and the electron is larger for K-shell according to Coulomb law..

It is also observed from figures (1,2,3,4and 5) when the distance is equal to zero the probability of finding an electron equal to zero (when r =0 , $D(r1) = 0$) this means that the electron is cannot be existed inside the nucleus and when the distance is far away the probability of finding an electron equal to zero also (when $r = \infty$, $D(r1) = 0$) this means that it is not possible of the electron to be existed outside the atom while note that when $r_{12} = 0$ the probability of the inter particle distribution function $f(r_{12}) = 0$ this means that the electron not be closed to another electron and when the distance is far away ($r_{12} = \infty$) the probability of the inter particle distribution function $f(r_{12})$ equal to zero also, This means that the diameter is not found out the atom..

According to the Fig (2), it is found that there are two peaks for L- shell. The first peak represents the probability of finding the electron in the K-shell, the second peak represents the probability of finding the electron in the L-shell also It is note in the Fig (4), it is found that there are two peaks, the first peak represents the probability of finding the electron in 1S, the second peak represents the probability of finding the electron in the 2S.

From table (2) it is noted that when n takes the values (-2,-1) the one-particle expectation value $\langle r_1^n \rangle$ increases where the atomic number Z increases, this is due to the attraction energy between the nucleus and electron increases . While when n takes the values(+1,+2) the one-expectation value $\langle r_1^n \rangle$ decreases by atomic number (Z) increases ,where the $\langle r_1^{-1} \rangle$ which represents the attraction energy expectation value $\langle V_{en} \rangle = -Z[\langle r_1^{-1} \rangle]$ and the $\langle r_1^{1} \rangle$ represents the distance between the nucleus and electron. When n equal to zero the one-particle expectation value $\langle r_1^n \rangle$ equal to unity for all studied systems this represented the normalization condition because the one-particle radial density distribution function D(r_1) is normalized [$\int_0^{\infty} D(r_1) r_1^n \, dr_1 = 1$], the one-expectation value $\langle r_1^n \rangle$ in the K-shell is larger than the another shells because effect electrons in this shells. From tables (4) when Z increases the inter-particle expectation value $\langle r_{12}^n \rangle$ increases when n takes values -2,-1 this leads to increases of the repulsion energy between two electrons, whereas decreases when n takes values +1,+2 this means the distance between pair electron increases.

Table (5) shows the expectation value energies of three-electron systems it is noted that all energies increase as nuclear charge increases. It is note that the attraction energy expectation values $\langle V_{en} \rangle$ are larger than the repulsion energy expectation value $\langle V_{ee} \rangle$ because the distances between the electrons and the nucleus are smaller than the distances between the electrons.

Conclusions

1. When the atomic number Z increases , the one-particle radial density distribution function $D(r_1)$ and the inter-particle distribution function $f(r_{12})$ are increased for three electrons systems.

2. For both one-particle expectation $\langle r_1^n \rangle$, and inter-particle expectation $\langle r_{12}^n \rangle$ are increased when Z increase for three electrons systems.

3. All the expectation values of the energies $\langle V_{en} \rangle$, $\langle V_{ee} \rangle$, $\langle V \rangle$, $\langle T \rangle$, $\langle E_{HF} \rangle$ and E_{corr} are increased when the atomic number increases for three electrons systems.

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