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ABSTRACT

We consider the neutrality in the framework of the average-atom model. It is shown that it is difficult to ensure the local neutrality inside the Wigner–Seitz sphere and the global neutrality inside all space. If we keep the neutrality of the Wigner–Seitz sphere, there is a small excess or deficit of charge in all space. Numerical examples are given for aluminum, iron, molybdenum, and gold for various compressions as a function of temperature. The small excess or deficit of charge in all space is noticeable in the warm dense matter regime. At high temperature, the neutrality inside the Wigner–Seitz sphere and in all space is restored.

I. INTRODUCTION

The microscopic description of hot dense plasmas is a complicated topic. A powerful and widespread tool to do this is the average-atom model. The first version was the semi-classical Thomas–Fermi model.[1] The quantum average-atom model[2–7] is a generalization of the Thomas–Fermi model. A self-consistent version is the one that employs the density functional theory (DFT) in local density approximation (LDA) at finite temperature. It converges quite easily and provides equation of state as well as transport coefficients in a large part of the density–temperature domain for a given element.

The key point of the average-atom model is the neutrality of the Wigner–Seitz sphere using a chemical potential. One usually does not bother to check the neutrality in all space, that is to say, globally. Only a local neutrality condition is ensured. The reason is that the global neutrality condition is difficult to check numerically. In this work, we consider the local and global neutralities in the quantum average-atom model. It is shown that it is difficult to satisfy both of them, and only the local neutrality condition based on the neutrality of the Wigner–Seitz sphere is ensured. This leads us with a non-neutrality in the whole space. It is difficult to see the consequences of this fact from a practical point of view. In most quantum average-atom models considered, only the Wigner–Seitz sphere is of practical interest and the global neutrality is simply not considered. We show that we can take into account local and global neutralities using a proper calculation of the phase shifts in the quantum average-atom interaction potential $V(r)$. A numerical tool is provided to obtain smooth phase shifts as a function of wavenumber for a given orbital number to calculate the continuum displaced charge $\bar{Z}_d$ due to the potential $V(r)$. We are, thus, able to calculate the excess charge that breaks the global neutrality condition once the local neutrality condition is satisfied. This excess charge is usually small compared to the nuclear charge in most thermodynamic conditions of practical interest.

This paper is organized as follows. In Sec. II, we present the theoretical formalism that is used to study the neutrality in the average-atom model. Section III is devoted to numerical applications. Section IV is the conclusion.

II. THEORY

We perform calculations in the non-relativistic approximation using an average-atom model in a muffin-tin approximation[1–7] for a given element at constant mass density ρ and electron temperature T. We assume that the ion and electron temperatures are equal and that the system is in local thermodynamic equilibrium. Using DFT in LDA at a finite temperature, the Schrödinger equation for the average atom reads

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + V(r)\right]\psi_a(\mathbf{r}) = \varepsilon_a\psi_a(\mathbf{r}), \tag{1}$$

where $\hbar$ is the reduced Planck constant, e is the elementary charge, and m_e is the electron mass. ε_a is the one-electron energy. $a = (n, \ell)$ for bound states and $a = (\varepsilon, \ell)$ for continuum states. In this case, the one-electron energy is simply ε. We use the sign of the one-electron energy to define a bound state or a free state. The one-electron potential

$$V(r) = -\frac{Ze^2}{r} + e^2 \int d\mathbf{r}' \frac{n(r')}{|\mathbf{r} - \mathbf{r}'|} + V_{xc}[n(r)] - V_{xc}[n(R_{WS})] \quad (2)$$

is equal to zero beyond the Wigner–Seitz radius R_{WS}. $4\pi R_{WS}^3 N_i/3 = 1$, where N_i is the ion density, $V_{at} = 4\pi R_{WS}^3/3$ is the Wigner–Seitz volume, Z is the nuclear charge, $n(r)$ is the total electron density of the average-atom, and V_{xc} is the finite-temperature exchange-correlation potential.[8] The wavefunction $\psi_a(\mathbf{r})$ is decomposed in a spherical basis

$$\psi_a(\mathbf{r}) = \frac{1}{r} P_a(r) Y_{\ell_a}^{m_a}(\theta, \phi) \chi_{\sigma_a}, \quad (3)$$

where $Y_\ell^m(\theta, \phi)$ is a spherical harmonic and χ_σ is a two-component electron spinor. The bound and free radial wavefunctions are normalized as

$$\int_0^{+\infty} dr P_{n\ell}(r) P_{n'\ell}(r) = \delta_{nn'} \quad (4)$$

and

$$\int_0^{+\infty} dr P_{\varepsilon\ell}(r) P_{\varepsilon'\ell}(r) = \delta(\varepsilon - \varepsilon'). \quad (5)$$

The total electron density of the average-atom $n(r)$ is equal to $n_b(r) + n_f(r)$, where

$$4\pi r^2 n_b(r) = \sum_{n\ell} \frac{2(2\ell+1)}{1 + e^{(\varepsilon_{n\ell} - \mu)/k_B T}} P_{n\ell}(r)^2 \quad (6)$$

and

$$4\pi r^2 n_f(r) = \sum_{\ell} \int_0^{+\infty} d\varepsilon \frac{2(2\ell+1)}{1 + e^{(\varepsilon - \mu)/k_B T}} P_{\varepsilon\ell}(r)^2. \quad (7)$$

k_B is the Boltzmann constant. The chemical potential μ is determined such that the system is neutral inside the Wigner–Seitz sphere, i.e.,

$$\int_0^{R_{WS}} 4\pi r^2 \left[n_b(r) + n_f(r)\right] dr = Z. \quad (8)$$

We consider various average ionizations. We can define $\bar{Z}_{WS,1}$ from the free electron density inside the Wigner–Seitz sphere, i.e.,

$$\bar{Z}_{WS,1} = \int_0^{R_{WS}} 4\pi r^2 n_f(r) dr, \quad (9)$$

and $\bar{Z}_{WS,2}$ from the electron density at R_{WS}, i.e.,

$$\bar{Z}_{WS,2} = n(R_{WS})/N_i = \frac{4}{3}\pi R_{WS}^3 n(R_{WS}). \quad (10)$$

Let us introduce $\bar{Z}_0$ deduced from the background electron density

$$n_0 = \frac{\sqrt{2}(m_e k_B T)^{3/2}}{\hbar^3 \pi^2} I_{1/2}(\eta), \quad (11)$$

where $\eta = \beta\mu$ is the reduced chemical potential and $\beta = 1/k_B T$. Moreover, $I_{1/2}(\eta)$ is the Fermi–Dirac integral of order 1/2, i.e.,

$$I_{1/2}(\eta) = \int_0^{+\infty} \frac{x^{1/2}}{1 + e^{x-\eta}} dx. \quad (12)$$

In clear,

$$\bar{Z}_0 = n_0/N_i = \frac{4}{3}\pi R_{WS}^3 n_0. \quad (13)$$

Let us now wonder about the neutrality in the average-atom model in all space. We have three terms. The first one is $\bar{Z}_0$ defined by Eqs. (11) and (13). The second one is the continuum displaced charge $\bar{Z}_d$ due to the potential $V(r)$, i.e.,

$$\bar{Z}_d = \int_0^{+\infty} 4\pi r^2 \left[n_f(r) - n_0\right] dr. \quad (14)$$

We can use[7] the Friedel formula to calculate $\bar{Z}_d$ introduced in Eq. (14), i.e.,

$$\bar{Z}_d = \beta \int_0^{+\infty} \frac{\hbar^2 k dk}{m_e} f(\varepsilon)[1 - f(\varepsilon)] \frac{2}{\pi} \sum_{\ell=0}^{\ell_>} (2\ell+1)\delta_\ell(k), \quad (15)$$

where $\varepsilon = \frac{\hbar^2 k^2}{2m_e}$. $\delta_\ell(k)$ is the phase shift. In Eq. (15), $f(\varepsilon)$ is the Fermi–Dirac statistic occupation number, i.e.,

$$f(\varepsilon) = \frac{1}{1 + e^{\beta\varepsilon - \eta}}. \quad (16)$$

The last term is the contribution of the bound electrons, i.e.,

$$Z_b = \int_0^{+\infty} 4\pi r^2 n_b(r) dr. \quad (17)$$

Consequently, the total number of electrons per ion is equal to

$$Z_{tot} = \bar{Z}_0 + \bar{Z}_d + Z_b, \quad (18)$$

i.e.,

$$Z_{tot} = \frac{4}{3}\pi R_{WS}^3 n_0 + \int_0^{+\infty} 4\pi r^2 \left[n_f(r) - n_0\right] dr + \int_0^{+\infty} 4\pi r^2 n_b(r) dr. \quad (19)$$

We can simplify this expression as follows. We find that

$$\begin{aligned} Z_{tot} = {} & \frac{4}{3}\pi R_{WS}^3 n_0 \\ & + \int_0^{R_{WS}} 4\pi r^2 \left[n_f(r) - n_0\right] dr + \int_{R_{WS}}^{+\infty} 4\pi r^2 \left[n_f(r) - n_0\right] dr \\ & + \int_0^{R_{WS}} 4\pi r^2 n_b(r) dr + \int_{R_{WS}}^{+\infty} 4\pi r^2 n_b(r) dr. \end{aligned} \quad (20)$$

Using the neutrality relation inside the Wigner–Seitz sphere (8), we find that

$$Z_{tot} = Z + \int_{R_{WS}}^{+\infty} 4\pi r^2 \left[n_f(r) - n_0\right] dr + \int_{R_{WS}}^{+\infty} 4\pi r^2 n_b(r) dr. \quad (21)$$

This is the main result of this work. In the Thomas–Fermi approximation,[1] we have

$$n_b(r) + n_f(r) = \frac{\sqrt{2}(m_e k_B T)^{3/2}}{\hbar^3 \pi^2} I_{1/2}[\eta - \beta V_e(r)], \quad (22)$$

where

$$V_e(r) = -\frac{Ze^2}{r} + e^2 \int d\mathbf{r}' \frac{n(r')}{|\mathbf{r} - \mathbf{r}'|}. \quad (23)$$

Since $V_e(r) = 0$ when $r \geq R_{WS}$, $n_b(r) + n_f(r) = n_0$ and $Z_{tot} = Z$. In the Thomas–Fermi approximation, we are neutral locally inside the Wigner–Seitz sphere and globally in the whole space. This is not the case in the quantum average-atom model. We are neutral locally inside the Wigner–Seitz sphere but not necessarily globally in the whole space. In Eq. (21), the two terms $\int_{R_{WS}}^{+\infty} 4\pi r^2 [n_f(r) - n_0] dr$ and $\int_{R_{WS}}^{+\infty} 4\pi r^2 n_b(r) dr$ are usually different from zero. The first one has no definite sign. It can be greater or smaller than zero depending on the potential $V(r)$. The second one is always positive. In general, these two terms are small compared to the nuclear charge Z. The term $\int_{R_{WS}}^{+\infty} 4\pi r^2 n_b(r) dr$ has a noticeable value when one bound orbital begins to delocalize, i.e., the bound electrons of this orbital go into the continuum by a dense plasma effect. In the following, we will give examples of the values of $Z_{tot} - Z$ in various thermodynamic conditions for various elements. The generalization to the relativistic domain is straightforward.[7,9]

III. NUMERICAL APPLICATIONS

To calculate Z_{tot}, we need to know $\bar{Z}_d$ and so the values of the phase shifts $\delta_\ell(k)$ (15). Numerically, the phase shift $\delta_\ell(k)$ is known within $N\pi$, where N is an integer. In practice, the function $k \to \delta_\ell(k)$ at given ℓ presents discontinuities at given k values and the discontinuities are equal to $N\pi$, where N varies with k. This means that we cannot calculate $\bar{Z}_d$ given by Eq. (15) if we keep the discontinuities. The computer program used in this work is written in Fortran 90. To regularize the function $k \to \delta_\ell(k)$ at given ℓ, we have written as small subroutine that works as follows. Let us fix ℓ and write the values of the function $k \to \delta_\ell(k)$ as $f(i)$, where the index i goes from 1 to $N_>$. We start with $i = 1$ and consider $f(i+1) - f(i)$. There may be a discontinuity at this point given by a multiple of π. So we use the Fortran function *NINT* and calculate $np_i = NINT[\frac{f(i+1)-f(i)}{\pi}]$. Once np_i is obtained, we subtract $np_i\pi$ from $f(j)$ where j goes from $i+1$ to $N_>$. When $i = N_>$, we have finished to regularize the curve $k \to \delta_\ell(k)$ at given ℓ. We now regularize the continuous curve $k \to \delta_\ell(k)$ at given ℓ by assuming that $\delta_\ell(0) = 0$. This is sufficient to calculate properly $\bar{Z}_d$ in Eq. (15). We, thus, calculate $np_1 = NINT[f(1)/\pi]$ and subtract $np_1\pi$ for the all values of $f(i)$ where $i = 1$ to $N_>$. We have, thus, obtained a smooth function $k \to \delta_\ell(k)$ at given ℓ with the convention $\delta_\ell(0) = 0$, and we can safely calculate $\bar{Z}_d$ from Eq. (15). We have used a portion of the Levinson theorem.[10] The exceptional case, where $\delta_\ell(0) = \pi\left(n_0 + \frac{1}{2}\right)$ for $\ell = 0$, has never been encountered in practice. If it happens, one should replace $\delta_0(k)$ in Eq. (15) by $\delta_0(k) - \frac{\pi}{2}$ or simply use the expression of $\bar{Z}_d$ involving $\frac{d\delta_\ell(k)}{dk}$ given in Ref. 7.

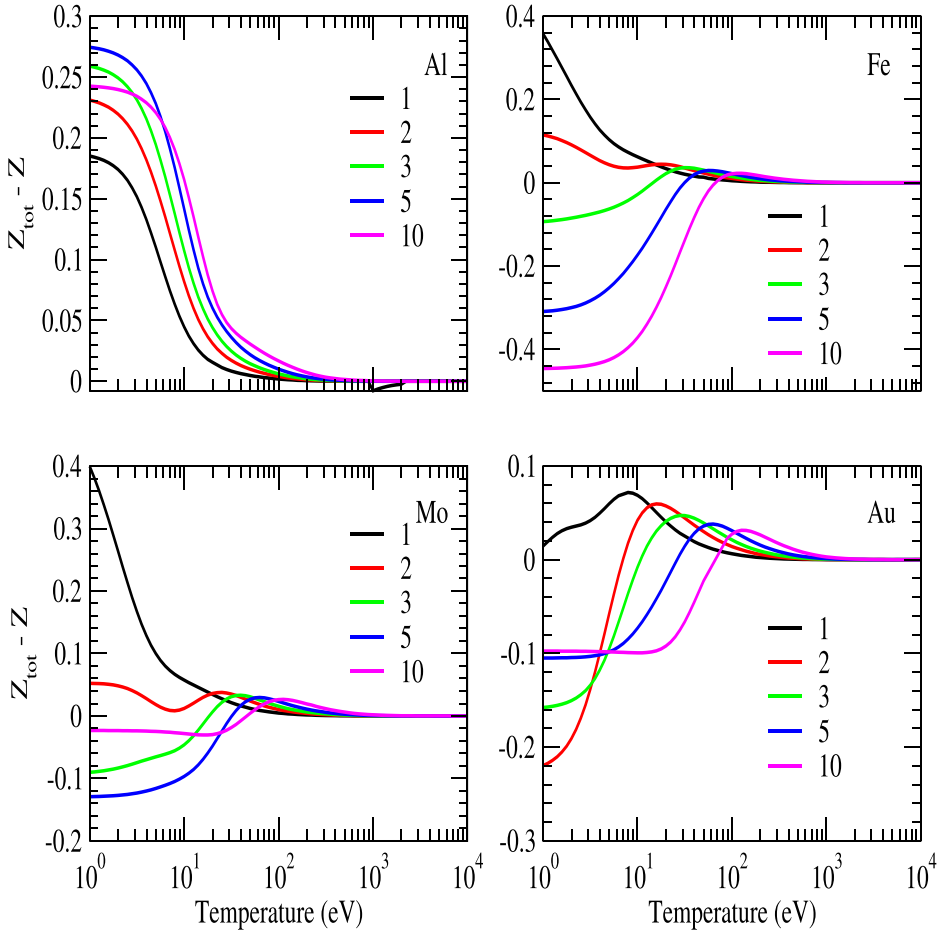

FIG. 1. $Z_{tot} - Z$ as a function of temperature for various compressions with respect to the mass density at cold solid density in aluminum, iron, molybdenum, and gold.

We plot in Fig. 1 $Z_{tot} - Z$ as a function of temperature for various compressions for aluminum, iron, molybdenum, and gold, respectively. By compression, we mean ρ/ρ_0, where ρ_0 is the mass density at cold solid density. We can see that the curves are smooth as a function of temperature and compression. For aluminum, $Z_{tot} - Z$ is positive except at compression one and beyond 1000 eV where it becomes slightly negative. For the other elements, at compression one, $Z_{tot} - Z$ is positive then it decreases and progressively changes sign when we increase the compression at low temperature. $Z_{tot} - Z$ is noticeable below 1000 eV. We can say that the neutrality in all space is broken in the warm dense matter regime. The behavior as a function of compression depends on the element. $(Z_{tot} - Z)/Z$ decreases with increasing nuclear charge.

It is difficult to provide an example of a physical consequence of the present results in an actual system due to a charge mismatch (excess or deficit). It is clear, however, that discontinuities using as ionization $\bar{Z}_0 + \bar{Z}_d$ may be found due to the localization or delocalization of bound orbitals because of pressure ionization. We can encounter this effect in the particular case of an s orbital for which $\int_{R_{WS}}^{+\infty} 4\pi r^2 n_b(r) dr$ can be significant as said above.

IV. CONCLUSION

We have studied the neutrality within the framework of the quantum average-atom model. We have shown that it is difficult to ensure a local neutrality, i.e., the neutrality within the Wigner–Seitz sphere, and a global neutrality, i.e., the neutrality in all space. This is a fundamental shortcoming of the quantum average-atom model. The semiclassical Thomas–Fermi model is neutral both locally and globally. We have given a formula to characterize the neutrality in all space using the neutrality in the Wigner–Seitz sphere. To use this formula in practical calculations, we need to know the phase shifts. A method has been given to provide smooth phase shifts that cancel in zero. They are, thus, appropriate to use the formula that characterize the neutrality in all space. Numerical examples have been given for light to heavy elements in which the neutrality in all space is broken in the warm dense matter regime. At high temperature, we have obtained local and global neutrality. We can obtain an excess of charge or a deficit of charge depending on the element and the thermodynamic conditions. The excess of charge or the deficit of charge is usually small and becomes smaller compared to the nuclear charge when we consider higher and higher nuclear charges.

AUTHOR DECLARATIONS

Conflict of Interest

The author has no conflicts to disclose.

Author Contributions

Gérald Faussurier: Conceptualization (equal); Formal analysis (equal); Methodology (equal); Software (equal); Validation (equal); Writing – original draft (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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