Variational method for ground-state energy of helium atom in N dimensions

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Summary. — The ground-state energy of the N-dimensional helium atom is presented by applying the variational principle. The calculations are made for the unscreened and screened cases. It is shown that, in both cases, the magnitude of the ground-state energy decreases (less negative) as the spatial dimension N increases. For the unscreened case, the relative contribution of the electron-electron interaction term to the ground-state energy is calculated for different dimensions, and it is found that this ratio approaches one half as $N \to \infty$. For the screened case, the effective nuclear charge is computed for different dimensions and its limiting value is found to be $3/2$ in the infinite-dimensional space. In addition, the relative contribution of screening to ground-state energy is calculated in different dimensions and it is shown that it reaches $1/8$ as $N \to \infty$. Furthermore, the asymptotic behavior of ground-state energy, contribution of electron-electron interaction and contribution of screening effect are presented.

PACS `03.65.-w` – Quantum mechanics.
PACS `03.65.Ca` – Formalism.
PACS `03.65.Ta` – Foundations of quantum mechanics; measurement theory.

1. – Introduction

The helium ground-state energy has been a subject of interest for a long time [1-7] and continues to attract the attention of many investigators [8-11]. The variational technique is considered as a powerful tool for estimating the ground-state energy of a quantum system. Over the last few years, this method has been applied to helium atom in different settings: Komasa and Rychlewski [12] considered correlated Gaussian functions in variational calculations to estimate the ground-state energy of helium dimmer, Banerjee [13] and Flores-Riveros *et al.* [14] studied energy spectrum of spherically confined helium atom, Theodorakis *et al.* [15] considered optimization method to find

approximate solutions of field equations, Lobanova *et al.* [16] and Biaye *et al.* [17] used variational method in calculating energies of excited states of helium to illustrate the importance of electron correlation effects. Hydrogen-like systems are considered a prototype of physical problems in N dimensions [18-20] and have an important role in different areas of physics: For example, in quantum field theory [21], in quantum chemistry [22], in quantum computation [23] and in nanotechnology [24]. In addition, the generalization of physical problems to higher space dimensions is useful in random walks [25], in Casimir effect [26], in harmonic oscillators [27-29] and in statistical mechanics [30, 31]. Furthermore, the N-dimensional radial Schrödinger equation has been examined for different kind of potentials [32-36]. In the present paper, we will derive an analytic expression for the ground-state energy for helium atom in N dimensions via the variational method. We do this for two cases: In the first case, we assume the nuclear charge to be unshielded by the electrons, and in the second case we consider screening of the nuclear charge by the electrons. The paper is organized as follows: in sect. **2**, we present some aspects of the N-dimensional hydrogenic system which are relevant to our work. In sect. **3**, we calculate the ground-state energy of helium atom in N dimensions by applying the variational method assuming no screening of the nuclear charge. In sect. **4**, we include the effect of screening on the ground-state energy. Section **5** is devoted for conclusions.

2. – The helium atom in N dimensions: preliminaries

We consider a helium atom which consists of two electrons and a nucleus with a charge Ze (with $Z = 2$). The Hamiltonian for this system (assuming infinite nuclear mass and ignoring fine structure and small corrections) is given by

$$(1) \qquad H = H_0 + V_{ee},$$

where H_0 is the sum of two Hamiltonians for one-electron hydrogenic-like atoms, given by

$$(2) \qquad H_0 = -\frac{\hbar^2}{2m} \left(\nabla_1^2 + \nabla_2^2 \right) - \frac{e^2 Z}{4\pi\varepsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right),$$

and V_{ee} represents the electron-electron interaction which is given by

$$(3) \qquad V_{ee} = \frac{e^2}{4\pi\varepsilon_0} \frac{1}{r_{12}},$$

with $r_{12} = 1/|\vec{r}_1 - \vec{r}_2|$. In the N-dimensional space, the Laplacian operator in the polar coordinates $(r, \theta_1, \theta_2, \ldots, \theta_{N-2}, \varphi)$ of R^N has the form

$$(4) \qquad \nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{(N-1)}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \Omega^2,$$

where Ω^2 is a partial differential operator on the unit hyper-sphere R^{N-1} and whose eigenvalues are $-\ell(\ell + N - 2)$. The angular solutions are the hyper-spherical harmonics $Y_\ell^{\{m\}}$ which depend on $(N-1)$ angular coordinates with ranges $0 \le \theta_j \le \pi$ and $0 \le \varphi \le 2\pi$. Each of these spherical harmonics is determined by $(N-1)$ integers $\ell, m_1, m_2, \ldots, m_{N-2}$ that can assume all values consistent with the inequalities

$\ell \geq m_1 \geq m_2 \geq \ldots \geq |m_{N-2}| \geq 0$. The eigenfunctions of H_0 are the product of the eigenfunctions of the one-electron Schrödinger equation for $\vec{r}_1$ and $\vec{r}_2$ coordinates, namely

$$\Phi^{(0)}(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_1)\psi(\vec{r}_2), \tag{5}$$

where

$$\psi(\vec{r}) = A R_{Nn\ell}(r) Y_\ell^m(\theta_j, \varphi). \quad j = 1, 2, 3, \ldots, N-2. \tag{6}$$

The functions $R_{Nn\ell}(r)$ are the solutions for the radial Schrödinger equation and are given by [37]

$$R_{Nn\ell}(r) = e^{-\rho/2} \rho^\ell L_{(n+\ell+N-3)}^{(2\ell+N-2)}(\rho), \tag{7}$$

where $L(\rho)$ is the associated Laguerre polynomial and $\rho = (8m(-E)/\hbar^2)^{1/2}$. The energy eigenvalues of H_0 are

$$E_{nN}^0 = (E_{nN}^0)_1 + (E_{nN}^0)_2 = \frac{2Z^2}{\left(n + \frac{N-3}{2}\right)^2} E_0, \tag{8}$$

where E_0 is the three-dimensional ground-state energy of a one hydrogen atom that is given by

$$E_0 = -\frac{e^2}{2a(4\pi\varepsilon_0)}, \tag{9}$$

whose value equals $-13.6\,\mathrm{eV}$ and $a = 4\pi\varepsilon_0\hbar^2/me^2$ is the Bohr radius. Since we are interested in the ground-state energy of the helium atom in N dimensions, eq. (8) gives the ground-state energy of H_0 by putting $Z = 2$ and $n = 1$, with the result

$$E_{1N}^0 = \frac{32}{(N-1)^2} E_0. \tag{10}$$

3. – Variational method without screening

In order to find the contribution of the electron-electron interaction term V_{ee} to the ground-state energy, we apply the variational principle by adopting the trial wave function

$$\phi(r_1, r_2) = A \exp\left[\frac{-2Z(r_1 + r_2)}{a(N-1)}\right], \tag{11}$$

where A is a normalization constant. Normalization requirement of the above trial wave function over the two sets of the N-dimensional electron coordinates gives

$$1 = A^2 \int \exp\left[-\frac{4Z(r_1 + r_2)}{a(N-1)}\right] r_1^{N-1} r_2^{N-1} \mathrm{d}r_1 \mathrm{d}r_2. \tag{12}$$

The integration over the r coordinates can be easily carried out by letting $x = 4Zr/a(N-1)$ and using

$$(13) \qquad \int_0^\infty x^{N-1} e^{-x} \mathrm{d}x = \Gamma(N),$$

which immediately gives the value of the constant A, namely

$$(14) \qquad A = \frac{1}{\Gamma(N)} \left[\frac{4Z}{a(N-1)} \right]^N.$$

We apply the variational principle, using the trial wave function given in eq. (11), to find the contribution of V_{ee} to the ground-state energy of the helium atom. This is given by

$$(15) \qquad \langle V_{ee} \rangle = \frac{e^2}{4\pi\varepsilon_0} A^2 \int \frac{1}{|\vec{r}_1 - \vec{r}_2|} \exp\left(-\frac{4Z(r_1+r_2)}{a(N-1)} \right) r_1^{N-1} r_2^{N-1} \mathrm{d}r_1 \mathrm{d}r_2 \mathrm{d}\Omega_1 \mathrm{d}\Omega_2.$$

It is helpful to expand $1/|\vec{r}_1 - \vec{r}_2|$ as [38]

$$(16) \qquad \frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{\ell=0}^\infty \frac{r_<^\ell}{r_>^{\ell+1}} C_\ell^{(N-2)/2}(\cos\theta),$$

where θ is the angle between $\vec{r}_1$ and $\vec{r}_2$ and $C_\ell^{(N-2)/2}$ are the Gegenbauer polynomials. The addition theorem for the M linearly independent hyperspherical harmonics Y_ℓ^m of degree ℓ on the S^{N-1} sphere has the form [39]

$$(17) \qquad C_\ell^{(N-2)/2}(\cos\theta) = \frac{N-2}{(2\ell+N-2)} \Omega(N) \sum_{m=1}^M Y_\ell^m(\Omega_1) Y_\ell^m(\Omega_2),$$

where $\Omega(N) = 2\pi^{N/2}/\Gamma(N/2)$ is the surface area of the N-dimensional unit sphere, and $M = (2\ell+N-2)(\ell+N-3)!/(N-3)!$. Therefore eq. (15) becomes

$$(18) \quad \langle V_{ee} \rangle = \frac{e^2}{4\pi\varepsilon_0} A^2 \sum_{\ell=0}^\infty \sum_m^M \frac{\Omega(N)(N-2)}{(2\ell+N-2)} \int Y_\ell^m(\Omega_1) Y_\ell^m(\Omega_2) \mathrm{d}\Omega_1 \mathrm{d}\Omega_2$$

$$\times \int \exp\left[-\frac{4Z(r_1+r_2)}{a(N-1)} \right] r_1^{N-1} r_2^{N-1} \mathrm{d}r_1 \mathrm{d}r_2$$

$$= \frac{e^2}{4\pi\varepsilon_0} A^2 \int_0^\infty r_1^{N-1} \mathrm{d}r_1 \int_0^\infty r_2^{N-1} \exp\left[-\frac{4Z(r_1+r_2)}{a(N-1)} \right] \frac{1}{r_>}$$

$$= \frac{e^2}{4\pi\varepsilon_0} A^2 \int_0^\infty r_1^{N-1} e^{\lambda r_1} \mathrm{d}r_1 \left[\frac{1}{r_1} \int_0^{r_1} r_2^{N-1} \mathrm{d}r_2 e^{\lambda r_2} + \int_{r_1}^\infty r_2^{N-2} \mathrm{d}r_2 e^{\lambda r_2} \right],$$

where we put $\lambda = -4Z/a(N-1)$ and used the orthonormality of hyperspherical harmonics [39]

$$(19) \qquad \int Y_\ell^{*m}(\Omega) Y_{\ell'}^{m'}(\Omega) \mathrm{d}\Omega = \delta_{\ell\ell'} \delta_{mm'}.$$

Using tables of integrals [40],

$$(20) \qquad \int x^n e^{ax} \mathrm{d}x = e^{ax} \sum_{j=0}^{n} \frac{(-1)^j x^{n-j}}{a^{j+1}} \frac{n!}{(n-j)!} \, ,$$

gives us

$$(21) \quad \int_0^{r_1} r_2^{N-1} \mathrm{d}r_2 e^{\lambda r_2} = \left[e^{\lambda r_1} \sum_{j=0}^{N-1} \frac{(-1)^j (N-1)!}{\lambda^{j+1}(N-1-j)!} r_1^{N-1-j} \right] - \frac{(-1)^{N-1}(N-1)!}{\lambda^N} \, ,$$

$$(22) \quad \int_{r_1}^{\infty} r_2^{N-2} \mathrm{d}r_2 e^{\lambda r_2} = -e^{\lambda r_1} \sum_{j=0}^{N-2} \frac{(-1)^j (N-2)!}{\lambda^{j+1}(N-2-j)!} r_1^{N-2-j} \, ,$$

and

$$(23) \qquad \int_0^{\infty} r_1^{(N-1)} e^{\lambda r_1} \mathrm{d}r_1 = -\frac{(-1)^{N-1}(N-1)!}{\lambda^N} \, .$$

Therefore, after some algebra, we get

$$(24) \quad \frac{1}{r_1} \int_0^{r_1} r_2^{N-1} e^{\lambda r_2} \mathrm{d}r_2 + \int_{r_1}^{\infty} r_2^{N-2} e^{\lambda r_2} \mathrm{d}r_2 = \frac{(-1)^{N-1}(N-1)!}{\lambda^N r_1}(e^{\lambda r_1} - 1)$$

$$+ e^{\lambda r_1} \sum_{j=o}^{N-2} \frac{(-1)^j j (N-2)!}{\lambda^{j+1}(N-1-j)!} r_1^{N-2-j} \, .$$

The integration over r_1, given in eq. (18), is now straightforward with the use of eq. (23) and the result is

$$(25) \qquad \langle V_{ee} \rangle = \frac{e^2}{4\pi\varepsilon_0} A^2 \frac{(-1)^{2N-3}(N-2)!}{\lambda^{2N-1}} \left[(N-1)! \left(1 - \frac{1}{2^{N-1}} \right) \right.$$

$$\left. - \sum_{j=0}^{N-2} \frac{j(2N-3-j)!}{2^{2N-2-j}(N-1-j)!} \right] ,$$

which upon the substitution of A and λ becomes

$$(26) \qquad \langle V_{ee} \rangle = \frac{e^2}{4\pi\varepsilon_0} \left(\frac{4Z}{a} \right) \frac{1}{(N-1)^3(N-2)!} \left[(N-1)! \left(1 - \frac{1}{2^{N-1}} \right) \right.$$

$$\left. - \sum_{j=0}^{N-2} \frac{j(2N-3-j)!}{2^{2N-2-j}(N-1-j)!} \right] .$$

The use of eq. (9) and after little manipulations, the above equation takes the form

$$(27) \qquad \langle V_{ee} \rangle = -\frac{8E_0 Z}{(N-1)^2} \left[(1 - 2^{1-N}) - \frac{1}{2^N (N-1)!} \sum_{j=0}^{N-2} \frac{j(2N-3-j)!}{2^{N-2-j}(N-1-j)!} \right] .$$

TABLE I. – *Ground-state energies in different space dimensions.*

N	E_{1N}^0	$\langle V_{ee} \rangle$	E_{1N}	$|\langle V_{ee} \rangle / E_{1N}^0|$
3	-108.800	34	-74.8	0.3125
4	-48.3555	16.6222	-31.7333	0.34374
5	-27.2	9.88125	-17.3187	0.36328
6	-17.408	6.562	-10.846	0.37695
7	-12.0889	4.6809	-7.408	0.3872
8	-8.88163	3.51058	-5.37104	0.39526
9	-6.8	2.7323	-4.06769	0.40181
10	-5.37284	2.188168	-3.18467	0.407264
11	-4.352	1.79259	-2.5594	0.4119
12	-3.5967	1.49588	-2.1008	0.4159
13	-3.0222	1.26755	-1.7546	0.4194
14	-2.5751	1.08802	-1.4871	0.4225
15	-2.2204	0.94428	-1.27611	0.42527

Our result clearly shows the dependence of the contribution of the electron-electron interaction on the space dimension N. Therefore, using eq. (10), the ground-state energy, which corresponds to the Hamiltonian H, in N-dimensional space is

$$(28) \qquad E_{1N} = E_{1N}^0 + \langle V_{ee} \rangle = \frac{32}{(N-1)^2} E_0 + \langle V_{ee} \rangle.$$

For the three-dimensional case ($N = 3$), eq. (27) gives $\langle V_{ee} \rangle = -5E_0 Z/4$ and thus $E_{1N} = 2Z^2 E_0 - 5E_0 Z/4$, which is an expected result [41]. It is constructive and il-luminating to compute E_{1N}^0, $\langle V_{ee} \rangle$ and E_{1N} for different values of N. We show these results in table I, where we used $E_0 = -13.6\,\text{eV}$ and $Z = 2$. It is interesting to calculate the relative contribution of the electron-electron interaction to the ground-state energy, namely $|\langle V_{ee} \rangle / E_{1N}^0|$, which we include in the last column of table I.

For comparison purposes, we include in the second column of table I the ground-state energy without $\langle V_{ee} \rangle$, which decreases as the space dimension N increases. This is due to the extra repulsive term in the effective potential which arises in dimensions greater than three, whose role has been emphasized by the present author more than a decade ago [37]. Furthermore, the results in the third column show that the contribution of the electron-electron interaction decreases as the space dimension increases. This is so since, as N increases, the repulsive extra term in the effective Hamiltonian tries to repel the electron away from the nucleus and hence the average of $1/r$ decreases. The fourth column gives the ground-state energies including the contribution $\langle V_{ee} \rangle$. The last column is interesting: It shows that the relative contribution of the electron-electron interaction, $|\langle V_{ee} \rangle / E_{1N}^0|$, increases as the space dimension increases. In fact, the terms in the curly bracket in eq. (27) goes to unity as $N \to \infty$ and thus, eq. (27), with $Z = 2$, gives

$$(29) \qquad \langle V_{ee} \rangle = -16E_0/(N-1)^2.$$

Therefore, with the use of eq. (10), the relative contribution of $\langle V_{ee} \rangle$ for large N is

$$(30) \qquad \lim_{N \to \infty} |\langle V_{ee} \rangle / E_{1N}^0| = 1/2.$$

One must notice that though each of $\langle V_{ee} \rangle$ and E_{1N}^0 vanishes as $N \to \infty$, yet their limiting ratio equals exactly one half.

4. – Variational method with screening

In this section, we consider the effect of electron screening of the nuclear charge. On the average, each electron represents a cloud of negative charge which partially shields the nucleus, so that the second electron sees an effective nuclear charge, Z. Therefore, we set Z a variational parameter in our variational calculations for the ground-state energies in different dimensions. We may write the Hamiltonian given in eq. (2) as

$$(31) \quad H = \frac{-\hbar^2}{2m} \left(\nabla_1^2 + \nabla_2^2 \right) - \frac{e^2}{4\pi\varepsilon_0} \left(\frac{Z}{r_1} + \frac{Z}{r_2} \right) + \frac{e^2}{4\pi\varepsilon_0} \left(\frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right).$$

The expectation value of the above Hamiltonian is clearly

$$(32) \qquad \langle H \rangle = 2Z^2 E_N^0 + 2(Z-2) \left(\frac{e^2}{4\pi\varepsilon_0} \right) \left\langle \frac{1}{r} \right\rangle + \langle V_{ee} \rangle,$$

where $E_N^0 = 4E_0/(N-1)^2$ is the ground-state energy of a one hydrogen atom in N dimensions. The expectation value of $1/r$ in the N-dimensional one-particle hydrogenic atom with nuclear charge Z is given by [37]

$$(33) \qquad \left\langle \frac{1}{r} \right\rangle = \frac{Z}{a \left(n + \frac{N-3}{2} \right)^2},$$

which gives for the ground state ($n = 1$)

$$(34) \qquad \frac{e^2}{4\pi\varepsilon_0} \left\langle \frac{1}{r} \right\rangle = \frac{e^2}{4\pi\varepsilon_0 a} \frac{4Z}{(N-1)^2} = -2Z E_N^0.$$

$\langle V_{ee} \rangle$ is given by eq. (27) which can be written as

$$(35) \qquad \langle V_{ee} \rangle = -2Z E_N^0 \left[(1 - 2^{1-N}) - \frac{1}{2^N (N-1)!} \sum_{j=0}^{N-2} \frac{j(2N-3-j)!}{2^{N-2-j}(N-1-j)!} \right].$$

The substitution of eqs. (34) and (35) into eq. (32) yields

$$(36) \qquad \langle H \rangle = \left(-2Z^2 + 8Z - 2Z \left[(1 - 2^{1-N}) \right. \right.$$
$$\left. \left. - \frac{1}{2^N (N-1)!} \sum_{j=0}^{N-2} \frac{j(2N-3-j)!}{2^{N-2-j}(N-1-j)!} \right] \right) E_N^0.$$

TABLE II. – *Effective charge Z, ground-state energy with screening, $\langle H \rangle$ and its deviation and percentage from that without screening.*

N	Z	$\langle H \rangle$	$\|\langle H \rangle - E_{1N}\|$	$\|\frac{\langle H \rangle - E_{1N}}{E_{1N}}\|100\%$
3	1.68750	−78.29	3.49	4.665
4	1.65625	−33.16180	1.4285	4.501
5	1.63672	−18.21617	0.89747	5.182
6	1.62300	−11.46373	0.6177	5.695
7	1.61279	−7.86111	0.4531	6.116
8	1.60474	−5.71795	0.3469	6.459
9	1.59819	−4.34216	0.2744	6.747
10	1.59273	−3.40746	0.2228	6.996
11	1.58809	−2.74395	0.18459	7.2125
12	1.58409	−2.25634	0.1555	7.404
13	1.58059	−1.88758	0.1329	7.578
14	1.57749	−1.60205	0.1149	7.7297
15	1.57472	−1.37652	0.10041	7.86817

We minimize $\langle H \rangle$ with respect to Z by setting $\frac{\partial}{\partial Z}\langle H \rangle = 0$ which immediately gives

$$(37) \qquad Z = 2 - \frac{1}{2}\left[(1 - 2^{1-N}) - \frac{1}{2^N(N-1)!}\sum_{j=0}^{N-2}\frac{j(2N-3-j)!}{2^{N-2-j}(N-1-j)!}\right].$$

Clearly, the above equation shows that the effective nuclear charge which is seen by the electron depends on the space dimension N, and for the three-dimensional space ($N = 3$) it yields an effective charge $Z = 27/16 = 1.6875$. With the help of eq. (37), it is tempting to calculate the effective nuclear charge Z, which minimizes $\langle H \rangle$, in different space dimensions. Then eq. (36) can be used to calculate the minimum of $\langle H \rangle$, which is just the ground-state energy that includes the screening effect. We also calculate the contribution of screening, $|\langle H \rangle - E_{1N}|$, and its percentage, $|\frac{\langle H \rangle - E_{1N}}{E_{1N}}|100\%$, to the ground-state energy. These results are presented in table II.

The results in table II show that as the space dimension N increases, the effective charge Z decreases (*i.e.* screening increases) and the corresponding ground-state energy, $\langle H \rangle$, decreases in magnitude (becomes less bound). In addition, comparison of column three in table II with that in table I shows that the ground-state energy with screening is more negative than the ground-state energy, E_{1N}, without screening. Furthermore, it is worth noticing that the ratio $|\frac{\langle H \rangle - E_{1N}}{E_{1N}}|$ increases as N increases. It is interesting to examine the very large N limit: As mentioned earlier, the curly bracket in eq. (27) goes to unity and thus eq. (37) yields an effective charge $Z = 3/2$, which upon its substitution into eq. (36), we get $\langle H \rangle = 18E_0/(N-1)^2$. As was shown in the previous section, the asymptotic behavior of the ground-state energy is $E_{1N} = 16E_0/(N-1)^2$ and therefore the ratio $|\frac{\langle H \rangle - E_{1N}}{E_{1N}}| = 1/8$ as $N \to \infty$, which represents the relative contribution of screening to the ground-state energy of the helium atom in the infinite-dimensional space.

5. – Conclusions

The variational method has been used to estimate the ground-state energy of an N-dimensional helium atom. This has been done for two cases: the first without screening and the second with screening. In the first case, the contribution of the electron-electron interaction term, $\langle V_{ee} \rangle$, to the ground-state energy, was shown to depend on the space dimension. Thus the ground-state energy decreases in magnitude (less negative) as N increases and it asymptotically behaves as $16E_0/N^2$. Our results also show that the relative contribution of V_{ee} to the ground-state energy E_{1N} increases as N increases and it approaches a value of one half in the infinite-dimensional space ($N \rightarrow \infty$) despite the vanishing limiting value of each of $\langle V_{ee} \rangle$ and E_{1N} in that limit. In the second case, the effective nuclear charge, due to electron screening, and its effect on the ground-state energy, were calculated in different dimensions. The results show that as N increases, the effective nuclear charge Z decreases (*i.e.* screening increases) and it approaches the value $3/2$ as $N \rightarrow \infty$, and the ground-state energy $\langle H \rangle$ decreases in magnitude and it behaves asymptotically as $18E_0/N^2$. It was also shown that the relative contribution of screening increases with increasing N and it approaches the value $1/8$ as $N \rightarrow \infty$.

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