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Comparison of the stabilized jellium model and the model with fixed point ions

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Abstract. A numerical analysis of the electron density and the electrostatic potential distribution in spherically symmetric bubbles of ionized hydrogen of nanometer size was made using density functional theory (DFT). Two models are considered: the stabilized jellium model, which allows to carry out one-dimensional computations for the spherically symmetric case, and the model with fixed point ions, where calculations are carried out in 3D geometry. For calculation in the point ions model Octopus and CP2K codes were used. One-dimensional computations in the jellium model require much less computational resources that allows to carry out calculations for systems with large number of electrons (about 10⁵). A conclusion about applicability of the stabilized jellium model for calculations of such systems. These calculations would be useful for studying inhomogeneities of the electric field, which affect ion motion during rapid compression of gas bubbles.

1. Introduction
In this work a numerical analysis of the electron density and the electrostatic potential distribution in spherically symmetric bubbles of ionized hydrogen of nanometer size with concentration 10²⁹÷10³¹ m⁻³ was made using density functional theory (DFT). These calculations would be useful for studying inhomogeneities of the electric field, which affect ion motion during rapid compression of gas bubbles. Two models were used. The first one is the stabilized jellium model [1], where ions are presented as a smooth positive charge distribution, that allows to carry out one-dimensional computations for the spherically symmetric case. The second one is the model with fixed point ions, which are homogeneously distributed inside the sphere and every ion is represented as a pseudopotential. In this case calculations are carried out in 3D geometry. Rough but allowing to carry out fast computations with large number of particles jellium model is compared to detailed but resource-intensive the point ion model to make a conclusion about its applicability. All computations were carried out for homogeneous spherically symmetric bubbles of hydrogen.

2. Description of used models

2.1. Stabilized jellium model
For spherically symmetric computations in the stabilized jellium model one-dimensional Kohn-Sham [2] equations are solved with the exchange-correlation functional PZ (Perdew, Zunger) [3] in the local density approximation (LDA). Single electron wavefunctions are presented as a product of radial and spherical wavefunctions. Kohn-Sham equation for radial wavefunctions:
\[-\frac{1}{2} \frac{d^2}{dr^2} + V_{KS}(r) + \frac{l(l+1)}{2r^2} \] \[P_{nl}(r) = E_{nl} P_{nl}(r), \] \[V_{KS} = V_{ion} + V_{H} + V_{xc} + \langle \delta v \rangle_{WS}, \] with border conditions \[P_{nl}(0) = 0, \quad P_{nl}(\infty) = 0, \] where \(V_{KS}\) is the effective Kohn-Sham potential, \(V_{H}\) and \(V_{ion}\) are electrostatic potentials arising from the electronic density and the jellium, respectively, \(V_{xc}\) is the exchange-correlation potential. In this section all electrostatic potentials are potentials for electrons, so they are multiplied by \(-1\).

Equation (1) is solved self-consistently using simple iteration method, at this a new value for electron density is obtained by mixing with values from previous iterations. A number of computed radial wavefunctions \(P_{nl}\), i.e a number of filled shells is much less than a number of electrons, for example, there are only \(~1000\) shells for \(10^5\) electrons.

In the stabilized jellium model there is a correction for the effective Kohn-Sham potential \(\langle \delta v \rangle_{WS}\), which is the difference between potential of the homogeneously charged ball with ion charge \(V(r)\) and the model pseudopotential averaged over the volume per ion \(Z/n_{ion}\)

\[\langle \delta v \rangle_{WS} = \frac{3}{4\pi r_0^3} \int_0^{r_0} dr 4\pi r^2 [\omega(r) - V(r)],\] \[r_0 = Z^{1/3} R = Z^{1/3} \left( \frac{3}{4\pi n_{ion}} \right)^{1/3}, \] where \(Z\) is the ion charge, \(n_{ion}\) is the positive charge concentration, \(V(r)\) is the potential of the homogeneously charged ball, \(\omega(r)\) is the model pseudopotential of interaction between an electron and an ion with charge \(Z\):

\[\omega(r) = \begin{cases} -Z/r, & r > r_c \\ 0, & r < r_c \end{cases} \] Further when we talk about the electrostatic potential in the jellium model it is the sum:

\[V_{ES} = V_{ion} + V_{H} + \langle \delta v \rangle_{WS}, \]

For computations an own code was used, which is specially created for spherically symmetric calculations using DFT. The program is checked by reproduction of results in papers [4] and [5]. Computations were carried out on grid with 5000 points and a border condition \(P_{nl}(R_{max}) = 0\), where \(R_{max}\) is several times more than the bubble radius, instead of the condition at infinity (3). In this work only calculations with the homogeneous ion distribution are considered. In the stabilized jellium model it looks like this: the ionic jellium density, which is also the positive charge density, equals the average density \(\tilde{n_e} = N(3/4\pi R^3)\) inside the sphere and 0 outside.

2.2. Discrete ion model
For computations with point ions Octopus [6] code and CP2K [7] code were used with the Hartwigsen-Goedecker-Hutter (HGH) [8] pseudopotential for ions. The modeling was carried out on three-dimensional cubic grid with spacing 0.2-0.4 a.u. (atomic units or bohr radius). In every case for the point ion model series of computations were carried out with different positions of ions, which are randomly homogeneously distributed inside the sphere. Distribution of ions inside the sphere is
presented in figure 1. At the same time, all ions are fixed and do not change their position, regardless of the forces acting on them.

Figure 1. Distribution of 450 (a) and 4500 (b) ions inside the sphere of radius 6.6 a.u.

So far as output of Octopus code for some quantity is the set of values on three-dimensional grid and electron density such as potentials are very inhomogeneous, to get the radius dependence and to compare the results to the jellium model averaging over directions is needed. Averaging over directions for potential carried out with weights equal to density to the 1/3 power.

\[
n_e(r_k) = \frac{\int_{|r|-r_k<|a|/2} n_e(r) d^3r}{\int_{|r|-r_k<|a|/2} d^3r},
\]

\[
V_{ES}(r_k) = \frac{\int_{|r|-r_k<|a|/2} V_{ES}(r)n_e^{1/3}(r) d^3r}{\int_{|r|-r_k<|a|/2} n_e^{1/3}(r) d^3r}, \quad r_k = ka,
\]

where \( k \) is a nonnegative integer, step \( a \) selected to be equal to the step of three-dimensional grid, which was used for calculation. In this way we get average values in several points. However, as a result of such averaging values at points near the center have large deviations, which depend on ion positions. Density and potentials obtained are very inhomogeneous and their values near the center depend strongly on whether the ion has got there or not as a result of a random distribution. This is connected to the fact, that averaging for every \( r_k \) is made over the area with volume \( \sim r_k^2 \) and near the center this area is very small.

With homogeneous random distribution of ions inside the sphere some of them could be very close to each other, as a result there would be large inhomogeneities of the electrostatic potential. The ion distribution should corresponds to the correlation function, so ions can be placed keeping the minimal distance between them as a simple analogue to such function.

Since individual ions do not act on themselves, to get the potential acting on ion we should exclude the potential of this ion from the electrostatic potential. For this the potential of the closest ion is excluded from the electrostatic potential in every point of three-dimensional grid. In figures 2–3 shown distribution of the full electrostatic potential and of the potential acting on individual ions in hydrogen bubbles of radius 6.6 a.u. with 450 and 4500 ions, that corresponds to density \( 2.5 \cdot 10^{30} \text{ m}^{-3} \) and \( 2.5 \cdot 10^{31} \text{ m}^{-3} \).
Figure 2. Distribution of the full electrostatic potential and potential, which acts on point ions, in the plane XY intersecting centre of the bubble with the radius 6.6 and the number of particles 450 shown two different ways.

Calculation for 450 ions was made with completely random ion distribution, but for 4500 with minimal distance between ions, which is close to the average distance between them. In the first case there are large inhomogeneities, in the second they are smaller. Also extracting a potential of the closest ion in every point a potential dispersion become less as well as value difference between the nearest points.

Figure 3. The same as figure 2 but for 4500 particles.

Figure 4 shows full electrostatic potentials and potentials acting on point ions averaged by directions, which are obtained using Octopus code with point ions for hydrogen bubble of radius 6.6 bohr and with 450 particles. There are displayed results for 15 random configurations of ions inside the sphere averaged using formulas (8), (9) and also its average value. One of these configurations was shown in figure 2.
Figure 4. The full electrostatic potential (a) and the potential excluding contribution of the closest ion (b) in hydrogen bubble of radius 6.6 a.u. and with 450 particles obtained using code Octopus. Potentials for all ion configurations shown separately by thin lines, average value over 15 configurations shown by thick line.

The electrostatic potential for ions averaged over directions differs from the full potential by a constant value. So further the full electrostatic potentials will be used for a comparison with the jellium model.

3. Comparison to the jellium model
In figure 5 the results shown for the electron density and the electrostatic potential obtained from the stabilized jellium model are compared to the results obtained from the point ions model using Octopus and CP2K codes. Averaging for the point ions model was made over 5 and 20 configurations, respectively. The computations were made for the hydrogen bubble of radius 17 a.u. with 450 particles. There were used two different programs for the point ions model to check the correctness of the results.

Figure 5. The electron density (a) and the electrostatic potential (b) in the jellium model compared to the results obtained for the point ions model using Octopus and CP2K codes.

In figures 6–8 shown the results for systems of radius 8.5 and 6.6 a.u. with 450 ions and also of radius 6.6 a.u. with 4500 ions, obtained for the jellium model and the point ions model using Octopus code. In case of the point ions model computations were carried out for 5, 15 and 6 ion configurations, respectively.
Figure 6. The electron density (a) and the electrostatic potential (b) in the jellium model compared to the point ions model for the hydrogen bubble of radius 8.5 a.u. with 450 ions, that is corresponds to density $1.2 \times 10^{30}$ m$^{-3}$.

Figure 7. The same as figure 6 but for radius 6.6 a.u.

Figure 8. The same as figure 6 but for radius 6.6 a.u. and with 4500 ions.

As we can see average values in the jellium model and in the point ions model are in a good agreement with each other. The deviations near the system center for the point ions model are connected with the fact that averaging in the center made over small volume. Distributions of the
electron density and potentials are very inhomogeneous, so average value near the center strongly
depends on specific ion configuration in this area. However, in the case of the point ion model
oscillations of density and potential have random behavior connected with ion distribution. So
determine oscillations, which are presented in the jellium model, are not visible in the results for the
point ions model. Probably, averaging over bigger number of ion configurations is needed.

4. Conclusion
The numerical researches carried out show that a simple model of the stabilized jellium is quite useful
for calculations of the electron density and the electric field in such spherically symmetric systems.
One-dimensional computations in the jellium model require much less computational resources than
three-dimensional computations with point ions. That fact allows to carry out calculations for systems
with large number of electrons (about $10^5$) in less time than three-dimensional require. In this way the
jellium model could be used to calculate the electrostatic potential, which acts on ion motion during
the gas bubbles of nanometer and micron size compression.

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