Energy of a finite three-dimensional electron gas of spinless electrons

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We study a finite three-dimensional electron gas system consisting of an arbitrary number of electrons embedded in a finite cubic domain. The electrons are treated as spinless particles implying that the system under consideration represents a fully spin-polarized Fermi quantum phase of electrons. The cubic region is uniformly filled with a positive background that ensures overall charge neutrality. We apply a Hartree-Fock approach that starts with a Slater determinant wave function of normalized plane wave orbitals. The treatment enables us to obtain the energy per particle of the finite system at any given number of electrons. The potential (exchange) energy is conveniently obtained by simplifying the calculation of the ensuing two-particle integrals over the finite cubic domain in terms of expressions that involve compact analytic auxiliary functions. Results are provided for both the kinetic and potential energy per particle for various numbers of electrons. It is shown that the kinetic and the potential energy per particle converge towards their bulk thermodynamic limit values in a non-monotonic way as a function of the number of particles. The results derived may apply to finite systems of delocalized electrons in alkali metal nanoclusters in which the positive ionic core is approximated as a cubic jellium region.

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I. INTRODUCTION

An infinite (bulk) three-dimensional electron gas (3DEG) model represents a system of N electrons contained in a space region with volume, V under the understanding that electron number density, $\rho_0 = N/V$ is finite in the thermodynamic limit of $N \to \infty$ and $V \to \infty$. One commonly assumes that the electrons are immersed in a background of uniformly distributed neutralizing positive charge (the jellium approximation). This way the whole system is guaranteed to be charge neutral. Work over many years has shed light on various properties of infinite 3DEG systems in the thermodynamic limit for a wide range of densities [1–8]. While studies of bulk properties of a 3DEG system are still of great relevance, recent progress in nanoscience and nanotechnology [9–11] has stimulated interest at the exactly opposite direction of small finite systems with few electrons in semiconductor quantum dots [12–18] or in metal nanoclusters [19].

In particular, studies of metal nanoclusters composed of less than a few hundred atoms have attracted a considerable interest over the last four decades [19]. The key subject of metal clusters research is to observe and quantify the influence of various finite-size effects on the physical properties of the system. However, past studies of metal clusters have shown that ab-initio calculations of such systems are very difficult [20–22]. Fortunately, it was found that various approximate methods work well for such systems and, thus, one can considerably simplify the calculations. A successful example of such methods is the jellium model in which a metal cluster is seen as made up of two constituent parts. One part is the ionic background (the core) whose positive charge is uniformly distributed over a given volume and the second part consists of delocalized valence electrons the feel the effect of the background. This model was used to explain many properties of alkali metal clusters [23, 24]. For such a case, it was assumed that the positive charge of the ionic core is uniformly spread over a given region of space. For instance, the observation of so-called electronic magic numbers [25] in certain metal nanoclusters was easily explained with a spherical jellium model of this nature. This means that the jellium model and its numerous refinements can be succesfully applied in the field of metal cluster physics [26]. Together with the simple spherical shape, it is also of great interest to study the electron's properties in jellium systems where the neutralizing background has many other different shapes [27]. In particular, background polyhedral shapes like octahedron, decahedron, etc. have been frequently used in numerical electronic structure calculations. For these choices, it is obvious that only the cubic shape is simple enough to allow for an analytic treatment of the problem (and even in this case up to a certain point). The layout specified above represents the motivation of this work where the focus of our attention is on the behavior and the properties of a finite 3DEG system consisting of an arbitrary number of N electrons in a finite cubic jellium background.

For this study, we adopt the Hartree-Fock (HF) approximation method which has proven its versatility in the context of an electron gas system in a uniform jellium background. In such a case, the underlying idea of the approach is to, basically, describe the system of electrons by a Slater determinant wave function of normalized plane wave orbitals [28]. Within this framework, the energy of a 3DEG system consists of two competing terms, kinetic

energy and potential (exchange) energy. Other energy terms arise from more elaborate calculations that go beyond the HF method. These additional energy terms represent the correlation energy and are more difficult to obtain [29–33]. Studies of alkali metal clusters of electrons in a positive ionic core have proven the validity of the HF approximation or similar variants [34] as a good first approximation even for the case of small finite systems of electrons in a jellium background. For example, even ultra-small electron-gas jellium clusters with 2 to 22 electrons has been successfully treated in the HF approximation by using a plane-wave basis as shown in the work of Ref.[26] where a deformable jellium background was employed. The HF method has its limitations since the mean field approximation is implied and the method neglects the Coulomb interaction between the electrons. However, the quantum electron exchange effect is accounted for exactly in the HF method.

The neglect of the Coulomb interaction between electrons is a well-known weakness of the method but any attempt to add interaction effects to a many-electron wave function generally leads to a problem that can be handled only via numerical treatments using sophisticated simulation methods, for example, variational Monte Carlo (MC) simulations with an added Jastrow factor in the wave function, density functional theory (DFT) calculations, etc. From this standpoint, the results presented in this work can, in no way, be expected to be as accurate as the results obtained via robust ab-initio methods (DFT, etc.) which are the preferred choices in the wider materials research community. The importance of this work stands on the fact that there are so few many-body problems that are exactly solvable that any model that allows an analytical treatment (up to a certain point) is worth investigating [35–38]. Analytic results, if available, represent useful benchmarks to test the validity of other more powerful tools and methods.

In a nutshell, despite its shortcomings, the HF method works reasonably well for various systems, it represents a good starting basis due to its simplicity and allows an analytical treatment of the problem up to certain degree. For all these reasons we employ it to calculate the energy of a finite 3DEG model in a cubic jellium background. We employ convenient mathematical transformations that enable us to obtain compact mathematical expressions for the kinetic and the potential (exchange) energy of such a finite 3DEG system. The total energy for systems with any given number of electrons is obtained by combining the result of the potential energy with that of the kinetic energy (that is easier to obtain). Throughout this work, for the sake of simplicity, we assume that the system of electrons is fully spin-polarized (spinless).

The article is organized as follows. In Section II we explain the model and the formalism adopted. In Section III we report the key results of the work and discuss the findings. In Section IV we briefly summarize the work and provide some concluding remarks.

II. MODEL AND ENERGY OF A FINITE 3DEG OF SPINLESS ELECTRONS

We consider a finite 3DEG model consisting of N spinless electrons confined in a positive uniformly charged three-dimensional cubic background represented by the region:

$$\Omega : \left\{ -\frac{L}{2} \leq x, y, z \leq +\frac{L}{2} \right\} \ . \tag{1}$$

For this choice of the geometry, the uniform density of the system is:

$$\rho_0 = \frac{N}{L^3} \ . \tag{2}$$

The Hamiltonian reads:

$$\hat{H} = \hat{T} + \hat{U} \ , \tag{3}$$

where $\hat{T}$ and $\hat{U}$ are, respectively, the kinetic and potential energy operators. The kinetic energy operator is written as

$$\hat{T} = \sum_{i=1}^{N} \frac{\hat{\vec{p}}_i^{\,2}}{2\,m} \ , \tag{4}$$

where $\hat{\vec{p}}_i$ is the quantum linear momentum operator of the i-th electron, m is the electron's mass and N is the finite number of electrons in the system. The potential energy operator is written as a sum of three terms

$$\hat{U} = \hat{U}_{ee} + \hat{U}_{eb} + \hat{U}_{bb} \ , \tag{5}$$

where $\hat{U}_{ee}$ represents the electron-electron (ee) interaction energy operator, $\hat{U}_{eb}$ represents the electron-background (eb) interaction energy operator and $\hat{U}_{bb}$ is the background-background (bb) Coulomb self-energy of the cubic jellium region that is a constant. In a more explicit form:

$$\hat{U}_{ee} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \hat{v}(|\vec{r}_i - \vec{r}_j|) \ . \tag{6}$$

A standard Coulomb interaction potential between point charges is assumed:

$$\hat{v}(|\vec{r}_i - \vec{r}_j|) = \frac{k_e\, e^2}{r_{ij}} \ , \tag{7}$$

where $-e$ ($e > 0$) is electron's charge, $r_{ij} = |\vec{r}_i - \vec{r}_j|$ is the separation distance between a pair of electrons and k_e is Coulomb's electric constant. It is easy to verify that the other two potential energy operator terms may be written, respectively, as:

$$\hat{U}_{eb} = -\rho_0 \sum_{i=1}^{N} \int_{\Omega} d^3 r' \, \hat{v}(|\vec{r}_i - \vec{r}\,'|) \ , \tag{8}$$

and

$$\hat{U}_{bb} = \frac{\rho_0^2}{2} \int_\Omega d^3r \int_\Omega d^3r' \; \hat{v}(|\vec{r} - \vec{r}\,'|) \; . \tag{9}$$

Within the framework of a HF approach, one can write a suitable normalized N-particle Fermi wave function as a Slater determinant of the form:

$$|\Psi\rangle = \frac{1}{\sqrt{N!}} \, Det\Big\{ \psi_{\alpha_1}(\vec{r}_1), \ldots, \psi_{\alpha_N}(\vec{r}_N) \Big\} \; , \tag{10}$$

constructed out of ortho-normalized single-particle space-spin orbitals where $\{\alpha_i\}$ represent the collective set of quantum numbers that define the i-th state of a particle. Periodic boundary conditions (PBC) are imposed in all directions. As a result, one has:

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{L^3}} \, e^{\, i \, \vec{k} \, \vec{r}} \; , \tag{11}$$

where $\vec{k} = (2\,\pi/L)\,\vec{n}$ and $\vec{n} = (n_x, n_y, n_z)$ has allowed values that correspond to $n_{x,y,z} = 0, \pm 1, \pm 2, \ldots$. The formalism adopted and the calculation of kinetic and potential energy for a spinless finite 3DEG system follows the same approach as that applied to its finite two-dimensional electron gas (2DEG) counterpart [39]. The expectation value of operator $\hat{U}_{ee}$ with respect to the given Slater determinant wave function, namely, $U_{ee} = \langle\Psi|\hat{U}_{ee}|\Psi\rangle/\langle\Psi|\Psi\rangle$, can be written as:

$$U_{ee} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \Big[\langle i\, j|\hat{v}|i\, j\rangle - \langle i\, j|\hat{v}|j\, i\rangle \Big] \; . \tag{12}$$

In compact notation:

$$\langle i\, j|\hat{v}|i\, j\rangle = \int_\Omega d^3r_1 \int_\Omega d^3r_2 \, \psi_i(\vec{r}_1)^* \, \psi_j(\vec{r}_2)^* \, \hat{v}(r_{12}) \, \psi_i(\vec{r}_1) \, \psi_j(\vec{r}_2) \tag{13}$$

where asterisk means complex conjugation. The first term in Eq.(12) is known as the (direct) Coulomb energy while the second one is the exchange counterpart. One has $\langle i\, i|\hat{v}|i\, i\rangle - \langle i\, i|\hat{v}|i\, i\rangle = 0$ when $j = i$ in Eq.(12). Thus, by dropping the $j \neq i$ restriction from Eq.(12), one obtains:

$$U_{ee} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \Big[\langle i\, j|\hat{v}|i\, j\rangle - \langle i\, j|\hat{v}|j\, i\rangle \Big] \; . \tag{14}$$

With some care, one can verify the correctness of the following result:

$$\begin{aligned} U_{ee} \; = \; & \frac{1}{2} \int_\Omega d^3r_1 \int_\Omega d^3r_2 \, \rho(\vec{r}_1) \, \hat{v}(r_{12}) \, \rho(\vec{r}_2) \\ & - \frac{1}{2} \int_\Omega d^3r_1 \int_\Omega d^3r_2 \, |\rho(\vec{r}_1, \vec{r}_2)|^2 \, \hat{v}(r_{12}) \; , \end{aligned} \tag{15}$$

where $\rho(\vec{r}_i)$ $(i = 1, 2)$ is known as the one-particle density function and $\rho(\vec{r}_1, \vec{r}_2)$ is the so-called one-particle density matrix. For the case of an ortho-normalized Slater determinant wave function of plane waves as in Eq.(10), one explicitly has:

$$\rho(\vec{r}) = \sum_{j=1}^{N} |\psi_{\vec{k}_j}(\vec{r})|^2 \tag{16}$$

and

$$\rho(\vec{r}_1, \vec{r}_2) = \sum_{j=1}^{N} \psi_{\vec{k}_j}(\vec{r}_1)^* \, \psi_{\vec{k}_j}(\vec{r}_2) \; . \tag{17}$$

Note that $\rho(\vec{r}_1 = \vec{r}, \vec{r}_2 = \vec{r}) = \rho(\vec{r})$. The result in Eq.(15) is valid only for the present calculation of the expectation value of the ee interaction energy operator (a two-body operator) with respect to a ortho-normalized Slater determinant wave function of plane waves.

However, quantities such as the one-particle density function, etc, can be quite generally defined for any given arbitrary wave function (not necessarily a Slater determinant wave function). For example, the general definition for the one-particle density function is:

$$\rho(\vec{r}_1) = N \, \frac{\int d^3r_2 \cdots \int d^3r_N \, |\Psi|^2}{\langle\Psi|\Psi\rangle} \; , \tag{18}$$

where $|\Psi\rangle = \Psi(\vec{r}_1, \ldots, \vec{r}_N)$ can be any given arbitrary wave function that describes a system of N particles. The corresponding expression for the one-particle density matrix is written as:

$$\rho(\vec{r}_1, \vec{r}_1{}') = N \, \frac{\int d^3r_2 \cdots \int d^3r_N \, \Psi(\vec{r}_1, \ldots, \vec{r}_N)^* \, \Psi(\vec{r}_1{}', \ldots, \vec{r}_N)}{\langle\Psi|\Psi\rangle} \; . \tag{19}$$

Such a formalism is explained in detail in Ref.[40] for the case of a one-dimensional electron gas (1DEG) and many definitions found there can readily be generalized (with proper modification of notation) to both 2DEG and 3DEG systems.

Similarly, the expectation value of $\hat{U}_{eb}$ with respect to the given Slater determinant wave function, namely U_{eb}, can be written as:

$$U_{eb} = -\rho_0 \int_\Omega d^3r_1 \, \rho(\vec{r}_1) \int_\Omega d^3r_2 \, \hat{v}(r_{12}) \; . \tag{20}$$

By combining all the three potential energy terms together, one can write the total potential energy (or, more precisely, the quantum expectation value of its corresponding operator with respect to the given Slater determinant wave function) for a fully spin-polarized (spinless) finite 3DEG system as:

$$\begin{aligned} U \; = \; & \frac{1}{2} \int_\Omega d^3r_1 \int_\Omega d^3r_2 \, \Big[\rho(\vec{r}_1) - \rho_0 \Big] \, \hat{v}(r_{12}) \, \Big[\rho(\vec{r}_2) - \rho_0 \Big] \\ & - \frac{1}{2} \int_\Omega d^3r_1 \int_\Omega d^3r_2 \, |\rho(\vec{r}_1, \vec{r}_2)|^2 \, \hat{v}(r_{12}) \; . \end{aligned} \tag{21}$$

Note that the values of the one-particle density function at any location $\vec{r}_1$ or $\vec{r}_2$ are always ρ_0, namely:

$$\rho(\vec{r}_1) = \rho(\vec{r}_2) = \rho_0 \; . \tag{22}$$

As a result, the expression in Eq.(21) reduces to:

$$U = -\frac{1}{2}\int_{\Omega} d^3r_1 \int_{\Omega} d^3r_2\, |\rho(\vec{r}_1,\vec{r}_2)|^2\, \hat{v}(r_{12}) \ . \tag{23}$$

One can explicitly write the total potential energy of the system with help from Eq.(17) as:

$$U = -\frac{k_e\, e^2}{2}\, \frac{1}{L^6} \sum_{i=1}^{N}\sum_{j=1}^{N} \int_{\Omega} d^3r_1 \int_{\Omega} d^3r_2\, \frac{e^{\,i\,(\vec{k}_i-\vec{k}_j)\,(\vec{r}_1-\vec{r}_2)}}{|\vec{r}_1-\vec{r}_2|} \ , \tag{24}$$

where Ω is the cubic domain of integration. The calculation of the quantity in Eq.(24) involves a two-electron multi-dimensional integral of the form:

$$I(\vec{k}) = \int_{\Omega} d^3r_1 \int_{\Omega} d^3r_2\, \frac{e^{\,i\,\vec{k}\,(\vec{r}_1-\vec{r}_2)}}{|\vec{r}_1-\vec{r}_2|} \ , \tag{25}$$

where, in this case, $\vec{k}$ denotes an arbitrary vector. It can be shown that the quantity in Eq.(25) can be written as a simple one-dimensional integral. To do so, one first uses the following transformation [41] to write $\frac{1}{|\vec{r}_1-\vec{r}_2|} = \frac{2}{\sqrt{\pi}}\int_0^{\infty} du\, e^{-u^2\,(\vec{r}_1-\vec{r}_2)^2}$. By substituting the expression above for $1/|\vec{r}_1-\vec{r}_2|$ into Eq.(25) one obtains:

$$I(\vec{k}) = \frac{2}{\sqrt{\pi}} \int_0^{\infty} du \int_{\Omega} d^3r_1 \int_{\Omega} d^3r_2\ e^{\,i\,\vec{k}\,(\vec{r}_1-\vec{r}_2)-u^2\,(\vec{r}_1-\vec{r}_2)^2} \ . \tag{26}$$

The next step is to write the quantity in Eq.(26) in such a way as to decouple the integrals over variables x_i from those over y_i and z_i. For simplicity, one introduces dimensionless variables: $X_i = x_i/L$, $Y_i = y_i/L$, $Z_i = z_i/L$, $t = u\,L$ and $\vec{q} = \vec{k}\,L$ where $i = 1$ and 2. After some algebra, the final result becomes:

$$I(\vec{q}) = \frac{2\,L^5}{\sqrt{\pi}} \int_0^{\infty} dt\ F(t,q_x)\ F(t,q_y)\ F(t,q_z) \ , \tag{27}$$

where $F(t,a)$ represents the following auxiliary function:

$$F(t,a) = \int_{-1/2}^{+1/2} dx \int_{-1/2}^{+1/2} dy\ e^{\,i\,a\,(x-y)-t^2\,(x-y)^2} \ . \tag{28}$$

This is the same function encountered in an earlier study of a finite 2DEG system where an exact analytic expression for it was also provided [39]. When $a = 0$ the function in Eq.(28) becomes:

$$F(t,0) = \sqrt{\pi}\, \frac{erf(t)}{t} + \frac{e^{-t^2}-1}{t^2} \ , \tag{29}$$

where $erf(t)$ is an error function.

The total kinetic energy for the system of N electrons is written as:

$$T = \frac{\hbar^2}{2\,m} \left(\frac{2\pi}{L}\right)^2 \sum_{i=1}^{N} |\vec{n}_i|^2 \ , \tag{30}$$

where the set of quantum numbers, $\vec{n} = (n_x, n_y, n_z)$ represents a given quantum state. Table. I displays the structure of the one-electron kinetic energies and the corresponding quantum states for a fully spin-polarized (spinless) 3DEG system with up to $N = 365$ electrons.

III. RESULTS

We now focus our attention on the calculation of the energy of a given finite 3DEG system where the number of spinless electrons has values of N as the ones listed in Table. I. These values of N yield completely filled energy shells. By using the result in Eq.(27), we write the expression for the total potential energy, namely, the quantitity in Eq.(24) as:

$$U = -\frac{k_e\, e^2}{L}\, \frac{1}{\sqrt{\pi}} \sum_{i=1}^{N}\sum_{j=1}^{N} R\Big(q_{ix}-q_{jx}, q_{iy}-q_{jy}, q_{iz}-q_{jz}\Big) \ , \tag{31}$$

where

$$R(a,b,c) = \int_0^{\infty} dt\, F(t,a)\, F(t,b)\, F(t,c) \ , \tag{32}$$

and $\vec{q}_i = \vec{k}_i\, L = 2\,\pi\,\vec{n}_i$, ($\vec{q}_j = \vec{k}_j\, L = 2\,\pi\,\vec{n}_j$). As a result, $\vec{q}_i - \vec{q}_j = 2\,\pi\,(\vec{n}_i - \vec{n}_j)$ where one should recall that:

$$\vec{n} = (n_x, n_y, n_z) \quad ; \quad n_{x,y,z} = 0, \pm 1, \pm 2, \ldots \tag{33}$$

For a fixed density, the total potential energy of the system scales with the number N of electrons. This means that the appropriate quantity to calculate is the potential energy per particle, U/N. For a fixed density, any change of the number of electrons in the system is reciprocated by a variation of the length of the cubic box which should scale with N as:

$$L = \left(\frac{N}{\rho_0}\right)^{1/3} \ . \tag{34}$$

One uses the fact that $1/L = (\rho_0/N)^{1/3}$ to write the potential energy per particle as:

$$u(N) = \frac{U}{N} = -\frac{k_e\, e^2}{N^{4/3}}\, \frac{{\rho_0}^{1/3}}{\sqrt{\pi}} \sum_{i=1}^{N}\sum_{j=1}^{N} R\Big(q_{ix}-q_{jx}, q_{iy}-q_{jy}, q_{iz}-q_{jz}\Big) \ . \tag{35}$$

The quantity $u(N)$ in Eq.(35) can be compared to the corresponding value of the potential energy per particle for an infinite system which is expressed solely in terms of the density:

$$u(N\to\infty) = \lim_{N\to\infty} \frac{U}{N} = -k_e e^2\, \frac{3}{4\,\pi}\, (6\,\pi^2\,\rho_0)^{1/3} \ . \tag{36}$$

One must recall that the Fermi wave vector, k_F for a fully spin-polarized (spinless) 3DEG system is:

$$k_F^3 = 6\,\pi^2 \rho_0 \ . \tag{37}$$

After some straightforward transformations one obtains:

TABLE I: Roman-numbered shells in increasing order of the kinetic energy, $E_{n_x,n_y,n_z} = \frac{\hbar^2}{2\,m}\,\left(\frac{2\,\pi}{L}\right)^2\,(n_x^2+n_y^2+n_z^2)$, degeneracy of each energy shell (N_s), total number of electrons (N) for a spinless 3DEG system and corresponding quantum states, $\vec{n} = (n_x, n_y, n_z)$.

Shell	$n_x^2+n_y^2+n_z^2$	N_s	N	$\vec{n} = (n_x, n_y, n_z)$
I	0	1	1	$(0,0,0)$
II	1	6	7	$(\pm1,0,0),(0,\pm1,0),(0,0,\pm1)$
III	2	12	19	$(\pm1,\pm1,0),(\pm1,0,\pm1),(0,\pm1,\pm1)$
IV	3	8	27	$(\pm1,\pm1,\pm1)$
V	4	6	33	$(\pm2,0,0),(0,\pm2,0),(0,0,\pm2)$
VI	5	24	57	$(\pm2,\pm1,0),(\pm2,0,\pm1),(0,\pm2,\pm1),(\pm1,\pm2,0),(\pm1,0,\pm2),(0,\pm1,\pm2)$
VII	6	24	81	$(\pm2,\pm1,\pm1),(\pm1,\pm2,\pm1),(\pm1,\pm1,\pm2)$
VIII	8	12	93	$(\pm2,\pm2,0),(\pm2,0,\pm2),(0,\pm2,\pm2)$
IX	9	30	123	$(\pm2,\pm2,\pm1),(\pm2,\pm1,\pm2),(\pm1,\pm2,\pm2),(\pm3,0,0),(0,\pm3,0),(0,0,\pm3)$
X	10	24	147	$(\pm3,\pm1,0),(\pm3,0,\pm1),(0,\pm3,\pm1),(\pm1,\pm3,0),(\pm1,0,\pm3),(0,\pm1,\pm3)$
XI	11	24	171	$(\pm3,\pm1,\pm1),(\pm1,\pm3,\pm1),(\pm1,\pm1,\pm3)$
XII	12	8	179	$(\pm2,\pm2,\pm2)$
XIII	13	24	203	$(\pm3,\pm2,0),(\pm3,0,\pm2),(0,\pm3,\pm2),(\pm2,\pm3,0),(\pm2,0,\pm3),(0,\pm2,\pm3)$
XIV	14	48	251	$(\pm3,\pm2,\pm1),(\pm3,\pm1,\pm2),(\pm1,\pm3,\pm2),(\pm2,\pm3,\pm1),(\pm2,\pm1,\pm3),(\pm1,\pm2,\pm3)$
XV	16	6	257	$(\pm4,0,0),(0,\pm4,0),(0,0,\pm4)$
XVI	17	48	305	$(\pm4,\pm1,0),(\pm4,0,\pm1),(0,\pm4,\pm1),(\pm1,\pm4,0),(\pm1,0,\pm4),(0,\pm1,\pm4),$ $(\pm3,\pm2,\pm2),(\pm2,\pm3,\pm2),(\pm2,\pm2,\pm3)$
XVII	18	36	341	$(\pm4,\pm1,\pm1),(\pm1,\pm4,\pm1),(\pm1,\pm1,\pm4),(\pm3,\pm3,0),(\pm3,0,\pm3),(0,\pm3,\pm3)$
XVIII	19	24	365	$(\pm3,\pm3,\pm1),(\pm3,\pm1,\pm3),(\pm1,\pm3,\pm3)$

$$\frac{u(N)}{u(N\to\infty)} = \frac{4\,\sqrt{\pi}}{3}\,\frac{1}{(6\,\pi^2)^{1/3}}\,\frac{1}{N^{4/3}}\,\sum_{i=1}^{N}\sum_{j=1}^{N} R\Big(q_{ix}-q_{jx}, q_{iy}-q_{jy}, q_{iz}-q_{jz}\Big)\;. \tag{38}$$

One can write the expression in Eq.(38) in a more convenient form as:

$$\frac{u(N)}{u(N\to\infty)} = \frac{4\,\sqrt{\pi}}{3}\,\frac{1}{(6\,\pi^2)^{1/3}}\,\frac{1}{N^{4/3}}\,\left[N\,R(0,0,0) + 2\,\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} R\Big(q_{ix}-q_{jx}, q_{iy}-q_{jy}, q_{iz}-q_{jz}\Big)\right]\;, \tag{39}$$

where

$$R(0,0,0) = \int_0^\infty dt\,F[t,0]^3\;. \tag{40}$$

The quantity, $R(0,0,0)$ in Eq.(40) can be calculated exactly if one choses to do so. The function $F(t,0)$ is given in Eq.(29). The integral in the right-hand-side of Eq.(40) is calculated exactly in Ref.[42] and is closely related to the expression for the Coulomb self-energy of a uniformly charged three-dimensional cube. The ratio of the finite potential energy per particle relative to its bulk counterpart, $u(N)/u(N\to\infty)$ is shown in Fig. 1. The results indicate that the value of the potential energy per particle, $u(N)$ tends quite slowly toward its bulk value in the thermodynamic limit, $u(N\to\infty)$ as N increases. An interesting observation is that the thermodynamic limit value of the potential energy is not reached in a monotonic way. The results obtained clearly suggest that $u(N)$ is a non-monotonic function of N. Furthermore, the cal-

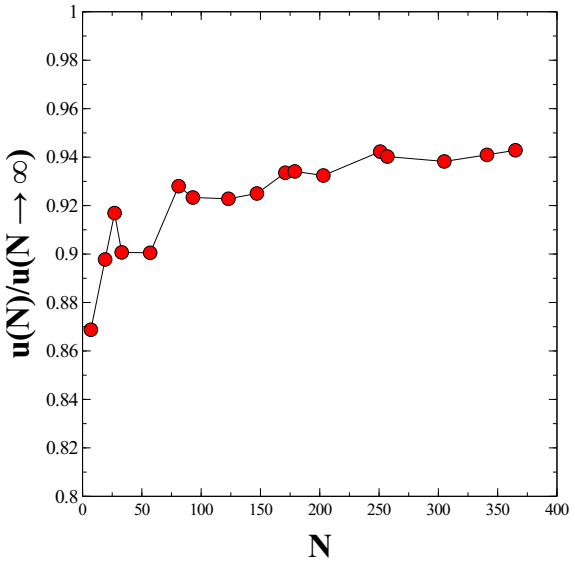

FIG. 1: Dependence of the potential energy per particle relative to its bulk thermodynamic value, $u(N)/u(N\to\infty)$ as a function of the number of electrons for a finite spinless 3DEG system with $N = 7, 19, \ldots, 365$ electrons.

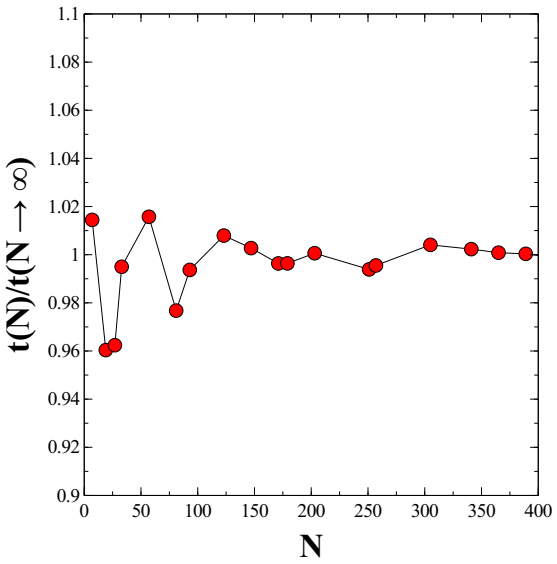

FIG. 2: Plot of the kinetic energy per particle relative to its bulk thermodynamic value, $t(N)/t(N\to\infty)$ for a finite spinless 3DEG system with $N = 7, 19, \ldots, 365$ electrons.

culations show that:

$$\frac{u(N)}{u(N\to\infty)} < 1 \ , \tag{41}$$

for all values of N considered in this work.

We also verified that the kinetic energy per particle of a finite 3DEG manifests a similar non-monotonic dependence as a function of N. In fact, we explicitly calculated the value of the kinetic energy per particle, $t(N) = T/N$ and expressed it relative to its thermodynamic limit counterpart to find out that such a ratio is a non-monotonic (sort of oscillatory) function of the number of electrons. One can expressly write this quantity as:

$$\frac{t(N)}{t(N\to\infty)} = C(N) \ , \tag{42}$$

where

$$C(N) = \frac{10}{9}\left(6\,\pi^2\right)^{1/3}\frac{1}{N^{5/3}}\sum_{\{\vec{n}\}}|\vec{n}|^2 \ . \tag{43}$$

The value of $C(N)$ changes with N, sometimes it is larger than 1 and sometimes it is smaller than 1. It is easy to verify by starting from Eq.(43) and converting the sum to an integral in the $N\to\infty$ limit that $\lim_{N\to\infty} C(N) = 1$. Note that the kinetic energy per particle for an infinite 3DEG system with N spinless electrons is written as:

$$t(N\to\infty) = \lim_{N\to\infty}\frac{T}{N} = \frac{3}{5}\frac{\hbar^2}{2\,m}\left(6\,\pi^2\rho_0\right)^{2/3} \ . \tag{44}$$

The quantity in Eq.(44) is the familiar expression for the kinetic energy per particle in the case of a free 3DEG, $(3/5)\hbar^2 k_F^2/(2\,m)$ where $k_F^3 = 6\,\pi^2\,\rho_0$. Fig. 2 shows the dependence of $t(N)/t(N\to\infty)$ as a function of the number of electrons. It is observed that, differently from the case of the potential energy where $u(N)/u(N\to\infty) < 1$, the kinetic energy values at a finite N do not follow this trend. With other words, it is found that the kinetic energy per particle, $t(N)$ is a kind of oscillating function of N around the bulk value of $t(N\to\infty)$. The value of $t(N)$ can be larger or smaller than $t(N\to\infty)$ depending on which value of N is considered. The observation of a non-monotonic variation of both potential and kinetic energy per particle of a spinless 3DEG as a function of N is similar to that of its finite 2DEG counterpart [43]. However, while such non-monotonic patterns seem common to both 2DEG and 3DEG systems, non-monotonic energy patterns of this nature are not general. For instance, the energy of a finite system of electrons under quantum Hall effect conditions (in a strong magnetic field) does not show any such energy patterns [44–48].

The energy per particle of the system in the thermodynamic limit can be written as $\epsilon(N\to\infty) = t(N\to\infty) + u(N\to\infty)$ and is given by:

$$\epsilon(N\to\infty) = \frac{3}{5}\frac{\hbar^2\,k_F^2}{2\,m} - \frac{3}{4\,\pi}k_F\,k_e\,e^2 \ . \tag{45}$$

The expression in Eq.(45) is equivalent to:

$$\epsilon(N\to\infty) = \left[\frac{3}{5}\left(k_F\,a_B\right)^2 - \frac{3}{2\,\pi}\left(k_F\,a_B\right)\right]\frac{k_e\,e^2}{2\,a_B} \ , \tag{46}$$

where $a_B = \hbar^2/(m\,k_e\,e^2)$ is the Bohr radius and the unit of energy used is the Rydberg (Ry):

$$1\,Ry = \frac{\hbar^2}{2\,m\,a_B^2} = \frac{k_e\,e^2}{2\,a_B} \ . \tag{47}$$

In conventional studies of a uniform electron gas, the parameter $(k_F\, a_B)$ is replaced by the dimensionless Wigner-Seitz radius parameter, r_s which, in the case of a 3DEG, is defined from the following expression:

$$\rho_0 = \frac{1}{\frac{4\,\pi}{3}\,(r_s\, a_B)^3}\ . \tag{48}$$

The uniform number density can also be written as $\rho_0 = k_F^3/(6\,\pi^2)$, an outcome that allows us to derive the following useful result:

$$(k_F\, r_s\, a_B)^3 = \frac{9\,\pi}{2}\ . \tag{49}$$

The expression above enables us to write the quantity in Eq.(46) as:

$$\epsilon(N\to\infty) = \left[\frac{3}{5}\left(\frac{9\,\pi}{2}\right)^{2/3}\frac{1}{r_s^2} - \frac{3}{2\,\pi}\left(\frac{9\,\pi}{2}\right)^{1/3}\frac{1}{r_s}\right]\frac{k_e\, e^2}{2\, a_B} \approx \left[\frac{3.5080}{r_s^2} - \frac{1.1545}{r_s}\right]\frac{k_e\, e^2}{2\, a_B}\ . \tag{50}$$

TABLE II: Energy per particle for a fully spin-polarized (spinless) 3DEG with $N = 81$ electrons as a function of the density parameter, r_s. The MC energy per particle computed with the pseudopotential derived from the random-phase approximation [49] (column two) is compared to the corresponding approximate HF energies (column 3). All energies are given in units of $k_e e^2/(2\, a_B)$ (in Rydbergs).

r_s	$\epsilon(N=81)$ [MC]	$\epsilon(N=81)$ [HF]
10.0	-0.10292	-0.07287
30.0	-0.04503	-0.03191
50.0	-0.02885	-0.02006

The energy per particle for a finite system, $\epsilon(N) = t(N) + u(N)$ depends on which specific value of N is considered since each of the terms $t(N)$ and $u(N)$ differs from its respective thermodynamic counterpart, $t(N\to\infty)$ and $u(N\to\infty)$.

Obviously, the approximation where the positive charges of the system are treated as a uniformly charged positive jellium background and the Coulomb interaction between electrons is neglected is only a start-off approximation that enables one to derive analytical results. The Coulomb interaction between electrons certainly plays an important role and its effect is worth estimating. At this juncture, we remind the reader that any form of energy that goes beyond the kinetic energy and the exchange potential energy of the system is called correlation energy. Its evaluation can be done only numerically via powerful tools such as DFT or MC simulation methods. Both DFT and MC methods are very accurate since they can reliably include the correlation energy in the overall result of the energy.

We choose a finite system with $N = 81$ electrons as a case study in order to estimate the magnitude of the correlation energy that is missing in the current approximate HF results. We wrote the HF energy per particle for a fully spin-polarized (spinless) 3DEG system of $N = 81$ electrons as:

$$\epsilon(N=81) = \left[\frac{3}{5}\left(\frac{9\,\pi}{2}\right)^{2/3}\frac{a}{r_s^2} - \frac{3}{2\,\pi}\left(\frac{9\,\pi}{2}\right)^{1/3}\frac{b}{r_s}\right]\frac{k_e\, e^2}{2\, a_B}\ , \tag{51}$$

where, earlier, we had found that:

$$a = \frac{t(N=81)}{t(N\to\infty)} = 0.97677\ \ ;\ \ b = \frac{u(N=81)}{u(N\to\infty)} = 0.92799\ . \tag{52}$$

The energy per particle, $\epsilon(N = 81)$ in Eq.(51) is compared to its more accurate MC counterpart that incorporates the missing correlation energy (the MC energy is computed with a highly correlated Jastrow-Slater trial wave function that incorporates very effectively the impact of particle correlations). We selected for consideration the same values of r_s as the ones reported in Ref.[49]. Results for such values of r_s are shown in Table. II. The first and second column of Table. II shows, respectively, the values of r_s and the corresponding MC energies found in Ref.[49]. The corresponding HF energies are listed in the third column of Table. II and are derived from Eq.(51). Comparison of the corresponding energy values is helpful to provide an estimate of the impact that the missing correlation energy has in the system.

IV. CONCLUSIONS

We adopted a HF approach (using a Slater determinant wave function of plane waves) and studied a finite spinless 3DEG system where a given number of electrons is confined in a cubic domain uniformly filled with positive jellium neutralizing background. We obtained compact mathematical expressions for the kinetic and the potential energy per particle corresponding to systems with an arbitrary number of electrons. The results derived can be used to understand the properties of finite 3DEG systems of electrons. As expected, it was noticed that the

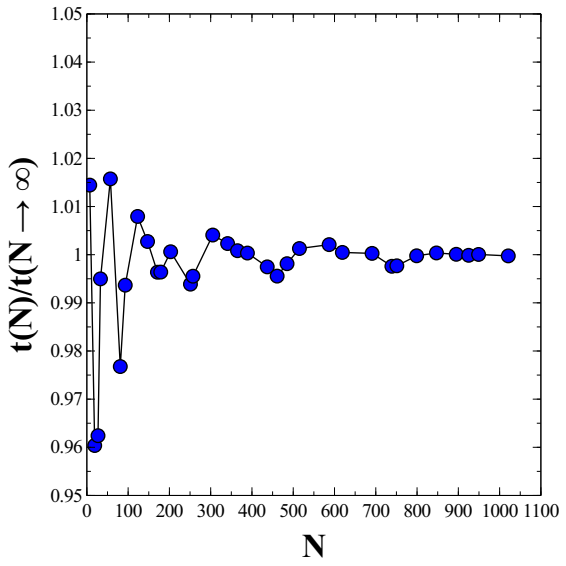

FIG. 3: Plot of the kinetic energy per particle relative to its bulk thermodynamic value, $t(N)/t(N \to \infty)$ for a finite spinless 3DEG system with up to $N = 1021$ electrons.

potential and kinetic energy per particle converge slowly towards their limiting bulk values as the size of the system increases. It is important to note that such a convergence process was non-monotonic in both cases. It is shown that the potential energy per particle approaches its bulk value slower than the kinetic energy per particle. For example, the value of the potential energy per particle is about 92 % of the bulk value for $N = 147$ electrons and grows to above 94 % of the bulk value as the size of the system increases to $N = 365$ electrons. On the other hand, the kinetic energy per particle for the same system sizes is much closer to its corresponding bulk value.

Applying PBC to electron's plane wave function in a finite potential well is presumed to work fine when the well's length is much larger than the wavelength of the electrons. The 3DEG model considered in this work conjectures that the length, L of the cubic box is directly proportional to $N^{1/3}$ for a fixed uniform density. This leads to a situation where one might argue that the source of the non-monotonic dependence of the kinetic and potential energies per particle as a function of N might be the small value of $N \propto 10^2$ electrons considered in the calculations shown in Fig. 1 and Fig. 2. We checked the likelihood of this possibility by increasing the size of the system under consideration to values of $N \propto 10^3$ electrons. The non-monotonic variation of both kinetic and potential energy per particle as a function of the number N of electrons seems not to be limited to only small values of N. Thus, we believe that this is not a finite small size effect. For instance, we verified in the case of the kinetic energy that the oscillating patterns of $t(N)/t(N \to \infty)$ persist up to the largest value of N considered in this work ($N = 1021$ electrons) as shown in Fig. 3.

The dependence of potential and kinetic energy per particle, respectively, $u(N)/u(N \to \infty)$ and $t(N)/t(N \to \infty)$ as a function of N for a finite 3DEG system shows similarities to its finite 2DEG counterpart in the sense that each of the two energy terms above converge non-monotonically towards their corresponding bulk values. However, there are also noticeable differences between the two cases. For instance, the potential and kinetic energy per particle of a finite 2DEG reaches the bulk value considerably faster than a finite 3DEG for approximately the same number of particles. We have calculated that $u(N = 149)/u(N \to \infty) \approx 0.98$ for a 2DEG while $u(N = 147)/u(N \to \infty) \approx 0.92$ for the 3DEG case. Note that since we have considered closed energy shells in our calculations the selected values of N for a closed energy shell of a 2DEG are not the same as those of a 3DEG. Similarly, we have seen that $t(N = 149)/t(N \to \infty) = 1.00074$ for a 2DEG while $t(N = 147)/t(N \to \infty) = 1.00274$ in the case of a 3DEG. While both kinetic energies have practically reached the bulk values, note that the value for the 2DEG is approximately one order of magnitude closer to the bulk estimate when compared to its 3DEG counterpart. We believe that the reason for this behavior is the reduced dimensionality that allows for a larger spatial extension of the 2DEG system for a given finite number of electrons.

Acknowledgments

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