

Heat capacity calculations for plasmas with
the finite-temperature Hartree-Fock-Slater
atomic model

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1 Introduction

A progress in developing power light sources leads us to constructing of X-ray free-electron lasers (XFEL). These lasers generate coherent X-ray radiation by single pass of an electron beam through a long undulator. XFEL combines high intensity of the pulse and high photon energy, therefore it offers new possibilities, which were unavailable before. Because of high intensity and short duration of a pulse, a target can be heated up to extremely high temperatures. Hence it is necessary to have a strong theoretical background to be able to describe behaviour of matter in such extreme conditions.

2 Non-relativistic Hartree-Fock-Slater equation

For pure hydrogen-like systems it is possible to solve the time-independent Schrödinger equation analytically.

$$\hat{H}(\mathbf{r})\Psi(\mathbf{r}) = E\Psi(\mathbf{r}), \quad (1)$$

Since most atomic systems have more than one electron, it is impossible to get precise solution of the equation (1). Major number of chemical elements are many-electron systems where state of one electron is correlated to states of all the others. In this case it is better to use approximate methods. One widely used method is a Hartree-Fock method [1, 2]. It is based on assumption that every electron moves in a mean field created by the nucleus and all other electrons. This leads us to a single-particle model, which essentially reduces the N-particle problem to problem of solving N single-particle equations.

To consider the Pauli exclusion principle, a wave function is chosen as a Slater determinant:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \dots & \psi_N(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \dots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \dots & \psi_N(\mathbf{x}_N) \end{vmatrix}, \quad (2)$$

where $\psi_i(\mathbf{x}_j)$ is a single-particle wavefunction of a particle j in a state i , $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$ —a set of space and spin variables. In this case if there are two identical lines or columns, determinant becomes zero. It corresponds to the Pauli exclusion principle—there is no possible states for two fermions with the same quantum properties.

Using the variational principle one could derive a Hartree-Fock equation:

$$\begin{aligned} \hat{h}_i \varphi_i(\mathbf{r}_i) + \sum_{i \neq j} \int \frac{\varphi_j^*(\mathbf{r}_j) \varphi_j(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d^3 r_j \varphi_i(\mathbf{r}_i) - \\ - \sum_{i \neq j} \int \frac{\varphi_j^*(\mathbf{r}_j) \varphi_i(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d^3 r_j \varphi_j(\mathbf{r}_i) = \varepsilon_i \varphi_i(\mathbf{r}_i), \end{aligned} \quad (3)$$

where \hat{h}_i is a single-particle Hamiltonian:

$$\hat{h}_i = -\frac{1}{2} \nabla_i^2 + \frac{Z}{r_i}. \quad (4)$$

The last term in the equation (3) stands for exchange interaction between electrons. Slater introduced an effective potential [3, 4], which corresponds to this interaction.

3 Total energy calculation

To provide all calculations we used XATOM [5]—an integrated toolkit for X-ray and atomic physics, which is able to calculate properties of warm and hot dense plasmas [6]. However, this program was not able to calculate a total energy of hot atomic system within the Wigner-Seitz radius.

Electrons start to occupy higher levels with increasing of the temperature. Hence it was essential to factor into contribution to energy only of those electrons, which are inside the Wigner-Seitz sphere. In the zero-order approximation we consider the total energy as the sum of orbital energies ε_i ,

$$\hat{h}_i \varphi_i = \varepsilon_i \varphi_i. \quad (5)$$

Since electrons have spin of $\pm 1/2$, they submit to the Fermi-Dirac distribution:

$$\tilde{n}_i = \frac{1}{e^{\frac{\varepsilon_i - \mu}{kT}}}. \quad (6)$$

From this set of statements we can derive evaluation for the total energy per Wigner-Seitz sphere in the zero-order approximation:

$$E_{WS} = \sum_i \tilde{n}_i \varepsilon_i \int_{r \leq R_{WS}} \varphi_i^* \varphi_i d^3 r_i. \quad (7)$$

4 Hot aluminum plasma energy calculation

After implementation this formula into the source code, the energy and the heat capacity of aluminum plasma were calculated, $\Delta E(T) = E(T) - E(0)$:

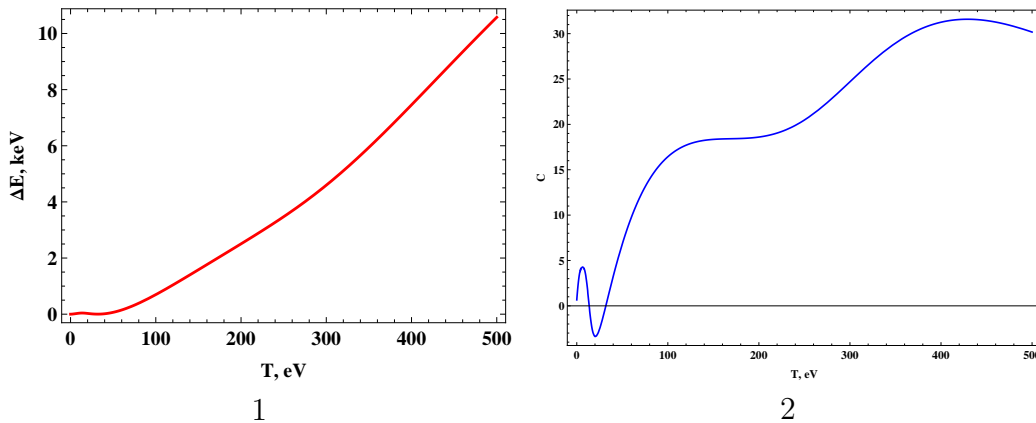


Figure 1: Dependence of the energy (1) and the heat capacity (2) on T for Al

From the Fig. 1 we can conclude that the heat capacity behaviour varies from expected. For low temperatures the heat capacity must be linear:

$$C = \gamma T + \beta T^3, \quad (8)$$

where the first term corresponds to the electron gas contribution and the second term—to the phonon contribution [9]. At the same time at high temperatures the Fermi-Dirac distribution transforms to the Boltzmann distribution, therefore electron gas becomes more and more ideal. Heat capacity for ideal gas is known well:

$$C = \frac{3}{2} N k_B = 19.5. \quad (9)$$

But on the plot we can see non-linear behaviour at low temperatures and the heat capacity goes higher than 19.5 at temperatures above 200 eV. Moreover we have a region with a negative heat capacity.

The easiest explanation of this result was in many approximations we have assumed in the source code: Hartree-Fock method [1, 2] with the Slater exchange potential [3, 4], muffin-tin potential for the average atom calculation [6]. Slater exchange potential does not depend on temperature, therefore it does not correspond to real orbital energies. To solve this issue we used two more types of the exchange potential: Rozsnyai exchange potential [7] and Perrot-Dharma-wardana (PDW) exchange potential [8]. The results are

shown below on the Fig. 2, green curve stands for Rozsnyai exchange potential, blue curve—for Perrot-Dharma-wardana exchange potential, red one—for Slater exchange potential:

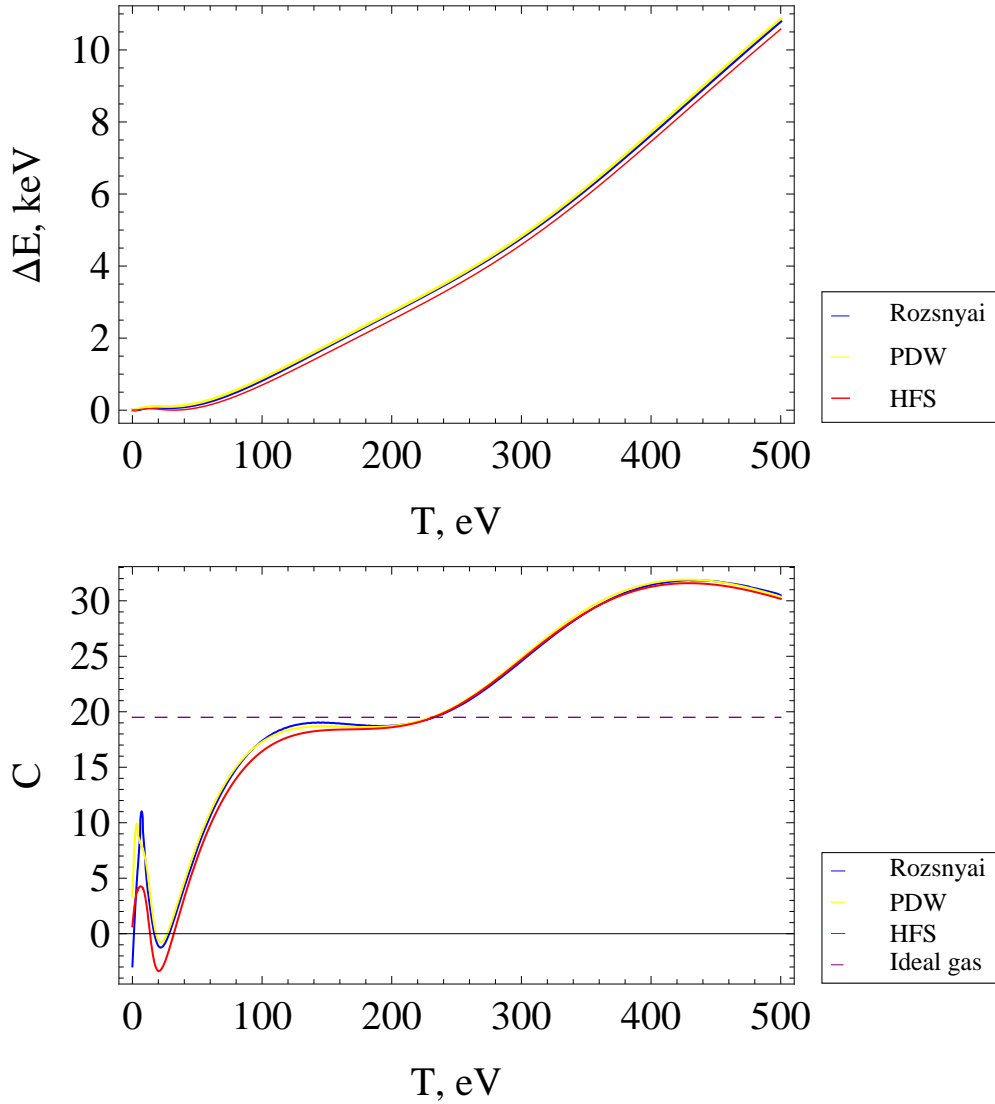


Figure 2: Comparison between Slater and thermal exchange potentials

We can conclude that difference between these three methods is not big and they describe behaviour of the energy with the same accuracy. However, using thermal exchange potentials we can reach better results in a region of 10 eV.

5 Cold aluminum plasma energy calculation

As it was already mentioned in (8), at low temperatures contribution to the total heat capacity from electron gas must be linear [9]:

$$C = \gamma T. \quad (10)$$

For aluminum $\gamma = 1.88$ in case of both energy and temperature units are eV.

We calculated the energy of aluminum plasma in a low temperature case with 3 different exchange potentials to figure out what approximation is better:

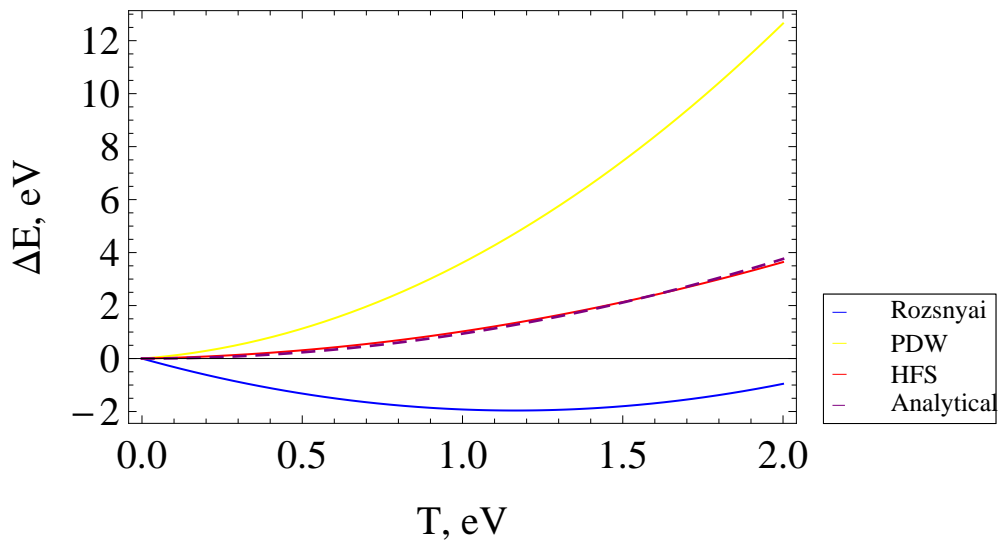


Figure 3: Dependence of the ΔE on T for Al in a low-temperature case

The red curve, which stands for the Slater exchange potential, fits the analytical expression (dashed curve) best of all.

6 Free-electron gas calculation

It was mentioned that in a high-temperature region the Fermi-Dirac distribution looks like the Boltzmann distribution. It means that electron gas in aluminum plasma becomes more and more ideal with the heat capacity of 19.5 (9) which corresponds to fully-ionized aluminum.

First, to calculate such a system we used a hydrogen atom with extra 12 electrons, which gives us an electronic configuration of aluminum, therefore

we calculated quasi-free electron gas (green curve). It was justified because of the value of the potential energy was much less than the kinetic energy. After that we managed to calculate a gas with no electron-electron interaction (blue curve) and with no electron-nucleus interaction (black curve). We did not manage to exclude both of this interactions because of the source code issues.

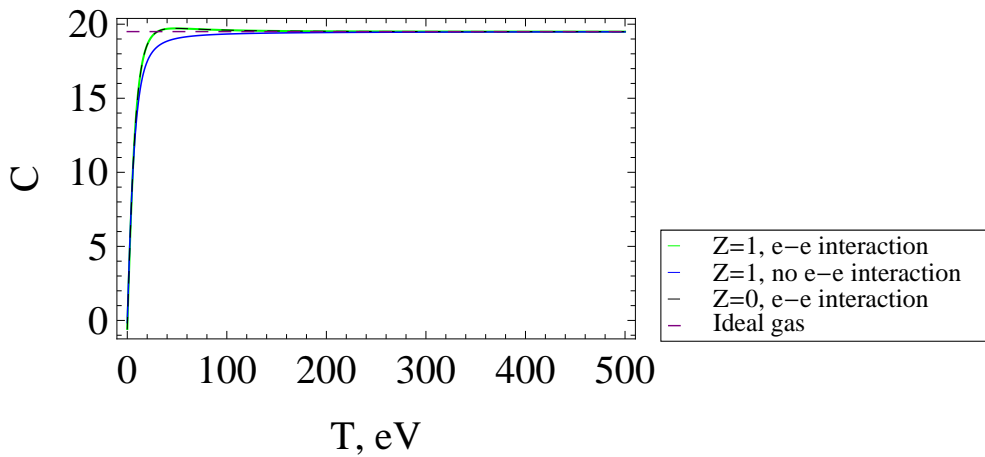
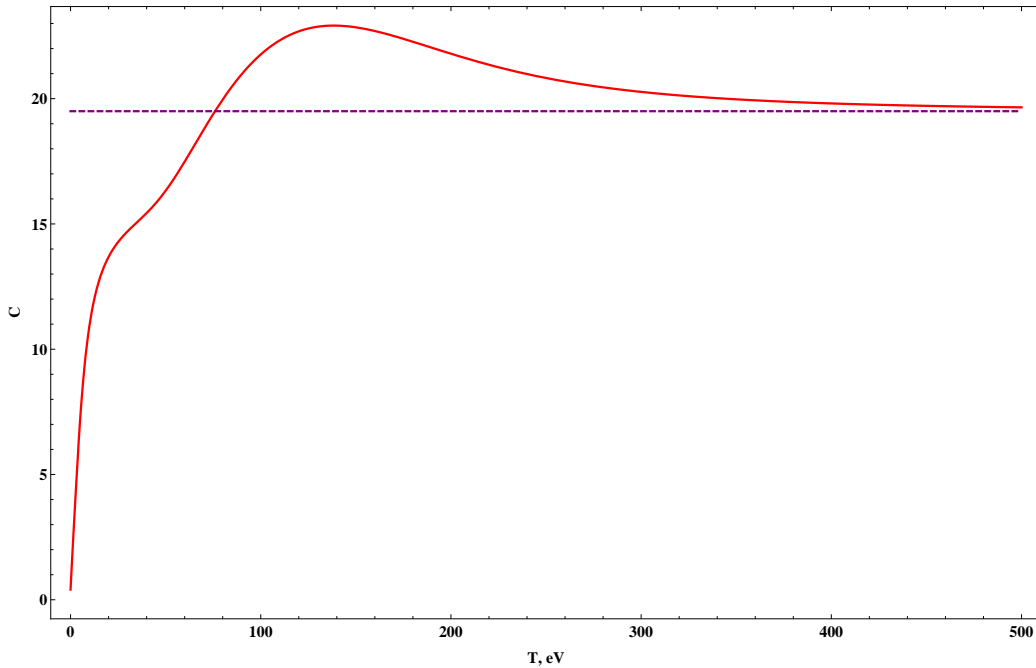


Figure 4: Calculations for different types of the quasi-free electron gas

Here we can see that all three curves reach an expected value of the heat capacity very fast. And this result allows us to conclude that the program works correctly.

Also we calculated an intermediate case—carbon with 7 additional electrons, the same trend was detected:



7 Conclusion

The XATOM was extended to be able to calculate the total energy of atomic system within the Wigner-Seitz radius. The results we got were quite unexpected and we were necessary to verify the calculation method using already known models. The results we took for carbon gives us confidence that the heat capacity for aluminum will reach the expected value with higher temperatures. Also there are unexplained phenomena, therefore all this results should be formalized.

8 Acknowledgements

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