

## ***Density Functional Molecular Dynamics of Hydrogen Plasma***

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Density functional molecular dynamics method is applied to the hydrogen plasma in the domain of liquid metallic hydrogen. Tentative results for the proton-proton pair distribution function and the electron-proton pair distribution function are obtained. It is shown that with the increase of the parameter  $r_s$ , we have increasingly strong screening of proton charge by electrons and the decrease of electron density in the domain between protons.

### **I. INTRODUCTION**

Owing to recent rapid increase in the computational power of microprocessors and developments in the method of parallel computation, numerical simulations seem to have established a position as the third method in scientific researches. As far as the classical systems are concerned, One can verify this statement by the fact that assemblies of more than  $10^7$  particles (atoms and molecules) are now analyzed in microscopic scales where we can observe directly the behavior of atoms and molecules. When the quantum mechanics or the quantum statistics play the essential role, however, the number of electrons in simulations is still limited within a few hundreds and there exists a large gap between simulations and real experiments.

The above situation prevails also in the field of plasma science where phenomena related to the generation of plasmas, the process of ionization, cannot be understood without quantum mechanics. In tenuous gases, the ionization occurs as an isolated process and the knowledge on atoms or molecules can be applied. In dense gases or liquids, on the other hand, the process is strongly influenced by surrounding particles, and atoms and molecules cannot be treated as isolated. The latter ionization process called the pressure ionization or the plasma phase transition is one of important subjects still unresolved.

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In addition to experiments by the shock-wave compression the results of which have been already accumulated, [1,2] recent developments in very short and very strong laser pulse, *Table-Top-Terawatt ( $T^3$ ) Lasers*, are expected to accelerate investigations on highly condensed matters, especially the pressure ionization of various materials. The results of these researches will be applied to the inertial confinement fusion.

We plan to clarify the behavior of high density and high temperature materials by large scale quantum simulations as well as theoretical approaches. The purpose of this paper is to present some results of molecular dynamics simulations of hydrogen plasma which have a possibility to be extended to large scale systems.

## II. CHARACTERISTIC PARAMETERS

In thermal equilibrium, the system composed of protons and electrons are characterized by two parameters:

$$\Gamma = \frac{e^2}{ak_B T}, \quad (2.1)$$

$$r_s = \frac{a}{a_B}. \quad (2.2)$$

Here  $T$  is the temperature,  $a = (3/4\pi n_p)$  is the mean distance between protons with the number density  $n_p$ , and  $a_B$  is the Bohr radius.

The critical point of the plasma phase transition is expected to be around [3–5]

$$r_s \sim 2.2, \text{ and } \Gamma \sim 12, \text{ (0.24g/cc, } 1.1 \cdot 10^4\text{K, 0.5Mbar)}. \quad (2.3)$$

At higher densities, we expect to have the metallic phase of hydrogen. There have been several quantum simulations with limited system size in the metallic domain. [6] There have been performed many experiments to observe the transition to metallic state but we seem to still lack clear experimental evidence. The  $T^3$  lasers will be helpful to identify the transition. To establish the parameters for pressure ionization is important from the viewpoint of the application of such a strong laser light itself.

## III. FORMULATION

The density functional molecular dynamics is a combination of density functional theory and the Car-Parrinello method. [7–10] In stead of treating the wave functions, the electron density itself is regarded as a dynamical variable and the time evolution is followed under the condition of the conservation of total electron number

$$\int d\mathbf{r}\rho(\mathbf{r}) = N_e. \quad (3.1)$$

The Lagrangian is given by

$$\mathcal{L} = \frac{1}{2}\mu \int d\mathbf{r}\dot{\rho}(\mathbf{r})^2 + \frac{1}{2} \sum_i M_i \dot{\mathbf{R}}_i^2 - F[\rho(\mathbf{r}), \{\mathbf{R}_i\}] + \alpha[\int d\mathbf{r}\rho(\mathbf{r}) - N_e], \quad (3.2)$$

where  $\alpha$  is the Lagrange's multiplier and  $\mu$  is the electronic 'mass' which is to be optimized. The 'potential' energy  $F$  is written as

$$F[\rho(\mathbf{r}), \{\mathbf{R}_i\}] = U_{ee} + U_{II} + U_{eI} + F_k + F_{xc} \quad (3.3)$$

and includes Coulomb energies between electrons and ions

$$U_{ee} + U_{II} + U_{eI} = \frac{e^2}{2} \iint d\mathbf{r}d\mathbf{r}' \frac{(\rho_{ion}(\mathbf{r}) - \rho(\mathbf{r}))(\rho_{ion}(\mathbf{r}') - \rho(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|}, \quad (3.4)$$

where  $\rho_{ion}(\mathbf{r})$  is the ion charge density

$$\rho_{ion}(\mathbf{r}) = \sum_i Z_i \delta(\mathbf{r} - \mathbf{R}_i), \quad (3.5)$$

the kinetic energy of electrons

$$F_k = F_{k0} + F_g, \quad (3.6)$$

and, exchange-correlation energy of electrons  $F_{xc}$ . Note that without terms with time derivatives, the maximum of the Lagrangian corresponds to the correct electron density in the usual (static) density functional theory.

The equations of motion are given by

$$\frac{d}{dt} \frac{\delta \mathcal{L}}{\delta \dot{\rho}(\mathbf{r})} = \mu \frac{d}{dt} \dot{\rho}(\mathbf{r}) = \frac{\delta \mathcal{L}}{\delta \rho(\mathbf{r})}, \quad (3.7)$$

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_i} = M_i \frac{d}{dt} \dot{\mathbf{R}}_i = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_i}. \quad (3.8)$$

The right hand of the above equations are calculated as

$$\frac{\delta \mathcal{L}}{\delta \rho(\mathbf{r})} = e^2 \int d\mathbf{r}' \frac{(\rho_{ion}(\mathbf{r}') - \rho(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} - \frac{\delta(F_k + F_{xc})}{\delta \rho(\mathbf{r})} + \alpha, \quad (3.9)$$

and

$$\frac{\partial \mathcal{L}}{\partial \mathbf{R}_i} = Ze^2 \int d\mathbf{r}' \frac{\mathbf{R}_i - \mathbf{r}'}{|\mathbf{R}_i - \mathbf{r}'|^3} (\rho_{ion}(\mathbf{r}') - \rho(\mathbf{r}')). \quad (3.10)$$

The Hamiltonian  $\mathcal{H}$  defined by

$$\mathcal{H} = \int d\mathbf{r}\dot{\rho}(\mathbf{r}) \frac{\delta \mathcal{L}}{\delta \dot{\rho}(\mathbf{r})} + \sum_i \dot{\mathbf{R}}_i \cdot \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_i} - \mathcal{L} \quad (3.11)$$

or

$$\mathcal{H} = \frac{1}{2}\mu \int d\mathbf{r}\dot{\rho}(\mathbf{r})^2 + \frac{1}{2} \sum_i M_i \dot{\mathbf{R}}_i^2 + F[\rho(\mathbf{r}), \{\mathbf{R}_i\}] - \alpha[\int d\mathbf{r}\rho(\mathbf{r}) - N_e] \quad (3.12)$$

is conserved in the course of time development.

#### IV. SIMPLE APPROXIMATIONS FOR $F_K$ AND $F_{XC}$

In this report, we adopt simple approximations for the density functionals. We expect that the behavior of liquid metallic hydrogen may not be deeply influenced by the simplicity of approximations and comparisons with other (sophisticated) forms will be given in later works.

##### A. Kinetic Energy of Electrons $F_k$

We apply the Thomas-Fermi approximation at zero temperature:

$$F_{k0}[\rho(\mathbf{r})] = c_k \int d\mathbf{r} \rho(\mathbf{r})^{5/3}, \quad (4.1)$$

$$c_k = \frac{3}{10} (3\pi^2)^{2/3} \frac{\hbar^2}{m_e}, \quad (4.2)$$

$$-\frac{\delta F_{k0}}{\delta \rho(\mathbf{r})} = -\frac{5}{3} c_k \rho(\mathbf{r})^{2/3}, \quad (4.3)$$

with or without the gradient correction

$$F_g[\rho(\mathbf{r})] = c_g \int d\mathbf{r} \frac{1}{\rho(\mathbf{r})} (\nabla \rho(\mathbf{r}))^2, \quad (4.4)$$

$$-\frac{\delta F_g}{\delta \rho(\mathbf{r})} = 2c_g \frac{1}{\rho(\mathbf{r})} \Delta \rho(\mathbf{r}) - c_g \frac{1}{\rho(\mathbf{r})^2} (\nabla \rho(\mathbf{r}))^2. \quad (4.5)$$

The value of  $c_g$  is estimated to be between

$$c_g = \frac{1}{72} \frac{\hbar^2}{m_e} \quad (4.6)$$

and

$$c_g = \frac{1}{40} \frac{\hbar^2}{m_e}. \quad (4.7)$$

##### B. Exchange-Correlation Energy of Electrons $F_{xc}$

We apply the lowest order exchange energy  $F_{ex}$  at zero temperature:

$$F_{ex}[\rho(\mathbf{r})] = c_{ex} \int d\mathbf{r} \rho(\mathbf{r})^{4/3}, \quad (4.8)$$

$$c_{ex} = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} e^2, \quad (4.9)$$

$$-\frac{\delta F_{ex}}{\delta \rho(\mathbf{r})} = -\frac{4}{3} c_{ex} \rho(\mathbf{r})^{1/3}. \quad (4.10)$$

### C. Equations of Motion

The equations of motion are written as

$$\begin{aligned} \mu \frac{d}{dt} \dot{\rho}(\mathbf{r}) &= e^2 \int d\mathbf{r}' \frac{(\rho_{ion}(\mathbf{r}') - \rho(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} \\ -\frac{5}{3} c_k \rho(\mathbf{r})^{2/3} + 2c_g \frac{1}{\rho(\mathbf{r})} \Delta \rho(\mathbf{r}) - c_g \frac{1}{\rho(\mathbf{r})^2} (\nabla \rho(\mathbf{r}))^2 - \frac{4}{3} c_{ex} \rho(\mathbf{r})^{1/3} + \alpha, \end{aligned} \quad (4.11)$$

$$M_i \frac{d}{dt} \dot{\mathbf{R}}_i = Z e^2 \int d\mathbf{r}' \frac{\mathbf{R}_i - \mathbf{r}'}{|\mathbf{R}_i - \mathbf{r}'|^3} (\rho_{ion}(\mathbf{r}') - \rho(\mathbf{r}')). \quad (4.12)$$

## V. NUMERICAL PROCEDURES

Here we list summary of numerical procedures. Some details are given in Appendix.

### A. Units

Atomic units are used except for the length in our procedures and a sense on the size of our system may be obtained through values given below.

mass	$m_e$ (electronic mass) = $9.109 \cdot 10^{-31}$ kg
charge	$e$ (elementary charge) = $1.602 \cdot 10^{-19}$ C
action	$\hbar = 1.055 \cdot 10^{-34}$ rrmJ · s
time	$t_0 = (m_e a_B^3 / e^2)^{1/2} = \hbar^3 / m_e e^4 = 2.419 \cdot 10^{-17}$ s
length	$La_B$ (side of simulation box)
energy	$m_e e^4 / \hbar^2 = 27.21$ eV

### B. Flow of Computation

- (0) Assume periodic boundary conditions of the simple cubic symmetry.
- (0') Apply the method of extended system (Nosé-Hoover thermostat) to protons.
- (1) Distribute mesh points uniformly in the simulation box.
- (2) Represent electron density by the values at mesh points, regarding it as uniform in the volume assigned to each mesh point.
- (3) Compute Fast Fourier transform of electronic and ionic charge densities.
- (4) Compute electrostatic potential at mesh points by the (inverse) Fast Fourier transform.
- (5) Compute electronic electrostatic energy in the Fourier space.
- (6) Compute electronic contribution for electrostatic force and potential at ion positions by The (inverse) Fast Fourier transform.

- (7) Compute ionic contribution for electrostatic force and potential at ion positions by the Ewald method.
- (8) Monitor the conservation of Hamiltonian by computations of energy corresponding to each method of force computation.

## VI. RESULTS AND CONCLUDING REMARKS

The above method is applied to hydrogen in the domain of metals. When the density is sufficiently high, our system is approximately described as the Yukawa system. Our previous results on Yukawa system has provided a basis for the present quantum simulations through comparisons of parameters in this domain. We have checked that the simulation with  $10^3$  protons is possible on the PC cluster of 8 CPU's in our laboratory. The number of proton is 128 in the results presented in this report.

When the plasma phase transition is approached from the high density side, we may observe the decrease of the degree of ionization as a signal of such transition. We here present some results obtained on this line of approach. In Fig. 1, the distributions of protons and electrons are shown. We observe the accumulation of electrons on protons and, at the same time, the decrease of electron density in the domain between protons. This tendency is clearly seen in Fig. 2 where the electron density around protons is plotted.

As for the proton distribution, the pair distribution functions are shown in Fig. 3. With the increase of the parameter  $r_s$ , we have enhanced screening of proton charge by electrons and the interaction between protons is expected to become weak. It seems that, however, the correlation between protons is not simply decreasing. More detailed analyses are now in progress.

The method of density functional molecular dynamics is shown to be a candidate for large scale quantum simulations of plasmas. In order to compare the results seriously with experiments, it is necessary to measure the accuracy of this approach by the *ab initio* molecular dynamics applying both to smaller systems. This is also in progress and will be reported elsewhere.

## ACKNOWLEDGEMENTS

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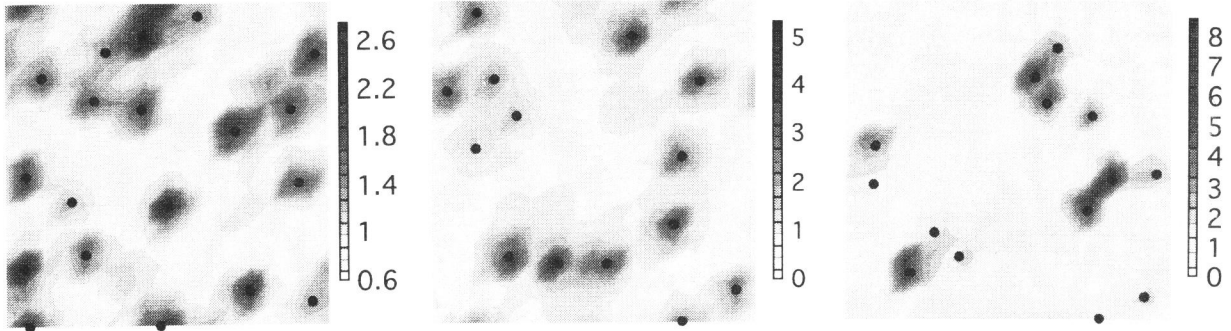


Fig.1. Distribution of protons and electrons. From left to right,  $(r_s = 0.5, \Gamma = 15)$ ,  $(r_s = 1.0, \Gamma = 15)$ , and  $(r_s = 1.8, \Gamma = 15)$ .

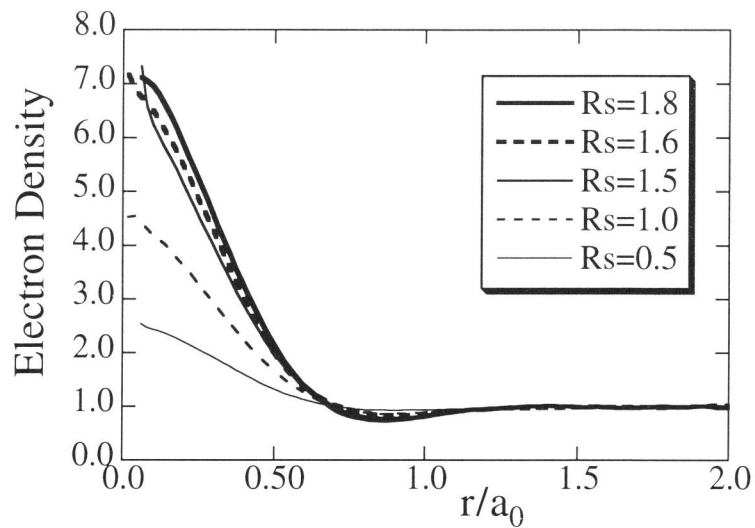


Fig.2. Distributions of electrons around protons.

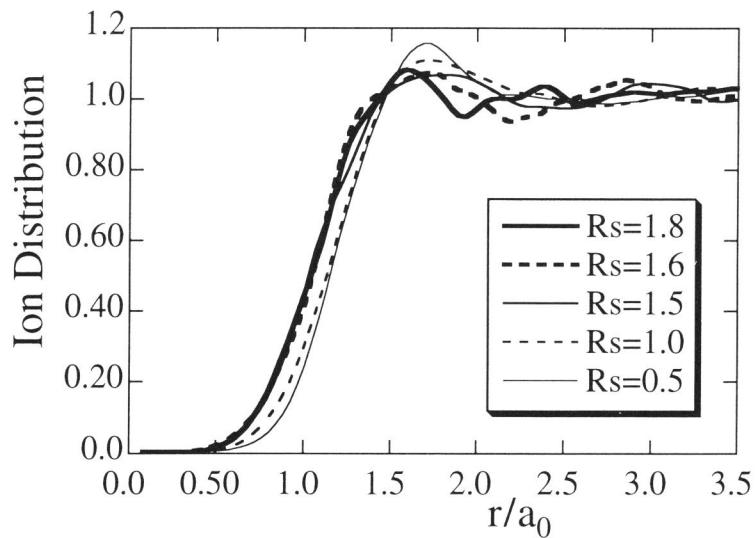


Fig.3. Pair distribution function of protons.

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## APPENDIX: EQUATIONS OF MOTION

Rewrite equations of motion into the form,

$$\begin{aligned} \frac{m_e a_B^5}{t_0^2 a_B^3} \frac{\mu}{m_e a_B^5} \frac{d^2}{dt^2/t_0^2} \rho(\mathbf{r}) a_B^3 &= \frac{e^2}{a_B} \int d(\mathbf{r}'/a_B) \frac{(\rho_{ion}(\mathbf{r}') - \rho(\mathbf{r}')) a_B^3}{|\mathbf{r} - \mathbf{r}'|/a_B} \\ &- \frac{1}{2} (3\pi^2)^{2/3} \frac{e^2}{a_B} \rho(\mathbf{r})^{2/3} a_B^2 + \frac{1}{36} \frac{e^2}{a_B} \frac{1}{\rho(\mathbf{r}) a_B^3} a_B^2 \Delta \rho(\mathbf{r}) a_B^3 - \frac{1}{72} \frac{e^2}{a_B} \frac{1}{\rho(\mathbf{r})^2 a_B^6} (a_B \nabla \rho(\mathbf{r}) a_B^3)^2 \\ &+ \left(\frac{3}{\pi}\right)^{1/3} \frac{e^2}{a_B} \rho(\mathbf{r})^{1/3} a_B + \alpha, \end{aligned} \quad (\text{A1})$$

$$\frac{m_e a_B}{t_0^2} \frac{M_i}{m_e} \frac{d^2}{dt^2/t_0^2} \mathbf{R}_i/a_B = Z \frac{e^2}{a_B^2} \int d(\mathbf{r}'/a_B) \frac{(\mathbf{R}_i - \mathbf{r}')/a_B}{|\mathbf{R}_i - \mathbf{r}'|/a_B} (\rho_{ion}(\mathbf{r}') - \rho(\mathbf{r}')) a_B^3, \quad (\text{A2})$$

or

$$\begin{aligned} \frac{\mu}{m_e a_B^5} \frac{d^2}{dt^2/t_0^2} \rho(\mathbf{r}) a_B^3 &= \int d(\mathbf{r}'/a_B) \frac{(\rho_{ion}(\mathbf{r}') - \rho(\mathbf{r}')) a_B^3}{|\mathbf{r} - \mathbf{r}'|/a_B} - \frac{1}{2} (3\pi^2)^{2/3} \rho(\mathbf{r})^{2/3} a_B^2 \\ &+ \frac{1}{36} \frac{1}{\rho(\mathbf{r}) a_B^3} a_B^2 \Delta \rho(\mathbf{r}) a_B^3 - \frac{1}{72} \frac{1}{\rho(\mathbf{r})^2 a_B^6} (a_B \nabla \rho(\mathbf{r}) a_B^3)^2 \\ &+ \left(\frac{3}{\pi}\right)^{1/3} \rho(\mathbf{r})^{1/3} a_B + \alpha, \end{aligned} \quad (\text{A3})$$



$$\frac{M_i}{m_e} \frac{d^2}{dt^2/t_0^2} \mathbf{R}_i/a_B = Z \int d(\mathbf{r}'/a_B) \frac{(\mathbf{R}_i - \mathbf{r}')/a_B}{|\mathbf{R}_i - \mathbf{r}'|^3/a_B^3} (\rho_{ion}(\mathbf{r}') - \rho(\mathbf{r}')) a_B^3. \quad (\text{A4})$$

When we take the side of our simulation box  $La_B$  as the unit of length, we have

$$\begin{aligned} \frac{1}{L^3} \frac{\mu}{m_e a_B^5} \frac{d^2}{dt^2/t_0^2} \rho(\mathbf{r}) L^3 a_B^3 &= \frac{1}{L} \int d\mathbf{r}'/La_B \frac{(\rho_{ion}(\mathbf{r}') - \rho(\mathbf{r}')) L^3 a_B^3}{|\mathbf{r} - \mathbf{r}'|/La_B} - \frac{1}{L^2} \frac{1}{2} (3\pi^2)^{2/3} \rho(\mathbf{r})^{2/3} L^2 a_B^2 \\ &+ \frac{1}{L^2} \frac{1}{36} \frac{1}{\rho(\mathbf{r}) L^3 a_B^3} L^2 a_B^2 \Delta \rho(\mathbf{r}) L^3 a_B^3 - \frac{1}{L^2} \frac{1}{72} \frac{1}{\rho(\mathbf{r})^2 L^6 a_B^6} (La_B \nabla \rho(\mathbf{r}) L^3 a_B^3)^2 \\ &+ \frac{1}{L} \left(\frac{3}{\pi}\right)^{1/3} \rho(\mathbf{r})^{1/3} La_B + \alpha, \end{aligned} \quad (\text{A5})$$

$$L \frac{M_i}{m_e} \frac{d^2}{dt^2/t_0^2} \mathbf{R}_i/La_B = Z \frac{1}{L^2} \int d\mathbf{r}'/La_B \frac{(\mathbf{R}_i - \mathbf{r}')/La_B}{|\mathbf{R}_i - \mathbf{r}'|^3/L^3 a_B^3} (\rho_{ion}(\mathbf{r}') - \rho(\mathbf{r}')) L^3 a_B^3. \quad (\text{A6})$$

Denoting normalized quantities and operations ( $\Delta$ ,  $\nabla$ ) by the same symbols in what follows, we have

$$\begin{aligned} \frac{1}{L^3} \mu \frac{d^2}{dt^2} \rho(\mathbf{r}) &= \frac{1}{L} \int d\mathbf{r}' \frac{(\rho_{ion}(\mathbf{r}') - \rho(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} - \frac{1}{L^2} \frac{1}{2} (3\pi^2)^{2/3} \rho(\mathbf{r})^{2/3} \\ &+ \frac{1}{L^2} \frac{1}{36} \frac{1}{\rho(\mathbf{r})} \Delta \rho(\mathbf{r}) - \frac{1}{L^2} \frac{1}{72} \frac{1}{\rho(\mathbf{r})^2} (\nabla \rho(\mathbf{r}))^2 \\ &+ \frac{1}{L} \left(\frac{3}{\pi}\right)^{1/3} \rho(\mathbf{r})^{1/3} + \alpha, \end{aligned} \quad (\text{A7})$$

$$L \frac{M_i}{m_e} \frac{d^2}{dt^2} \mathbf{R}_i = Z \frac{1}{L^2} \int d\mathbf{r}' \frac{(\mathbf{R}_i - \mathbf{r}')}{|\mathbf{R}_i - \mathbf{r}'|^3} (\rho_{ion}(\mathbf{r}') - \rho(\mathbf{r}')). \quad (\text{A8})$$

The above notations apply in programs.

The Hamiltonian  $\mathcal{H}$  is written in the form

$$\begin{aligned} \mathcal{H} &= \frac{1}{L^3} \frac{1}{2} \mu \int d\mathbf{r} \dot{\rho}(\mathbf{r})^2 + L^2 \frac{1}{2} \sum_i M_i \dot{\mathbf{R}}_i^2 \\ &+ \frac{1}{L} (U_{ee} + U_{II} + U_{eI}) + \frac{1}{L^2} F_k[\rho(\mathbf{r})] + \frac{1}{L} F_{ex}[\rho(\mathbf{r})] - \alpha \left[ \int d\mathbf{r} \rho(\mathbf{r}) - N_e \right] \end{aligned} \quad (\text{A9})$$

where

$$U_{ee} + U_{II} + U_{eI} = \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{(\rho_{ion}(\mathbf{r}) - \rho(\mathbf{r})) (\rho_{ion}(\mathbf{r}') - \rho(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|}, \quad (\text{A10})$$

$$F_k[\rho(\mathbf{r})] = \frac{3}{10} (3\pi^2)^{2/3} \int d\mathbf{r} \rho(\mathbf{r})^{5/3} + \left(\frac{c_g}{\hbar^2/m_e}\right) \int d\mathbf{r} \frac{1}{\rho(\mathbf{r})} (\nabla \rho(\mathbf{r}))^2, \quad (\text{A11})$$

$$F_{ex}[\rho(\mathbf{r})] = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int d\mathbf{r} \rho(\mathbf{r})^{4/3}. \quad (\text{A12})$$