

Electron density separations in nonideal plasmas: Structure of Thomas-Fermi-like bound states and the Mott transition

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Starting from a general free energy functional, the chemical picture for nonideal plasmas arises from a certain separation of the electron density. Defining a bound state and its electrostatically screening plasma environment as a subsystem, a simple theory for plasma-correspondent bound state structure can be formulated. This provides the possibility to derive adjustable parameters for the interactions in the chemical picture. The Mott transition corresponds to the violation of the normalization condition due to plasma influences.

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I. INTRODUCTION: THE CHEMICAL PICTURE OF PLASMAS

The equilibrium properties of Coulombic matter have been studied since the early days of statistical physics. Depending on the position in the density-temperature plane, Coulomb matter—or plasmas, in the vocabulary of this work—presents itself in vastly differing shapes; examples are as far adrift as stellar interiors, electron-hole plasmas in semiconductors, the Wigner crystal, classical electrolytes, and so forth. Naturally, emphases and toolkits of theoretical approaches differ accordingly: dilute systems are successfully described by the assumption that electrons and ions are grouped into bound states which themselves form the molecular chaos of a gas. The ionization processes in this gas can be thought of as chemical reactions between free electrons and different ions. Hence this approach is usually referred to as the “chemical picture” (see, e.g., [1]). Dense systems, on the other hand, connect to solid state physics with ionic crystalline order (or the remnants of it as, for instance, in liquid metals) and itinerant electrons [2,3]. Non-ideal plasmas, which are characterized by notable corrections to the ideal kinetic energy due to the Coulomb interaction, are located in the region of the density-temperature plane that connects to both limits of theory buildup. A consistent plasma theory should, therefore, contain a principal bridge from molecular chaos to long-range order. Despite a number of attempts (for instance, a hydrogen theory [4]), such a theory is, rather unsurprisingly, in general still elusive. Its general theme, however, has to be the consistency of structural and energetical description. This paper will present a route toward improved consistency starting from the chemical picture employing the spirit of density functional theory (DFT). Since its foundation in 1964 and 1965 [5–7], DFT has been applied successfully to a wide variety of Coulomb matter problems (see anthologies [8–10]). Since both the success and the theoretical beauty of DFT lie in its self-consistency (a charge density generates a potential that in turn determines the distribution of the charges), it seems tailor-made for addressing the problem sketched above. In a system of N_i pointlike, Z -fold charged nuclei and $N_e = ZN_i$ electrons the Helmholtz free energy can be formulated as a functional of ionic and electron densities, $n_i(r)$ and $n_e(r)$,

respectively, where the origin has been fixed without loss of generality on an arbitrary nucleus with the temperature T as parameter (a.u.):

$$F[n_e(r), n_i(r); T] = F^{id}[n_e(r)] + F^{id}[n_i(r)] + \int_0^1 d\xi \langle V_{ee} + V_{ii} + V_{ei} \rangle_\xi + \int d\vec{r} \frac{Z}{r} [Zn_i(r) - n_e(r)]. \quad (1)$$

The charging expression via the coupling constant ξ of the interaction potential V holds for both classical and quantum statistics [11]. With the choice of origin, the normalizations

$$\int d\vec{r} n_i(r) = N_i - 1, \quad (2)$$

$$\int d\vec{r} n_e(r) = N_e = ZN_i$$

follow. Consequently, the electron density $n_e(r)$ balances the ionic charge in the plasma [second line of Eq. (1)] as well as the nuclear field of the charge at the origin (third line). In the chemical picture, $n_e(r)$ is assumed to separate generating bound states [the one at the origin with density $n_{ZN}(r)$ and those in the plasma labeled by their net charge z] and itinerant plasma electrons:

$$n_e(r) = n_{ZN}(r) + \sum_z (Z - z)n_z(r) + n^*(r),$$

$$n_{ZN}(r \rightarrow \infty) \rightarrow 0, \quad (3)$$

$$n^*(r \rightarrow \infty) \rightarrow \rho^* = \text{const.}$$

Inevitably, a free energy reformulated in this separation contains a mixing term due to the interaction of the bound state with the surrounding plasma:

$$\begin{aligned}
F[n_{ZN}, n^*, \vec{n}_z; T] &= F^{\text{id}}[n_{ZN}; T] + F^{\text{id}}[n^*, \vec{n}_z; T] \\
&+ F^{\text{mix}}[n_{ZN}, n^*, \vec{n}_z; T] + F^{\text{int}}[n^*, \vec{n}_z; T] \\
&- \int d\vec{r} \frac{Z}{r} n_{ZN}(r) \\
&+ \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{n_{ZN}(r) n_{ZN}(r')}{|\vec{r} - \vec{r}'|}. \quad (4)
\end{aligned}$$

Otherwise, ideal and interaction contributions can be assigned to the bound state *or* the plasma. Equation (4) suggests already the shape of the theory as it will be developed below; assuming $T=0$ for the bound electrons, $F^{\text{id}}[n_{ZN}; T]$ plus the last two terms in Eq. (4) present a bound state problem that can be tackled by Thomas-Fermi-like methods. Via the mixing term F^{mix} , this bound state is coupled to the plasma, which itself is in a “chemical” (i.e., ionization) equilibrium determined by $F^{\text{int}}[n^*, \vec{n}_z; T]$. The adjustment of the bound state to the surrounding plasma presents an—albeit simple—step toward improved consistency of structure and energy in the sense addressed above. Nonideality corrections to the ionization energy are complemented by an according change of structure [alterations of $n_{ZN}(r)$]. Most especially, the so-called Mott transition [12,1], which describes the delocalization of initially bound electrons, is hoped to be better understood by such a consistency. (Mott transition and the composition of hot, dense plasmas have been of scientific interest for many decades. Approaches similar to the one presented here, involving the work of Perrot and Dharma-Wardana [13,14], Rosenfeld [15] and, recently, Chiu and Ng [16], are exemplarily quoted.) It has to be cautioned, though, that the separation [Eq. (3)] is an approximation. In particular, the boundary condition $n_{ZN}(r \rightarrow \infty)$ is not substantiated by any physical argument and will lead to problems.

Four comments have to be made at this point. First, the separation [Eq. (3)] “aggregates,” so to speak, the initially pure Coulomb interaction, together with the quantum character of the particles, into “chemical interactions”; van der Waals interactions will, for instance, enter $F^{\text{int}}[n^*, \vec{n}_z; T]$. Usually, this aggregated interaction is formulated with the help of parameters; in the case of the van der Waals equation of state (EOS), for instance, the parameters are the hard sphere radii of the bound states. The spirit of the free energy [Eq. (3)] is to make these radii correspond to the surrounding plasma. It is in this sense that the consistency improvements of the overall plasma description will be understood.

Second, the applicability of Thomas-Fermi (TF) theory has to be discussed. It may be interesting to note that, albeit being formulated some 40 years earlier, TF theory can be understood as a special case of DFT. The well-known anomalies of TF theory originate from the crude approximation of the kinetic energy. This, however, can be corrected [17–20], with the resulting binding energies being surprisingly accurate (further corrections account for the exchange energy of the electrons [21]). Formally, the corrections can be grouped into an \hbar expansion [22,8] which leads, at least in principle, to a full quantum theory. Nevertheless, it has to be kept in mind that TF theory describes a statistical atom, whence its applicability for small Z is principally limited.

As a third comment, it should be noted that the arbitrary separation [Eq. (3)] potentially contains the onset of long-range order if a suitable structure theory for the heavy particles is employed in the formulation of the plasma free energy (see, e.g., [2,3]). In the framework of this paper, however, the consistency notion shall be restricted to the bound state and its immediate environment. This is for Boltzmann statistics in $F^{\text{id}}[n^*, \vec{n}_z; T]$ in leading order given by electrostatic screening and will be shown below to reproduce, under certain approximations, the famous theory of Debye and Hückel (DH) [23]. Generalizing $F^{\text{id}}[n^*]$ to its full Fermi function expression presents an immediate means to extend the concept of electrostatic screening beyond DH (an example is the well-known Thomas-Fermi screening in a fully degenerate electron gas [10,1]).

Finally, the conundrum presented by the mixing term $F^{\text{mix}}[n_{ZN}, n^*, \vec{n}_z; T]$ has to be addressed. With respect to the chemical description of the plasma, two choices can be made: either the plasma effects are regarded as modifying the binding energy of the bound state, thus altering its sum of states, or this is left at its ideal value and the difference is subsumed into the nonideality contributions to the plasma thermodynamical potentials. For hydrogenlike systems both descriptions are energetically equivalent: the solutions of the mass action law (MAL) are the same since the differences of the chemical potentials for bound and plasma electrons stay the same. Furthermore, hydrogenlike systems imply the use of the Bethe-Salpeter equation, a two-particle quantum equation of motion. Subsuming the plasma effects into an effective Hamiltonian, a consistent two-particle picture can be developed (see [24], as a more recent work, e.g., [25]). Starting from the notion of individual particles (rather than densities, as in DFT), energetic effects based on the symmetry properties of the wave function (correlation, phase-space occupation) and the dynamics of the screening process can be expressed. The naturally arising challenge to unify DFT with propagator-based plasma pictures has been acknowledged and addressed, e.g., in [8]. Recently, new progress has been made in this area ([26] and references therein). Certain one-particle concepts as, e.g., the continuum edge are, however, not viable in the context of statistical atoms where ionization is described by comparing systems with N and $N-1$ bound electrons, where N has to remain large. Excitation phenomena in statistical atoms can, of course, not be studied on the grounds of DFT or TF theory, which are zero temperature theories, but must employ the DFT extension of Mermin [7]. For more than one bound electron, furthermore, the screening will also affect the mutual repulsion of the electrons in the core (see [28] for a heliumlike theory). Since the “chemical reaction” for the ionization of bound state species z ,

$$z \Leftrightarrow (z+1) + e^-, \quad (5)$$

is necessarily a one-electron (i.e., a hydrogenlike) model, the equivalence of both pictures is maintained only up to leading (i.e., net charge) order. Also, and in the context of this work of crucial importance, the corresponding structure will differ. Simultaneously obtaining an effective binding energy and the according structures $n_{ZN}(r)$, $n^*(r)$, and $\vec{n}_z(r)$ is another illustration of the kind of consistency improvement this paper strives to achieve.

II. THOMAS-FERMI-LIKE BOUND STATES IN DEBYE-HÜCKEL PLASMAS

As already hinted at in the Introduction, for the bound state portion of the free energy [Eq. (4)] zero temperature shall be assumed (from here on, atomic units shall be adopted):

$$\begin{aligned} E_{ZN}[n_{ZN}] &= F_{ZN}[n_{ZN}; T=0] \\ &= F^{\text{idr}}[n_{ZN}; T=0] - \int d\vec{r} \frac{Z}{r} n_{ZN}(r) \\ &\quad + \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{n_{ZN}(r)n_{ZN}(r')}{|\vec{r}-\vec{r}'|}. \end{aligned} \quad (6)$$

Then, the bound state structure is found by seeking a stationary value of the functional [Eq. (4)] with respect to variation of n_{ZN} and inclusion of a Lagrange multiplier λ_N for the normalization condition:

$$\frac{\delta(E_{ZN}[n_{ZN}] + F^{\text{mix}}[n_{EN}, n^*, \vec{n}_z; T])}{\delta n_{ZN}(r)} + \lambda_N = 0. \quad (7)$$

In Eq. (7) an effective potential v_e^{eff} emerges:

$$v_e^{\text{eff}}(r) = -\frac{Z}{r} + \int d\vec{r}' \frac{n_{ZN}(r')}{|\vec{r}-\vec{r}'|} + \frac{\delta F^{\text{mix}}}{\delta n_{ZN}}. \quad (8)$$

In atomic TF theory, v_e^{eff} is related, via the Poisson equation, to the electron density n_{ZN} and thus the famous TF differential equation is found. In the plasma context, however, part of the effective potential is given rise to by the charge distribution of the plasma around the bound state. Acknowledging this, the following Poisson relation derives:

$$\nabla^2 v_e^{\text{eff}} = 4\pi \left[Z\delta(\vec{r}) - n_{ZN} - n^* + \sum_z z n_z \right]. \quad (9)$$

Equations equivalent to Eq. (9) for the variations with respect to n^* and the n_z generate a complete system of equations. It should be noted that atomic TF theory as well as conventional DH theory are contained in Eq. (9) as limits. For $n^*, n_z \rightarrow 0$, the plasma effects from F^{mix} vanish and the description of an isolated bound state remains. For $Z=N$ and a δ -like electron distribution n_{ZN} , Eq. (9) presents the stage of DH theory before the Maxwell-Boltzmann ansatz and linearization [23,1]. Performing the DH procedure on Eq. (9) destroys, however, the self-consistency of the bound state and plasma charge densities. In the spirit of DH theory, a pointlike test charge generates the electrostatic screening. The approximation imminent in applying the DH line of thought is, consequently, to treat the extended bound state as $[Z\delta(\vec{r}) - n_{ZN}(r)] \rightarrow (Z-N)\delta(\vec{r})$. Thus with

$$\begin{aligned} n^* &\sim \exp[-v_e^{\text{eff}}/k_B T], \\ n_z &\sim \exp[zv_e^{\text{eff}}/k_B T], \end{aligned} \quad (10)$$

and linearization Eq. (9) changes to

$$\begin{aligned} \nabla^2 v_e^{\text{eff}} &= \kappa^2 v_e^{\text{eff}} - 4\pi n_{ZN}, \\ \kappa^2 &= 4\pi\tau^{-1}[\rho^* + z^2\rho_z], \end{aligned} \quad (11)$$

where the ρ are the thermodynamical limits of the distributions $n^*(r)$ and $n_z(r)$, and τ is the dimensionless temperature $k_B T/Ry$.

One convinces oneself easily that the Poisson equation [Eq. (11)] is solved by a certain shape of the energy functional:

$$E_{ZN}[\eta_{ZN}] + F^{\text{mix}}[n_{ZN}, n^*, n_z; T] = \tilde{E}_{ZN}[n_{ZN}; \kappa], \quad (12)$$

where in \tilde{E}_{ZN} all Coulombic terms are screened in the usual DH fashion:

$$\begin{aligned} \tilde{E}_{ZN}[n_{ZN}; \kappa] &= \tilde{T} + \tilde{E}_{eZ} + \tilde{E}_{ee} \\ &= \frac{3}{10}(3\pi^2)^{2/3} \int d\vec{r} n_{ZN}(r)^{5/3} \\ &\quad - \int d\vec{r} \frac{Z \exp[-\kappa r]}{r} n_{ZN}(r) \\ &\quad + \frac{1}{2} \int \int d\vec{r} d\vec{r}' \frac{n_{ZN}(r)n_{ZN}(r')}{|\vec{r}-\vec{r}'|} \\ &\quad \times \exp[\kappa|\vec{r}-\vec{r}'|]. \end{aligned} \quad (13)$$

At this stage the physical interpretation has to be reiterated. As is well known, expectation values of $e^{-\kappa r}/r$ must not be constructed since the acting potential can only be Coulombic. Consequently, the Yukawa-like factors in Eq. (13) must be understood as belonging to neither the potential nor the density. The functional \tilde{E}_{ZN} has rather to be thought of as the special form of the energies $E_{ZN} + F^{\text{mix}}$ with presupposed DH structure for the plasma charges around the bound state considered. Equation (11), together with

$$\frac{\delta \tilde{E}_{ZN}[n_{ZN}; \kappa]}{\delta n_{ZN}(r)} + \lambda_N = 0, \quad (14)$$

describes, thus, an adaptable bound state embedded in a Debye-Hückel plasma within the chemical picture:

$$\begin{aligned} \frac{1}{2} [3\pi^2 n_{ZN}(r)]^{2/3} - \frac{Z e^{-\kappa r}}{r} + \frac{2\pi}{\kappa r} \int dr' r' n_{ZN}(r') \\ \times [e^{\kappa|r-r'|} - e^{\kappa|r+r'|}] + \frac{\lambda_N}{2} = 0. \end{aligned} \quad (15)$$

It should be mentioned that immediate improvement to simple DH theory is readily at hand by extending Boltzmann statistics to the full Fermi function expressions for quantum particles in Eq. (10) and/or perturbation theory for a test charge with extended charge distribution. As already suggested above, treating the kinetic energy in \tilde{E}_{ZN} locally as that of a homogeneous, fully degenerate electron gas generates TF theory.

Referring the reader to the above-quoted texts (see also [29]) for details, the usual TF analysis is straightforward. Introducing the so-called TF screening function,

$$\eta(r) \frac{Z}{r} = \frac{1}{2} [3\pi^2 n_{ZN}(r)]^{2/3}, \quad (16)$$

the differential equation

$$\eta'' - \kappa^2 \left[\eta + \frac{\lambda_N r}{2Z} \right] - \frac{8}{3\pi} \sqrt{\frac{2Z}{r}} \eta^{3/2} = 0 \quad (17)$$

with the boundary conditions

$$\begin{aligned} \eta(0) &= 1, \\ \eta(r=R_{ZN}) &= 0 \end{aligned} \quad (18)$$

is established as determining the structure of a TF-like bound state in a DH plasma. The second boundary condition points, again, to the chemical picture: chemical species can only be sensibly defined if they are spatially limited ensembles of ions and electrons. This has been taken care of by introducing the radius R_{ZN} . It should also be mentioned that the transition $\kappa \rightarrow 0$ in Eq. (17) reproduces correctly the atomic TF differential equation as had to be expected from the discussion of the Poisson relation [Eq. (9)]. Equations (17) and (18) entail a number of implications that highlight the problem of bound states in a plasma.

A. Asymptotics

First, the famous asymptotic solution $\eta \sim r^{-3}$ [27] for the isolated TF atom, giving it an infinite radius, is disallowed in Eq. (17). One convinces oneself easily, however, that $\eta \sim \text{const } r$ is an exact solution that corresponds (cf. the definition of η) to a constant n_{ZN} . This solution does not agree with the above definition of the chemical picture and has to be disregarded within the framework of this paper. It points, however, to a physical picture where the electron density in the plasma is not (artificially) divided into bound and free parts but is described by *one* correlation function.

For the boundary condition (18), Eq. (17) delivers furthermore $\eta''(R_{ZN}) > 0$ for $\lambda_N > 0$ (see below). Together with the linear term in r , this prevents R_{ZN} from tending toward infinity.

B. Debye-Hückel chemical potential: linear approximation

Second, it should be noted that any plasma effect in the solution of Eq. (17) is of order $O(\kappa^2)$. If, however, in the energy functional (13) the exponential is expanded, a linear term arises (the problems of an expansion under the integral can be controlled, remembering that $n_{ZN} \rightarrow 0$ for larger r):

$$\begin{aligned} -Z \int n_{ZN} \frac{\exp[-\kappa r]}{r} &\simeq -Z \int \frac{n_{ZN}}{r} + Z\kappa N, \\ \frac{1}{2} \int \int \frac{n_{ZN}(\vec{r}) n_{ZN}(\vec{r}')}{|\vec{r} - \vec{r}'|} \exp[-\kappa r] & \\ \simeq \frac{1}{2} \int \int \frac{n_{ZN}(\vec{r}) n_{ZN}(\vec{r}')}{|\vec{r} - \vec{r}'|} - \frac{1}{2} \kappa N^2. & \end{aligned} \quad (19)$$

In TF ideology, the ionization energies are found as the differences of the ground state energies for N and $N-1$ bound

electrons. Remembering that the objective of TF theory is a “statistical” atom, i.e., one with large N , this corresponds to the derivative with respect to N . As discussed in the Introduction, the correction to the ionization energy due to κ can be identified as the Debye-Hückel chemical potential. The linear expressions above reproduce, thus immediately the Debye-Hückel chemical potential $\mu_{ZN}^{\text{DH}}/R_{ZN} = -2(Z-N)\kappa$, depending only on the net charge of the bound state. Reassuringly, in this limit the chemical picture, which is a theory for net charge interactions, and the DH limiting law are reinstated. The full solution of Eq. (17) will, however, provide higher order energy corrections as well as the corresponding structure changes in the shape of $\eta(r)$.

C. Lagrange multiplier: linear approximation

Third, the Lagrange multiplier λ_N has to be discussed. The definition of the chemical picture includes $n_{ZN}(R_{ZN}) = 0$ for some radius R_{ZN} [with, possibly, $R_{ZN} \rightarrow \infty$, see Eq. (18)]. At that point, Eq. (15) immediately yields

$$\begin{aligned} \frac{\lambda_N}{2} &= \frac{e^{-\kappa R_{ZN}}}{R_{ZN}} \left[Z - \frac{2\pi}{\kappa} \int_0^{R_{ZN}} dr' r' n_{ZN}(r') \right. \\ &\quad \left. \times [e^{-\kappa|\vec{r}-\vec{r}'|} - e^{-\kappa(\vec{r}+\vec{r})}] \right] \\ &= \frac{Z-N}{R_{ZN}} e^{-\kappa R_{ZN}} + O(\kappa^2). \end{aligned} \quad (20)$$

Similar to the chemical potential μ_{ZN} , linear approximation produces a net charge dependence. Again, the full solution will acknowledge simultaneously higher order effects and structure. For vanishing κ , the well-known value $(Z-N)/R_{ZN}$ is recovered. For the isolated neutral atom, this means $\lambda_Z = 0$; the neutral atom in a plasma will be discussed below.

Regarding the chemical potentials μ_{ZN} and λ_N , confusion must be avoided. Whereas λ_N corresponds to the normalization of the bound electron density, μ_{ZN} couples the bound state to the plasma by describing—due to the formal choice discussed in the Introduction—either the ionization energy correction or the limiting law.

D. Normalization and delocalization

Fourth, the normalization of the bound electron density $n_{ZN}(r)$

$$\int_0^{R_{ZN}} 4\pi r^2 dr n_{ZN}(r) \stackrel{!}{=} N \quad (21)$$

can, by integration by parts, and use of the TF differential equation [Eq. (17)], be expressed as

$$0 \stackrel{!}{=} \eta'(R_{ZN}) R_{ZN} + \frac{Z-N}{Z} - \kappa^2 \int_0^{R_{ZN}} dr r \eta(r) - \frac{\lambda_N \kappa^2 R_{ZN}^3}{6Z}. \quad (22)$$

The last term in natural units, $\frac{1}{6}[\lambda_N/(Ze^2/R_{ZN})](\kappa R_{ZN})^2$, reveals the interplay of a structural nonideality parameter (κR_{ZN}) and an energetic one that measures the chemical potential λ_N against the potential energy of an electron located at the radius R_{ZN} of the bound state. Since the slope of η at R_{ZN} and the third term on the right-hand side Eq. of (22) are necessarily nonpositive, the linear approximation for λ_N from Eq. (20) gives a simple delocalization criterion:

$$0 \stackrel{!}{=} \eta'(R_{ZN})R_{ZN} - \kappa^2 \int_0^{R_{ZN}} dr r \eta(r) + \frac{Z-N}{Z} \left[1 - \frac{(\kappa R_{ZN})^2}{3} \right], \quad (23)$$

such that for

$$(\kappa R_{ZN}) > \sqrt{3} \quad (24)$$

no bound states can be formed anymore. Since Eq. (24) has been derived from the linear approximation, which certainly has to be judged rather poor at the actual point of delocalization (it leaves the structure unperturbed), the validity of this criterion should be put in perspective. Furthermore, Eq. (23) leads to the astonishing assertion that the neutral atom $N=Z$, is, even for arbitrarily weak screening, unstable. This result must be understood as an artifact of TF theory. As mentioned above, the isolated neutral atom has an infinite radius $R_{ZZ}=\infty$; in other words, the bound electron density is already delocalized. It seems to be plausible that this state cannot be delocalized further. Further insight can be gained from the differential equation itself [Eq. (17)]: the stronger curvature in comparison with $\eta(\kappa=0)$ means steeper slopes at the origin and, simultaneously, that less electronic density can be accommodated in the region near the nucleus. Since R_{ZZ} is already infinite, this cannot be compensated for in the outer regions, resulting again in a no-binding notion.

Physically, the mechanism of delocalization in the spirit of this paper becomes transparent: in the outer region of the atom the mutual repulsion of two elements of the core electron density is hardly effected by the electrostatic screening if the distance between those is small. At the same time, the distance to the nucleus is large, and consequently the attraction to it strongly effected by the Yukawa-like cutoff of the potential. In the overall energy balance, then, the repulsion \tilde{E}_{ee} remains larger in comparison with \tilde{E}_{eZ} and forces the density $n_{ZN}(r)$ to extend to higher R_{ZN} .

Hence for positive ions $N < Z$, R_{ZN} increases with κ up to a point where the delocalization criterion (23) is violated. As will be commented on in the numerical example below, this point is numerically extremely difficult to access due to the simultaneous transitions $\lambda_N \rightarrow$ small, and $R_{ZN} \rightarrow$ large.

E. Ground state energy

For evaluating the double integral in the ground state energy functional (13), the differential equation can be used in a similar way as in the normalization discussed above. Then, the total energy \tilde{E}_{ZN} of the electron gas in the field of a nucleus at $r=0$ and the electrostatic plasma charge cloud is found as

$$\begin{aligned} \tilde{E}_{ZN}/\text{Ry} = & \frac{8\sqrt{2}}{15\pi} Z^{5/2} \int_0^{R_0} dr \eta(r)^{5/2} r^{-1/2} \\ & - \frac{8\sqrt{2}}{3\pi} Z^{5/2} \int_0^{R_0} dr \eta(r)^{3/2} r^{-1/2} e^{-\kappa r} - \frac{\lambda_N}{2} N. \end{aligned} \quad (25)$$

For the isolated TF atom ($N=Z$, $\kappa=0$), the ground state energy has been shown to scale with $Z^{7/3}$. This is of limited interest since the neutral atom has been shown to be unstable in any plasma environment. The ground state energies of positive ions $N < Z$ have been shown to scale as $E_{ZN} \sim Z^{7/3} f(N/Z)$ [30,31]. The different contributions to \tilde{E}_{ZN} are easily found to be related by

$$E_{ee} = -\frac{1}{2}[\lambda_N N + E_{eZ} + \frac{5}{3}T]. \quad (26)$$

The factor 1/2 in Eq. (26) is hidden in the difference of exponentials in the effective potential v_e^{eff} : if these, for instance, in Eq. (13), are expanded, an exactly compensating factor of 2 arises in the linear term to reproduce the virial theorem for isolated bound states. Equation (26) must not, however, be interpreted as a virial theorem, since in the total energy import from the plasma is included. It would be of interest to extract the screening contribution from \tilde{E}_{ZN} and study the relations of the remaining terms. This, however, is not possible in a transparent way.

F. Numerical example: $Z=10$

The above discussion shall be illustrated with the numerical example $Z=10$. This number is large enough to justify the statistical approach to the binding problem, yet small enough to circumvent relativistic corrections that become necessary for large nuclear attraction [32,33]. It may be interesting to note that, with all available corrections applied, even the hydrogen atom ground state energy can be reproduced to within 8% by TF theory [29]. Together with the proof by Lieb [34,35] that for $Z \rightarrow \infty$ TF theory is exact; this makes $Z=1$ a rather good approximation for infinity. Also, TF theory is thus asserted as a useful tool for binding problems for the majority of chemical elements.

In the numbers and figures that follow, the apparatus as developed above will be illustrated. Due to the nature of the approximations made and the decisive fault of the instability of the neutral atom, the presented example cannot have any meaning for real plasmas. Such a work will be a natural follow-up to this work, with a more refined description of the bound state and the charge cloud around it; especially, however, of the kinetic energy T . The essence of the presented theory can, however, already be seen from the simple variant presented in this paper.

Figure 1 shows the dependence of the ground state energy on the plasma inverse screening length κ for the first three positive ions $N=9$, $N=8$, and $N=7$. The ionization energy, as has been pointed out above, is given by the difference of these energies. Figure 1 clearly shows the diminishing of the ionization gap for increasing κ . However, delocalization—as defined above by the violation of the normalization condition [Eq. (23)]—occurs before the energy curves cross (cf. Fig.

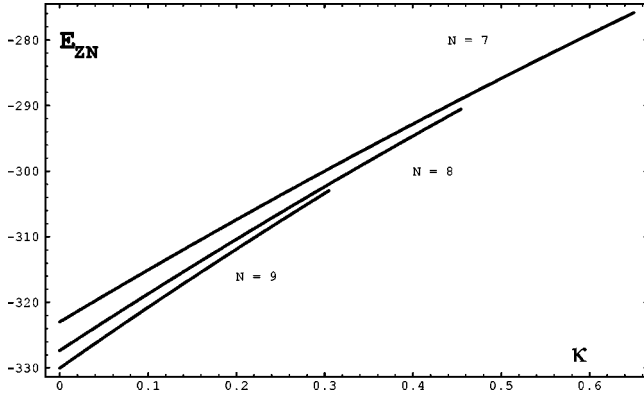


FIG. 1. Ground state energy (in Ry) of positive ions $N=9,8,7$ as a function of the screening parameter κ (in a_B^{-1}). Note that ionization occurs *before* the curves intersect.

3). This demonstrates the importance of treating structure on the same footing as the energy corrections. Furthermore, Fig. 1 clearly shows a nonlinear behavior of the energies, thus surpassing the linear approximation as given in Eq. (19). Figure 2 shows, for the $N=9$ ion, the difference of the full \tilde{E}_{ZN} and the linear approximation as in Eq. (19), which corresponds thermodynamically to the DH limiting law. It is quite obvious that even for very small values of κ the linear law is insufficient.

The structure changes due to the plasma, as described in the formalism developed above, is documented in Fig. 3. In contrast to hydrogenlike bound states, where $R_{1,1}$ really tends toward infinity, the discussion in the context of Eq. (23) showed that for many-electron atoms delocalization must not be understood as removing the electron to infinity but rather as the nuclear field becoming too weak to bind the number of electrons prescribed by the definition of the chemical species. Figure 3 shows that while $R_{10,9}$ nearly doubles before ionization, the next higher ions are much less effected.

Figure 4 shows the dependence of the chemical potentials λ_N on κ . Inspection of Eqs. (23) and (20) shows that the R_{ZN} being finite at the point of ionization necessarily means $\lambda_N > 0$ as well, as is clearly visible in Fig. 4. In the usual interpretation of the chemical potential, this would provoke the

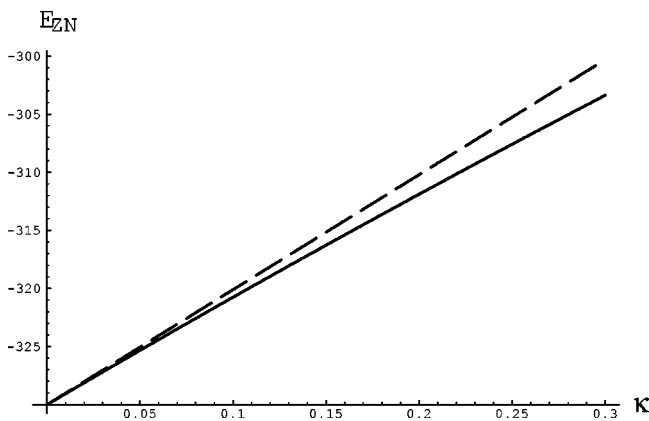


FIG. 2. Difference of self-consistent (solid line) and perturbative (dashed) ground state energy (in rydbergs) for the $N=9$ ion; κ in a_B^{-1} ; nonlinearity effects are clearly established even for small κ values.

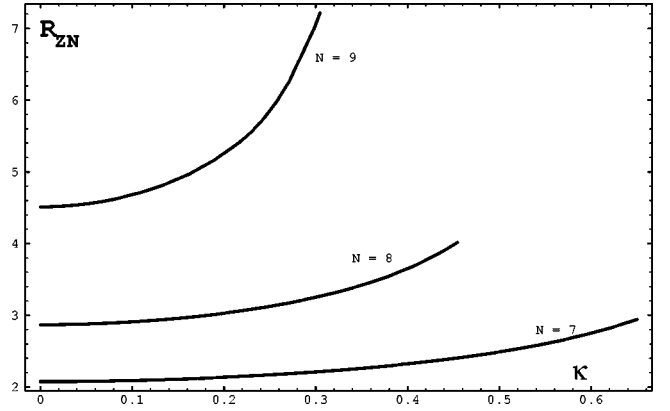


FIG. 3. κ dependence (in units of a_B^{-1}) of ionic radii $N=9,8,7$ (in a_B).

statement that, at the point of ionization, energy can still be gained from adding electronic density to the bound state, which is, of course, in open contradiction to the idea of ionization. The answer lies, again, in the electron density separation [Eq. (3)] and the definition of \tilde{E}_{ZN} , Eq. (12). The finite λ_N signify, then, the energy of the plasma hidden in \tilde{E}_{ZN} . Similar to those in Fig. 1, the λ_N -curves are notably nonlinear, which underlines the necessity of a sound structural theory for bound states in plasmas. Finally, it should be pointed out that the κ effects already start to play a significant role at rather small values. Although this may be an artifact of TF theory, it seems to signal, again, the importance of an appropriate treatment of the screening effects in the outer regions of the bound-electron density.

III. THERMODYNAMICS

In the Introduction, the treatment of the bound states as laid out above was motivated by the desire to construct plasma-correspondent parameters for the ‘‘aggregated’’ chemical interactions. It seems obvious that with the changing of bound electron density, for instance, hard sphere radii and polarizabilities will change. If molecules were to be included, i.e., the radial symmetry broken, further contributions to $F^{\text{int}}[n^*, \tilde{n}_z; T]$ would arise, the parameters of which

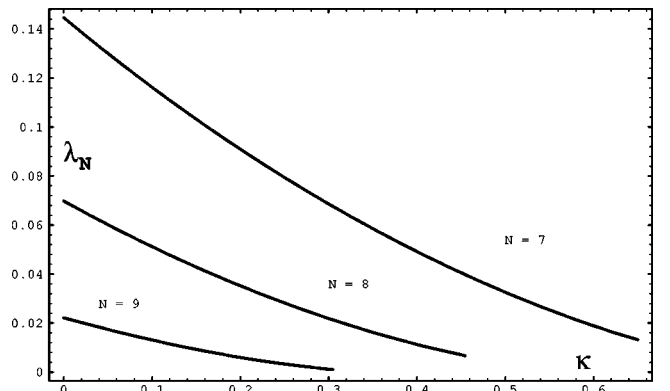


FIG. 4. Chemical potentials λ_N in rydbergs as functions of κ (in a_B^{-1}). Note that the λ_N are nonzero at ionization; explanations are found in the text.

would depend on the bound state structure as well. The mechanism of the thus adjusted chemical picture is most easily demonstrated with the help of van der Waals' EOS:

$$\left(p - \frac{a}{V^2}\right)(V - b) = Nk_B T. \quad (27)$$

Equation (27) contains two empirical corrections to ideal gas behavior. The parameter a describes the lowering of the pressure p due to mutual attraction of the molecules, whereas b describes the space taken up by the extended molecules themselves. Parameters a and b thus stand for an energetical and a structural effect, respectively. The van der Waals reasoning can now immediately be applied to the above discussed quantum plasmas. Obviously, the parameter a corresponds to the lowering of the ionization energy due to the electrostatic screening, whereas b links to the radii R_{ZN} (Fig. 3). It is then possible to define an analogous parameter b_q as

$$\frac{b_q}{V} = \sum_z^{Z-1} \frac{4\pi}{3} \rho_z R_{Z,Z-z}^3. \quad (28)$$

It can be stated at this point that the effective volume term and the energetic correction have been derived on exactly the same footing, which is in contrast to usual ionization equilibrium theories formulated in the chemical picture (e.g., [24,36,37]). Introducing the effective particle densities

$$\tilde{\rho}_i = \frac{\rho_i}{1 - b_q}, \quad i = *, 0, 1, \dots, 2, \quad (29)$$

the MAL can be formulated as

$$\begin{aligned} \mu_{i+1}^{id}(\tilde{\rho}_{i+1}) + [\tilde{E}_{Z,Z-(i+1)}(\kappa) - \tilde{E}_{Z,Z-(i+1)}(\kappa=0)] + \mu^* \\ = \mu_i^{id}(\tilde{\rho}_i) + [\tilde{E}_{Z,Z-i}(\kappa) - \tilde{E}_{Z,Z-i}(\kappa=0)], \\ i = 0, 1, \dots, Z-1. \end{aligned} \quad (30)$$

The system (30) has, obviously, to be solved iteratively since the densities $\tilde{\rho}_i$ depend on the solution. In Ref. [38] an equivalent one-electron problem has been solved and clearly showed the effect that is expected in Eq. (30) as well: starting with the isolated bound state value $b_q(\kappa=0)$, the plasma composition will yield a finite κ . This, in turn, increases the R_{ZN} and produces a new plasma composition with yet another κ . Potentially, this loop contains the point where the plasma composition becomes unstable, which is a thermodynamical expression of the Mott transition discussed above. A numerical example for this phenomenon can, within the framework of this work, however, not be given due to the decisive fault of the neutral TF atoms being unstable and has to be left to subsequent work. In the MAL (30) the plasma chemical potential μ^* may contain further contributions due

to exchange and correlation effects in the plasma [1,24] which correspond, in a general sense, also to van der Waals' parameter a . Thus, a picture of a van der Waals-like description of quantum plasmas emerges.

IV. CONCLUSION

Starting from a general functional of the free energy of a system of quantum electrons and classical nuclei, the chemical picture has been shown to arise for a certain separation ansatz for the electron density. This separation entails necessarily a mixing term that cannot, on physical grounds, be assigned to *either* the plasma *or* the bound state. In the presented evaluation, this mixing term was treated in analogy to the famous theory of Debye and Hückel [23], which led to the definition of a functional describing the bound state plus its electrostatically screening environment. Assuming further the kinetic energy of the bound electrons to be Thomas-Fermi-like, a simple analysis was made possible. Unsurprisingly, this showed the usual flaws of TF theory, even enhanced up to the point of generally unstable neutral atoms. A number of features such as the delocalization mechanism or the difference with one-electron ionization theories could, however, be discussed and illustrated. The bound state analysis, then, provided a means to construct plasma-correspondent parameters for the chemical picture. In the spirit of the van der Waals EOS this produced, finally, a consistent description of energetical and structural corrections to ideal gas behavior.

Concerning the approximations made, it should be noted that Thomas-Fermi theory can not only be corrected for its well-known anomalies, but even turned into a surprisingly accurate theory. Furthermore, the Debye-Hückel treatment of the electrostatic screening can be improved as well. It has to be stressed again that the assumptions of Eqs. (10)–(12) destroy the self-consistency initially contained in Eq. (9). With a proper ionic structure theory inserted there instead of the Debye-Hückel ansatz, the presented framework can indeed be extended to long-range order phenomena. It has to be stated that the presupposed Debye-Hückel-like form of the charge cloud around a bound state restricts the theory to a nondegenerate, weakly interacting plasma. Despite the restrictive character of the approximations, it can be registered as a general result of this work that for chemical species, which can—due to the number of bound electrons—be labeled statistical, the interaction of the outer regions of the core electronic density with the plasma is of great importance. Delocalization and a correspondent understanding of the Mott transition follow.

The aim of this paper was not to present a numerically accurate theory but to highlight the general problem of consistency of structural and energetical changes when applying the chemical picture to nonideal plasmas. In this respect the MAL (30) presents the desired improvement in consistency.

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