

Correlated-basis-functions theory of metal surfaces

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A new method for treating metal surfaces is presented which will complement the conventional density-functional theory. It makes use of the correlated-basis-functions approach, which has proven useful for treating liquid and solid helium, nuclear matter, and homogeneous and mildly inhomogeneous Coulomb systems. It is a variational theory that deals directly with the wave function—one that contains in a balanced way both single-particle elements and explicit many-particle correlation factors. The surface-energy expression does not require a density-gradient expansion. It does not draw information from independent work on the homogeneous electron liquid and is thus totally self-contained. Discrete ion-lattice effects are accounted for without the need to invoke a low-order perturbation theory. Systematic improvements are possible, either through the introduction of higher-order irreducible correlation factors or through a diagrammatic perturbation theory in the correlated representation. Most importantly, approximate many-particle wave functions for describing the ground-state and low-lying excitations are made available. They can be used for determining adsorption properties such as the substrate-mediated interaction between adatoms. In this paper we describe the theory in detail and report on numerical results obtained for the entire range of metals, $2 \leq r_s \leq 6$. Our surface energies show slight improvement over those obtained with density-functional methods. Our work functions are not quite as good at small r_s ; there the electron-density profiles display slightly higher peaks and longer tails. We discovered no new startling results and had not expected to do so. The main accomplishment is the establishment of a self-contained theory and a basis for future calculations considered impossible or difficult in the density-functional formalism. Discussions are carried out in that spirit.

I. INTRODUCTION

A. Formulation of the problem

The system under consideration consists of N/Z charge- Z ions and N electrons in a volume of order Ω closed on all sides except one. On this side, we have a free surface that results from a cleaving process. For convenience, let us take $Z = 1$ throughout.

The full Hamiltonian has the form

$$H = \sum_{\alpha=1}^N \frac{-\hbar^2}{2M} \nabla_{\alpha}^2 + \sum_{i=1}^N \frac{-\hbar^2}{2m} \nabla_i^2 + \sum_{\substack{\alpha, \beta=1 \\ \alpha < \beta}}^N v_{II}(\alpha, \beta) + \sum_{\alpha=1}^N \sum_{i=1}^N v_{Ie}(\alpha, i) + \sum_{\substack{i, j=1 \\ i < j}}^N v_{ee}(i, j), \quad (1)$$

where M and m denote, respectively, the ion and electron masses. In the simplest model, one assumes that the ion lattice is static and represents it by a distribution function $n_+(\vec{r})$. The Hamiltonian reduces to

$$H = \sum_{i=1}^N \frac{-\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \int d\vec{r} d\vec{r}' n_+(\vec{r}) n_+(\vec{r}') v_{II}(\vec{r}, \vec{r}') + \sum_{i=1}^N \int d\vec{r} n_+(\vec{r}) v_{Ie}(\vec{r}, \vec{r}_i) + \sum_{\substack{i, j=1 \\ i < j}}^N \frac{e^2}{|\vec{r}_i - \vec{r}_j|}, \quad (2)$$

the second term being a constant.

Single-particle theories, such as band theory, keep the first and third terms together and solve the one-particle Schrödinger equation in detail. The choice of v_{Ie} reflects realistically the effect of overlap between core and valence electrons, and $n_+(\vec{r})$ contains information on both the lattice symmetry and the spread of ion wave functions. Coulomb interactions between the electrons are then brought in as a correction. Conventional many-particle theories, on the other hand, combine the first and fourth terms with a semi-infinite uniform charged background to form a jellium model, calculate the latter's properties, and then treat the deviation of $n_+(\vec{r})$ from uniformity as a perturbation. In either case, the information to be deduced includes at least the electron-density profile $n(\vec{r})$, the surface energy σ , the work function ϕ , and the excitation spectrum.

B. Density-functional theory

In the original density-functional theory calculation (DFT) for metal surfaces by Lang and Kohn,¹ the energy functional

$$E[n(\vec{r})] = \int v(\vec{r}) n(\vec{r}) d\vec{r} + \frac{1}{2} \int \frac{e^2 n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + T_S[n(\vec{r})] + \int \epsilon_{xc}[n(\vec{r})] n(\vec{r}) d\vec{r} \quad (3)$$

is minimized with respect to the electron-density profile $n(\vec{r})$ for a jellium model. This can be done by solving an auxiliary self-consistent single-particle Schrödinger equation

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\vec{r}) \right] \varphi_{\vec{\mu}}(\vec{r}) = \epsilon_{\vec{\mu}} \varphi_{\vec{\mu}}(\vec{r}), \quad (4)$$

with

$$v_{\text{eff}}(\vec{r}) = v(\vec{r}) + \int \frac{e^2 n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + \left. \frac{d[n\epsilon_{\text{xc}}(n)]}{dn} \right|_{n=n(\vec{r})} \quad (5)$$

and

$$n(\vec{r}) = \sum_{\vec{\mu}} |\varphi_{\vec{\mu}}(\vec{r})|^2. \quad (6)$$

From here,

$$T_S[n(\vec{r})] = \sum_{\vec{\mu}} \epsilon_{\vec{\mu}} - \int v_{\text{eff}}(\vec{r}) n(\vec{r}) d\vec{r}. \quad (7)$$

The substitution of Eq. (7) into Eq. (3) yields the ground-state energy.

In this calculation, the exchange-correlation energy density $\epsilon_{\text{xc}}[n(\vec{r})]$ is to be taken from bulk electron liquid calculations, which yield $\epsilon_{\text{xc}}(n)$ at uniform densities n . Such a local-density approximation (LDA) is expected to be good for systems with slow variations or small inhomogeneities. Metal surfaces do not satisfy either requirement. Yet when lattice corrections on the jellium model are accounted for in a first-order perturbation theory, the LDA is found to yield surface energies and work functions in rather good agreement with experimental data.¹⁻³

The LDA and the first-order perturbation treatment for the discrete lattice have been two sources of concern to theorists in the field. During the last decade, many authors have attempted to make improvements on these aspects of the original Lang-Kohn calculation. A few examples will be mentioned here.

To correct the LDA, Rasolt and co-workers^{4,5} included in $E[n(\vec{r})]$ the leading density-gradient correction

$$\int \epsilon_{\text{xc}}^{(2)}[n(\vec{r})] [\nabla n(\vec{r})]^2 d\vec{r},$$

and found the surface energy increased by 20% or more, depending on the value of r_s . Gupta and Singwi⁶ added the term

$$\int \epsilon_{\text{xc}}^{(4)}[n(\vec{r})] \vec{\nabla} n(\vec{r}) \cdot \vec{\nabla} [\nabla^2 n(\vec{r})] d\vec{r},$$

and reduced the total correction to a few percent. Langreth and Perdew⁷ replaced the density-gradient expansion with a wave-vector analysis, interpolating the exchange-correlation energy between the LDA at short wavelengths and the random phase approximation (RPA) at long wavelengths. They found surface energies at values approximately 10% above those of the LDA including a first-order perturbative correction (LDA-FPC).

On improving the treatment for the ion lattice, Sahni and co-workers⁸ carried out variational calculations using trial density functions generated by a parametrized $v_{\text{eff}}(\vec{r})$.

Monnier and Perdew,⁹ on the other hand, parametrized only the discrete-lattice correction term in the self-consistent potential, and used the solutions of the self-consistent equation to generate trial density functions for their variational calculation. In each case, a general lowering of the surface energy was found, which tended to offset the increases caused by correcting LDA-FPC. This probably explains why the LDA results including first-order perturbative correction for the discrete lattice, i.e., Lang-Kohn, stand so close to the best DFT results and to experimental data.

A large number of three-dimensional band calculations using realistic ion lattices exist in the literature.¹⁰⁻¹⁸ Diverse methods have been used for treating the exchange-correlation energy functional. Since it is generally believed by band theorists that many-particle effects are small, the exchange-correlation density functional is given simple forms. Few reported on the density profiles or the surface energies. Their interest lies mainly in the structure of the energy band, especially the surface states.

C. The correlated basis-functions approach

The method of correlated basis functions (CBF) seeks to incorporate into the basis functions as much information about the system as is practicable, without unduly restricting the outcome of the calculation. Correlations in the system can be long-ranged, as in crystals or superconductors, or short-ranged, as in liquid helium or nuclear matter. The wave functions come in the form of two or more factors. For example, one factor will be the "model function," defined as an optimum independent particle (or quasiparticle) description for the system. In the case of a system without long-range order, it will be a properly symmetrized product of plane waves. For a solid, it may be a product of Gaussians localized on lattice sites, Bloch states, or phonons. In the case of a superfluid of fermions, it can be a product of paired functions in the momentum space—a BCS wave function. For a Fermi system with a surface, as in the present case, it should be a determinant whose elements are solutions of a single-particle Hamiltonian that contains some reasonable model surface potential, such as (but surely not limited to) the set $\{\varphi_{\vec{\mu}}(\vec{r})\}$ that appears in Eq. (4).

The other factor is a "correlation factor," which features interparticle (or interquasiparticle) correlations. A popular example is a function in the Jastrow-Feenberg form,

$$\prod_{i < j} f(r_{ij}),$$

which accounts for pair-reducible many-particle correlations. One can also include higher-order functions designed to account for irreducible multiparticle correlations. In the present case, as was shown in calculations performed for electron correlations in bulk metal—both CBF (Refs. 19 and 20) and t matrix (Ref. 21)—the Jastrow-Feenberg form will be quite adequate.

The two factors serve to cast single-particle and many-particle properties in balanced roles. The model function emphasizes the first and third terms of the Hamiltonian

(2). It takes exchange into account. The correlation factor stresses the importance of the last term in the Hamiltonian and thus the interparticle correlations. No assumption need be made on their relative significance. The competition between these two factors will ultimately determine the best microscopic description for the system. For example, if correlations are truly unimportant, the CBF variational calculation will result in a $\prod_{i < j} f(r_{ij})$ that deviates little from unity when the best $\{\varphi_{\vec{\mu}}(\vec{r})\}$ are used in forming the model function. For details and general reviews of the CBF theory, we refer the reader to Refs. 22–25 and recent conference proceedings.²⁶

An immediate question arises. The DFT has worked rather well, so why should a new formalism be attempted? It is our belief that the CBF method has become sufficiently well developed for application to metal surface and adsorption calculations. If successfully carried out, it can provide a useful complement to the DFT for the following reasons:

(i) In the CBF, the variational procedure is applied directly on the ground-state wave function rather than the density.

(ii) The wave function is constructed to explicitly account for single-particle and many-particle features in a balanced way, as described above.

(iii) The energy expectation value will be expressed in closed, integrable forms. The theory will be free of density-gradient expansion or interpolation schemes.

(iv) The homogeneous bulk appears as a limiting case of the inhomogeneous system [when the model surface potential is taken as a constant, and thus $\{\varphi_{\vec{\mu}}(\vec{r})\}$ turn into plane waves]. They are treated on equal footing. The theory is self-contained: It need not draw upon results of independent work on the homogeneous system.

(v) The model for the lattice can be altered at will. It enters the variational calculation through the Hamiltonian (2). For the best effect, the symmetry of the model function should be chosen to match the lattice, but there remains much flexibility in varying the model function. One need not employ a low-order perturbation theory to account for the discreteness of the lattice.

(vi) Systematic improvements are possible in two ways: by including higher-order correlation factors in the trial wave function, or by carrying out perturbative calculations in the correlated representation, using nondiagonal matrix elements of the Hamiltonian (2) as perturbation.

(vii) The availability of a set of many-electron wave functions enables us to use the theory for studying adsorption phenomena, in particular for obtaining the substrate-mediated interaction between a pair of adsorbed atoms/molecules. It also makes the theory applicable to situations where interparticle correlations exert dominant influences.

We have approached the development of such a theory with much caution. The long-range nature of Coulomb correlations was expected to give rise to spurious divergences. In addition, inhomogeneities as sharp as those near the surfaces of metals would require accurate approximation schemes.

Our first step was to apply CBF to Coulomb correla-

tions in a homogeneous Fermi system. We derived and solved an integral equation [hereafter to be referred to as the Chakravarty-Woo (CW) equation] for the homogeneous electron liquid.¹⁹ The results obtained were in good agreement with those obtained with conventional methods throughout the range of metallic densities (e.g., by Singwi and co-workers^{27,28}). The same integral equation in the configuration representation was next applied to nuclear matter. An initial attempt²⁹ gave results that deviated from Fermi hypernetted chain calculations (FHNC/4).^{30,31} Subsequent diagrammatic analyses suggested improvement on an approximation, which turned out to be important for liquid helium and nuclear matter. Its inclusion led to results that agreed closely with FHNC/4, thereby confirming the validity of the CW equation.³² It was shown that this improvement is not needed for long-range systems such as the electron liquid. We then moved on to inhomogeneous electron liquids, deriving in the process coupled CW equations²⁰ that contain the homogeneous system as a limiting case. The first application of this theory was on a system with relatively mild inhomogeneities: metallic hydrogen.²⁰ Our results agreed well with those obtained using a standard perturbation theory³³ and using the DFT.³⁴ At that point, we decided that the time had finally arrived for proceeding to metal surface calculations.

II. THE ONE-ELECTRON MODEL PROBLEM

We take for our correlated wave function (suppressing spin functions)

$$\psi(1, 2, \dots, N) = \prod_{\substack{i, j=1 \\ i < j}}^N \exp[\frac{1}{2}u(r_{ij})] D[\varphi], \quad (8)$$

where $D[\varphi]$ denotes a determinant with single-particle elements $\{\varphi_{\vec{k}}(\vec{r})\}$. Variation is to be conducted on $u(r)$ and $\varphi_{\vec{k}}(\vec{r})$. $u(r)$ will be a subject of discussion in Sec. III. In this section, we focus our attention on the model function $D[\varphi]$, calculating for later use an “uncorrelated” density distribution and its attending contribution to the surface energy.

The single-particle elements $\{\varphi_{\vec{k}}(\vec{r})\}$ should form a complete set. The most convenient way to parametrize such a set of functions is to take them as eigenstates of a Hamiltonian that contains a parametrizable potential $V(\vec{r})$:

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \varphi_{\vec{k}}(\vec{r}) = \epsilon_{\vec{k}} \varphi_{\vec{k}}(\vec{r}). \quad (9)$$

$V(\vec{r})$ should have the appearance of a surface potential. It is, however, only a device to assist us in constructing a variational wave function. There is no reason for it to be the effective surface potential experienced by an electron in an actual metal. We will discuss this later.

In preliminary calculations,^{35–37} we experimented with several simple forms of $V(\vec{r})$, all of which are dependent upon only one variable, z , the distance from the electronic

Gibbs surface (to be defined presently). Here we shall employ a two-parameter hyperbolic tangent form:

$$V(z) = \frac{V_0}{2} \left[1 + \tanh \left[\frac{z - z_0}{2a} \right] \right]. \quad (10)$$

The two parameters are V_0 and a , which measure, respectively, the depth and width of the model potential. The third parameter z_0 determines the location of the potential, but cannot be considered free, as will be seen later in this section and in Sec. III.

We adopt periodic boundary conditions in x and y directions, each with period L . In the z direction, we confine the electron to a region bounded at $z = -L$ by an infinite barrier, but we let the wave functions decay freely outside the surface, i.e., beyond the region $z \approx 0$.

The solutions of Eq. (9), with $V(\vec{r})$ given by Eq. (10), can be written as

$$\varphi_{\vec{k}}(\vec{r}) \equiv \varphi_{k_x, k_y, k}(x, y, z) = \frac{1}{L} e^{i(k_x x + k_y y)} \varphi_k(z), \quad (11)$$

where

$$k_x = \frac{2\pi m_x}{L}, \quad k_y = \frac{2\pi m_y}{L}, \quad (12)$$

m_x and m_y being integers, both positive and negative. $\varphi_k(z)$ then satisfies the one-dimensional Schrödinger equation

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dz^2} + V(z) \right] \varphi_k(z) = \frac{\hbar^2 k^2}{2m} \varphi_k(z) \quad (13)$$

and can be expressed in terms of ${}_2F_1$, the hypergeometric function³⁸:

$$\varphi_k(z) = C \frac{e^{ikz}}{(1+\xi)^{\mu+\nu}} {}_2F_1 \left[\mu + \nu, \mu + \nu + 1, 2\nu + 1, \frac{1}{1+\xi} \right], \quad (14)$$

where

$$\mu = ika, \quad \nu^2 = \left[\frac{2mV_0}{\hbar^2} - k^2 \right] a^2, \quad (15)$$

$$\xi = \exp[(z - z_0)/a], \quad (16)$$

and

$$C = \frac{|\Gamma(\mu + \nu)| |\Gamma(\mu + \nu + 1)|}{2\Gamma(2\nu + 1) |\Gamma(2\mu)|}. \quad (17)$$

The requirement that $\varphi_k(z)$ decay exponentially outside the surface means that we must take $\nu > 0$. Deep into the bulk, as $z \rightarrow -\infty$, $\varphi_k(z)$ takes on its asymptotic form of a cosine wave of unit amplitude:

$$\lim_{z \rightarrow -\infty} \varphi_k(z) = \cos[k(z - z_0) - \gamma(k)], \quad (18)$$

where $\gamma(k)$ denotes the phase shift:

$$\gamma(k) = \frac{i}{2} \ln \left[\frac{\Gamma(\mu + \nu) \Gamma(\mu + \nu + 1) \Gamma(-2\mu)}{\Gamma(\nu - \mu) \Gamma(\nu - \mu + 1) \Gamma(2\mu)} \right], \quad (19)$$

a continuous function of k in the range of allowed values of k , with the property

$$\gamma(0) = -\frac{\pi}{2}. \quad (20)$$

Also, since $\mu(k) = -\mu(-k)$ and $\nu(k) = \nu(-k)$, we have

$$\gamma(-k) = -\gamma(k). \quad (21)$$

The eigenvalues k can be determined from the boundary condition

$$\varphi_k(z) |_{z=-L} = 0. \quad (22)$$

Using the asymptotic condition (18),

$$k_m(L + z_0) + \gamma(k_m) = (2m + 1) \frac{\pi}{2}, \quad m = 0, \pm 1, \pm 2, \dots$$

From Eq. (13), k and $-k$ correspond to the same energy. Since the energy eigenstates for a one-dimensional Schrödinger equation cannot be degenerate, we take only $k \geq 0$. Also, by Eq. (21), $m \geq 0$. Thus the quantization condition of k_m reads

$$k_m = \frac{(2m + 1)\pi}{2(L + z_0)} - \frac{\gamma(k_m)}{L + z_0}, \quad m = 0, 1, 2, \dots \quad (23)$$

Now let us look at an N -electron system. Suppose we have a set of N noninteracting electrons moving under the influence of the same model potential $V(z)$. The density of such a noninteracting system will be given by

$$n_0(\vec{r}) \equiv n_0(z) = 2 \sum_{m=1}^M \sum_{m_x, m_y} |\varphi_{k_x, k_y, k_m}(x, y, z)|^2, \quad (24)$$

where the upper limit M corresponds to k_M , the maximum value of k_m when N electrons fill up the N lowest single-particle states. Straightforward counting gives

$$N = 2 \sum_{m=0}^M \sum_{m_x, m_y} 1 = 2 \sum_{m=0}^M \frac{L^2}{4\pi^2} \int_0^{(k_M^2 - k_m^2)^{1/2}} 2\pi k dk = \frac{L^2}{2\pi} \sum_{m=0}^M (k_M^2 - k_m^2) = \frac{L^2(L + z_0)}{\pi^2} \left[\frac{k_M^3}{3} + \frac{1}{L} \int_0^{k_M} \gamma(k) k dk \right]. \quad (25)$$

To lend this uncorrelated density function a more concrete interpretation—one that will become useful later when we discuss the interacting system described by the wave function (8)—we now introduce an imaginary “posi-

tive charge” background. The background is brought up here merely to facilitate counting. It is *not* to add an external field and alter our single-particle calculation. Therefore it does not matter how we distribute these ima-

ginary charges as long as they are confined between two planes $z=0$ and $z=-L+\delta$ and they give us an average density $\langle n_+(\vec{r}) \rangle$ equal to the bulk density n_B of the noninteracting electrons:

$$n_B \equiv \frac{N}{\Omega} \equiv \frac{N}{L^2(L-\delta)}. \quad (26)$$

$z=-L+\delta$ gives the location of the asymptotic Gibbs surface of the electron system. That the latter is not at $z=-L$ is because a short distance, on the order of 2δ , is needed for the electron density $n_0(z)$ to fall from its bulk value at large negative z to zero at $z=-L$. (See Fig. 1.) To preserve charge neutrality, the imaginary background must end on a plane that matches this asymptotic Gibbs surface. Of course, the same is true near the free surface; we shall address that question a little later.

Equation (26) enables us to relate k_M to k_F , the Fermi momentum of the bulk, defined as usual by

$$n_B = \frac{k_F^3}{3\pi^2}. \quad (27)$$

Equations (25)–(27) yield

$$k_M = k_F - \frac{1}{L} \left[\frac{\delta+z_0}{3} k_F + \frac{1}{k_F^2} \int_0^{k_F} \gamma(k) k dk \right]. \quad (28)$$

$$n_0(z) \rightarrow \frac{1}{\pi^2} \int_0^{k_F} (k_F^2 - k^2) \sin^2[k(z+L)] dk$$

$$= n_B \left[1 + \frac{3}{4k_F^2(z+L)^2} \cos[2k_F(z+L)] - \frac{3}{8k_F^3(z+L)^3} \sin[2k_F(z+L)] \right]. \quad (30)$$

Using this, the charge-neutrality condition renders

$$\delta = \frac{3\pi}{8k_F}. \quad (31)$$

Moving now to the free end, take a point $z=-l$ such that $-L \ll -l \ll -1/k_F$, in other words, a point deep in the bulk. Charge neutrality requires

$$\int_{-l}^{\infty} n_0(z) dz = n_B l. \quad (32)$$

Since $n_0(z) \rightarrow n_B$ when $z \ll -1/k_F$, Eq. (32) does not depend on l . The transformation $z' = z - z_0$ then yields

$$\begin{aligned} \int_{-l-z_0}^{\infty} n_0(z'+z_0) dz' &= \int_{-l-z_0}^{-l} n_B dz' + \int_{-l}^{\infty} n_0(z'+z_0) dz' \\ &= n_B z_0 + \int_{-l}^{\infty} n_0(z'+z_0) dz'. \end{aligned}$$

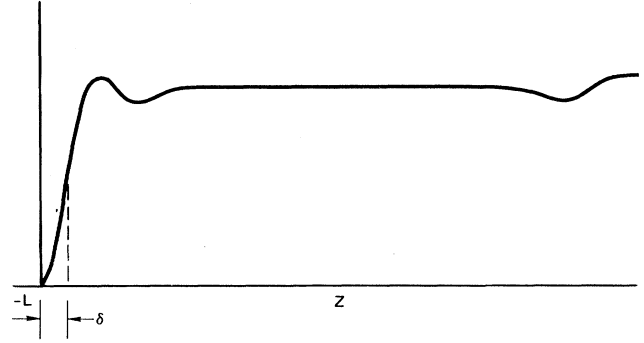


FIG. 1. Asymptotic Gibbs surface.

Note that caution must be taken everywhere with regard to terms of order L^{-1} when we perform surface calculations. Following the same counting procedure as that of Eq. (25), and making use of the Euler-Maclaurin formula, we find from Eq. (24) to order L^{-1}

$$n_0(z) = \frac{1}{\pi^2} \int_0^{k_F} (k_F^2 - k^2) |\varphi_k(z)|^2 dk. \quad (29)$$

Asymptotically, as $z \rightarrow -L$,

Or, by Eq. (32),

$$z_0 = l - \int_{-l}^{\infty} \frac{n_0(z'+z_0)}{n_B} dz'. \quad (33)$$

Since the positive background has been taken to terminate at $z=0$, the electronic Gibbs surface must also be at $z=0$. Equation (33) tells us that to guarantee the latter we must choose z_0 to satisfy Eq. (33). Thus z_0 is not a free parameter.

The ground-state energy of the noninteracting system is given by

$$\begin{aligned} T_1 &\equiv 2 \sum_{\vec{k}} \epsilon_{\vec{k}} = \frac{\hbar^2}{m} \sum_{m=0}^M \sum_{m_x, m_y} (k_x^2 + k_y^2 + k_m^2) = \frac{\hbar^2}{m} \frac{L^2}{4\pi^2} \sum_{m=0}^M \int_0^{(k_M^2 - k_m^2)^{1/2}} 2\pi k (k^2 + k_m^2) dk \\ &= \frac{\hbar^2 L^2}{8m\pi} \sum_{m=0}^M (k_M^4 - k_m^4) = \frac{\hbar^2 L^2 (L+z_0)}{2m\pi^2} \left[\frac{k_M^5}{5} + \frac{1}{L} \int_0^{k_M} \gamma(k) k^3 dk \right]. \end{aligned} \quad (34)$$

Equation (28) converts T_1 to the form

$$T_1 = \frac{\hbar^2 L^3}{2m\pi^2} \left[\left[\frac{1}{5} - \frac{2z_0}{15L} - \frac{\delta}{3L} \right] k_F^5 + \frac{1}{L} \int_0^{k_F} \gamma(k)(k^2 - k_F^2)k dk \right]. \quad (35)$$

For the bulk system, similar calculations as described above lead to

$$k = \frac{m\pi}{2L}, \quad m = 1, 2, \dots$$

$$k_M = k_F + \frac{\pi}{8L} - \frac{\delta}{3L} k_F,$$

and

$$\begin{aligned} T_1^B &= \frac{\hbar^2 L^3}{m\pi^2} \left[\frac{k_M^5}{5} - \frac{\pi k_M^4}{16L} \right] \\ &= \frac{\hbar^2 L^3}{m\pi^2} \left[\left[\frac{1}{5} - \frac{\delta}{3L} \right] k_F^5 + \frac{1}{L} \frac{\pi k_F^4}{16} \right]. \end{aligned} \quad (36)$$

Thus, the surface energy per unit area is given by

$$\begin{aligned} t_1 &\equiv \frac{T_1 - \frac{1}{2} T_1^B}{L^2} \\ &= \frac{\hbar^2}{2m\pi^2} \left[-\frac{2}{15} z_0 k_F^5 + \int_0^{k_F} k(k^2 - k_F^2) \right. \\ &\quad \left. \times \left[\gamma(k) + \frac{\pi}{4} \right] dk \right]. \end{aligned} \quad (37)$$

Once again we emphasize that this section has dealt with choosing a set of model functions $\{\varphi_{\vec{k}}(\vec{r})\}$ for use in the variational wave function $\psi(1, 2, \dots, N)$. The purpose of introducing an imaginary neutralizing background after the completion of the eigenvalue calculation was to establish a proper counting procedure. In the process, several concepts and formulas emerged, which will prove useful in later sections.

III. DENSITY FOR AN INTERACTING ELECTRON SYSTEM

For describing an interacting electron system, we go back to the correlated wave function of Eq. (8). First, we will discuss the choice of $u(r)$.

In Ref. 19, we took for a homogeneous electron liquid

$$u(r) = -\frac{\alpha}{r}(1 - e^{-br}), \quad \alpha = \frac{2e^2}{\hbar\omega_p} \quad (38)$$

where $\omega_p \equiv (4\pi n_B e^2/m)^{1/2}$ denotes the plasmon frequency and b a variational parameter. The latter was determined for every value of r_s . It was shown in Ref. 19 that such a $u(r)$ satisfied the required sum rule. We shall adopt the same form of $u(r)$ in this work to ensure that the bulk will be eliminated exactly in our calculation of the surface energy. Of course, for each r_s , b will have to be accorded

its value as determined in Ref. 19.

Offhand, it appears that a better choice of $u(r)$ would be one that varies with the local density. In other words, n_B in ω_p should probably be replaced by the local electron density $n(r)$. Closer inspection indicates that such a simple local density dependence would not be quite correct, because $n(\vec{r})$ does not approximate the density of a *locally neutral system*. It is better, at least for now, to leave n_B in its place.

A. Chakravarty-Woo equation for the density

We now define for $\psi(1, 2, \dots, N)$ the n -particle distribution functions $p(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n)$. With spin indices and summations suppressed throughout,

$$p(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) = \frac{N!}{(N-n)!} \frac{\int |\psi|^2 d\vec{r}_{n+1} \cdots d\vec{r}_N}{\int |\psi|^2 d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_N}. \quad (39)$$

Note that the one-particle distribution function

$$p(\vec{r}_1) = N \frac{\int |\psi|^2 d\vec{r}_2 \cdots d\vec{r}_N}{\int |\psi|^2 d\vec{r}_1 \cdots d\vec{r}_N} \quad (40)$$

is precisely the density function $n(\vec{r}_1)$. In the special case of $u(r) = 0$, $p(\vec{r})$ reduces to the density $n_0(\vec{r})$ of an uncorrelated electron system. For later use, we write down explicitly the two- and three-particle distribution functions:

$$\begin{aligned} p(\vec{r}_1, \vec{r}_2) &= N(N-1) \frac{\int |\psi|^2 d\vec{r}_3 \cdots d\vec{r}_N}{\int |\psi|^2 d\vec{r}_1 \cdots d\vec{r}_N} \\ &\equiv p(\vec{r}_1)p(\vec{r}_2)g(\vec{r}_1, \vec{r}_2) \end{aligned} \quad (41)$$

and

$$\begin{aligned} p(\vec{r}_1, \vec{r}_2, \vec{r}_3) &= N(N-1)(N-2) \frac{\int |\psi|^2 d\vec{r}_4 \cdots d\vec{r}_N}{\int |\psi|^2 d\vec{r}_1 \cdots d\vec{r}_N} \\ &\equiv p(\vec{r}_1)p(\vec{r}_2)p(\vec{r}_3)g(\vec{r}_1, \vec{r}_2, \vec{r}_3). \end{aligned} \quad (42)$$

In this section, our task is to obtain $p(\vec{r})$, or $n(\vec{r})$, for an interacting system described by the correlated wave function ψ .

A most direct procedure would be by integration, using, for example, a Monte Carlo method³⁹ and the definition of $p(\vec{r})$ [Eq. (40)]. We choose, however, to use an integro-differential equation approach: the generalized CW equation. Unlike Ref. 20, we shall do it in the configuration representation, as in Ref. 40. First, we define a "strength parameter" λ for the correlation and form a λ -dependent wave function:

$$\psi(1,2,\dots,N|\lambda) = \prod_{\substack{i,j=1 \\ i < j}}^N \exp[\frac{1}{2}\lambda u(r_{ij})] D[\varphi]. \quad (43)$$

Then we define λ -dependent distribution functions $p(\vec{r}_1|\lambda)$, $p(\vec{r}_1, \vec{r}_2|\lambda)$, $p(\vec{r}_1, \vec{r}_2, \vec{r}_3|\lambda)$, etc., as in Eqs. (40)–(42). The equations that we derive will be for these λ -dependent distribution functions. The solutions for these equations taken in the full-strength limit $\lambda=1$ are then the functions we seek. In particular, $p(\vec{r}|\lambda=1)$

$=n(\vec{r}) \equiv n(z)$. They will be related to the functions at the uncorrelated limit, $\lambda=0$, e.g., $p(\vec{r}|\lambda=0) = n_0(\vec{r}) \equiv n_0(z)$.

The generalized CW equation is the first of a hierarchy obtained by differentiating the definition of $p(\vec{r}_1|\lambda)$ with respect to λ , introducing into the results the definitions of $p(\vec{r}_1, \vec{r}_2|\lambda)$ and $p(\vec{r}_1, \vec{r}_2, \vec{r}_3|\lambda)$, and then reintegrating with respect to λ . Straightforward algebra leads to the nonlinear integral equation

$$p(\vec{r}_1|\lambda) = p(\vec{r}_1|\lambda=0) \exp \left[\int_0^\lambda d\lambda' \int u(r_{12}) p(\vec{r}_2|\lambda') g(\vec{r}_1, \vec{r}_2|\lambda') d\vec{r}_2 \right. \\ \left. + \frac{1}{2} \int_0^\lambda d\lambda' \int u(r_{23}) p(\vec{r}_2|\lambda') p(\vec{r}_3|\lambda') [g(\vec{r}_1, \vec{r}_2, \vec{r}_3|\lambda') - g(\vec{r}_2, \vec{r}_3|\lambda')] d\vec{r}_2 d\vec{r}_3 \right]. \quad (44)$$

The second of the hierarchy of CW equations would be obtained by performing a similar operation on $p(\vec{r}_1, \vec{r}_2|\lambda)$. This becomes very complicated. It is a project that we plan to undertake in the future. For the present, we intend to approximate $p(\vec{r}_1, \vec{r}_2|\lambda)$ in a manner to be described in Sec. III E and truncate the hierarchy by imposing further a convolution approximation on $p(\vec{r}_1, \vec{r}_2, \vec{r}_3|\lambda)$:

$$g(\vec{r}_1, \vec{r}_2, \vec{r}_3|\lambda) \approx 1 + h_{12}(\lambda) + h_{23}(\lambda) + h_{31}(\lambda) + h_{12}(\lambda)h_{23}(\lambda) + h_{23}(\lambda)h_{31}(\lambda) + h_{31}(\lambda)h_{12}(\lambda) \\ + \int p(\vec{r}_4|\lambda) h_{14}(\lambda) h_{24}(\lambda) h_{34}(\lambda) d\vec{r}_4, \quad (45)$$

where

$$h_{ij}(\lambda) \equiv g(\vec{r}_i, \vec{r}_j|\lambda) - 1. \quad (46)$$

Equation (44) then becomes

$$\ln \frac{p(\vec{r}_1|\lambda)}{p(\vec{r}_1|\lambda=0)} = \sum_{i=1}^6 A_i(\vec{r}_1|\lambda), \quad (47)$$

with

$$A_1(\vec{r}_1|\lambda) = \int_0^\lambda d\lambda' \int d\vec{r}_2 u(r_{12}) p(\vec{r}_2|\lambda'), \quad (48)$$

$$A_2(\vec{r}_1|\lambda) = \int_0^\lambda d\lambda' \int d\vec{r}_2 u(r_{12}) p(\vec{r}_2|\lambda') h_{12}(\lambda'), \quad (49)$$

$$A_3(\vec{r}_1|\lambda) = \int_0^\lambda d\lambda' \int d\vec{r}_2 d\vec{r}_3 u(r_{23}) p(\vec{r}_2|\lambda') p(\vec{r}_3|\lambda') h_{13}(\lambda'), \quad (50)$$

$$A_4(\vec{r}_1|\lambda) = \int_0^\lambda d\lambda' \int d\vec{r}_2 d\vec{r}_3 u(r_{23}) p(\vec{r}_2|\lambda') p(\vec{r}_3|\lambda') h_{12}(\lambda') h_{23}(\lambda'), \quad (51)$$

$$A_5(\vec{r}_1|\lambda) = \frac{1}{2} \int_0^\lambda d\lambda' \int d\vec{r}_2 d\vec{r}_3 u(r_{23}) p(\vec{r}_2|\lambda') p(\vec{r}_3|\lambda') h_{12}(\lambda') h_{13}(\lambda'), \quad (52)$$

and

$$A_6(\vec{r}_1|\lambda) = \frac{1}{2} \int_0^\lambda d\lambda' \int d\vec{r}_2 d\vec{r}_3 d\vec{r}_4 u(r_{23}) p(\vec{r}_2|\lambda') p(\vec{r}_3|\lambda') p(\vec{r}_4|\lambda') h_{14}(\lambda') h_{24}(\lambda') h_{34}(\lambda'). \quad (53)$$

Careful inspection shows that in the convolution approximation the CW equation preserves the asymptotic behavior of the density function. In other words, all A_i 's approach zero deep into the bulk. This is extremely important for a nontrivial interpretation of the solution.

B. Source of spurious divergences

$u(r_{ij})$ is long-ranged, but h_{ij} is short-ranged. We thus find A_2, A_4, A_5 , and A_6 finite, and A_1 and A_3 divergent. The divergences are expected to be spurious.

First, by combining A_1 and A_3 we can demonstrate that the most divergent parts cancel. Let us write A_3 as

$$A_3(\vec{r}_1|\lambda) = \int_0^\lambda d\lambda' \int d\vec{r}_2 d\vec{r}_3 u(|\vec{r}_{12} - \vec{r}_{13}|) p(\vec{r}_2|\lambda') p(\vec{r}_3|\lambda') h_{13}(\lambda') \\ = \int_0^\lambda d\lambda' \int d\vec{r}_2 d\vec{r}_3 \{ u(r_{12}) + \vec{r}_{13} \cdot [\vec{\nabla}_{23} u(r_{23})]_{\vec{r}_3 = \vec{r}_1} + \dots \} p(\vec{r}_2|\lambda') p(\vec{r}_3|\lambda') h_{13}(\lambda'). \quad (54)$$

The definitions (40) and (41) give rise to an obvious sequential relation (or sum rule):

$$\int p(\vec{r}_1, \vec{r}_3 | \lambda) d\vec{r}_3 = (N-1)p(\vec{r}_1 | \lambda). \quad (55)$$

But since

$$\begin{aligned} \int p(\vec{r}_1, \vec{r}_3 | \lambda) d\vec{r}_3 &= \int p(\vec{r}_1 | \lambda) p(\vec{r}_3 | \lambda) g(\vec{r}_1, \vec{r}_3 | \lambda) d\vec{r}_3 \\ &= p(\vec{r}_1 | \lambda) \left[\int p(\vec{r}_3 | \lambda) [g(\vec{r}_1, \vec{r}_3 | \lambda) - 1] d\vec{r}_3 + \int p(\vec{r}_3 | \lambda) d\vec{r}_3 \right] \\ &= p(\vec{r}_1 | \lambda) \left[\int p(\vec{r}_3 | \lambda) h_{13}(\lambda) d\vec{r}_3 + N \right], \end{aligned}$$

Eq. (55) becomes

$$\int p(\vec{r}_3 | \lambda) h_{13}(\lambda) d\vec{r}_3 = -1. \quad (56)$$

Using this relation in A_3 , the first term becomes

$$\int_0^\lambda d\lambda' \int d\vec{r}_2 d\vec{r}_3 u(r_{12}) p(\vec{r}_2 | \lambda') p(\vec{r}_3 | \lambda') h_{13}(\lambda') = - \int_0^\lambda d\lambda' \int d\vec{r}_2 u(r_{12}) p(\vec{r}_2 | \lambda'), \quad (57)$$

which cancels A_1 exactly. The second term in A_3 is not as divergent, nor are the higher-order terms in the expansion.

This is, however, not the way to handle the divergence problem. Having been convinced in this manner that the divergences are spurious, we seek a more rigorous way of removing them.

To proceed, we shall simplify the notations and the calculations by recognizing that in the models to be considered, the density profile will depend only on z —normal to the surface. We write $p(z | \lambda)$ in place of $p(\vec{r} | \lambda)$. Also, $h_{1i}(\lambda)$ depends on r_{1i} as well as z_1 and z_i . We shall suppress z_1 and z_i in the notation and write it as $h(r_{1i} | \lambda)$. Bringing Eq. (56) into A_1 , we find

$$\begin{aligned} A_1 + A_3 &= \int_0^\lambda d\lambda' \int d\vec{r}_2 u(r_{12}) p(\vec{r}_2 | \lambda') \left[- \int d\vec{r}_3 p(\vec{r}_3 | \lambda') h_{13}(\lambda') \right] \\ &\quad + \int_0^\lambda d\lambda' \int d\vec{r}_2 d\vec{r}_3 u(r_{23}) p(\vec{r}_2 | \lambda') p(\vec{r}_3 | \lambda') h_{13}(\lambda') \\ &= \int_0^\lambda d\lambda' \int d\vec{r}_3 p(z_3 | \lambda') h_{13}(\lambda') \int d\vec{r}_2 p(z_2 | \lambda') [u(r_{23}) - u(r_{12})] \\ &= 2\pi \int_0^\lambda d\lambda' \int d\vec{r}_3 p(z_3 | \lambda') h(r_{13} | \lambda') \int dz_2 p(z_2 | \lambda') \int_{|z_{23}|}^{|z_{21}|} \xi u(\xi) d\xi \\ &= (2\pi)^2 \int_0^\lambda d\lambda' \int dz_3 p(z_3 | \lambda') \mathcal{H}_{\lambda'}(|z_{13}|) \int dz_2 p(z_2 | \lambda') \int_{|z_{23}|}^{|z_{21}|} \xi u(\xi) d\xi, \end{aligned} \quad (58)$$

where

$$\mathcal{H}_{\lambda'}(|z|) = \int_{|z|}^\infty \xi h(\xi | \lambda) d\xi. \quad (59)$$

Now, using $u(r)$ as given in Eq. (38), $A_1 + A_3$ reduces to two terms:

$$A_1 + A_3 = \mathcal{A}_1(z_1 | \lambda) + \mathcal{A}_3(z_1 | \lambda), \quad (60)$$

with

$$\mathcal{A}_1(z_1 | \lambda) = (2\pi)^2 \int_0^\lambda d\lambda' \int dz_3 p(z_3 | \lambda') \mathcal{H}_{\lambda'}(|z_{13}|) \int dz_2 p(z_2 | \lambda') \int_{|z_{23}|}^{|z_{21}|} \xi \left[\frac{-\alpha}{\xi} \right] d\xi \quad (61)$$

and

$$\mathcal{A}_3(z_1 | \lambda) = (2\pi)^2 \frac{\alpha}{b} \int_0^\lambda d\lambda' \int dz_3 p(z_3 | \lambda') \mathcal{H}_{\lambda'}(|z_{13}|) \int_{-\infty}^\infty dz_2 (e^{-b|z_{23}|} - e^{-b|z_{21}|}) p(z_2 | \lambda'). \quad (62)$$

\mathcal{A}_3 is well behaved. We shall later reduce it further along with A_2 , A_4 , A_5 , and A_6 . For now let us concentrate on \mathcal{A}_1 , which would diverge if the calculation is carried out without due regard to the order in which several length scales are taken to their infinite limit.

C. Removal of divergences in $\mathcal{A}_1(z_1 | \lambda)$

Consider the cleaving process, which results in two free surfaces. Let us abandon the coordinate system used in Sec. II for the moment and adopt one that is symmetric,

i.e., one whose origin sits midway between the two free surfaces, as defined by two Gibbs surfaces at $z = -z_G$ and $z = +z_G$. The asymptotic boundaries will be placed at $z = -L$ and $z = +L$. (We ignore δ , since asymptotic boundary behavior does not enter present arguments.)

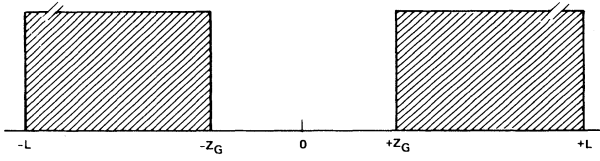


FIG. 2. Cleaving.

Figure 2 helps to define these points on the z axis.

There are three length scales involved: the size of the system, the spacing between the two cleaved surfaces, and the range of the Coulomb correlation. The former two are

measured by L and z_G , respectively. The latter can be described by modifying $u(r)$ with an exponential factor $e^{-\epsilon r}$, measured by the length ϵ^{-1} . All three approach infinity. It is important to take the limits in the right order.

In accordance with customary practices, we bring $e^{-\epsilon\xi}$ into the right-hand side of Eq. (61) and postpone taking the limit $\epsilon \rightarrow 0$ until the final stage of calculation. Separating out the deviation from the average bulk density, we define $f(z|\lambda)$ by

$$p(z|\lambda) = n_B [\Theta(-z_G - z) + f(z|\lambda) + \Theta(z - z_G)] . \quad (63)$$

Thus,

$$\begin{aligned} \mathcal{A}_1(z_1|\lambda) = & -(2\pi n_B)^2 \alpha \int_0^\lambda d\lambda' \int dz_3 [\Theta(-z_G - z_3) + f(z_3|\lambda') + \Theta(z_3 - z_G)] \mathcal{H}_{\lambda'}(|z_{13}|) \\ & \times \int dz_2 [\Theta(-z_G - z_2) + f(z_2|\lambda') + \Theta(z_2 - z_G)] \int_{|z_{23}|}^{|z_{21}|} e^{-\epsilon\xi} d\xi . \end{aligned} \quad (64)$$

Take z_1 on the left of the cleaving plane; then the term $\Theta(z_3 - z_G)$ can be omitted from the integral over z_3 , since $\mathcal{H}_{\lambda'}(|z_{13}|)$ is short ranged and the separation between the free surfaces is macroscopic. \mathcal{A}_1 splits into four terms:

$$\mathcal{A}_1 = \mathcal{A}_{11} + \mathcal{A}_{12} + \mathcal{A}_{13} + \mathcal{A}_{14} , \quad (65)$$

with

$$\mathcal{A}_{11}(z_1|\lambda) = -(2\pi n_B)^2 \alpha \int_0^\lambda d\lambda' \int dz_3 \Theta(-z_G - z_3) \mathcal{H}_{\lambda'}(|z_{13}|) \int dz_2 [\Theta(-z_G - z_2) + \Theta(z_2 - z_G)] \int_{|z_{23}|}^{|z_{21}|} e^{-\epsilon\xi} d\xi , \quad (66)$$

$$\mathcal{A}_{12}(z_1|\lambda) = -(2\pi n_B)^2 \alpha \int_0^\lambda d\lambda' \int dz_3 f(z_3|\lambda') \mathcal{H}_{\lambda'}(|z_{13}|) \int dz_2 [\Theta(-z_G - z_2) + \Theta(z_2 - z_G)] \int_{|z_{23}|}^{|z_{21}|} e^{-\epsilon\xi} d\xi , \quad (67)$$

$$\mathcal{A}_{13}(z_1|\lambda) = -(2\pi n_B)^2 \alpha \int_0^\lambda d\lambda' \int dz_3 \Theta(-z_G - z_3) \mathcal{H}_{\lambda'}(|z_{13}|) \int dz_2 f(z_2|\lambda') \int_{|z_{23}|}^{|z_{21}|} e^{-\epsilon\xi} d\xi , \quad (68)$$

and

$$\mathcal{A}_{14}(z_1|\lambda) = -(2\pi n_B)^2 \alpha \int_0^\lambda d\lambda' \int dz_3 f(z_3|\lambda') \mathcal{H}_{\lambda'}(|z_{13}|) \int dz_2 f(z_2|\lambda') \int_{|z_{23}|}^{|z_{21}|} e^{-\epsilon\xi} d\xi . \quad (69)$$

\mathcal{A}_{13} and \mathcal{A}_{14} can be evaluated immediately. The results will be given presently. In \mathcal{A}_{11} and \mathcal{A}_{12} , there remains a small complication. As the two free surfaces are given increased separation, i.e., as $2z_G \rightarrow \infty$, one should not allow the Coulomb correlation factor to be distorted. Hence if z_1 is on the left side of the cleaving plane, the factor $e^{-\epsilon\xi}$ should be replaced by $e^{-\epsilon(\xi - 2z_G)}$ when an integration is performed over the region on the right of the cleaving plane. Thus

$$\mathcal{A}_{11} = \mathcal{A}_{11L} + \mathcal{A}_{11R} ,$$

$$\mathcal{A}_{11L}(z_1|\lambda) = \lim_{\epsilon \rightarrow 0} \lim_{L \rightarrow \infty} (2\pi n_B)^2 \alpha \int_0^\lambda d\lambda' \int_{-L}^{-z_G} dz_3 \mathcal{H}_{\lambda'}(|z_{13}|) \int_{-L}^{-z_G} dz_2 \frac{1}{\epsilon} (-e^{-\epsilon|z_{23}|} + e^{-\epsilon|z_{21}|}) ,$$

$$\mathcal{A}_{11R}(z_1|\lambda) = \lim_{\epsilon \rightarrow 0} \lim_{L \rightarrow \infty} (2\pi n_B)^2 \alpha \int_0^\lambda d\lambda' \int_{-L}^{-z_G} dz_3 \mathcal{H}_{\lambda'}(|z_{13}|) \int_{z_G}^L dz_2 \frac{1}{\epsilon} (-e^{-\epsilon z_{23}} + e^{-\epsilon z_{21}}) e^{2\epsilon z_G} .$$

Combining these expressions, it can be seen that there will be a contribution only if z_1 is located outside the Gibbs surface:

$$\mathcal{A}_{11}(z_1|\lambda) = (2\pi n_B)^2 \alpha \int_0^\lambda d\lambda' \Theta(z_1 + z_G)(z_1 + z_G)^2 \int_{-\infty}^{-z_G - z_1} \mathcal{H}_{\lambda'}(|z|) dz . \quad (70)$$

Likewise,

$$\mathcal{A}_{12} = \mathcal{A}_{12L} + \mathcal{A}_{12R} ,$$

$$\mathcal{A}_{12L} = \lim_{\epsilon \rightarrow 0} \lim_{L \rightarrow \infty} \left[-(2\pi n_B)^2 \alpha \int_0^\lambda d\lambda' \int_{-L}^L dz_3 f(z_3|\lambda') \mathcal{H}_{\lambda'}(|z_{13}|) \int_{-L}^L dz_2 \Theta(-z_G - z_2) \int_{|z_{23}|}^{|z_{21}|} e^{-\epsilon\xi} d\xi \right] ,$$

$$\mathcal{A}_{12R} = \lim_{\epsilon \rightarrow 0} \lim_{L \rightarrow \infty} \left[-(2\pi n_B)^2 \alpha \int_0^\lambda d\lambda' \int_{-L}^L dz_3 f(z_3|\lambda') \mathcal{H}_{\lambda'}(|z_{13}|) \int_{-L}^L dz_2 \Theta(z_2 - z_G) \int_{|z_{23}|}^{|z_{21}|} e^{-\epsilon(\xi - 2z_G)} d\xi \right] .$$

Combining,

$$\begin{aligned} \mathcal{A}_{12}(z_1 | \lambda) = & (2\pi n_B)^2 \alpha \int_0^\lambda d\lambda' \left[\Theta(z_1 + z_G)(z_1 + z_G)^2 \int_{-\infty}^\infty f(z_1 + z | \lambda') \mathcal{H}_{\lambda'}(|z|) dz \right. \\ & \left. - \int_{-z_G - z_1}^\infty f(z + z_1 | \lambda') \mathcal{H}_{\lambda'}(|z|)(z_1 + z + z_G)^2 dz \right]. \end{aligned} \tag{71}$$

Finally, the charge neutrality condition, now in the form

$$\int_{-\infty}^\infty f(z | \lambda) dz = 0, \tag{72}$$

leads Eqs. (68) and (69) to the expressions

$$\begin{aligned} \mathcal{A}_{13}(z_1 | \lambda) = & (2\pi n_B)^2 \alpha \int_0^\lambda d\lambda' \int_0^\infty \{ \Theta(-z_G - z - z_1) [\mathcal{F}_{\lambda'}(z_1 + z) - \mathcal{F}_{\lambda'}(z_1)] \\ & + \Theta(-z_G + z - z_1) [\mathcal{F}_{\lambda'}(z_1 - z) - \mathcal{F}_{\lambda'}(z_1)] \} \mathcal{H}_{\lambda'}(z) dz \end{aligned} \tag{73}$$

and

$$\begin{aligned} \mathcal{A}_{14}(z_1 | \lambda) = & (2\pi n_B)^2 \alpha \int_0^\lambda d\lambda' \int_0^\infty \{ f(z_1 + z | \lambda') [\mathcal{F}_{\lambda'}(z_1 + z) - \mathcal{F}_{\lambda'}(z_1)] \\ & + f(z_1 - z | \lambda') [\mathcal{F}_{\lambda'}(z_1 - z) - \mathcal{F}_{\lambda'}(z_1)] \} \mathcal{H}_{\lambda'}(z) dz, \end{aligned} \tag{74}$$

where

$$\mathcal{F}_{\lambda}(z) = 2 \int_z^\infty f(z' | \lambda)(z' - z) dz'. \tag{75}$$

D. Remaining parts of the Chakravarty-Woo equation

Straightforward integration yields

$$\mathcal{A}_3(z_1 | \lambda) = (2\pi)^2 \frac{\alpha}{b} \int_0^\lambda d\lambda' \int_0^\infty \{ p(z_1 + z | \lambda') [\mathcal{P}_{\lambda'}(z_1 + z) - \mathcal{P}_{\lambda'}(z_1)] + p(z_1 - z | \lambda') [\mathcal{P}_{\lambda'}(z_1 - z) - \mathcal{P}_{\lambda'}(z_1)] \} \mathcal{H}_{\lambda'}(z) dz, \tag{76}$$

where

$$\mathcal{P}_{\lambda}(z) = \int_0^\infty [p(z + z' | \lambda) + p(z - z' | \lambda)] e^{-bz'} dz'. \tag{77}$$

A_2 and A_4 can be combined in much the same manner as A_1 and A_3 . In other words, multiply the integrand of $A_2(\vec{r}_1 | \lambda)$ by $-\int d\vec{r}_3 p(\vec{r}_3 | \lambda') h_{13}(\lambda')$ and add the results to $A_4(\vec{r}_1 | \lambda)$. We find by straightforward integration

$$\begin{aligned} A_2(z_1 | \lambda) + A_4(z_1 | \lambda) = & 2\pi \int_0^\lambda d\lambda' \int_0^\infty \{ p(z_1 + z | \lambda') [\mathcal{B}_{\lambda'}(z_1 + z) - \mathcal{B}_{\lambda'}(z_1)] \\ & + p(z_1 - z | \lambda') [\mathcal{B}_{\lambda'}(z_1 - z) - \mathcal{B}_{\lambda'}(z_1)] \} \mathcal{H}_{\lambda'}(z) dz, \end{aligned} \tag{78}$$

where

$$\mathcal{B}_{\lambda}(z) = 2\pi \int_0^\infty [p(z + z' | \lambda) + p(z - z' | \lambda)] \mathcal{C}_{\lambda}(z') dz' \tag{79}$$

and

$$\mathcal{C}_{\lambda}(|z|) = \int_{|z|}^\infty \xi h(\xi | \lambda) u(\xi) d\xi. \tag{80}$$

A_5 and A_6 consist of complicated integrals. The following expansion turns out to be useful:

$$\begin{aligned} & \int d\vec{r} p(z | \lambda) u(|\vec{r} - \vec{r}_\alpha|) h(|\vec{r} - \vec{r}_\beta| | \lambda) \\ & = \int d\vec{r} p(z | \lambda) \{ u(|\vec{r}_\beta - \vec{r}_\alpha|) + (\vec{r} - \vec{r}_\beta) \cdot [\vec{\nabla} u(|\vec{r} - \vec{r}_\alpha|)]_{\vec{r} = \vec{r}_\beta} + \dots \} h(|\vec{r} - \vec{r}_\beta| | \lambda) \\ & = -u(r_{\beta\alpha}) + u'(r_{\beta\alpha}) \frac{\vec{r}_{\beta\alpha}}{r_{\beta\alpha}} \cdot \int d\vec{r} (\vec{r} - \vec{r}_\beta) p(z | \lambda) h(|\vec{r} - \vec{r}_\beta| | \lambda) + \dots \\ & = -u(r_{\beta\alpha}) + u'(r_{\beta\alpha}) \frac{z_\beta - z_\alpha}{r_{\beta\alpha}} \int d\vec{r} (z - z_\beta) p(z | \lambda) h(|\vec{r} - \vec{r}_\beta| | \lambda) + \dots \\ & = - \left[u(r_{\beta\alpha}) + u'(r_{\beta\alpha}) \frac{z_\beta - z_\alpha}{r_{\beta\alpha}} \mathcal{D}_{\lambda}(z_\beta) + \dots \right], \end{aligned} \tag{81}$$

where

$$\mathcal{D}_\lambda(z) = -2\pi \int_0^\infty [p(z+z'|\lambda) - p(z-z'|\lambda)] \mathcal{H}_\lambda(z') z' dz' . \quad (82)$$

Substitution of Eq. (81) into A_5 and A_6 leads to

$$A_5(z_1|\lambda) \approx -\frac{1}{2}A_2(z_1|\lambda) + \delta A_5(z_1|\lambda) , \quad (83)$$

where

$$\delta A_5(z_1|\lambda) = \frac{1}{2} \int_0^\lambda d\lambda' \mathcal{D}_{\lambda'}(z_1) \mathcal{G}_{\lambda'}(z_1) , \quad (84)$$

$$\mathcal{G}_\lambda(z) = 2\pi \int_0^\infty [p(z+z'|\lambda) - p(z-z'|\lambda)] \mathcal{F}_\lambda(z') z' dz' , \quad (85)$$

$$\mathcal{F}_\lambda(|z|) = \int_{|z|}^\infty h(\xi|\lambda) u'(\xi) d\xi , \quad (86)$$

and to

$$A_6(z_1|\lambda) \approx -\frac{1}{2}A_4(z_1|\lambda) + \delta A_6(z_1|\lambda) , \quad (87)$$

where

$$\delta A_6(z_1|\lambda) = \pi \int_0^\lambda d\lambda' \int_0^\infty [p(z_1+z|\lambda') \mathcal{D}_{\lambda'}(z_1+z) \mathcal{G}_{\lambda'}(z_1+z) + p(z_1-z|\lambda') \mathcal{D}_{\lambda'}(z_1-z) \mathcal{G}_{\lambda'}(z_1-z)] \mathcal{H}_{\lambda'}(z) dz . \quad (88)$$

In Eqs. (83) and (87), only the two leading terms of A_5 and A_6 have been retained. Numerical computations give results that show the expansion converges reasonably well, and since A_5 and A_6 are relatively small to begin with, truncation after two terms does not significantly affect the accuracy of the calculation. (See Table I.)

E. Sum-rule approximation for $g(\vec{r}_1, \vec{r}_2|\lambda)$. Typical results

It should be clear by now that if the one-particle CW equation is already so difficult to solve, determining $g(\vec{r}_1, \vec{r}_2|\lambda)$ by actually solving the two-particle CW equation would pose far too prohibitive a task at this stage. In preliminary work,³⁵⁻³⁷ we simply employed for each r_s the pair distribution function of a bulk electron liquid, $g_B(r_{12})$, determined at the same r_s in Ref. 19. Such a g does not take into account local variations of the density in the surface region.

In this work we bring about an improvement, still taking results from the bulk calculation, but using for each r_s and λ the entire set of $g_B(r)$ with densities ranging from 0 to the peak value of $n(\vec{r})$, and λ' ranging from 0 to λ . We let the local density enter through the following approximation method. Let

$$g(\vec{r}_1, \vec{r}_2|\lambda) \approx g_B(r_{12}, \lambda | \tilde{n}(z_1)) , \quad (89)$$

where $g_B(r_{12}, \lambda | \tilde{n}(z_1))$ denotes a bulk $g_B(r_{12}, \lambda)$ at a particular density \tilde{n} that depends on z_1 through the sequential relation (or sum rule), Eq. (56), namely,

$$\int n(\vec{r}_2|\lambda) [g_B(r_{12}, \lambda | \tilde{n}(z_1)) - 1] d\vec{r}_2 = -1 . \quad (90)$$

In actual practice, instead of solving Eq. (90), we permit g_B to scale with n_B and determine the scale parameter by requiring it to satisfy Eq. (90). Such an approximation would not be too inaccurate since g_B does scale reasonably well as long as the density is not too high. (See the results given in Ref. 19.) In addition, we interpolate between the fully interacting g_B and the Hartree-Fock g_B , both from

Ref. 19, to give g_B its λ dependence. More sophisticated approximation schemes are planned to be attempted in future work.

A word about the relocation of the Gibbs surface. Equation (44) comes from the definition of the density function, Eq. (40), which is the same as that for the uncorrelated system [with $u(r)$ set to zero]. So, if $n_0(\vec{r}) \equiv p(\vec{r}|\lambda=0)$ observes charge neutrality, so does $n(\vec{r}) \equiv p(\vec{r}|\lambda=1)$. In principle, then, the Gibbs surface would not shift.

However, approximations must be made to bring Eq. (44) into its final, usable form. There is no guarantee that the Gibbs surface located at $z=0$ in Sec. II would remain at $z=0$. As a check on the approximations, we require the shift to be slight. It turns out to indeed be the case. Nevertheless, it is still necessary to relocate the Gibbs surface in accordance with the dictates of $n(\vec{r})$ in order to ensure exact charge neutrality so that the energy and work function calculated will be meaningful.

In actual computation, Eqs. (47)–(53) are solved iteratively. The iteration process begins with $p(\vec{r}|\lambda=0)$ replacing $p(\vec{r}|\lambda)$ on the right-hand side of the equations. Once a new $p(\vec{r}|\lambda)$ emerges on the left-hand side of Eq. (47), it is translated along the z axis until the charge neutrality condition (72) is satisfied. This is done for every value of λ . In other words, in each case, the Gibbs surface will be maintained at the origin. That z_G appears in the results for $\mathcal{A}_1(z|\lambda)$ should be of no concern. The coordinate system considered in Sec. III C was devised to facilitate the removal of spurious divergences. As soon as the limits are taken properly, we stop worrying about the cleaving process and return to dealing with one side of the cleaving plane, as in the evaluation of $\mathcal{A}_3, A_2, A_4, A_5$, and A_6 . In the final results for \mathcal{A}_1 , i.e., in Eqs. (70), (71), (73), and (74), $-z_G$ always appears in the role of a reference point for z coordinates. It may simply be set to zero as a result of relocating the Gibbs surface.

TABLE I. Solving the density profile equation. $r_s = 3.28$, $V_0 = 1.08(\hbar^2 k_F^2 / 2m)$, $\alpha = 0.08 \text{ \AA}$.

z (k_F^{-1})	\mathcal{A}_{11}	\mathcal{A}_{12}	\mathcal{A}_{13}	\mathcal{A}_{14}	\mathcal{A}_3	$\frac{1}{2}(A_2 + A_4)$	δA_5	δA_6	$\sum_{l=1}^6 A_l$	$\frac{p(z \lambda=0)}{n_B}$	$\frac{p(z \lambda=1)}{n_B}$
3.36	0.1333	-0.0851	-0.0005	0.0021	0.0007	-0.1505	0.0000	-0.0001	-0.1001	0.0004	0.0003
3.16	0.1210	-0.0851	-0.0005	0.0021	0.0008	-0.1629	0.0000	-0.0000	-0.1247	0.0006	0.0005
2.96	0.0941	-0.0904	-0.0005	0.0019	0.0008	-0.1686	0.0000	0.0000	-0.1627	0.0009	0.0008
2.76	0.0543	-0.0900	-0.0003	0.0013	0.0005	-0.1651	0.0000	0.0001	-0.1993	0.0014	0.0012
2.56	0.0049	-0.0847	-0.0001	0.0018	-0.0001	-0.1561	-0.0000	0.0002	-0.2358	0.0022	0.0018
2.36	-0.0497	-0.0754	0.0002	-0.0015	-0.0014	-0.1493	-0.0001	0.0003	-0.2769	0.0035	0.0027
2.16	-0.1042	-0.0630	0.0007	-0.0038	-0.0036	-0.1394	-0.0002	0.0004	-0.3132	0.0055	0.0040
1.96	-0.1533	-0.0484	0.0012	-0.0069	-0.0072	-0.1316	-0.0005	0.0006	-0.3461	0.0087	0.0062
1.76	-0.1916	-0.0327	0.0018	-0.0108	-0.0126	-0.1217	-0.0010	0.0008	-0.3678	0.0137	0.0095
1.56	-0.2144	-0.0172	0.0026	-0.0155	-0.0203	-0.1119	-0.0018	0.0011	-0.3774	0.0216	0.0148
1.36	-0.2184	-0.0033	0.0034	-0.0209	-0.0307	-0.1089	-0.0028	0.0013	-0.3803	0.0342	0.0234
1.16	-0.2027	0.0079	0.0043	-0.0267	-0.0440	-0.0973	-0.0042	0.0016	-0.3612	0.0543	0.0378
0.96	-0.1691	0.0158	0.0052	-0.0325	-0.0602	-0.0876	-0.0059	0.0019	-0.3325	0.0861	0.0617
0.76	-0.1226	0.0202	0.0060	-0.0375	-0.0783	-0.0738	-0.0077	0.0021	-0.2917	0.1366	0.1021
0.56	-0.0716	0.0215	0.0068	-0.0401	-0.0966	-0.0659	-0.0095	0.0023	-0.2532	0.2140	0.1661
0.36	-0.0271	0.0207	0.0072	-0.0379	-0.1122	-0.0545	-0.0111	0.0024	-0.2125	0.3180	0.2571
0.16	-0.0023	0.0188	0.0073	-0.0276	-0.1225	-0.0433	-0.0121	0.0024	-0.1794	0.4366	0.3649
-0.04	0.0000	0.0166	0.0068	-0.0115	-0.1258	-0.0325	-0.0125	0.0024	-0.1564	0.5593	0.4783
-0.24	0.0000	0.0144	0.0061	0.0025	-0.1217	-0.0225	-0.0122	0.0024	-0.1310	0.6784	0.5951
-0.44	0.0000	0.0121	0.0054	0.0106	-0.1109	-0.0112	-0.0111	0.0024	-0.1028	0.7877	0.7107
-0.64	0.0000	0.0099	0.0047	0.0131	-0.0951	-0.0101	-0.0096	0.0024	-0.0846	0.8822	0.8106
-0.84	0.0000	0.0079	0.0042	0.0111	-0.0765	-0.0074	-0.0077	0.0025	-0.0659	0.9586	0.8975
-1.04	0.0000	0.0060	0.0037	0.0063	-0.0573	0.0019	-0.0057	0.0025	-0.0464	1.0153	0.9690
-1.24	0.0000	0.0044	0.0032	0.0004	-0.0399	0.0012	-0.0039	0.0024	-0.0322	1.0522	1.0189
-1.44	0.0000	0.0030	0.0028	-0.0050	-0.0255	0.0070	-0.0025	0.0024	-0.0178	1.0709	1.0520
-1.64	0.0000	0.0018	0.0023	-0.0089	-0.0147	0.0064	-0.0014	0.0022	-0.0121	1.0742	1.0613
-1.84	0.0000	0.0010	0.0018	-0.0106	-0.0075	0.0052	-0.0006	0.0020	-0.0087	1.0657	1.0565
-2.04	0.0000	0.0003	0.0014	-0.0103	-0.0031	0.0009	-0.0002	0.0018	-0.0093	1.0493	1.0396
-2.24	0.0000	-0.0002	0.0009	-0.0083	-0.0009	0.0017	-0.0001	0.0015	-0.0052	1.0291	1.0238
-2.44	0.0000	-0.0005	0.0006	-0.0052	0.0001	0.0041	-0.0000	0.0013	0.0004	1.0086	1.0090
-2.64	0.0000	-0.0006	0.0003	-0.0018	0.0005	0.0051	-0.0000	0.0010	0.0045	0.9907	0.9952
-2.84	0.0000	-0.0006	0.0001	0.0013	0.0007	0.0053	-0.0000	0.0008	0.0075	0.9774	0.9847
-3.04	0.0000	-0.0006	0.0000	0.0037	0.0007	0.0048	-0.0000	0.0006	0.0092	0.9697	0.9787
-3.24	0.0000	-0.0005	0.0000	0.0051	0.0008	0.0040	-0.0000	0.0004	0.0098	0.9677	0.9772
-3.44	0.0000	-0.0004	-0.0001	0.0054	0.0008	0.0031	-0.0000	0.0002	0.0092	0.9709	0.9798
-3.64	0.0000	-0.0002	-0.0001	0.0049	0.0007	0.0023	-0.0000	0.0001	0.0077	0.9779	0.9854
-3.84	0.0000	-0.0002	-0.0001	0.0035	0.0006	0.0016	0.0000	0.0000	0.0056	0.9871	0.9926
-4.04	0.0000	-0.0001	-0.0000	0.0018	0.0004	0.0012	0.0000	-0.0000	0.0033	0.9970	1.0002
-4.24	0.0000	-0.0000	-0.0000	0.0000	0.0002	0.0009	0.0000	-0.0000	0.0011	1.0059	1.0070
-4.44	0.0000	-0.0000	0.0000	-0.0015	0.0001	0.0007	0.0000	-0.0001	-0.0008	1.0128	1.0121

Table I shows typical results in a density profile calculation. The particular case shown is for $r_s=3.28$ (Li). Detailed results will be given in Sec. V.

IV. SURFACE ENERGY AND WORK FUNCTION

The Hamiltonian of the interacting electron system was given in Eq. (2):

$$H = \sum_{i=1}^N \frac{-\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \int d\vec{r} d\vec{r}' n_+(\vec{r}) n_+(\vec{r}') v_{II}(\vec{r}, \vec{r}') + \sum_{i=1}^N \int d\vec{r} n_+(\vec{r}) v_{Ie}(\vec{r}, \vec{r}_i) + \sum_{\substack{i,j=1 \\ i < j}}^N \frac{e^2}{r_{ij}} .$$

In this section, we wish to evaluate its expectation value in the correlated wave function $\psi(1, 2, \dots, N)$ of Eq. (8):

$$E \equiv \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} . \quad (91)$$

Subtracting from E the bulk energy $\frac{1}{2} E^B$, the remainder, which is proportional to L^2 , will be the total surface energy E^S . The surface energy per unit area is then $\sigma \equiv E^S/L^2$.

It is convenient to separate H into two parts: a jellium-model part H_J and a lattice correction part ΔH ,

$$H = H_J + \Delta H . \quad (92)$$

We begin with H_J :

$$H_J = \sum_{i=1}^N \frac{-\hbar^2}{2m} \nabla_i^2 + \frac{e^2}{2} \int \frac{n_+(\vec{r}_1) n_+(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 - e^2 \sum_{i=1}^N \int \frac{n_+(\vec{r})}{|\vec{r}_i - \vec{r}|} d\vec{r} + \sum_{\substack{i,j=1 \\ i < j}}^N \frac{e^2}{r_{ij}} , \quad (93)$$

where $n_+(\vec{r})$ now denotes a semi-infinite uniform positive charge distribution:

$$E_J \equiv \frac{\langle \psi | H_J | \psi \rangle}{\langle \psi | \psi \rangle} \equiv \langle T \rangle + \langle V_{II} \rangle_J + \langle V_{Ie} \rangle_J + \langle V_{ee} \rangle_J \equiv \langle T \rangle + U_{es} + U_c \quad (94)$$

(es denotes the electrostatic contribution, c denotes correlation), where

$$\langle T \rangle = T_1 + T_2 + T_3 + T_4 , \quad (95)$$

with

$$T_1 = 2 \sum_{\vec{k}} \epsilon_{\vec{k}} , \quad (96)$$

$$T_2 = - \int n(\vec{r}) V(\vec{r}) d\vec{r} , \quad (97)$$

$$T_3 = \frac{\hbar^2}{8m} \int p(\vec{r}_1, \vec{r}_2) [\vec{\nabla}_1 u(r_{12})]^2 d\vec{r}_1 d\vec{r}_2 , \quad (98)$$

$$T_4 = \frac{\hbar^2}{8m} \int p(\vec{r}_1, \vec{r}_2, \vec{r}_3) \vec{\nabla}_1 u(r_{12}) \cdot \vec{\nabla}_1 u(r_{13}) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 , \quad (99)$$

$$\langle V_{II} \rangle_J = \frac{e^2}{2} \int d\vec{r}_1 d\vec{r}_2 \frac{n_+(\vec{r}_1) n_+(\vec{r}_2)}{r_{12}} , \quad (100)$$

$$\langle V_{Ie} \rangle_J = -e^2 \int d\vec{r}_1 n(\vec{r}_1) \int d\vec{r}_2 \frac{n_+(\vec{r}_2)}{r_{12}} , \quad (101)$$

and

$$\langle V_{ee} \rangle_J = \frac{e^2}{2} \int d\vec{r}_1 d\vec{r}_2 \frac{p(\vec{r}_1, \vec{r}_2)}{r_{12}} . \quad (102)$$

$\langle V_{II} \rangle_J$, $\langle V_{Ie} \rangle_J$, and $\langle V_{ee} \rangle_J$ can be combined and rewritten as $U_{es} + U_c$, where

$$U_{es} = \frac{e^2}{2} \int d\vec{r}_1 d\vec{r}_2 \frac{[n(\vec{r}_1) - n_+(\vec{r}_1)][n(\vec{r}_2) - n_+(\vec{r}_2)]}{r_{12}} \quad (103)$$

and

$$U_c = \frac{e^2}{2} \int d\vec{r}_1 d\vec{r}_2 \frac{n(\vec{r}_1) n(\vec{r}_2) [g(\vec{r}_1, \vec{r}_2) - 1]}{r_{12}} . \quad (104)$$

We shall first work on the kinetic-energy contributions T_l , $l=1, \dots, 4$. T_1 was given in Sec. II, Eq. (34). The corresponding bulk contribution T_1^B was given in Eq. (36). The contribution to the surface energy per area, t_1 , is thus given as in Eq. (37):

$$t_1 \equiv \frac{T_1 - \frac{1}{2} T_1^B}{L^2} = \frac{\hbar^2}{2m\pi^2} \left[-\frac{2}{15} z_0 k_F^5 + \int_0^{k_F} k(k^2 - k_F^2) [\gamma(k) + \frac{1}{4}\pi] dk \right] . \quad (105)$$

Next,

$$T_2 = -L^2 \int n(z) V(z) dz \quad (106)$$

and

$$T_2^B = 0 . \quad (107)$$

Hence

$$t_2 = \frac{T_2 - \frac{1}{2} T_2^B}{L^2} = - \int n(z) V(z) dz . \quad (108)$$

T_3 and T_4 are divergent and complicated to evaluate. We shall give an outline below and refer the reader to Appendices A–D for details.

With the use of the convolution approximation for $p(\vec{r}_1, \vec{r}_2, \vec{r}_3)$, as shown in Eq. (45) except that now we deal with the full-correlation limit $\lambda=1$, T_4 can be separated into three parts:

$$T_4 = T_{41} + T_{42} + T_{43},$$

$$T_{41} = \frac{\hbar^2}{8m} \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 n(z_1) n(z_2) n(z_3) \times g_{12} g_{13} \vec{\nabla}_1 u(r_{12}) \cdot \vec{\nabla}_1 u(r_{13}), \quad (109)$$

$$T_{42} = \frac{\hbar^2}{8m} \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 n(z_1) n(z_2) n(z_3) \times g_{12} h_{23} \vec{\nabla}_1 u(r_{12}) \cdot \vec{\nabla}_1 u(r_{13}), \quad (110)$$

$$T_{43} = \frac{\hbar^2}{8m} \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 n(z_1) n(z_2) n(z_3) \times \left[h_{23} h_{31} + \int d\vec{r}_4 n(z_4) h_{14} h_{24} h_{34} \right] \times \vec{\nabla}_1 u(r_{12}) \cdot \vec{\nabla}_1 u(r_{13}), \quad (111)$$

where $g_{ij} \equiv g(\vec{r}_i, \vec{r}_j)$ and $h_{ij} \equiv g_{ij} - 1$ as before. Note that we shall again take g in the form of a bulk g that is scaled to satisfy the sum rule locally, as in Sec. III E.

A. Kinetic energy—short-range part

First we consider T_{42} , T_{43} , and T_3 , since they all contain the short-range factor h_{ij} , making their evaluation easier to carry out. T_{41} is where all the difficulties arise; we shall discuss it in Sec. IV B.

Let us begin by showing that the divergent parts of T_3 and T_{42} cancel. By rewriting T_{42} in the form

$$T_{42} = \frac{\hbar^2}{8m} \int d\vec{r}_1 d\vec{r}_2 n(z_1) n(z_2) g_{12} \times \vec{\nabla}_1 u(r_{12}) \cdot \vec{\nabla}_1 \int d\vec{r}_3 n(z_3) h_{23} u(r_{13})$$

and calling forth the expansion (81), one finds

$$T_3 + T_{42} \approx \frac{-\hbar^2}{8m} \int d\vec{r}_1 d\vec{r}_2 n(z_1) n(z_2) g_{12} \mathcal{D}_1(z_2) \times \vec{\nabla}_1 u(r_{12}) \cdot \vec{\nabla}_1 \left[u'(r_{12}) \frac{z_2 - z_1}{r_{12}} \right]. \quad (112)$$

The definition of $\mathcal{D}_1(z)$, Eq. (82), indicates that it would vanish if $p(z)$ is constant, which is the case for the homogeneous bulk. Thus $T_3 + T_{42}$ vanishes. Combining this result with Eq. (112) and reducing it further algebraically, we obtain

$$t_3 + t_{42} \equiv \frac{(T_3 + T_{42}) - \frac{1}{2}(T_3^B + T_{42}^B)}{L^2} \approx \frac{-\hbar^2}{8mL^2} \int d\vec{r}_1 d\vec{r}_2 n(z_1) n(z_2) g_{12} \mathcal{D}_1(z_2) \frac{z_2 - z_1}{r_{12}} u'(r_{12}) u''(r_{12}). \quad (113)$$

Next, the second term in T_{43} can be rewritten as

$$\frac{\hbar^2}{8m} \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_4 n(z_1) n(z_2) n(z_4) h_{14} h_{24} \vec{\nabla}_1 u(r_{12}) \cdot \vec{\nabla}_1 \int d\vec{r}_3 n(z_3) h_{34} u(r_{13})$$

and expanded as in Eq. (81). Its first contribution cancels the first term in T_{43} , leaving only its second contribution in the expansion. It reads

$$\frac{-\hbar^2}{8m} \int d\vec{r}_1 d\vec{r}_2 n(z_1) n(z_2) \vec{\nabla}_1 u(r_{12}) \cdot \left\{ \int d\vec{r}_4 n(z_4) h_{24} \left[h_{14} \mathcal{D}_1(z_4) \vec{\nabla}_1 \left[u'(r_{14}) \frac{z_4 - z_1}{r_{14}} \right] \right] \right\}.$$

The existence of the short-range factor h_{24} permits the coordinate \vec{r}_4 in the curly brackets to be replaced by \vec{r}_2 , which leads to further simplification and the result

$$T_{43} \approx \frac{\hbar^2}{8m} \int d\vec{r}_1 d\vec{r}_2 n(z_1) n(z_2) h_{12} \mathcal{D}_1(z_2) \vec{\nabla}_1 u(r_{12}) \cdot \vec{\nabla}_1 \left[u'(r_{12}) \frac{z_2 - z_1}{r_{12}} \right]. \quad (114)$$

Once again, because of $\mathcal{D}_1(z)$, T_{43}^B vanishes. Thus,

$$t_{43} \equiv \frac{T_{43} - \frac{1}{2} T_{43}^B}{L^2} \approx \frac{\hbar^2}{8mL^2} \int d\vec{r}_1 d\vec{r}_2 n(z_1) n(z_2) h_{12} \mathcal{D}_1(z_2) \frac{z_2 - z_1}{r_{12}} u'(r_{12}) u''(r_{12}). \quad (115)$$

Combining Eqs. (113) and (115),

$$\begin{aligned} t_3 + t_{42} + t_{43} &\approx \frac{-\hbar^2}{8mL^2} \int d\vec{r}_1 d\vec{r}_2 n(z_1) n(z_2) \mathcal{D}_1(z_2) \frac{z_2 - z_1}{r_{12}} u'(r_{12}) u''(r_{12}) \\ &= \frac{-\hbar^2}{8m} \int dz_1 dz_2 n(z_1) n(z_2) \mathcal{D}_1(z_2) (z_2 - z_1) \int_{|z_{12}|}^{\infty} 2\pi u'(r) u''(r) dr \\ &= \frac{\pi \hbar^2}{8m} \int dz_1 dz_2 n(z_1) n(z_2) \mathcal{D}_1(z_2) (z_2 - z_1) [u'(|z_{12}|)]^2. \end{aligned} \quad (116)$$

This leaves T_{41} .

B. Kinetic energy—long-range part

We refer to T_{41} as the long-range part of the kinetic energy, since the integrand contains no short-range factor to ensure its convergence. In fact, direct integration would give rise to divergences that are obviously spurious. We return to procedures similar to those employed in Sec. III for removing divergences in the density equation.

Figure 2 once again becomes helpful. We shall write $n(z)$ as the sum of two parts: a left piece

$$L(z) \equiv n_B [\Theta(-z_G - z) + f_L(z)] \quad (117)$$

and its mirror image

$$R(z) \equiv n_B [\Theta(z - z_G) + f_R(z)]. \quad (118)$$

Note that $f_L(z) = f_R(-z)$. Each piece dies off in the region between the free surfaces, i.e., $-z_G < z < z_G$. f_L and f_R each satisfies the charge neutrality condition, with Gibbs surfaces falling on $z = -z_G$ and $z = z_G$, respectively. The sum of f_L and f_R gives $f(z | \lambda = 1)$ of Eq. (63), but it is more convenient here to write f in two parts:

$$T_{41} = \frac{\hbar^2}{8m} \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 n(z_1) n(z_2) n(z_3) \times g_{12} g_{13} \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1}. \quad (119)$$

Enter $n(z) \equiv L(z) + R(z)$. Applying the symmetry with respect to exchanging \vec{r}_2 and \vec{r}_3 . Next apply the symmetry $L(z) = R(-z)$. One finds

$$T_{41} = \frac{2\hbar^2 L^2}{m} (W_1 + W_2 + W_3), \quad (120)$$

with

$$W_1 = \frac{1}{8} \int dz_1 \int d\vec{r}_2 d\vec{r}_3 g_{12} g_{13} \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} \times L(z_1) L(z_2) L(z_3), \quad (121)$$

$$W_2 = \frac{1}{4} \int dz_1 \int d\vec{r}_2 d\vec{r}_3 g_{12} g_{13} \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} \times L(z_1) L(z_2) R(z_3), \quad (122)$$

$$W_3 = \frac{1}{8} \int dz_1 \int d\vec{r}_2 d\vec{r}_3 g_{12} g_{13} \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} \times L(z_1) R(z_2) R(z_3), \quad (123)$$

where all integrations are from $-z_G - L$ to $z_G + L$.

For T_{41} , $L(z)$ is replaced by $n_B \Theta(-z)$, $R(z)$ by $n_B \Theta(z)$, and g_{ij} by g_{ij}^B , which stands for the bulk g_{ij} at the homogeneous density n_B . The integrations are from $-L$ to L . We refer to these contributions as W_1^B , W_2^B , and W_3^B .

In such a configuration

$$t_{41} \equiv \frac{T_{41} - T_{41}^B}{2L^2} = \frac{\hbar^2}{m} [(W_1 - W_1^B) + (W_2 - W_2^B) + (W_3 - W_3^B)]. \quad (124)$$

$W_1 - W_1^B$ and $W_2 - W_2^B$ will be evaluated in Appendix A, with the most tedious part appearing separately in Appendix B; another part is given in Appendix D. $W_3 - W_3^B$ will be evaluated in Appendix C, with one part appearing in Appendix D. The final results are given below. It should be noted that while T_{41} and T_{41}^B both diverge as $L \rightarrow \infty$, their difference per unit area is finite, as expected. We have, at the end,

$$t_{41} = \frac{\hbar^2}{m} [(\delta W_1 + \delta W_2) + W'_1 + (W'_2 + W'_3)] = \frac{\hbar^2}{m} \frac{n_B^3}{8} (2\pi)^2 \int_{-\infty}^0 dz [\mathcal{H}(z)]^2 + \frac{\hbar^2}{m} W_1, \quad (125)$$

where

$$\mathcal{H}(z) = \int_{-\infty}^0 (z - z') \mathcal{F}_1(|z - z'|) dz'.$$

W_1 consists of many integrals. It is given in Appendix B and will not be reproduced here.

C. U_{es}

In the jellium model, $n_+(\vec{r})$ is merely a step function. We need to deal with only one side of the cleaved plane, say, the left side. Equations (103) and (117) yield

$$U_{es} = \frac{e^2 n_B^2}{2} \int d\vec{r}_1 d\vec{r}_2 \frac{f_L(z_1) f_L(z_2)}{r_{12}},$$

or

$$\frac{en_B}{2} \int d\vec{r} f_L(z) \Phi(z), \quad (126)$$

where

$$\Phi(z_1) = \int d\vec{r}_2 \frac{en_B f_L(z_2)}{r_{12}}. \quad (127)$$

Using

$$\nabla^2 \Phi(z) = -4\pi en_B f_L(z) \quad (128)$$

in Eq. (126) and then integrating by parts, we find

$$U_{es} = \frac{1}{8\pi} \int d\vec{r} (\nabla \Phi)^2 \equiv \frac{1}{8\pi} \int d\vec{r} E^2.$$

Finally, with Gauss's law

$$E(z) = 4\pi en_B \int_{-\infty}^z dz' f_L(z'),$$

we obtain

$$U_{es} = 2\pi e^2 n_B^2 L^2 \int_{-\infty}^{\infty} dz \left[\int_{-\infty}^{\infty} dz' f_L(z') \right]^2. \quad (129)$$

Obviously $U_{es}^B = 0$. Thus the electrostatic contribution to the surface energy per unit area is given by

$$u_{es} \equiv \frac{U_{es}}{L^2} = 2\pi e^2 n_B^2 \int_{-\infty}^{\infty} dz \left[\int_{-\infty}^z dz' f_L(z') \right]^2. \quad (130)$$

D. U_c

We define

$$U_c^H = \frac{e^2}{2} \int d\vec{r}_1 \int d\vec{r}_2 n(z_1) n(z_2) \frac{g_B(r_{12}) - 1}{r_{12}}.$$

Then,

$$U_c - \frac{1}{2} U_c^B = (U_c - U_c^H) + (U_c^H - \frac{1}{2} U_c^B). \quad (131)$$

From Eq. (104), $U_c - U_c^H = L^2 \tilde{u}_c$, where

$$\tilde{u}_c = \frac{e^2}{2} \int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_2 n(z_1) n(z_2) \times \int_{|z_{12}|}^{\infty} 2\pi [g(\vec{r}_1, \vec{r}_2) - g_B(r)] dr. \quad (132)$$

$g(r_1, r_2)$ takes the form of Eqs. (89) and (90); it is a function of r and of z_1 through $\tilde{n}(z_1)$. We have

$$\begin{aligned} U_c^H - \frac{1}{2} U_c^B &= L^2 \frac{e^2}{2} \int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_2 [n(z_1) n(z_2) - n_B^2 \Theta(-z_1)] \int_{|z_{12}|}^{\infty} 2\pi [g_B(r) - 1] dr \\ &= L^2 \pi e^2 n_B^2 \int_0^{\infty} dr [g_B(r) - 1] [\gamma_1(r) + \gamma_2(r) + \gamma_3(r)], \end{aligned} \quad (133)$$

where

$$\begin{aligned} \gamma_1(r) &= \int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_2 \Theta(r - |z_{12}|) [\Theta(-z_1) \Theta(-z_2) - \Theta(-z_1)] \\ &= - \int_{-\infty}^0 dz_1 \int_0^{\infty} dz_2 \Theta(r - |z_{12}|) = - \int_{-r}^0 dz_1 \int_0^{z_1+r} dz_2 = - \frac{r^2}{2}, \end{aligned} \quad (134)$$

$$\begin{aligned} \gamma_2(r) &= 2 \int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_2 \Theta(r - |z_{12}|) \Theta(-z_1) f_L(z_2) \\ &= 2 \int_{-\infty}^0 dz_1 \left[\int_{-\infty}^{z_1} dz_2 f_L(z_2) \Theta(r - z_1 + z_2) + \int_{z_1}^{\infty} dz_2 f_L(z_2) \Theta(r - z_2 + z_1) \right] \\ &= 2 \int_{-\infty}^0 dz_1 \left[\int_{z_1-r}^{z_1} dz_2 f_L(z_2) + \int_{z_1}^{z_1+r} dz_2 f_L(z_2) \right] = 2 \int_{-\infty}^0 dz_1 \int_{z_1-r}^{z_1+r} dz_2 f_L(z_2), \end{aligned} \quad (135)$$

and

$$\begin{aligned} \gamma_3(r) &= \int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_2 \Theta(r - |z_{12}|) f_L(z_1) f_L(z_2) = 2 \int_{-\infty}^{\infty} dz_1 f_L(z_1) \int_{-\infty}^{z_1} dz_2 f_L(z_2) \Theta(r - |z_{12}|) \\ &= 2 \int_{-\infty}^{\infty} dz_1 f_L(z_1) \int_{z_1-r}^{z_1} dz_2 f_L(z_2). \end{aligned} \quad (136)$$

The contribution to the surface energy per unit area is

$$\begin{aligned} u_c &\equiv \frac{1}{L^2} (U_c - \frac{1}{2} U_c^B) \\ &= \frac{e^2 n_B^2}{8} + \pi e^2 n_B^2 \int_0^{\infty} dr [g_B(r) - 1] [\gamma_2(r) + \gamma_3(r)] + \tilde{u}_c. \end{aligned} \quad (137)$$

E. Lattice correction term

We have

$$\Delta E \equiv \frac{\langle \psi | \Delta H | \psi \rangle}{\langle \psi | \psi \rangle}, \quad (138)$$

where $\Delta H \equiv H - H_J$. Note that ΔH contains changes from H_J that come from two independent sources. First, $n_+(\vec{r})$ will now be a semi-infinite positively charged lattice, $n_+^L(\vec{r}) \Theta(-z)$, instead of a uniform distribution. Second, the ion-electron interaction v_{Ie} will now differ

from a pure Coulomb interaction. We shall follow the Lang-Kohn calculation¹ and adopt the local ion pseudopotential proposed by Ashcroft⁴¹ (with ionic charge $Z=1$):

$$v_{Ie}(\vec{r}) \approx v_{ps}(\vec{r}) = \begin{cases} 0, & r \leq r_c \\ -\frac{e^2}{r}, & r > r_c \end{cases} \quad (139)$$

where r_c is a cutoff radius determined for each metal to give a reasonable description of its bulk properties.

There is no correction to the kinetic energy terms. This can be seen by a quick inspection of Eqs. (95)–(99): Neither the positive charge distribution nor the electron-ion interaction appears in those equations. To avoid confusion, let us remind the reader that the “kinetic energy” here is that for a *chosen form of the trial wave function* ψ , as are the distribution functions $n(\vec{r})$, $p(\vec{r}_1, \vec{r}_2)$, and $p(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ that appear in the kinetic energy expressions. To improve the quantitative aspects of our theory, we may

wish to widen our variational space at some time to better accommodate the lattice model.

The corrections are for

$$\langle V \rangle_J \equiv \langle V_{II} \rangle_J + \langle V_{Ie} \rangle_J + \langle V_{ee} \rangle_J.$$

Since the ions are assumed static and nonoverlapping, we can use a pure Coulomb interaction for V_{II} , as in Eq.

(100). The pseudopotential enters only in V_{Ie} . The lattice correction is given by

$$\Delta E = \langle V \rangle_L - \langle V \rangle_J, \quad (140)$$

where

$$\begin{aligned} \langle V \rangle_L &= \langle V_{II} \rangle_L + \langle V_{Ie} \rangle_L + \langle V_{ee} \rangle_L \\ &= \frac{e^2}{2} \int d\vec{r}_1 d\vec{r}_2 \frac{n_+^L(\vec{r}_1)n_+^L(\vec{r}_2)\Theta(-z_1)\Theta(-z_2)}{r_{12}} + \frac{e^2}{2} \int d\vec{r}_1 d\vec{r}_2 \frac{n(\vec{r}_1)n(\vec{r}_2)}{r_{12}} + U_c \\ &\quad - e^2 \int d\vec{r}_1 d\vec{r}_2 \frac{n(\vec{r}_1)n_+^L(\vec{r}_2)\Theta(-z_2)}{r_{12}} \Theta(r_{12}-r_c) \end{aligned} \quad (141)$$

and

$$\langle V \rangle_J = \frac{e^2}{2} \int d\vec{r}_1 d\vec{r}_2 \frac{n_B^2\Theta(-z_1)\Theta(-z_2)}{r_{12}} + \frac{e^2}{2} \int d\vec{r}_1 d\vec{r}_2 \frac{n(\vec{r}_1)n(\vec{r}_2)}{r_{12}} + U_c - e^2 \int d\vec{r}_1 d\vec{r}_2 \frac{n(\vec{r}_1)n_B\Theta(-z_2)}{r_{12}}. \quad (142)$$

There is of course the bulk counterpart to remove:

$$\frac{1}{2}\Delta E^B = \frac{1}{2}[\langle V \rangle_L^B - \langle V \rangle_J^B], \quad (143)$$

where

$$\langle V \rangle_L^B = \frac{e^2}{2} \int d\vec{r}_1 d\vec{r}_2 \frac{n_+^L(\vec{r}_1)n_+^L(\vec{r}_2)}{r_{12}} + \frac{e^2}{2} \int d\vec{r}_1 d\vec{r}_2 \frac{n_B^2}{r_{12}} + U_c^B - e^2 \int d\vec{r}_1 d\vec{r}_2 \frac{n_B n_+^L(\vec{r}_2)}{r_{12}} \Theta(r_{12}-r_c) \quad (144)$$

and

$$\langle V \rangle_J^B = U_c^B. \quad (145)$$

Combining and rearranging, we find the contribution to the surface energy per unit area to be

$$\begin{aligned} \frac{1}{L^2}(\Delta E - \frac{1}{2}\Delta E^B) &= \frac{e^2}{2L^2} \left[\int d\vec{r}_1 d\vec{r}_2 \frac{n_+^L(\vec{r}_1)n_+^L(\vec{r}_2)\Theta(-z_1)\Theta(-z_2)}{r_{12}} \right. \\ &\quad - 2 \int d\vec{r}_1 d\vec{r}_2 \frac{n_B n_+^L(\vec{r}_2)\Theta(-z_1)\Theta(-z_2)}{r_{12}} \Theta(r_{12}-r_c) + \int d\vec{r}_1 d\vec{r}_2 \frac{n_B^2\Theta(-z_1)\Theta(-z_2)}{r_{12}} \\ &\quad \left. - \frac{1}{2} \left[\int d\vec{r}_1 d\vec{r}_2 \frac{n_+^L(\vec{r}_1)n_+^L(\vec{r}_2)}{r_{12}} - 2 \int d\vec{r}_1 d\vec{r}_2 \frac{n_B n_+^L(\vec{r}_2)}{r_{12}} \Theta(r_{12}-r_c) + \int d\vec{r}_1 d\vec{r}_2 \frac{n_B^2}{r_{12}} \right] \right] \\ &\quad + \frac{e^2}{L^2} \left[\int d\vec{r}_1 d\vec{r}_2 \frac{n_B n_+^L(\vec{r}_2)\Theta(-z_1)\Theta(-z_2)}{r_{12}} \Theta(r_{12}-r_c) - \int d\vec{r}_1 d\vec{r}_2 \frac{n_B^2\Theta(-z_1)\Theta(-z_2)}{r_{12}} \right. \\ &\quad \left. - \int d\vec{r}_1 d\vec{r}_2 \frac{n(\vec{r}_1)n_+^L(\vec{r}_2)\Theta(-z_2)}{r_{12}} \Theta(r_{12}-r_c) + \int d\vec{r}_1 d\vec{r}_2 \frac{n(\vec{r}_1)n_B\Theta(-z_2)}{r_{12}} \right]. \end{aligned} \quad (146)$$

It should be noted that the first set of six terms in the square brackets corresponds to

$$[E(\text{lat}, \text{lat}) + E(-, \text{lat}) + E(-, -)]$$

$$- \frac{1}{2}[E_{\text{inf}}(\text{lat}, \text{lat}) + E_{\text{inf}}(-, \text{lat}) + E_{\text{inf}}(-, -)]$$

of Lang and Kohn, or $\delta\sigma_{\text{cl}}$. The second set of four terms corresponds to $\delta\sigma_{\text{ps}}$ of Lang and Kohn, since the latter was given by

$$\delta\sigma_{\text{ps}} = - \int_{-\infty}^{\infty} \delta v(z)[n(z) - n_B\Theta(-z)]dz, \quad (147)$$

which came from averaging the following expression over the xy plane:

$$- \frac{e}{L^2} \int [\Phi^L(\vec{r}_1) - \Phi^J(\vec{r}_1)][n(\vec{r}_1) - n_B\Theta(-z_1)]d\vec{r}_1, \quad (148)$$

where

$$\Phi^L(\vec{r}_1) = \int \frac{en_+^L(\vec{r}_2)\Theta(-z_2)}{r_{12}} \Theta(r_{12}-r_c) d\vec{r}_2 \quad (149)$$

and

$$\Phi^J(\vec{r}_1) = \int \frac{en_B\Theta(-z_2)}{r_{12}} d\vec{r}_2. \quad (150)$$

These results should not be surprising, since a first-order perturbation theory using the jellium wave function as unperturbed is totally equivalent to a variational calculation *restricted to using a trial wave function determined from the jellium calculation*. If we restrict our ψ to that which minimizes E_J , our resulting expression for $E \equiv E_J + \Delta E$ should agree with that of Lang and Kohn. In that sense, we would merely have given a more systematic derivation of the Lang-Kohn correction term. What enhances our variational calculation is that ψ need not be thus restricted. We minimize the total $E \equiv E_J + \Delta E$ with respect to the variational parameters in ψ rather than using the ψ that minimizes E_J . In fact, had we given the form of ψ sufficient flexibility, our procedure would have provided a quantitative check on the accuracy of the first-order perturbation calculation. Unfortunately, our present choice for $\{\varphi_{\vec{k}}(\vec{r})\}$ is too restrictive for this purpose. We will discuss this later.

The computation of our correction terms follows exactly the procedure prescribed by Lang and Kohn. The formulas are too lengthy to reproduce here. The reader is referred to Ref. 1, Sec. III, and Appendixes C and D.

F. Work function

To obtain the work function, we should (i) calculate the energy of an N -electron system with a surface, (ii) calculate the energy of a system with $N-1$ electrons to the left of the surface and one electron at infinity, and (iii) obtain the difference between these two energies. Each energy should be calculated with a variational correlated wave function.

In practice, since formally the evaluation of an expectation value of $H_J + \Delta H$ is exactly like carrying out a first-order perturbation theory, we can adopt the Lang-Kohn procedure as presented by Sahni and co-workers⁸ or Monnier and Perdew.⁹ There, the work function ϕ is given by

$$\phi = \Delta\Phi - \bar{\mu} - \langle \delta v \rangle. \quad (151)$$

$\Delta\Phi$ stands for the electronic relaxation dipole barrier and can be calculated from the static potential (127) or

$$\Phi(\vec{r}) = \int \frac{e[n(\vec{r}') - n_B\Theta(-z')]}{|\vec{r} - \vec{r}'|} d\vec{r}'. \quad (152)$$

Thus

$$\begin{aligned} \Delta\Phi &= e\Phi(+\infty) - e\Phi(-\infty) \\ &= 4\pi e^2 \int_{-\infty}^{\infty} z[n(z) - n_B\Theta(-z)] dz. \end{aligned} \quad (153)$$

$\bar{\mu}$ is the chemical potential of the bulk metal:

$$\bar{\mu} = \frac{\hbar^2 k_F^2}{2m} + \frac{d[n\epsilon_{xc}(n)]}{dn}. \quad (154)$$

In this case, for consistency's sake, we take $\epsilon_{xc}(n)$ from the CBF calculation for bulk electron liquids (see Ref. 19).

$\langle \delta v \rangle$ is as defined in Eqs. (147)–(150) and averaged over the xy plane. For the Ashcroft pseudopotential,

$$\langle \delta v \rangle = \pi n_B \left[2r_c^2 - \frac{d^2}{6} \right], \quad (155)$$

where d denotes the interplanar spacing. We have not made an attempt at this stage to use a more sophisticated expression for the work function, e.g., the “displaced-profile” work function of Ref. 8.

V. RESULTS AND DISCUSSION

As input to the calculation, we need for each metal its value of r_s or k_F . Once a crystal lattice structure is identified, we have the lattice cell size and the interplanar spacing d . These are physical parameters. In addition, we have the Ashcroft pseudopotential parameter r_c .

We then need the bulk parameters a and b , as determined in an earlier calculation¹⁹ for every value of r_s . (In Sec. III we explained why there was no attempt to revise these parameters.) We also take the bulk pair distribution functions $g_B(r|n_B)$ from the CBF calculation in Ref. 19. In the surface region, they are accorded local dependences as explained in Sec. IV E.

In the model single-particle wave functions $\{\varphi_{\vec{k}}(\vec{r})\}$, there exist the variational parameters V_0 and a . They are subject to variation. The single-particle energy spectrum $\epsilon_{\vec{k}}$ and the density profile of the uncorrelated model system $n_0(z)$ are evaluated in Sec. II.

There are no other inputs to the theory. All numerical calculations proceed in accordance with the equations and formulas derived in Secs. III and IV. Appendix E lists the various special functions defined for solving the density profile equation and evaluating the surface energy. They are assembled for the convenience of the reader.

We refer the reader to Table I for typical intermediate results from an iteration of the CW equation. Shown, except for the last two columns, are results obtained from the first iteration of a calculation at $r_s = 3.28$ (Li), with $V_0 = 1.80(\hbar^2 k_F^2 / 2m)$ and $a = 0.08$ Å. The last two columns give the density profiles for the noninteracting and interacting systems, respectively.

Table II lists the model parameters, bulk parameters, and optimum variational parameters for all the metals considered. Figure 3 shows density profiles obtained for two extreme cases: $r_2 = 2.07$ (Al) and 5.65 (Cs). Figure 4 contrasts the density profile obtained for $r_s = 3.99$ (Na) against that obtained by Lang and Kohn for $r_s = 4.00$.

In Table III, we list the surface energies and work functions determined in this work and compare them to the DFT results of Lang and Kohn,¹ Sahni and co-workers,⁸ and Monnier and Perdew.⁹ Experimental results^{42–48} are also shown. In the case of surface energies, “experimental” results refer to data extrapolated or inferred from surface tension measurements performed on liquid metals or

TABLE II. Parameters in the calculations.

Metal	Model parameters				Bulk parameters		Optimized variational parameters	
	r_s	Face	d (Å)	r_c (a.u.)	α (Å)	b (Å ⁻¹)	$V_0 \left[\frac{\hbar^2 k_F^2}{2m} \right]$	a (Å)
Al	2.07	fcc (111)	2.34	1.12	1.82	1.40	1.24	0.18
Zn	2.30	hcp (0001)	2.47	1.27	2.13	1.32	1.33	0.17
Pb	2.30	fcc (111)	2.86	1.12	2.13	1.32	1.41	0.14
Mg	2.66	hcp (0001)	2.60	1.39	2.65	1.21	1.45	0.16
Li	3.28	bcc (110)	2.47	1.06	3.63	1.11	1.80	0.08
Na	3.99	bcc (110)	2.99	1.67	4.87	1.00	2.06	0.03
K	4.96	bcc (110)	3.70	2.14	6.75	0.91	2.24	0.03
Rb	5.23	bcc (110)	3.95	2.61	7.29	0.89	2.29	0.03
Cs	5.65	bcc (110)	4.28	2.93	8.21	0.87	2.30	0.04

solid-liquid interfaces. This accounts for the rather large uncertainties.

Figure 5 shows surface energies plotted against r_s . Our results for the surface energies appear to be slightly improved over those of the DFT calculations. The work functions are not quite as good at small r_s . Since all the results are presented here, we shall allow the reader to draw his own conclusions.

A discussion of these results may prove useful when carried out in reference to features that are special to our CBF theory. Let us return, then, to some of the points raised in Sec. I C.

A. Wave functions

Unlike the DFT, our theory begins with the Hamiltonian and with a trial wave function for the ground state. The expectation value of the Hamiltonian is formed. The variational calculation that minimizes this expectation value is performed on the wave function rather than the density. That the latter is important is because one is liable to construct density functions that do not correspond

to wave functions. While the solution of the self-consistent equation would yield valid density functions—provided that the approximations are accurate—free variations of parametrized density functions do not lend us that assurance. On the other hand, direct variations on parametrized wave functions always uphold the minimum principle, provided again that the approximations are accurate. This we consider a desirable feature of the CBF theory.

The form of the correlated wave function, Eq. (8), imposes unfortunate restrictions on the choice of trial wave functions. At the very least we should have set the single-particle orbitals $\{\varphi_{\vec{k}}(\vec{r})\}$ free. Even if we had to take $\{\varphi_{\vec{k}}(\vec{r})\}$ as the eigenfunctions of some model potential $V(\vec{r})$, it would have been better to solve a self-consistent equation such as

$$\frac{\delta E}{\delta V(\vec{r})} = 0 \quad (156)$$

along with

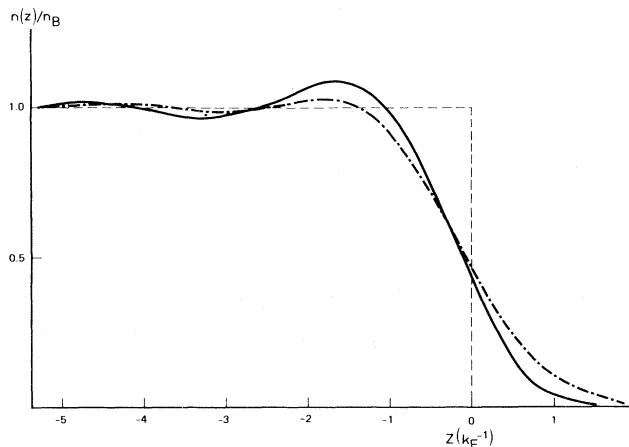


FIG. 3. Density profiles. — $r_s = 5.65$ (Cs); - - - - $r_s = 2.07$ (Al).

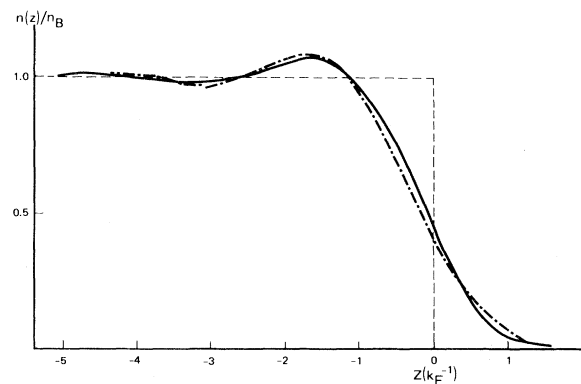


FIG. 4. Density profiles. — $r_s = 3.99$ (Na); - - - - $r_s = 4.00$ from Lang and Kohn (Ref. 1).

TABLE III. Surface-energy and work-function results.

r_s	Metal	Face	Surface energy (erg/cm ²)				Expt.
			Lang and Kohn (Ref. 1)	DFT Sahni and co-workers (Ref. 8)	Monnier and Perdew (Ref. 9)	CBF	
2.07	Al	(111)	730	692–852	795	977	1143, ^a 1170, ^b 965 ^c
2.30	Zn	(0001)	480	509–627	590	547	913, ^a 1040, ^b 350 ^d
2.30	Pb	(111)	1140	779–886	456	1118	593, ^a 690 ^b
2.66	Mg	(0001)	546	552–629	619	672	785, ^a 712 ^c
3.28	Li	(110)	380	371–409	392	465	522, ^a 470 ^e
3.99	Na	(110)	230	227–248	247	264	261, ^a 275, ^b 220 ^f
4.96	K	(110)	140	136–147	148	124	145, ^a 135, ^b 125 ^f
5.23	Rb	(110)	120	107–116	117	107	117, ^a 95 ^f
5.65	Cs	(110)	102	85–93	93	92	95, ^a 80 ^f

$$\frac{\delta E}{\delta u(r)} = 0 \quad (157)$$

instead of fixing $u(r)$ and parametrizing $V(\vec{r})$. The expressions shown in Appendixes A–D should, however, convince the reader why it would be unthinkable in practical terms to attempt solving such a self-consistency. In addition, our experience with several drastically different forms of $V(\vec{r})$ indicates that such free variations may not be necessary, at least for $r_s \gtrsim 3$ where the calculation is not terribly sensitive to the choice of $V(\vec{r})$.

We do expect to bring about several improvements in the future. One is to allow periodicity in $V(\vec{r})$ in the z direction. This will require new derivations for the one-electron model problem (Sec. II) and new computations for the remaining work, but no formal changes. Another is to adopt results of three-dimensional band calculations by other authors and use them in place of our own one-electron model. What is needed includes the uncorrelated

density profile and the single-particle spectrum (density of states). The exact form of the single-particle wave functions need not be known.

The CBF theory offers a set of approximate wave functions for the excited states of the many-body system. They are in the form (8), with $D[\varphi]$ representing determinants whose elements are selected from the complete set $\{\varphi_{\vec{k}}(\vec{r})\}$. These correlated wave functions correspond to “unperturbed” particle-hole states. Linear combinations of these functions can be constructed to give rise to collective excitations, e.g., surface plasmons, in ways not unlike the Feynman phonon emerging from correlated basis functions for a Bose system.⁴⁹ At present we are working on adsorption problems in which these excited state functions are actually employed for calculating adatom self-energies and substrate-mediated interatomic potentials. We feel that these wave functions are more representative of the excitations than determinants made up of single-particle solutions of the self-consistent equation in the DFT.

In Secs. IA and IC we spoke of our motivation to cast single-particle and many-particle properties in balanced roles. In many cases, single-particle properties dominate, and a good three-dimensional one-electron calculation would suffice. If necessary, the results can be put into a DFT to account for correlation effects. In other cases, many-particle correlations can be dominant. There is no reason, however, for us to insist on prejudging the relative importance of single- versus many-particle effects. Wave functions such as (8) do not require prejudgment. They include all independent particle models as limiting cases [in the limit $u(r) \rightarrow 0$].

B. Surface-energy expressions

In Eqs. (95)–(102), all contributions to the surface energy are seen as expressed in terms of integrals containing one-, two-, and three-particle distribution functions. They are in closed forms. No density-gradient expansion is needed.

As these expressions become reduced to usable forms, approximation schemes are introduced. The convolution approximation for $p(\vec{r}_1, \vec{r}_2, \vec{r}_3)$, for example, corresponds

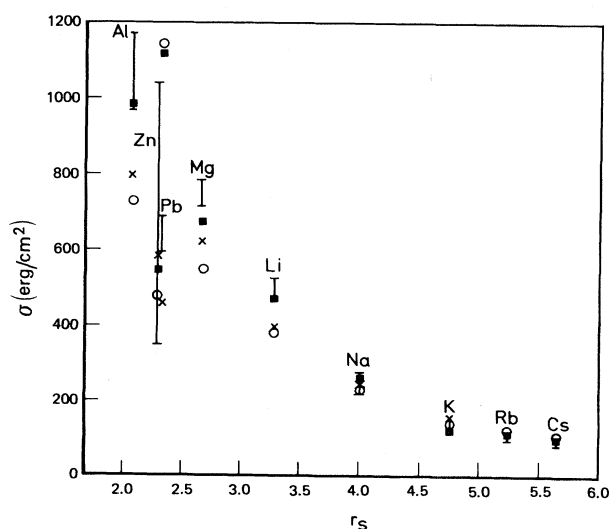


FIG. 5. Surface energy plotted against r_s . \circ , “experiment”; \circ , Lang and Kohn (DFT); \times ; Monnier and Perdew (DFT); \blacksquare , present calculation (CFG). Where \times disappears, it falls between \circ and \blacksquare .

TABLE III. (Continued.)

r_s	Metal	Face	Work function (eV)				CBF	Expt. ^g
			Lang and Kohn (Ref. 1)	DFT Sahni and co-workers (Ref. 8)	Monnier and Perdew (Ref. 9)			
2.07	Al	(111)	4.05	3.47–3.92	4.0	3.6	4.19	
2.30	Zn	(0001)	4.15	3.65–4.07	4.2	3.0	4.33	
2.30	Pb	(111)	3.85	5.23–3.65	3.9	5.9	4.01	
2.66	Mg	(0001)	4.05	3.88–4.01	4.2	3.0	3.66	
3.28	Li	(110)	3.55	3.87–3.58	3.5	3.6	2.32, 3.1	
3.99	Na	(110)	3.10	3.33–3.08	3.3	2.9	2.7	
4.96	K	(110)	2.75	3.01–2.72	2.9	2.7	2.39	
5.23	Rb	(110)	2.20	2.72–2.49	2.6	2.2	2.21	
5.65	Cs	(110)	2.25	2.56–2.35	2.5	2.1	2.12	

^aReference 42^bReference 43.^cReference 44.^dReference 45.^eReference 46.^fReference 47.^gReference 48.

to a partial summation of cluster contributions to infinite orders. Accuracy may be at issue, but not convergence. Since accuracy can be checked out numerically, by using stochastic methods or by comparing different approximation schemes, we are on safer grounds than calling in corrections one term at a time, as in many DFT calculations.

It should be admitted that some of the contributions in our surface energy are evaluated on the basis of keeping just the leading terms in a Taylor expansion. (See T_{42} and T_{43} in Sec. IV A.) We did take care to ensure that the numerical errors that result are acceptably small. It is quite possible to avoid using these expansions altogether if more computer time is placed at our disposal. The nature of our approximations is numerical, unlike the density-gradient expansion in the DFT.

In Sec. III A, where the convolution approximation was employed for the CW equation, we mentioned in passing that the asymptotic behavior of the density function was preserved. This deserves additional emphasis. It is important that the right-hand side of Eq. (47) approach zero as $z_1 \rightarrow -\infty$, since otherwise the bulk limit of the correlated density function would be macroscopically different from that of the uncorrelated density function, leading to a macroscopic surplus or deficit of negative charge. Of the commonly used approximation schemes for multiparticle distribution functions, the convolution approximation is the only one that satisfies this particular requirement.

We remarked earlier that in the CBF theory the homogeneous bulk appears as a limiting case of the inhomogeneous system. When $V(\vec{r})$ is taken to be zero or constant, $\{\varphi_{\vec{k}}(\vec{r})\}$ reduces to plane waves. We have then a wave function suitable for describing the homogeneous electron liquid, as in Ref. 19. When seen in this light, our present theory for the metal surface is completely self-contained. No input from other authors' bulk calculations is needed. Whatever approximation schemes used in the homogeneous system are also those used in the inhomogeneous system.

Even when an approximation scheme is deemed numerically less than satisfactory, the fact that the same scheme is used for *both* the homogeneous and the inhomogeneous system tends to reduce the magnitude of the error by compensation. In the calculation of the surface energy, for example, terms of order L^3 in the system and in the bulk cancel out exactly as required.

C. Systematic improvements; applications

Systematic improvements come in two forms: on the model and on the theory. As far as the model is concerned, we intend to adopt a three-dimensional static lattice of positive ions. Many reliable one-electron theories are available.^{10–18} There is no need for us to define a new parametrized $V(\vec{r})$ and solve for $\{\varphi_{\vec{k}}(\vec{r})\}$. By taking one-electron spectra and density profiles from other calculations, we no longer vary the single-particle part of the correlated wave function. More attention will be paid to the determination of the correlation factor u . In a previous paper on the theory of quantum crystals,⁵⁰ we studied the effects of lattice symmetry and anisotropy on pair correlations. Part of the formalism can be adapted for present use.

As for improvements on the theory, the basic question is on the form of the correlated wave function. We feel that the form (8) has been shown to be adequate for describing the ground state. In other words, there is little need for introducing, e.g., three-particle correlation factors, nor is it necessary to use the entire set and perform a perturbation theory in the correlated basis. Where more work is in order is in the description of collective excitations. Proper linear combinations of the correlated basis functions need to be constructed. Readers who are interested in examining the importance of multiparticle correlated factors may wish to consult Refs. 51–53 and 25.

Ongoing work in our group consists of the application of the CBF theory to three types of problems. The first is adsorption, in particular, the adsorption energy and electron configuration of a single adatom, and the substrate-mediated interaction between two adatoms. In the former case, a wave function can be constructed as a product of the N -electron correlated wave function given in this paper and a hydrogen orbital, or it can be that for an $(N+1)$ -electron correlated wave function in a background made up of N ions in a semi-infinite lattice and one ion at a short distance from the outermost lattice plane. These extremes in bonding provide us with a way of studying the transition of an adatom from a physisorbed to a chemisorbed state. In the latter case, we shall begin with the simpler model of two physisorbed hydrogen atoms at moderate to long distances from each other. The wave function employed is then simply the product of the N -electron wave function and two separately centered hydrogen orbitals, properly symmetrized.

In both cases, particle-hole states of the substrate surface will then enter. The vertices depicting the interaction between an adatom and the substrate will be nondiagonal matrix elements calculated directly from the Hamiltonian and the product wave functions, in a manner not unlike the way in which the diagonal matrix element (expectation value) was evaluated in this paper. The calculation will be more difficult, but we have had some experience with it in our earlier work on metallic hydrogen.^{20,54} Indications from our CBF formalism for ^3He - ^4He solutions⁵⁵ are that the adatom-adatom interaction will be highly nonlocal.

A second type of ongoing work deals with defects in or on metals. One model calculation attempts to describe the effect of a point-charge defect in a jellium, using the same

theoretical framework as in this paper but for the coordinate system. This will serve as a starting point for a theory of hydrogen in metal, vacancy, or indeed a large atom.

A third type of ongoing work is strictly formal in nature: a study on the relation between DFT and CBF. Initial work focuses on a relatively simple model—that of a low-density system of bosons interacting via a well-behaved pairwise potential. Input needed for the CBF theory is available from earlier results relating CBF to field-theoretic methods⁵⁶ (which proved to be reasonably successful).

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APPENDIX A: EVALUATION OF $W_1 - W_1^B$ AND $W_2 - W_2^B$

W_1 contains $L(z_1)L(z_2)L(z_3)$. Since $L(z)$ vanishes in the region $-z_G + L < z < z_G + L$, we can replace the upper limit in the z_1 integration by $-z_G + L$. A translation of the origin to $-z_G$ gives rise to

$$\begin{aligned} W_1 &= \frac{n_B^3}{8} \int_{-L}^L dz_1 \int_{-L}^L d\vec{r}_2 \int_{-L}^L d\vec{r}_3 g_{12} g_{13} \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} [\Theta(-z_1)\Theta(-z_2)\Theta(-z_3) + l_1(z_1, z_2, z_3)] \\ &= W_1^B + \delta W_1 + W_1', \end{aligned} \quad (\text{A1})$$

where

$$\begin{aligned} \delta W_1 &= \frac{n_B^3}{8} \int_{-L}^0 dz_1 \int_{-L}^0 d\vec{r}_2 \int_{-L}^0 d\vec{r}_3 (g_{12} g_{13} - g_{12}^B g_{13}^B) \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} \\ &= \frac{n_B^3}{8} \int_{-L}^0 dz_1 \int_{-L}^0 d\vec{r}_2 \int_{-L}^0 d\vec{r}_3 [(h_{12} h_{13} - h_{12}^B h_{13}^B) + 2(h_{12} - h_{12}^B)] \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1}, \end{aligned} \quad (\text{A2})$$

$$W_1' = \frac{n_B^3}{8} \int_{-L}^L dz_1 \int_{-L}^L d\vec{r}_2 \int_{-L}^L d\vec{r}_3 g_{12} g_{13} \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} l_1(z_1, z_2, z_3), \quad (\text{A3})$$

and

$$\begin{aligned} l_1(z_1, z_2, z_3) &= \Theta(-z_1)\Theta(-z_2)f_L(z_3) + \Theta(-z_1)f_L(z_2)\Theta(-z_3) + f_L(z_1)\Theta(-z_2)\Theta(-z_3) \\ &\quad + \Theta(-z_1)f_L(z_2)f_L(z_3) + f_L(z_1)\Theta(-z_2)f_L(z_3) + f_L(z_1)f_L(z_2)\Theta(-z_3) + f_L(z_1)f_L(z_2)f_L(z_3). \end{aligned} \quad (\text{A4})$$

W_2 can likewise be separated into two parts. The first part,

$$W_{21} = \frac{n_B^3}{4} \int_{-z_G-L}^{z_G+L} dz_1 \int_{-z_G-L}^{z_G+L} d\vec{r}_2 d\vec{r}_3 g_{12} g_{13} \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} \Theta(-z_G-z_1) \Theta(-z_G-z_2) \Theta(z_3-z_G),$$

can be written with g_{13} replaced by unity, since in this integral $|z_{13}| \gtrsim 2z_G$, which becomes macroscopic as the cleaved surfaces become separated. Thus

$$W_{21} = \frac{n_B^3}{4} \int dz_1 \Theta(-z_G-z_1) \int d\vec{r}_2 g_{12} \frac{\partial u(r_{12})}{\partial z_1} \Theta(-z_G-z_2) \int_{z_G}^{z_G+L} d\vec{r}_3 \frac{\partial u(r_{13})}{\partial z_1}.$$

$u(r)$ has the form of Coulomb's interaction. By Gauss's law the "field" at z_1 (which is less than $-z_G$) will not change if the "charged region" is moved from $[z_G, z_G+L]$ to $[-z_G, -z_G+L]$. This permits us to change the limits on the z_3 integration. A further shift of origin to $-z_G$ leads to

$$W_{21} = \frac{n_B^3}{4} \int_{-L}^L dz_1 \int_{-L}^L d\vec{r}_2 \int_{-L}^L d\vec{r}_3 g_{12} \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} \Theta(-z_1) \Theta(-z_2) \Theta(z_3). \quad (\text{A5})$$

Now, since W_2^B can be written as

$$W_2^B = \frac{n_B^3}{4} \int_{-L}^L dz_1 \int_{-L}^L d\vec{r}_2 \int_{-L}^L d\vec{r}_3 g_{12}^B \left[\frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} + h_{13}^B \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} \right] \Theta(-z_1) \Theta(-z_2) \Theta(z_3), \quad (\text{A6})$$

we have

$$W_{21} = W_2^B + \delta W_2 + W_2', \quad (\text{A7})$$

where

$$\begin{aligned} \delta W_2 &= \frac{n_B^3}{4} \int_{-L}^L dz_1 \int_{-L}^L d\vec{r}_2 \int_{-L}^L d\vec{r}_3 (g_{12} - g_{12}^B) \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} \Theta(-z_1) \Theta(-z_2) \Theta(z_3) \\ &= \frac{n_B^3}{4} \int_{-L}^0 dz_1 \int_{-L}^0 d\vec{r}_2 \int_0^L d\vec{r}_3 (h_{12} - h_{12}^B) \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1}, \end{aligned} \quad (\text{A8})$$

$$W_2' = \frac{-n_B^3}{4} \int_{-L}^L dz_1 \int_{-L}^L d\vec{r}_2 \int_{-L}^L d\vec{r}_3 g_{12}^B h_{13}^B \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} \Theta(-z_1) \Theta(-z_2) \Theta(z_3). \quad (\text{A9})$$

The remaining part of W_2 is

$$W_{22} = \frac{n_B^3}{4} \int dz_1 \int d\vec{r}_2 d\vec{r}_3 g_{12} g_{13} \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} l_2(z_1, z_2, z_3), \quad (\text{A10})$$

where

$$\begin{aligned} l_2(z_1, z_2, z_3) &= [f_L(z_1) \Theta(-z_G-z_2) \Theta(z_3-z_G) + \Theta(-z_G-z_1) f_L(z_2) \Theta(z_3-z_G) + \Theta(-z_G-z_1) \Theta(-z_G-z_2) f_R(z_3) \\ &\quad + \Theta(-z_G-z_1) f_L(z_2) f_R(z_3) + f_L(z_1) \Theta(-z_G-z_2) f_R(z_3) \\ &\quad + f_L(z_1) f_L(z_2) \Theta(z_3-z_G) + f_L(z_1) f_L(z_2) f_R(z_3)]. \end{aligned} \quad (\text{A11})$$

It vanishes upon term-by-term inspection. This is realized by first noting that since $|z_{13}| \gtrsim 2z_G \rightarrow \infty$, one can set g_{13} to unity and $u(r_{13})$ to $-\alpha/r_{13}$. W_{22} now reads

$$W_{22} = W_{221} + W_{222} + W_{223}, \quad (\text{A12})$$

with

$$\begin{aligned} W_{221} &= \frac{n_B^3}{4} \int dz_1 \int d\vec{r}_2 d\vec{r}_3 \frac{\partial}{\partial z_1} \left[\frac{-\alpha}{r_{12}} \right] \frac{\partial}{\partial z_1} \left[\frac{-\alpha}{r_{13}} \right] l_2(z_1, z_2, z_3) \\ &= \frac{n_B^3}{4} (2\pi\alpha)^2 \int dz_1 \int dz_2 \frac{z_{12}}{|z_{12}|} \int dz_3 \frac{z_{13}}{|z_{13}|} l_2(z_1, z_2, z_3), \end{aligned} \quad (\text{A13})$$

$$\begin{aligned} W_{222} &= \frac{n_B^3}{4} \int dz_1 \int d\vec{r}_2 d\vec{r}_3 \frac{\partial}{\partial z_1} \left[\frac{\alpha}{r_{12}} e^{-br_{12}} \right] \frac{\partial}{\partial z_1} \left[\frac{-\alpha}{r_{13}} \right] l_2(z_1, z_2, z_3) \\ &= \frac{-n_B^3}{4} (2\pi\alpha)^2 \int dz_1 \int dz_2 \frac{z_{12}}{|z_{12}|} e^{-b|z_{12}|} \int dz_3 \frac{z_{13}}{|z_{13}|} l_2(z_1, z_2, z_3), \end{aligned} \quad (\text{A14})$$

$$\begin{aligned}
W_{223} &= \frac{n_B^3}{4} \int dz_1 \int d\vec{r}_2 d\vec{r}_3 h_{12} \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial}{\partial z_1} \left[\frac{-\alpha}{r_{13}} \right] l_2(z_1, z_2, z_3) \\
&= \frac{n_B^3}{4} \frac{2\pi\alpha}{L^2} \int d\vec{r}_1 d\vec{r}_2 h_{12} \frac{\partial u(r_{12})}{\partial z_1} \int dz_3 \frac{z_{13}}{|z_{13}|} l_2(z_1, z_2, z_3).
\end{aligned} \tag{A15}$$

Each of these expressions contains seven terms, by Eq. (A11). In each case, the first pair of terms cancel, while all remaining terms vanish, either because the integral over z_3 can be isolated in the form $\int_{-z_G}^{z_G+L} dz_3 f_R(z_3)$, which vanishes on account of charge neutrality, or because an odd integrand can be identified.

In summary, then, from Eqs. (A1) and (A7), one finds

$$(W_1 - W_1^B) + (W_2 - W_2^B) = \delta W_1 + \delta W_2 + W'_1 + W'_2, \tag{A16}$$

where from Eqs. (A2) and (A8),

$$\begin{aligned}
\delta W_1 + \delta W_2 &= \frac{n_B^3}{8} \int_{-L}^0 dz_1 \left[\left[\int_{-L}^0 d\vec{r}_2 h_{12} \frac{\partial u(r_{12})}{\partial z_1} \right]^2 - \left[\int_{-L}^0 d\vec{r}_2 h_{12}^B \frac{\partial u(r_{12})}{\partial z_1} \right]^2 \right] \\
&\quad + \frac{n_B^3}{4} \int_{-L}^0 dz_1 \int_{-L}^0 d\vec{r}_2 (h_{12} - h_{12}^B) \frac{\partial u(r_{12})}{\partial z_1} \left[\int_{-L}^0 d\vec{r}_3 \frac{\partial u(r_{13})}{\partial z_1} + \int_0^L d\vec{r}_3 \frac{\partial u(r_{13})}{\partial z_1} \right].
\end{aligned}$$

The second term vanishes since $\partial u(r_{13})/\partial z_1$ is odd, leaving

$$\delta W_1 + \delta W_2 = \frac{n_B^3}{8} (2\pi)^2 \int_{-\infty}^0 dz \{ [\mathcal{X}(z)]^2 - [\mathcal{X}^B(z)]^2 \}, \tag{A17}$$

where

$$\mathcal{X}(z) = \int_{-\infty}^0 (z - z') \mathcal{F}_1(|z - z'|) dz'. \tag{A18}$$

The superscript B implies that $\mathcal{F}_1^B(|z - z'|)$ be used in (A18) for defining $\mathcal{X}^B(z)$ and that in turn $h^B(\xi|1)$ be used in Eq. (86) for the definition of $\mathcal{F}_1^B(|z|)$.

W'_1 consists of many contributions. We reserve it for Appendix B. W'_2 combines neatly with W'_3 : a term from $W_3 - W_3^B$. We reserve it for Appendix D.

APPENDIX B: EVALUATION OF W'_1

Equations (A3) and (A4) give, by virtue of symmetries in some of the terms,

$$W'_1 = 2W'_{11} + W'_{12} + W'_{13} + 2W'_{14} + W'_{15}, \tag{B1}$$

with

$$2W'_{11} = \frac{n_B^3}{4} \int_{-L}^0 dz_1 \int_{-L}^0 d\vec{r}_2 \int_{-L}^L d\vec{r}_3 g_{12} g_{13} \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} f_L(z_3) \equiv \sum_{l=1}^4 w_{1l}, \tag{B2}$$

$$W'_{12} = \frac{n_B^3}{8} \int_{-L}^L dz_1 f_L(z_1) \int_{-L}^0 d\vec{r}_2 \int_{-L}^0 d\vec{r}_3 g_{12} g_{13} \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} \equiv \sum_{l=1}^4 w_{2l}, \tag{B3}$$

$$W'_{13} = \frac{n_B^3}{8} \int_{-L}^0 dz_1 \int_{-L}^L d\vec{r}_2 \int_{-L}^L d\vec{r}_3 g_{12} g_{13} \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} f_L(z_2) f_L(z_3), \tag{B4}$$

$$2W'_{14} = \frac{n_B^3}{4} \int_{-L}^L dz_1 \int_{-L}^0 d\vec{r}_2 \int_{-L}^L d\vec{r}_3 g_{12} g_{13} \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} f_L(z_1) f_L(z_3) \equiv \sum_{l=1}^4 w_{4l}, \tag{B5}$$

and

$$W'_{15} = \frac{n_B^3}{8} \int_{-L}^L dz_1 \int_{-L}^L d\vec{r}_2 \int_{-L}^L d\vec{r}_3 g_{12} g_{13} \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} f_L(z_1) f_L(z_2) f_L(z_3). \tag{B6}$$

Equations (B2), (B3), and (B5) each breaks down the right-hand side to four contributions, corresponding to the four terms from $g_{12}g_{13} = 1 + h_{12} + h_{13} + h_{12}h_{13}$, respectively. We find, after some algebraic work,

$$\begin{aligned}
w_{11} &= \frac{n_B^3}{4} \int_{-L}^0 dz_1 \int_{-L}^0 d\vec{r}_2 \frac{\partial u(r_{12})}{\partial z_1} \int_{-L}^L d\vec{r}_3 \frac{\partial u(r_{13})}{\partial z_1} f_L(z_3) \\
&= \frac{n_B^3}{8} (2\pi\alpha)^2 \left[L \left[\int_{-L}^0 dz f_L(z) \frac{2}{b} e^{bz} + \int_0^L dz f_L(z) \frac{2}{b} e^{-bz} \right] \right. \\
&\quad \left. + \int_{-L}^0 dz f_L(z) \left[-\frac{2}{b^2} + \frac{3}{b^2} e^{bz} - \frac{2z}{b} e^{bz} \right] + \int_0^L dz f_L(z) \left[\frac{2}{b^2} - \frac{1}{b^2} e^{-bz} \right] \right], \tag{B7}
\end{aligned}$$

$$w_{12} = \frac{n_B^3}{4} \int_{-L}^0 dz_1 \int_{-L}^0 d\vec{r}_2 h_{12} \frac{\partial u(r_{12})}{\partial z_1} \int_{-L}^L d\vec{r}_3 \frac{\partial u(r_{13})}{\partial z_1} f_L(z_3) = \frac{n_B^3}{4} (2\pi)^2 \int_{-L}^0 dz \mathcal{K}(z) \mathcal{M}(z), \tag{B8}$$

where

$$\mathcal{M}(z) = - \int_{-\infty}^{\infty} (z-z') f_L(z') u(|z-z'|) dz', \tag{B9}$$

$$\begin{aligned}
w_{13} &= \frac{n_B^3}{4} \int_{-L}^0 dz_1 \int_{-L}^0 d\vec{r}_2 \frac{\partial u(r_{12})}{\partial z_1} \int_{-L}^L d\vec{r}_3 h_{13} \frac{\partial u(r_{13})}{\partial z_1} f_L(z_3) \\
&= \frac{n_B^3}{4} (2\pi\alpha) \left[-L \int_{-L}^L dz_3 f_L(z_3) \int_{-L}^0 d\vec{r}_1 h_{13} \frac{\partial u(r_{13})}{\partial z_3} - \frac{2\pi}{b} \int_{-L}^0 dz e^{bz} \mathcal{L}(z) \right], \tag{B10}
\end{aligned}$$

where

$$\mathcal{L}(z) = \int_{-\infty}^{\infty} (z-z') f_L(z') \mathcal{J}_1(|z-z'|) dz', \tag{B11}$$

$$w_{14} = \frac{n_B^3}{4} \int_{-L}^0 dz_1 \int_{-L}^0 d\vec{r}_2 h_{12} \frac{\partial u(r_{12})}{\partial z_1} \int_{-L}^L d\vec{r}_3 h_{13} \frac{\partial u(r_{13})}{\partial z_1} f_L(z_3) = \frac{n_B^3}{4} (2\pi)^2 \int_{-L}^0 dz \mathcal{K}(z) \mathcal{L}(z), \tag{B12}$$

$$\begin{aligned}
w_{21} &= \frac{n_B^3}{8} \int_{-L}^L dz_1 f_L(z_1) \int_{-L}^0 d\vec{r}_2 \frac{\partial u(r_{12})}{\partial z_1} \int_{-L}^0 d\vec{r}_3 \frac{\partial u(r_{13})}{\partial z_1} \\
&= \frac{n_B^3}{8} (2\pi\alpha)^2 \left[L \left[- \int_{-L}^0 dz f_L(z) \frac{2}{b} e^{bz} - \int_0^L dz f_L(z) \frac{2}{b} e^{-bz} \right] + \int_{-L}^0 dz f_L(z) \frac{1}{b^2} e^{2bz} \right. \\
&\quad \left. + \int_0^L dz f_L(z) \frac{1}{b^2} e^{-2bz} \right], \tag{B13}
\end{aligned}$$

$$\begin{aligned}
w_{22} &= \frac{n_B^3}{8} \int_{-L}^L dz_1 f_L(z_1) \int_{-L}^0 d\vec{r}_2 h_{12} \frac{\partial u(r_{12})}{\partial z_1} \int_{-L}^0 d\vec{r}_3 \frac{\partial u(r_{13})}{\partial z_1} \\
&= \frac{n_B^3}{8} (2\pi\alpha) \left[L \int_{-L}^L dz_3 f_L(z_3) \int_{-L}^0 d\vec{r}_1 h_{31} \frac{\partial u(r_{13})}{\partial z_3} - \frac{2\pi}{b} \left[\int_{-L}^0 dz f_L(z) e^{bz} \mathcal{K}(z) + \int_0^L dz f_L(z) e^{-bz} \mathcal{K}(z) \right] \right], \tag{B14}
\end{aligned}$$

$$w_{23} = \frac{n_B^3}{8} \int_{-L}^L dz_1 f_L(z_1) \int_{-L}^0 d\vec{r}_2 \frac{\partial u(r_{12})}{\partial z_1} \int_{-L}^0 d\vec{r}_3 h_{13} \frac{\partial u(r_{13})}{\partial z_1} = w_{22}, \tag{B15}$$

$$w_{24} = \frac{n_B^3}{8} \int_{-L}^L dz_1 f_L(z_1) \int_{-L}^0 d\vec{r}_2 h_{12} \frac{\partial u(r_{12})}{\partial z_1} \int_{-L}^0 d\vec{r}_3 h_{13} \frac{\partial u(r_{13})}{\partial z_1} = \frac{n_B^3}{8} (2\pi)^2 \int_{-L}^L dz f_L(z) [\mathcal{K}(z)]^2, \tag{B16}$$

$$\begin{aligned}
w_{41} &= \frac{n_B^3}{4} \int_{-L}^L dz_1 f_L(z_1) \int_{-L}^0 d\vec{r}_2 \frac{\partial u(r_{12})}{\partial z_1} \int_{-L}^L d\vec{r}_3 \frac{\partial u(r_{13})}{\partial z_1} f_L(z_3) \\
&= \frac{n_B^3}{4} (2\pi)^2 \frac{\alpha}{b} \left[- \int_{-L}^0 dz f_L(z) e^{bz} \mathcal{M}(z) - \int_0^L dz f_L(z) e^{-bz} \mathcal{M}(z) \right], \tag{B17}
\end{aligned}$$

$$\begin{aligned}
w_{42} &= \frac{n_B^3}{4} \int_{-L}^L dz_1 f_L(z_1) \int_{-L}^0 d\vec{r}_2 h_{12} \frac{\partial u(r_{12})}{\partial z_1} \int_{-L}^L d\vec{r}_3 \frac{\partial u(r_{13})}{\partial z_1} f_L(z_3) \\
&= \frac{n_B^3}{4} (2\pi)^2 \int_{-L}^L dz f_L(z) \mathcal{K}(z) \mathcal{M}(z), \tag{B18}
\end{aligned}$$

$$\begin{aligned}
w_{43} &= \frac{n_B^3}{4} \int_{-L}^L dz_1 f_L(z_1) \int_{-L}^0 d\vec{r}_2 \frac{\partial u(r_{12})}{\partial z_1} \int_{-L}^L d\vec{r}_3 h_{13} \frac{\partial u(r_{13})}{\partial z_1} f_L(z_3) \\
&= -\frac{n_B^3}{4} (2\pi)^2 \frac{\alpha}{b} \left[\int_{-L}^0 dz f_L(z) e^{bz} \mathcal{L}(z) + \int_0^L dz f_L(z) e^{-bz} \mathcal{L}(z) \right], \tag{B19}
\end{aligned}$$

and

$$\begin{aligned}
w_{44} &= \frac{n_B^3}{4} \int_{-L}^L dz_1 f_L(z_1) \int_{-L}^0 d\vec{r}_2 h_{12} \frac{\partial u(r_{12})}{\partial z_1} \int_{-L}^L d\vec{r}_3 h_{13} \frac{\partial u(r_{13})}{\partial z_1} f_L(z_3) \\
&= \frac{n_B^3}{4} (2\pi)^2 \int_{-L}^L dz f_L(z) \mathcal{H}(z) \mathcal{L}(z). \tag{B20}
\end{aligned}$$

Also,

$$W'_{13} = \frac{n_B^3}{8} \int_{-L}^0 dz_1 \left[\int_{-L}^L d\vec{r}_2 (1+h_{12}) \frac{\partial u(r_{12})}{\partial z_1} f_L(z_2) \right]^2 = \frac{n_B^3}{8} (2\pi)^2 \int_{-L}^0 dz [\mathcal{M}(z) + \mathcal{L}(z)]^2 \tag{B21}$$

and

$$W'_{15} = \frac{n_B^3}{8} \int_{-L}^L dz_1 f_L(z_1) \left[\int_{-L}^L d\vec{r}_2 (1+h_{12}) \frac{\partial u(r_{12})}{\partial z_1} f_L(z_2) \right]^2 = \frac{n_B^3}{8} (2\pi)^2 \int_{-L}^L dz f_L(z) [\mathcal{M}(z) + \mathcal{L}(z)]^2. \tag{B22}$$

This completes the calculation for W'_1 . It is interesting to note that in the calculation for w_{21} we actually encountered a term of order L^2 . It dropped out, however, because it appeared with a coefficient $\int_{-L}^L f_L(z) dz$, which vanished on account of charge neutrality. Also, in the final results for w_{11} , there exist two terms of order L . They are cancelled exactly by like terms in w_{21} . w_{13} contains a term of order L , which is cancelled exactly by the leading term in w_{22} and that in w_{23} . All surviving contributions are of order 1, as expected. In this manner, we have removed the spurious divergences in W_1 .

APPENDIX C: EVALUATION OF $W_3 - W_3^B$

We have

$$\begin{aligned}
W_3 &= \frac{1}{8} \int dz_1 \int d\vec{r}_2 d\vec{r}_3 g_{12} g_{13} \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} L(z_1) R(z_2) R(z_3) \\
&= \frac{1}{8} \int dz_1 \int d\vec{r}_2 d\vec{r}_3 \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_2} L(z_1) R(z_2) R(z_3)
\end{aligned}$$

since in this integral $|z_{12}| \gtrsim 2z_G \rightarrow \infty$ and $|z_{13}| \gtrsim 2z_G \rightarrow \infty$, and thus $g_{12} \rightarrow 1$ and $g_{13} \rightarrow 1$. As for W_2 , we now separate W_3 into two parts. One part gives

$$\begin{aligned}
W_{31} &= \frac{n_B^3}{8} \int dz_1 \int d\vec{r}_2 d\vec{r}_3 \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} \Theta(-z_G - z_1) \Theta(z_2 - z_G) \Theta(z_3 - z_G) \\
&= \frac{n_B^3}{8} \int_{-z_G - L}^{-z_G} dz_1 \int_{z_G}^{z_G + L} d\vec{r}_2 \frac{\partial u(r_{12})}{\partial z_1} \int_{z_G}^{z_G + L} d\vec{r}_3 \frac{\partial u(r_{13})}{\partial z_1}.
\end{aligned}$$

Again, as in W_{21} , we change the limits on z_2 and z_3 by Gauss's law, shifting them to $[-z_G, -z_G + L]$. Then a translation of the origin leads to

$$W_{31} = \frac{n_B^3}{8} \int_{-L}^0 dz_1 \int_0^L d\vec{r}_2 \frac{\partial u(r_{12})}{\partial z_1} \int_0^L d\vec{r}_3 \frac{\partial u(r_{13})}{\partial z_1}. \tag{C1}$$

Now,

$$\begin{aligned}
W_3^B &= \frac{n_B^3}{8} \int dz_1 \int d\vec{r}_2 d\vec{r}_3 g_{12}^B g_{13}^B \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} \Theta(-z_1) \Theta(z_2) \Theta(z_3) \\
&= \frac{n_B^3}{8} \int_{-L}^0 dz_1 \int_0^L d\vec{r}_2 \frac{\partial u(r_{12})}{\partial z_1} \int_0^L d\vec{r}_3 \frac{\partial u(r_{13})}{\partial z_1} - W'_3, \tag{C2}
\end{aligned}$$

where

$$W'_3 = -\frac{n_B^3}{8} \int_{-L}^0 dz_1 \int_0^L d\vec{r}_2 \int_0^L d\vec{r}_3 (2h_{13}^B + h_{12}^B h_{13}^B) \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} . \quad (C3)$$

We shall proceed to show that the other part of W_3 vanishes:

$$W_{32} = \frac{n_B^3}{8} \int dz_1 \int d\vec{r}_2 d\vec{r}_3 \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} l_3(z_1, z_2, z_3) , \quad (C4)$$

where

$$\begin{aligned} l_3(z_1, z_2, z_3) = & f_L(z_1) \Theta(z_2 - z_G) \Theta(z_3 - z_G) + \Theta(-z_G - z_1) f_R(z_2) \Theta(z_3 - z_G) \\ & + \Theta(-z_G - z_1) \Theta(z_2 - z_G) f_R(z_3) + \Theta(-z_G - z_1) f_R(z_2) f_R(z_3) \\ & + f_L(z_1) \Theta(z_2 - z_G) f_R(z_3) + f_L(z_1) f_R(z_2) \Theta(z_3 - z_G) + f_L(z_1) f_R(z_2) f_R(z_3) . \end{aligned} \quad (C5)$$

The proof is exceedingly simple. Since $u(r_{12}) \rightarrow -\alpha/r_{12}$ and $u(r_{13}) \rightarrow -\alpha/r_{13}$ here,

$$\begin{aligned} W_{32} = & \frac{n_B^3}{8} \int dz_1 \int d\vec{r}_2 d\vec{r}_3 \frac{\partial}{\partial z_1} \left[\frac{-\alpha}{r_{12}} \right] \frac{\partial}{\partial z_1} \left[\frac{-\alpha}{r_{13}} \right] l_3(z_1, z_2, z_3) \\ = & \frac{n_B^3}{8} (2\pi\alpha)^2 \int dz_1 \int dz_2 \frac{z_{12}}{|z_{12}|} \int dz_3 \frac{z_{13}}{|z_{13}|} l_3(z_1, z_2, z_3) \\ = & \frac{n_B^3}{8} (2\pi\alpha)^2 \int dz_1 \int dz_2 \int dz_3 l_3(z_1, z_2, z_3) , \end{aligned} \quad (C6)$$

since $z_2 > z_1$ and $z_3 > z_1$. The limits of integration are from $-z_G - L$ to $z_G + L$, or from $-\infty$ to ∞ . Since each term in Eq. (C5) contains at least one factor of f_L or f_R that will be separated out for integration in Eq. (C6), every term vanishes as a result of charge neutrality. Thus,

$$W_{32} = 0 . \quad (C7)$$

Equations (C1), (C2), and (C7) yield

$$W_3 - W_3^B \equiv W_{31} + W_{32} - W_3^B = W'_3 . \quad (C8)$$

W'_3 will be evaluated in Appendix D along with W'_2 .

APPENDIX D: EVALUATION OF W'_2 AND W'_3

From Eq. (A9),

$$W'_2 = W'_{21} + W'_{22} , \quad (D1)$$

where

$$W'_{21} = \frac{-n_B^3}{4} \int_{-L}^0 dz_1 \int_{-L}^0 d\vec{r}_2 \int_0^L d\vec{r}_3 h_{13}^B \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} \quad (D2)$$

and

$$W'_{22} = \frac{-n_B^3}{4} \int_{-L}^0 dz_1 \int_{-L}^0 d\vec{r}_2 \int_0^L d\vec{r}_3 h_{12}^B h_{13}^B \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} . \quad (D3)$$

From Eq. (C3),

$$W'_3 = W'_{31} + W'_{32} , \quad (D4)$$

where

$$W'_{31} = \frac{-n_B^3}{4} \int_{-L}^0 dz_1 \int_0^L d\vec{r}_2 \int_0^L d\vec{r}_3 h_{13}^B \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1} \quad (D5)$$

and

$$W'_{32} = \frac{-n_B^3}{8} \int_{-L}^0 dz_1 \int_0^L d\vec{r}_2 \int_0^L d\vec{r}_3 h_{12}^B h_{13}^B \frac{\partial u(r_{12})}{\partial z_1} \frac{\partial u(r_{13})}{\partial z_1}. \quad (\text{D6})$$

Thus

$$W'_{21} + W'_{31} = \frac{-n_B^3}{4} \int_{-L}^0 dz_1 \int_{-L}^L d\vec{r}_2 \frac{\partial u(r_{12})}{\partial z_1} \int_0^L d\vec{r}_3 h_{13}^B \frac{\partial u(r_{13})}{\partial z_1} = 0, \quad (\text{D7})$$

since the integrand for the \vec{r}_2 integration is odd. This is interesting since separately W'_{21} and W'_{31} are both divergent. We again have an exact cancellation of spurious divergences.

Next,

$$\begin{aligned} W'_{22} + W'_{32} &= \frac{-n_B^3}{4} \int_{-L}^0 dz_1 \int_{-L}^L d\vec{r}_2 h_{12}^B \frac{\partial u(r_{12})}{\partial z_1} \int_0^L d\vec{r}_3 h_{13}^B \frac{\partial u(r_{13})}{\partial z_1} \\ &\quad + \frac{n_B^3}{8} \int_{-L}^0 dz_1 \int_0^L d\vec{r}_2 h_{12}^B \frac{\partial u(r_{12})}{\partial z_1} \int_0^L d\vec{r}_3 h_{13}^B \frac{\partial u(r_{13})}{\partial z_1}. \end{aligned} \quad (\text{D8})$$

The first term vanishes since the integrand for the r_2 integrand is again odd. This leaves

$$W'_2 + W'_3 = \frac{n_B^3}{8} \int_{-L}^0 dz_1 \left[\int_0^L d\vec{r}_2 h_{12}^B \frac{\partial u(r_{12})}{\partial z_1} \right]^2.$$

As $L \rightarrow \infty$, the integral in the large parentheses can be shown to equal $-2\pi \int_{-\infty}^0 (z-z') \mathcal{F}_1^B(|z-z'|) dz'$ or $-2\pi \mathcal{X}^B(z)$. Thus

$$W'_2 + W'_3 = \frac{n_B^3}{8} (2\pi)^2 \int_{-\infty}^0 dz [\mathcal{X}^B(z)]^2. \quad (\text{D9})$$

APPENDIX E: GLOSSARY OF SPECIAL FUNCTIONS

We have

$$\begin{aligned} \mathcal{H}_\lambda(|z|) &= \int_{|z|}^{\infty} \xi h(\xi|\lambda) d\xi, \\ \mathcal{C}_\lambda(|z|) &= \int_{|z|}^{\infty} \xi h(\xi|\lambda) u(\xi) d\xi, \\ \mathcal{F}_\lambda(|z|) &= \int_{|z|}^{\infty} h(\xi|\lambda) u'(\xi) d\xi, \\ \mathcal{I}_\lambda(z) &= 2 \int_z^{\infty} f(z'|\lambda)(z'-z) dz', \\ \mathcal{L}(z) &= \int_{-\infty}^{\infty} f_L(z') \mathcal{F}_1(|z-z'|)(z-z') dz', \\ \mathcal{M}(z) &= - \int_{-\infty}^{\infty} f_L(z') u(|z-z'|)(z-z') dz', \\ \mathcal{X}(z) &= \int_{-\infty}^0 \mathcal{F}_1(|z-z'|)(z-z') dz', \\ \mathcal{D}_\lambda(z) &= -2\pi \int_0^{\infty} [p(z+z'|\lambda) - p(z-z'|\lambda)] \mathcal{H}_\lambda(z') z' dz', \\ \mathcal{G}_\lambda(z) &= 2\pi \int_0^{\infty} [p(z+z'|\lambda) - p(z-z'|\lambda)] \mathcal{F}_\lambda(z') z' dz', \\ \mathcal{B}_\lambda(z) &= 2\pi \int_0^{\infty} [p(z+z'|\lambda) + p(z-z'|\lambda)] \mathcal{C}_\lambda(z') dz', \\ \mathcal{P}_\lambda(z) &= \int_0^{\infty} [p(z+z'|\lambda) + p(z-z'|\lambda)] e^{-bz'} dz'. \end{aligned}$$

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