The wide-range model of shell effects in hot plasma with semiclassical approximation for bound electrons

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Abstract. The state-of-the-art density functional theory (DFT) methods provide high quality data about materials properties at extremes. The cost for this is the days of modern supercomputers operation to obtain a set of particular points on a phase diagram. Moreover, the low density region is usually unreachable for these methods due to convergence issues. We demonstrate that an adequate wide-range model of electron subsystem may be constructed using the simple Thomas–Fermi approach corrected by introducing semiclassical bound states instead of continuous ones. The obtained thermodynamic properties are compared to Saha and Kohn–Sham DFT data with good agreement thus covering the region between low and normal densities of hot plasma.

1. Introduction
Wide-range equations of state are of high demand in various applications of modern physics. The interaction of intense energy fluxes with condensed matter, such as irradiation by short laser pulses, high velocity impact, or explosion of wires heated by electric current pulses lead to the formation of non-ideal plasma with degenerate electrons. It is quite difficult to develop an adequate theory which takes into account electron correlations in these conditions. However, experimental research of material properties for fluid dynamics simulations of materials in extremes is even more difficult or almost impossible to conduct nowadays.

The existing theoretical methods are valid only within a limited region of the phase diagram as shown in figure 1, and the proper account for quantum effects is the most challenging problem. The chemical Saha model of plasma, which is based on equilibrium equations for atoms, various ions and electrons, is strictly formulated only for the ideal system of hot rarefied plasma. Only approximate form of corrections which takes into account the non-ideality is obtained. The chemical model is also depends much on data for ionization potentials, obtained in experiments or calculations. Thus, the ab-initio quantum methods seems to be the most promising ones [1].

The simplest quantum-statistical approach of Thomas and Fermi to determine the electron density and thermodynamic properties at arbitrary temperatures [2] uses the rough assumption of the continuity of the electron spectrum, therefore it is applicable only at high temperatures and compressions. In its basic form it is applied to a single average atom, but may be extended to a system of nuclei and electrons in orbital-free density functional theory (OF-DFT) [3]. The Kohn–Sham density functional theory (KS-DFT) [4] along with quantum molecular dynamics...
2. Semiclassical bound states in the Thomas–Fermi potential

The Thomas–Fermi approximation for electron density within an average atom is

\[
n_{\text{TF}}(r) = \frac{(2T)^{3/2}}{2\pi^2} I_{1/2} \left( \frac{\mu_{\text{TF}} + U_{\text{TF}}(r)}{T} \right),
\]

where \( T \) is the temperature; \( \mu_{\text{TF}} \) and \( U_{\text{TF}}(r) \) are the chemical and self-consistent potentials defined in accordance with the boundary problem [6]:

\[
\begin{align*}
\frac{1}{r} \frac{d}{dr} \left( r U_{\text{TF}} \right) & = \frac{2}{\pi} (2T)^{3/2} I_{1/2} \left( \frac{U_{\text{TF}}(r) + \mu_{\text{TF}}}{T} \right), \\
r U_{\text{TF}}(r)_{|r=0} & = Z, U_{\text{TF}}(r_0) = 0, U'_{\text{TF}}(r)_{|r=r_0} = 0,
\end{align*}
\]

where \( I_k(x) \) is the Fermi–Dirac function.
The electron density within a spherical cell of an average atom is expressed by the following expression:

\[ n(r) = \frac{2}{4\pi r^2} \sum_{n,l} (2l + 1) |R_{nl}(r)|^2 \left[ 1 + \exp \left( \frac{\varepsilon_{nl} - \mu}{T} \right) \right]^{-1}, \tag{3} \]

where \( n, l \) are the principal and orbital quantum numbers; \( R_{nl} \) is the radial wave functions; \( \varepsilon_{nl} \) is the energy level corresponding to the quantum numbers \( n, l \); \( \mu \) is the chemical potential.

The energy levels may be found in the Thomas–Fermi potential using the Bohr–Sommerfeld quantization condition without solution of the Shrödinger equation:

\[ S_{nl} = \int_{r_i}^{r_o} p_{nl}(r) \, dr = \pi(n - l - 1/2), \tag{4} \]

where \( S_{nl} \) is the semiclassical action for electron with energy \( \varepsilon_{n,l} \); \( r_i, r_o \) are the inner and outer rotate points; \( p_{nl}(r) \) is the semiclassical momentum:

\[ p_{nl}(r) = \sqrt{2 \left[ \varepsilon_{nl} + U_{TF}(r) - \frac{(l + 1/2)^2}{2r^2} \right]}. \tag{5} \]

The example of energy levels evaluation is shown in figure 2(a).

The wave functions of electrons in a spherically symmetric potential may be approximated using Jeffreys–Wentzel–Kramers–Brillouin method (JWKB) which is found to be very close to the solution of the corresponding Shrödinger equation [6]:

\[ R_{nl}^{(i)}(r) = \begin{cases} \frac{C_i}{\sqrt{3}} \frac{\xi_i}{|p|} K_{1/3}(\xi_i) & (r \leq r_i), \\ \frac{C_i}{\pi} \frac{\xi_i}{p} \left[ J_{-1/3}(\xi_i) + J_{1/3}(\xi_i) \right] & (r_i \leq r \leq r_o), \end{cases} \tag{6} \]
Figure 3. (a) The Thomas–Fermi model electron density; (b) the semiclassical electron density. Calculations are performed for Au atom at various temperatures.

\[ R_{nl}(o) = \begin{cases} 
C_o \left( \frac{\xi_o}{\rho} \right)^{\frac{1}{3}} \int^{r_o} [J_{-1/3}(\xi_o) + J_{1/3}(\xi_o)] 
& (r_i < r \leq r_o), \\
C_o \left( \frac{\xi_o}{p} \right)^{\frac{1}{3}} K_{1/3}(\xi_o) 
& (r \geq r_o).
\end{cases} \]  
\tag{7}

Here \( J_{-1/3}(x) \), \( J_{1/3}(x) \) are the Bessel functions of the first kind, \( K_{1/3}(x) \) is the modified Bessel function of the second kind,

\[ \xi_i(r) = \left| \int_{r_i}^{r} |p_{nl}(r')| dr' \right|, \quad \xi_o(r) = \left| \int_{r_o}^{r} |p_{nl}(r')| dr' \right|. \]  
\tag{8}

The authors of monograph [6] also recommend using the following combination for the complete wave function:

\[ R_{nl}(r) = [1 - a(r)] R_{nl}^{(i)}(r) + a(r) R_{nl}^{(o)}(r), \quad a(r) = \xi_i(r)/\xi_i(r_o). \]  
\tag{9}

The signs of the inner \( R_{nl}^{(o)}(r) \) and outer \( R_{nl}^{(i)}(r) \) wave functions here should be consistent:

\[ C_i = C_o \text{sign}\{J_{-1/3}[\xi_i(r_o)] + J_{1/3}[\xi_i(r_o)]\}. \]  
\tag{10}

The constant \( C = |C_i| = |C_o| \) is defined from the normalization condition:

\[ \int_0^{r_o} |R_{nl}(r)|^2 dr = 1. \]  
\tag{11}

The examples of calculated wave functions for the average atom of gold are shown in figure 2(b).

The electron density by the Thomas–Fermi approximation \( n_{TF}(r) \) (1) and discrete summation (3) with the semiclassical wave functions and energy levels in the Thomas–Fermi potential \( n_{sc}(r) \) for average atom of gold are shown in figure 3. One can notice the specific oscillations in the semiclassical variant which correspond electron shells and are absent in the Thomas–Fermi approximation. With the temperature growth these shells disappear sequentially starting from the outer ones.
3. Shell corrections

The difference between the Thomas–Fermi model electron density (1) and the semiclassical one (3) calculated for the average Thomas–Fermi atom is the shell correction:

$$\delta n_{sh}(r) = \frac{1}{2\pi r^2} \sum_{n,l} (2l + 1)|R_{nl}(r)|^2 \left[ 1 + \exp\left(\frac{\varepsilon_{nl} - \mu_{TF}}{T}\right)\right]^{-1} - n_{TF}(r).$$

(12)

Being calculated, this correction disturbs the boundary problem for the potential (2) providing the additional equation for the potential $\delta U_{sh}$ and chemical potential $\delta \mu_{sh}$ corrections:

$$\begin{cases} \frac{1}{r} \frac{d^2}{dr^2}(r \delta U_{sh}) &= 4\pi \left( n_{TF} \frac{\delta U_{sh} + \delta \mu_{sh}}{T} + \delta n_{sh} \right), \\ r \delta U_{sh} |_{r=0} &= 0, \quad \delta U_{sh}(r_0) = 0, \quad \delta U_{sh}'(r) |_{r=r_0} = 0. \end{cases}$$

(13)

The main issue here is limiting the calculations of discrete spectrum at high temperatures where occupation numbers for large quantum numbers are not negligible. The idea is to limit the spectrum by the energy $\varepsilon_b$ which is the solution of the equation [6]:

$$\sum_{n,l} (2l + 1)\theta(\varepsilon_b - \varepsilon_{nl}) = \int \int \theta(\varepsilon_b - \varepsilon) \frac{d^3p}{(2\pi)^3} d^3r.$$ 

(14)

Here $\theta$ is the Heaviside function, and, as soon as the main contribution to shell effects is provided by the difference between the semiclassical and Thomas–Fermi bound states (with $\varepsilon_{nl} < 0$), it is enough to use the first appropriate solution with $\varepsilon_b > 0$. With these limitations the shell correction to density is

$$\delta n_{sh}(r) = n_{sc}(r) |_{\varepsilon_{nl} < \varepsilon_b} - n_{TF}(r) |_{\varepsilon < \varepsilon_b}. $$

(15)

The approach proposed here has certain advantages and drawbacks. It is less precise than the HFS model which consistently evaluates the potential, wave functions and energy levels during an iterative procedure. From the other hand, our approach takes much less efforts to perform calculations and achieve reasonable results: the discrete spectrum and wave functions are calculated only once without solving the Shrödinger equation. The problem of singular behavior of the Thomas–Fermi electron density at the nucleus is also eliminated with the proposed semiclassical correction to the electron density. It is worth noting that the amplitude

Figure 4. The shell corrections to (a) electron density and (b) potential of the Thomas–Fermi. Calculations are performed for Au atom at various temperatures.
of shell corrections should be less than the basic thermodynamic quantities calculated using the Thomas–Fermi model. This restricts the region of its validity from rarefied plasma of temperatures higher than 1 eV to hot dense matter of about 10–100 eV and higher similar to the Thomas–Fermi model with quantum and exchange corrections (TFC) [8].

It is convenient to calculate thermodynamic functions using the expressions [10] for pressure

$$\delta P_{sh} = \rho_{TF}(r_0)\delta \mu_{sh}$$

and internal energy

$$\delta E_{sh} = \left[ \frac{3}{2}Z - \int_0^{r_0} (\mu_{TF} + U_{TF}) \frac{\partial \rho_{TF}}{\partial \mu} 4\pi r^2 dr \right] \delta \mu_{sh}.$$  

They are obtained in linear expansion of the basic Thomas–Fermi thermodynamic functions and may be applied for hot plasma states below normal densities.

4. Applications at low and normal densities

The absence of discrete spectrum in the Thomas–Fermi approximation has the most noticeable effect on isochors calculations for the rarefied plasma ($\rho/\rho_0 \lesssim 0.1$) where electrons are localized near the nuclei at $T = 0$ and do not form the band structure. In that case the existence of electronic shells leads to the nonhomogeneous ionization under heating. Such behavior takes effect on thermodynamic functions which experience similar oscillations.

The behavior of rarefied plasma is properly reproduced by the chemical model which is used as reference for that case. It should be noted that the ab-initio Thomas–Fermi model with semiclassical discrete spectrum requires only basic constants, cell radius $r_0$, temperature $T$, and atomic number $Z$ to perform calculations. The ideal gas contribution of nuclei to the equation of state is used ($P_i = n_i T$).

In figure 5, the thermal equation of state is calculated for aluminum plasma at $\rho/\rho_0 = 10^{-3}$ using Saha model in comparison to the Thomas–Fermi model with the quantum, exchange, and shell corrections. The shell correction reproduces the stepwise character of the dependences.
due to plasma ionization, which indirectly demonstrates that ionization potentials calculated in semiclassical approximation are close to the experimental ones.

The Thomas–Fermi model provides adequate thermodynamic properties of matter in a wide region of the phase diagram. It has the proper asymptotics for the degenerate gas of electrons (high compressions) and for the classic one (high temperatures). However, the proper description of normal densities and average temperatures could be challenging. In this conditions it is appropriate to use KS-DFT data as a reference. The calculations of thermal pressure for copper are performed using VASP software [9] with the exchange-correlation functional in the form of GGA PBE with 17 valence electrons.

The thermal pressure in the Thomas–Fermi approximation grows much faster than that one calculated using KS-DFT approach. It seems that the continuous approximation for bound states results in the increased amount of electrons at the atomic cell boundary, which in reality is lower due to a shell oscillations minimum. Quantum and exchange corrections change the value of thermal pressure, but the tendency to the fast pressure growth remains. However, shell correction seems to provide the slope much closer to that of the KS-DFT pressure curve. The overall relative error eliminates with the temperature growth and is less than 5% at 30 eV.

5. Conclusion
We have developed the method for wide-range evaluation of the shell corrections to the Thomas–Fermi potential, electron density, and thermodynamic functions using the high quality JWKB semiclassical approximation for wave functions of bound electrons. The method is shown to be valid for the evaluation of thermodynamic properties of hot plasma below normal densities as shown in direct comparison with the Saha and KS-DFT models. We expect that better results could be achieved by introducing the self-consistent evaluation of potential with the semiclassical electron density. The tables of thermodynamic functions of electrons for practical use may be calculated using the simulation tools [12] developed by the authors.

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References
[1] Desjarlais M P, Graziani F, Redmer R and Trickey S B 2014 Frontiers and Challenges in Warm Dense Matter Lecture Notes in Computational Science and Engineering (Springer)
[2] Feynman R P, Metropolis N and Teller E 1949 Phys. Rev. 75 1561–73
[3] Zéraah G, Clérouin J and Pollock E L 1992 Phys. Rev. Lett. 69 446–9
[4] Kohn W and Sham L J 1965 Phys. Rev. A 140 1133–41
[5] Kresse G and Hafner J 1993 Phys. Rev. B 47 558–61
[6] Nikiforov A F, Novikov V G and Uvarov V B 2005 Quantum-Statistical Models of Hot Dense Matter. Methods for Computation Opacity and Equation of State (Birkhäuser Basel)
[7] Starret C E and Saumon D 2014 High Energy Density Phys. 10 35–42
[8] Dyachkov S A, Levashov P R and Minakov D V 2016 Phys. Plasmas 23 112705
[9] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169–86
[10] Shipakova Veva G V 2012 Phys. Usp. 55 429
[11] Dyachkov S A and Levashov P R 2014 Phys. Plasmas 21 052702
[12] Source code for calculations of electronic structure and thermodynamic properties of an average atom using various models. URL https://github.com/dya4kov/average-atom-toolkit