

Evaluation of the atomic properties for like-ions of He-atom using Hartree-Fock method for the Closed Shells in position space

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Abstract:

In this research we studied some atomic properties of the like ions of the He-atom in the closed shells by using Hartree-Fock(HF)wave function,In this research we calculated(i)non-relativistic energy (Hartree-Fock energy E_{HF}) for the(N^{5+} , O^{6+} ,and F^{7+} ions) and we found the correlation energy of the (N^{5+} – ion -44.73664 Hartree , O^{6+} -ion -59.11233 Hartree and for the F^{7+} -ion -75.486 Hartree) and we compared these results with some experimental results. we found large agreement .(ii)Nuclear Magnetic Shielding Constant was found (σ_{dia} for $N^{5+}=1.187 \times 10^{-4}$, $O^{6+}=1.365 \times 10^{-4}$ and for $F^{7+}=1.542 \times 10^{-4}$),and (iii) we examined the influence of the atomic number on some atomic properties where $Z=7$ for N^{5+} – ion $Z=8$ for O^{6+} -ion and $Z=9$ for F^{7+} ions .

حساب الخواص الذرية للأيونات الشبيهة بذرة الهليوم باستخدام طريقة هارترى-فوك للأغلفة المغلقة في فضاء الموقع

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الخلاصة :

درسنا في هذا البحث بعض الخواص الذرية للأيونات الذرية الشبيهة بذرة الهليوم للأغلفة المغلقة باستخدام دالة هارترى-فوك في هذا البحث حسبنا: (1) الطاقة غير النسبية (طاقة هارترى-فوك) لأيون النتروجين وأيون الأوكسجين وأيون الفلور وجدنا أن طاقة الارتباط لأيون النتروجين هي(-44.73664 Hartree) الأوكسجين هي (-59.11233 Hartree) بينما لأيون الفلور(-75.486 Hartree) قارنا هذه النتيجة مع القيمة التجريبية فوجدنا تقارب كبير (2) ثابت الحجب المغناطيسي النووي فوجدنا لأيون النتروجين 1.187×10^{-4} وأيون الأوكسجين 1.365×10^{-4} ولأيون الفلور 1.542×10^{-4} (3) تفحصنا تأثير العدد الذري في دراسة بعض الخواص الذرية حيث $Z=7$ لأيون النتروجين , $Z=8$ لأيون الأوكسجين و $Z=9$ لأيون

1.Introduction

The Schrödinger equation for atoms (ions) with more than one electron has not been solved analytically. Approximate methods must be applied in order to obtain the wave functions or another physical attributes from quantum mechanical calculation[1].

The Hartree-Fock(HF) equations were first proposed by Fock in 1930.since then, the Hartree-Fock method has taken a central role in studies of atomic and molecular electronic structure the development of effective computational methods for Hartree-Fock equations there are two computation methods for Hartree-Fock equations: numerical and algebraic [2]. Numerical computational methods for atomic HF equations have been developed by Froese Fischer [3,4].

The Hartree-Fock method(HF) is known to be successful in calculating properties of electron systems, in particular , the ground state properties of atoms. Based on a variational principle ,the HF method estimate the ground state energy E of the electron system ,from above,i.e $E_{HF} \geq E$,where E_{HF} is the ground state energy calculated within the *HFmethod* if the ground state wave function of N- electrons is approximated by a single N-electron Slater determinant, the HF solution delivers minimum value E_{HF} on the set of all such determinants. Agreement, or otherwise, with the HF result is often used to estimate the success of other approximate computational schemes[5].

In this paper the radial wave functions for single-electron orbitals are obtained by self-consistent field method [6] .

Hartree SCF calculation, assumes that the instantaneous electron-electron interaction can be approximated by an average and the correlation between two electrons in their motions is neglected. Nevertheless, an error is introduced by this approximation in the determination of the ground-state energy,which is called the correlation energy and defined as [7]

$$E_c(Z) = E(Z) - E_{HF}(Z). \quad (1)$$

where $E(Z)$ is the ground state energy and $E_{HF}(Z)$. is the one obtained by Hartree SCF method.

i.e. the difference between the correlated(the exact solution to the non-relativistic Schrödinger equation[8]) and the Hartree-Fock energies[9] The correlation energy is not a physical quantity but the measure of the energy error due to the neglect of correlation in a certain approximation [10].

2.theory

The Hartree-Fock (HF) approximation ignores the correlation between electrons but gives roughly 99% of the total electronic energy[11]. We start from the standard N-electron Hamiltonian (in Hartree atomic units , $\hbar=m=a_o=e=1$,used throughout)[12,13]

$$H = T + V_{ee} + V_{ne} \quad (2)$$

where T is the kinetic energy:

$$T = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 \quad (3)$$

∇_i^2 the Laplace operator

V_{ee} is the two-electron Coulomb repulsion operator :

$$V_{ee} = \frac{1}{2} \sum_{i \neq j}^N \frac{1}{|r_i - r_j|} \quad (4)$$

V_{ne} attractive electron-nucleus potential operator:

$$V_{ne} = \sum_{i=1}^N V_{ne}(r_i) \quad (5)$$

The expectation value of the non-relativistic atomic Hamiltonian can be computed readily :

$$\langle H \rangle = \left\langle \phi \left| -\frac{1}{2} \sum_{i=1}^N (\nabla_i^2 + \frac{Z}{r_i}) \right| \phi \right\rangle \left\langle \phi \left| \sum_{i < j}^N \frac{1}{r_{ij}} \right| \phi \right\rangle \quad (6)$$

This can be reduced to one and two -body integerls that can be computed analytically because we are using Slater-type orbitals[14].

Notice that :

$$\sum_{i < j}^N r_{ij}^{-1} \equiv \sum_{i=j}^N \sum_{j=i+1}^N r_{ij}^{-1} = \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N r_{ij}^{-1} \quad (7)$$

holds the constraint $i < j$ ensures that each electron-electron interaction is counted only one time the same holds for the nucleus-nucleus interaction[15] .Hartree-Fock wave function is taken to be the Slater determinant in order to obey the antisymmetry principle characterizing the fermions or the Pauli exclusion principle [17].

A Slater determinant $|\psi\rangle$, consisting of N orthonormal spin orbits $|\psi_i(j)\rangle$, is defined by

$$\begin{aligned}
|\psi\rangle &= \frac{1}{\sqrt{N!}} \begin{vmatrix} |\psi_1(1)\rangle & |\psi_2(1)\rangle & \dots & |\psi_i(1)\rangle & \dots & |\psi_N(1)\rangle \\ |\psi_1(2)\rangle & |\psi_2(2)\rangle & \dots & |\psi_i(2)\rangle & \dots & |\psi_N(2)\rangle \\ \vdots & \vdots & & \vdots & & \vdots \\ |\psi_1(i)\rangle & |\psi_2(i)\rangle & \dots & |\psi_i(i)\rangle & \dots & |\psi_N(i)\rangle \\ \vdots & \vdots & & \vdots & & \vdots \\ |\psi_1(N)\rangle & |\psi_2(N)\rangle & \dots & |\psi_i(N)\rangle & \dots & |\psi_N(N)\rangle \end{vmatrix} \\
&= \frac{1}{\sqrt{N!}} \hat{A}(\prod_{i=1}^N |\psi_i(i)\rangle) \quad (8)
\end{aligned}$$

$$= \frac{1}{\sqrt{N!}} \sum_{p=1}^{N!} (-1)^p \hat{P}((\prod_{i=1}^N |\psi_i(i)\rangle) \quad (9)$$

$$= \frac{1}{\sqrt{N!}} \sum_{p=1}^{N!} (-1)^p \hat{P}((\prod_{i=1}^N |\psi_i(\hat{P}_i)\rangle) \quad (10)$$

(permutation of the row indices ,i.e. electron coordinates).

$$= \frac{1}{\sqrt{N!}} \sum_{p=1}^{N!} (-1)^p \hat{P}((\prod_{i=1}^N |\psi_i(\hat{P}_i)\rangle) \quad (11)$$

(permutation of the column indices, i.e. spin orbital indices).The factor $(\sqrt{N!})^{-1}$ is normalization constant and it ensures that the normalization condition [15].Using the Hartree-Fock description of a system with N-electrons we write the wave function ψ as

$$\psi = \frac{1}{\sqrt{N!}} \sum_{p=1}^{N!} (-1)^p P(\phi_1, \phi_2, \dots, \phi_N), \quad (12)$$

P being the antisymmetrization operator and $\{\phi_i\}_{i=1}^N$ being a set of spin-orbitals (one-electron functions)[16].

the basis functions are expressed as linear combinations $(x_{p\lambda\alpha})$ by

$$x_{i\lambda\alpha} = \sum_p x_{p\lambda\alpha} c_{pi\lambda} \quad (13)$$

where designates the orbital angular momentum magnitude quantum number and α designates the orbital angular momentum component quantum number (commonly m_l) .this basis function are expressed as products of radial and angular factors[18], $c_{pi\lambda}$ the expansion coefficients[19] The Slater –type functions (STFs) defined by[20]

$$\chi_{nlm}(r, \xi) = R_n(r; \xi) Y_{lm}(\theta, \phi), \quad (14)$$

$$R_n(r; \xi) = \frac{(2\xi)^{n+\frac{1}{2}}}{[\Gamma(2n+1)]^{\frac{1}{2}}} r^{n-1} \exp(-\xi r) \quad (15)$$

where r, θ, ϕ are the stander spherical coordinates, n is the principle quantum number, l is the azimuthal quantum number, m is the magnetic quantum number[21]. $Y_{lm}(\theta, \phi)$ is a spherical harmonic, $\Gamma(x)$ the gamma function, and ξ the orbital exponent. $\Gamma(2n+1)$ simplifies to a factorial $(2n)!$ in this case[20].

3.Atomic properties

3.1 one –electron radial density function $D(r_1)$ and two-electron radial density function $D_2(r_1, r_2)$:

In an N-electron atom ($N \geq 2$), the one-electron radial density $D(r)$ represents the probability density function of finding an electron at a distance r from the coordinate origin, i.e., the nucleus. The density function $D(r)$, normalized to N, is expressible as

$$D(r) = \frac{2}{N-1} \int_0^\infty dr_2 D_2(r, r_2), \quad (16)$$

$$D_2(r_1, r_2) = \frac{N(N-1)}{2} r_1^2 r_2^2 \int ds_1 ds_2 d\Omega_1 d\Omega_2 dx_3, \dots, dx_N |\psi(x_1, \dots, x_N)|^2, \quad (17)$$

is the two-electron radial density function normalized to $\frac{N(N-1)}{2}$, the number of electron pairs. in Eq() $\psi(x_1, \dots, x_N)$ is a normalized N-electron wave function, $x_i = (r_i, s_i)$ is the combined position –spin coordinate of the electron i , and (r_i, Ω_i) is the polar coordinate of the vector r_i the function $D_2(r_1, r_2)$ is the probability density of finding an electron at a radial r_1 and another electron at r_2 simultaneously[22]

3.2 Inter –particle distribution function $f(r_{12})$

The inter–particle distribution function associated with the spin-orbital pair (i,j) is given by [23].

$$f_{ij}(r_{12}) = \int \Gamma_{ij}(r_1, r_2) dr_1 dr_2 \quad (18)$$

Where $\square$ is the level width[24] The function $f(r_{12})$ times the volume $4\pi r_{12}^2 dr_{12}$ is the proportional to the probability density for the particle-particle distance in a system of N electron in the state ψ , and normalized to the number of electron pairs, $\frac{N(N-1)}{2}$. this quantity fully determines the expectation value of the electronic Coulomb repulsion (in Hartree-atomic units used throughout)[25].

3.3 one –particle expectation and inter-particle value:

The one-particle expectation value can be calculated from[26].

$$\langle r_1^n \rangle = \int D_{ij}(r_1) r_1^n dr_1 \quad (19)$$

The inter-particle expectation values can be calculated from[27].

$$\langle r_{12}^n \rangle = \int f_{ij}(r_{12}) r_{12}^n dr_{12} \quad (20)$$

3.4 Standard deviation

The standard deviation of distance of the test electron from the nucleus r_1 is defined as[28].

$$\Delta r_1 = \sqrt{\langle r_1^2 \rangle - \langle r_1 \rangle^2} \quad (21)$$

While the standard deviation of the inter electronic distance of the two electrons, is defined as[29].

$$\Delta r_{12} = \sqrt{\langle r_{12}^2 \rangle - \langle r_{12} \rangle^2} \quad (22)$$

3.5 energy expectation value $\langle E \rangle$:

The energy expectation value associated with the Hamiltonian operator can be written as follows [30].

$$E = \langle \hat{H} \rangle = \int \psi^* \hat{H} \psi dt \quad (23)$$

for the N-electron system is given by:

$$H = -\frac{1}{2} \sum_{i=1}^N (\nabla_i^2 + \sum_{i=1}^N \frac{Z}{r_i} + \sum_{i<j}^N \frac{1}{r_{ij}}) \quad (24)$$

Since $E = T + V_{ee} + V_{ne}$, equation (23) is used to find the expectation value of the kinetic and potential energies , and is given by:

$$\langle T \rangle = \frac{1}{2} \int \psi \left[\sum_{i=1}^N \nabla_i^2 \right] \psi dt \quad (25)$$

$$\langle V \rangle = \int \psi \left[\sum_i^N \frac{Z}{r_i} + \sum_{i<j}^N \frac{1}{r_{ij}} \right] \quad (26)$$

3.5 Nuclear Magnetic Shielding Constant σ_{dia}

Hartree-Fock equations are solved with a Hamiltonian, which takes into account the influence of the magnetic field[31]. the nuclear magnetic shielding constant is determined from the formula[32]:

$$\sigma_d = \frac{1}{3} \alpha^2 \langle \psi | \sum_{i=1}^n (r_i)^{-1} | \psi \rangle \quad (27)$$

We use atomic units($m, \hbar, e=1$)throughout this research;in this units,the fine structure constant $\alpha = \frac{1}{c} \cong 137.036$ [31]

4.Result and discussion

In this research we used the atomic data for Hartree-fock function for iso-electronic of He-atom Clementi and Roetti[33].

Table(1) parameters of the $N_2^{5+} - ion$

n	ξ	C
1	6.45215	0.95445
1	11.69880	0.05228
1	19.74440	-0.00096

Table(2) parameters of the $O^{6+} - ion$

n	ξ	C
1	7.45601	0.96175
1	13.66210	0.04445
1	22.59050	-0.00121

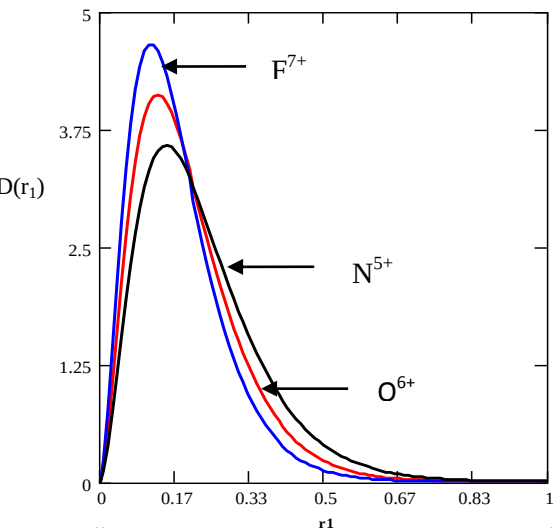
Table(3) parameters of $F^{7+} - ion$

n	ξ	C
1	8.44950	0.96398
1	15.20300	0.04150
1	24.63050	-0.00103

The atomic properties such as inter-particle distribution function $f(r_{12})$, one-particle radial distribution function $D(r_1)$, two-particle radial density function $D(r_1, r_2)$, all expectation values $\langle r_1^n \rangle, \langle r_{12}^n \rangle, \langle V \rangle, \langle T \rangle, \langle E \rangle$ the values of nuclear magnetic shielding constant χ_{dia} were obtained numerically by using Mathcad 2001i.

Each plot in this work was normalized to unity and all result of the expectation values checked according to the normalization condition. Also we used the atomic units in our calculates in this work

We calculated the one-particle radial density function by using equation (15) and table(4) indicated the maximum values of the $D(r_1)$ and values of the positions, from these results we noticed when the atomic number increased the maximum values of $D(r_1)$ was increasing and the values of the position decreased because the effect of nuclear charge increased, Fig(1) and Fig(2) show the relation between $D(r_1)$ and position we found when $r_1 = 0$; $D(r_1) = 0$ and when $r_1 = \infty$, $D(r_1) = 0$ that means the electron was not found in the nucleus or out the orbitals



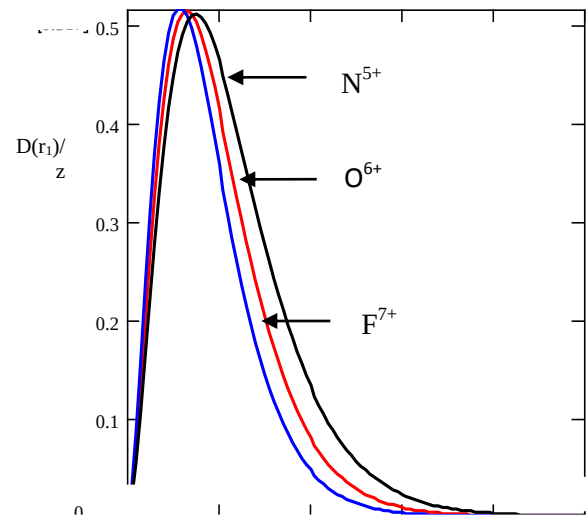
Fig(1)the one- particle radial density distribution function for like-ions of He-atom

Table(4)values of positions and maximum values of one-particle radial density distribution function

Ion	r_1	$D(r_1)$	$D(r_1)/z$
N^{5+}	0.15	3.572	0.510
O^{6+}	0.13	4.114	0.514
F^{7+}	0.11	4.645	0.516

Table (5) inter -particle density distribution function For like-ions of the He-atom

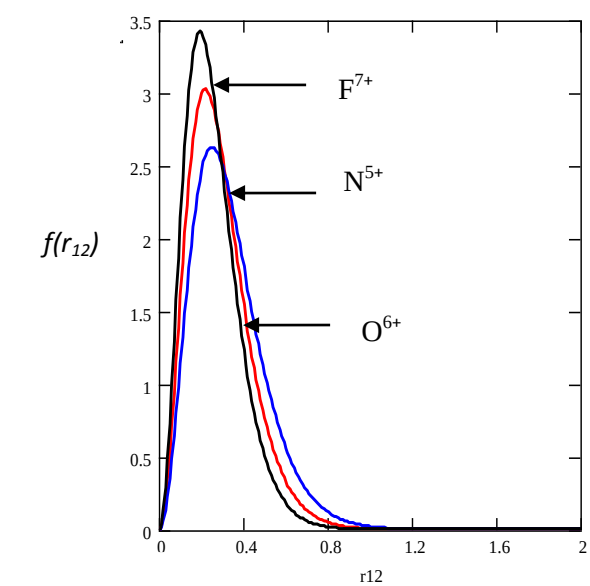
Ion	r_{12}	$f(r_{12})$	$\frac{\chi(\chi_{12})}{\chi}$
N^{5+}	0.375	2.623	0.25
O^{6+}	0.378	3.021	0.22
F^{7+}	0.380	3.419	0.19



Fig(2)the effect atomic number on one- particle radial density distribution function for like-ions He-atom for

The same interpretation was concluded for table (5) and fig(3) and fig(4) where the values of two

particles radiad were compared with the exact results we found large agreement

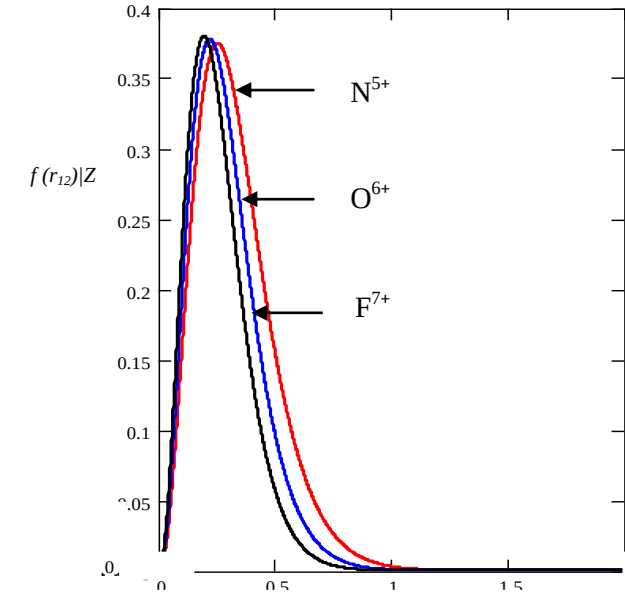


Fig(3) the inter-particle density distribution function for like –ions of the He-atom

density distribution function was calculated by using equation (17).

The one-particle expectation values and inter-particle expectation values were calculated by using equation(18)and(19),while the values of the standard deviation are calculated by using equation(21) and (22) and the results were tabulated in the tables (6)and(7),From these results we noted that as atomic number increases the values of $\langle \square_I^0 \rangle$ increased for (n) negative values and inverse for (n) positive values ,the values.of the standard deviation decreased as atomic number increased and same thing for the values of inter-particle expectation values

The expectation values of energy $\langle \square \rangle$, $\langle \square \rangle$, $\langle \square \rangle$ were calculated by using equation (24)and (25) and the results were tabulated in table (8) ,From these results we noted that as the atomic number increased all the energies increased for all systems because the nuclear charge effect increased and the values 41 the total energy for all systems .



Fig(4) the effect atomic number inter-particle density distribution function for like-ions of the He-atom

Table(6) values of one-particle expectation and standard deviation for like ions of He-atom.

Ion	$\langle \square^{-2} \rangle$	$\langle \square_I^{-1} \rangle$	$\langle \square_I^0 \rangle$	$\langle \square_I^1 \rangle$	$\langle \square_I^2 \rangle$	$\Delta \square I$
N ⁵⁺	90.572	6.687	1	0.226	0.068	0.132
O ⁶⁺	119.488	7.687	1.00001	0.196	0.051	0.114
F ⁷⁺	152.401	8.687	1.00001	0.173	0.040	0.101

Ion	$\langle \square_{I2}^{-2} \rangle$	$\langle \square_{I2}^{-1} \rangle$	$\langle \square_{I2}^0 \rangle$	$\langle \square_{I2}^1 \rangle$	$\langle \square_{I2}^2 \rangle$	$\Delta \square I2$
N ⁵⁺	29.597	4.152	1	0.330	0.137	0.168
O ⁶⁺	39.148	4.777	1.00002	0.287	0.103	0.145
F ⁷⁺	50.031	5.402	1.00003	0.253	0.081	0.128

Table(7) radial expectation values for tow-particle and standard deviation

table (8) expectation values of the potential , Kinetic energy, Hartree-Fock energy and correlation energy and comparison with exact value ,All values are in Hartree unit.

Ion	$\langle V \rangle$	$\langle V_{ee} \rangle$	$\langle V_{ne} \rangle$	$\langle T \rangle$	E_{HF}	$E_{exact}^{(a)}$	E_{corr}
N^{5+}	-89.473	4.152	13.375	44.736	-44.736	-44.781	-0.044
O^{6+}	-118.228	4.777	15.375	59.112	-59.112	-59.156	-0.044

(a)reference (34).

The values of nuclear magnetic shielding constant were calculated by using equation(26) and the results were tabulated in the table(9) ,From these results we noted that the value of the nuclear magnetic shielding constant increased as atomic number increased because the nuclear charge are increased.

Conclusions

- 1) When $r_1=0$ or $r_1=\infty$ the values of $D(r_1)=0$ and when $r_{12}=0$ or $r_{12}=\infty$ the values of the $f(r_{12})=0$
- 2)As Z increased the maximum values of inter-particle distribution function $f(r_{12})$ and one-particle radial density distribution function $D(r_1)$ increased and the positions of these maximum values decreased with Z increased . values and decrease for n positive values.

- 3) As Z increased the values of $\langle \square_I^{\square} \rangle, \langle \square_{I2}^{\square} \rangle$ increased for n negative values and decreased for n positive values.
- 4) For the systems the standard deviation $\Delta \square_I$, $\Delta \square_{I2}$ decreased as Z increased.
- 5) As Z increased, all the energies increased for all systems

Table(9) nuclear magnetic shielding constant

Ions	Nuclear magnetic shielding constant $\square_{dia}$
N^{5+}	1.187×10^{-4}
O^{6+}	1.365×10^{-4}
F^{7+}	1.542×10^{-4}

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