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Variational Calculation of the Image Potential near a Metal Surface

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We have calculated the interaction energy of a static point charge with a metal surface. The metal surface is treated in the jellium approximation with the positive ions replaced by a uniform background and the electrons characterized parametrically by their total charge density. The energy of the system is written as a functional of the total electron density, including that induced by the point charge external to the metal. The distribution of this induced charge is varied to minimize the energy and thus calculate the image potential. We find that we can write the image potential for $D > 2$ Å as $-Q^2/4(D-d)$, where Q is the size of the point charge, D the distance of the point charge from that jellium discontinuity, and d an origin shift which is a function of the electron density at the metal surface. For smaller distances the potential no longer scales as Q^2 and saturation sets in.

I. INTRODUCTION

There has in the last few years been renewed interest in studying the interaction of a point charge with a metallic surface.[1–5] The precise form of this interaction is of importance for a number of phenomena, such as field evaporation and desorption,[6–8] electron tunneling,[9] field emission,[10] low-energy-electron scattering,[11] etc. From classical electrostatics, one knows that the interaction energy of a point charge of strength Q with an ideal conductor is just $-Q^2/4D$, where D is the distance of the charge from the metal surface. Since this expression is singular as one approaches the metal surface it is very important to know in what way the energy saturates for a real metal surface as $D \to 0$. In addition, the very long-range nature of the image potential makes it important to know the asymptotic corrections to the $1/D$ behavior.

Corrections to the image potential can be classified as static or dynamic in origin. The latter arise when the point charge is traveling at velocities comparable or greater than those of metallic electrons; it is then important to include the nonadiabatic response of the electrons to the point charge. We will have essentially nothing to say about these corrections. The static corrections arise because the charge induced in the metal is not a planar surface charge, but has finite extent in the direction of the surface normal. This leads to dipolar and higher multipolar interactions between the point charge and its induced charge and to saturation of the interaction energy at very small distances. Furthermore, modifications of the charge density in the region of the metal surface result in changes in the total kinetic, exchange, and correlation energy of the metal electrons which must be included in a complete theory.

Recently both Newns[1] and Beck and Celli[2] have treated the static problem by studying the response of a metal to the point charge using a random-phase-approximation (RPA) dielectric function for a semi-infinite metal. There are two potentially serious limitations associated with their approaches. First, their method is linear, and therefore breaks down when the electrons approach too close to the surface. The second, and we believe more severe, restriction is that the surface is highly artificial, in that the wave functions are constrained to vanish exactly at a fixed point outside the positive jellium background. It is the aim of this paper to partially remove both these restrictions.

The approach we take to the problem is variational, exploiting the fact that we can write the energy of the metal as a functional of the density.[12] The method, in its broadest outline, proceeds as follows: We write down the energy of the metal as a functional of density, making certain assumptions about the exchange, correlation, and kinetic terms. We then parametrize the density in the metal in the presence of the external point charge, choosing a form for the density consistent with classical image theory among other requirements. We then minimize the total energy of the system with respect to the parameters of the electron density for fixed metal–point-charge separation. This energy minimum is then studied as a function of metal–point-charge separation.

The remainder of the paper is divided up as follows: In Sec. II we discuss our choice for the energy functional and introduce and motivate two possible choices for the electron density. The methods and approximations used in evaluating the functional for these choices are given in Sec. III and Sec. IV. These sections may be omitted by the casual reader without loss of continuity.

In Sec. V we present our results for the image potential, a discussion of them, and a comparison of this work with that of previous authors.

II. ENERGY AND CHARGE DENSITY

We adopt for the metal surface a jellium model in which the positive ions are smeared out into a uniform background which has a step-function discontinuity at the hypothetical metal surface. An expression for the energy of this model has been written down recently by Smith.[13] He uses a gradient expansion for the exchange- and kinetic-energy terms, an expression due to Kirzhnits[14] involving the square root of the gradient of the density for the correlation energy, and of course, the exact expression for the Coulomb self-energy.

The expansions for the exchange and correlation energy Smith uses are at best asymptotic, and are particularly suspect at low electron densities. In place of them we adopt Wigner's[15] interpolation expression for the exchange and correlation energy, which is a local functional of the density. This choice is consistent with that of Lang and Kohn,[16] who have studied the jellium model through the self-consistent solution of Schrödinger's and Poisson's equations. It has the further advantage of simplicity. For the kinetic terms we have found it necessary to go beyond the local-density approximation and have retained the first two terms in the gradient expansion as written down by Smith. If we had only retained the leading term, i.e., the Thomas-Fermi approximation, we would find that the system would go unstable at low electron densities. This is because the physical requirement that one pay an infinite penalty in kinetic energy to produce a step-function discontinuity in the electron density is not incorporated into the local-density approximation.

The expression we adopt in this paper for the surface energy is then (we use atomic units throughout)

$$E_s = E_{\mathrm{kin}} + E_{\mathrm{x\text{-}c}} + E_{\mathrm{Coul}} \ , \tag{2.1}$$

where

$$E_{\mathrm{kin}} = 2.871 \int n^{5/3}(\vec{r})\, d^3r + \frac{1}{72} \int \frac{|\vec{\nabla} n(\vec{r})|^2}{n(\vec{r})}\, d^3r , \tag{2.2}$$

$$E_{\mathrm{x\text{-}c}} = -0.738 \int n^{4/3}(\vec{r}) \left(1 + \frac{0.959}{1 + 12.57 n^{1/3}(\vec{r})} \right) d^3r , \tag{2.3}$$

$$E_{\mathrm{Coul}} = \frac{1}{2} \int \frac{\bar{n}(\vec{r})\bar{n}(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\, d^3r\, d^3r^1 \ . \tag{2.4}$$

In the above, $n(\vec{r})$ denotes the electron density and $\bar{n}(\vec{r})$ the total charge density

$$\bar{n}(\vec{r}) = n(\vec{r}) - n_0 \theta(-z) \ , \tag{2.5}$$

where n_0 is the positive jellium background, related to the Wigner-Seitz radius r_s by

$$n_0 = 3/4\pi r_s^2 \ . \tag{2.6}$$

As a preliminary step, we examine the properties of the metal surface which result from our choice for the energy—Eqs. (2.1)–(2.4). To this end we adopt the trial density

$$n(\vec{r}) = \tfrac{1}{2} n_0 (1 - \tanh \beta z) \ , \tag{2.7}$$

which depends on the single parameter β.

This expression is similar to that of Smith's trial density,[13] in that it varies monotonically and approaches its asymptotes exponentially. It differs from Smith's choice in that it is analytically well behaved at $z = 0$, a feature which we will find useful when we consider the external point charge.

Inserting $n(\vec{r})$ into (2.1)–(2.4), the integrals can all be done exactly, leading to a polynomial in β. Minimizing E with respect to β fixes β for a given r_s. In Table I we show the values of β and the dipole moment associated with (2.7) for $r_s = 2$, 3, and 5 and compare it with Lang and Kohn. Notice the results are in reasonable agreement with Lang and Kohn's, especially considering the simplicity of (2.7), lending support to our assumption that (2.1) and (2.7) represent a reasonable starting point for studying the image potential.

If we now introduce into the problem a point charge Q a distance D from the surface we expect the electron density $n(\vec{r})$ given by (2.7) to be modified. A physically reasonable choice for $n(\vec{r})$, consistent with the cylindrical symmetry of the problem, is

$$n(r) = \tfrac{1}{2} n_0 \{ 1 - \tanh \beta(r) [z - z_0(r)] \} \ . \tag{2.8}$$

What we are allowing for in (2.8) is for the unperturbed electron density to distort both by stretching (contracting) through $\beta(r)$ and by simultaneously shifting by $z_0(r)$. It is important to realize that changing $\beta(r)$ does not change the net charge on the metal—that is only accomplished by $z_0(r)$. The functions $\beta(r)$ and $z_0(r)$ are not arbitrary, but are constrained in the following ways:

$$\beta(r) \to \beta_0 \quad \text{as } r \to \infty , \tag{2.9a}$$

$$z_0(r) \to 0 \quad \text{as } r \to \infty \ . \tag{2.9b}$$

TABLE I. We have listed for $r_s = 2, 3$, and 5 our calculated values of $1/\beta$ and $\varphi_{\mathrm{dipole}}$, the electrostatic-surface-dipole layer, and compared them to $\varphi_{\mathrm{dipole}}$ calculated by Lang and Kohn (Ref. 16).

	This calculation		Lang and Kohn
r_s	$1/\beta$ (Å)	$\varphi_{\mathrm{dipole}}$ (eV)	$\varphi_{\mathrm{dipole}}$ (eV)
2	0.626	5.97	6.8
3	0.626	1.77	2.32
5	0.610	0.36	0.35

These two requirements arise because the metal must look the same infinitely far from the point charge as it did in its absence. Clearly β_0 is the value of β for the free jellium surface. The equation

$$2\pi n_0 \int_0^\infty z_0(r)\, r\, dr = Q \tag{2.9c}$$

simply states that the induced charge on the metal is opposite that of the point charge.

The simplest way to proceed is to define $z_0(r)$ and $\beta(r)$ parametrically, building into them the requirements (2.9a)–(2.9c) as well as a number of others to be discussed below. For $z_0(r)$ we choose

$$z_0(r) = \frac{Q}{2\pi n_0} \frac{R}{(r^2+R^2)^{3/2}} \quad , \tag{2.10}$$

and for $\beta(r)$,

$$\beta(r) = \beta_0 + c z_0(r) \ , \tag{2.11}$$

in which c and R are variational parameters.

The choices (2.10) and (2.11) clearly satisfy (2.9). Furthermore, in the limit that $\beta_0 \to \infty$ (ideal classical metal) $z_0(r)$ correctly gives the induced surface charge if one sets $R = D$. Our choice for $\beta(r)$ was motivated by the following reasoning: The zeroth-order dipole moment associated with (2.7) is proportional to $1/\beta_0^2$. Small shifts of β from β_0 therefore induce shifts in the dipole moment proportional to the changes in β. Since we expect the local dipole moment to be proportional to the applied field (in the weak-field limit), which in turn is proportional to $z_0(r)$, it follows that $\beta(r) - \beta_0 \propto z_0(r)$.

Our trial density (2.8) must now be inserted into an expression for the total energy, which in the presence of the point charge is just

$$E_T = E_S + Q \int [\bar{n}(\vec{\mathrm{r}})/\,|\vec{\mathrm{r}} - D|\,]\, d^3r \, . \tag{2.12}$$

Equation (2.12) omits the exchange and correlation interaction between the point charge and metal electrons in the case where the point charge is an electron. We will return to this subject in Sec. V.

Unfortunately we have been unable to exactly evaluate (2.12) as an explicit function of c and R and have had to use an expansion procedure on the Coulomb terms which limits our ability to let D become very small.

In order to examine this region we have adopted the following alternative trial density:

$$n(r) = \tfrac{1}{2} n_0 (1 - \tanh\beta_0 z) + \tfrac{1}{2} n_0 z_0(r) \beta_0 \,\mathrm{sech}^2 \beta_0 z \, . \tag{2.13}$$

For a positive point charge (2.13) is positive definite, and using (2.13) we can evaluate (2.12) for arbitrary values of R or D. For a negative point charge (2.13) becomes negative at some point, and this clearly presents a lower limit on the size of R.

It will be obvious to the reader that $n(r)$ given by (2.13) can be obtained from (2.8) by setting $c = 0$ and expanding (2.8) to lowest order in $z_0(r)$. It must be pointed out, however, that (2.13) is a bonafide trial density in its own right, and its use does not imply a perturbational approach.

III. EVALUATION OF ONE-PARAMETER VARIATIONAL ENERGY

The bulk of the effort in performing this calculation is involved in evaluating integrals. The particular choice of variational function was, in fact, made to facilitate this as much as possible. The integrals to be dealt with are of three types, each of which presents its special problems. The first type arises from the local functional terms (2.2) and (2.3). The second is the point-charge interaction with the added charge density. The third is the self-interaction of the added charge, coming from (2.4). Another term arising from this integral is the interaction of the added charge with the unperturbed charge distribution. When the positive background is included, however, this term vanishes identically by symmetry.

A. Local Terms

The leading term in the kinetic energy (2.2) contains a nonintegral power of the density. The exchange-correlation integral (2.3) contains a similar term multiplied by a slowly varying function. For the present purpose, we simplify this integral by replacing that part of the functional with a constant α adjusted to make β_0 agree with the result obtained using the full functional. This approximation is commonly employed in band-structure calculations, where the coefficient of the Slater exchange is adjusted to fit some key feature.[17]

Therefore we must evaluate two integrals of the form

$$I_\gamma = (\tfrac{1}{2} n_0)^\gamma (2\pi) \int dz \int r\, dr \{ [1 - \tanh\beta_0 z + \beta_0 z_0(r) \,\mathrm{sech}^2 \beta_0 z]^\gamma - [1 - \tanh\beta_0 z]^\gamma \}, \tag{3.1}$$

where $\gamma = \frac{4}{3}$ or $\frac{5}{3}$, and $z_0(r)$ is given by (2.10). Note that the unperturbed expression must be subtracted to obtain convergence. We develop a series representation for the integral by expanding the first radical in a binomial series, putting the $\beta_0 z_0$ term in the numerators. Each term is a product of a function of r times a function of z. The r integrals are of the form

$$\int_0^\infty r\, dr\, [z_0(r)]^n = \left(\frac{Q}{2\pi n_0 R^2} \right)^n \frac{R^2}{(3n-2)} \, . \tag{3.2}$$

In the z integrals, changing to the variable $y = \tanh\beta_0 z$ yields

$$\int_{-1}^{1} dy\, (1 - y^2)^{n-1} (1 - y)^{-n+\gamma} = 2^{n+\gamma-1} [\Gamma(n)\Gamma(\gamma)/\Gamma(\gamma+n)] \, , \tag{3.3}$$

where Γ is the gamma function. The series is

$$I_\gamma = n_0^\gamma \pi R^2 \sum_{n=1}^{\infty} \frac{x^n}{n(3n-2)} \frac{\gamma(\gamma-1)\cdots(\gamma-n+1)}{\gamma(\gamma+1)\cdots(\gamma+n-1)}, \quad (3.4)$$

where

$$x = QB_0/\pi n_0 R^2 . \quad (3.5)$$

The first term of the series gives a R-independent contribution to the energy, and arises from the first term in the expansion of the energy about the unperturbed charge density. The sum of all such contributions must vanish because of the variational choice of β_0, so we will drop these terms.

The series diverges for $|x| \geq 1$ because the variational electron density (2.13) can become negative for a negative point charge and R sufficiently small. The series represents functions with a branch point on the negative real axis. We can continue the series for $x > 1$ most easily by using a rational approximation. The second approximant, computed from the series using a standard algorithm, is accurate to 0.2% for $x = 10$, and is more than adequate for our purposes. The results are

$$I'_{5/3} = \pi n_0^{5/3} R^2 \frac{0.03125\,x^2 + 0.00191\,x^3}{1 + 0.09528\,x - 0.00191 x^2}, \quad (3.6)$$

$$I'_{4/3} = \alpha \pi n_0^{4/3} R^2 \frac{0.01786\,x^2 + 0.00171\,x^3}{1 + 0.17805\,x - 0.00171\,x^2}, \quad (3.7)$$

where the prime denotes the subtraction of the R-independent term, and α is the adjustable coefficient. (The pole in these approximants at large positive x is an artifact which moves to larger x as higher approximants are taken. It is far beyond any x values that occur in the calculation.)

The kinetic-energy-gradient term in (2.3) is given by

$$I'_{\rm gr} = \frac{\pi n_0}{72} \int_{-1}^{1} dy \int_0^\infty r\,dr\,\beta_0(1+y) \times \frac{4\,\beta_0 z_0 y + 4\beta_0^2 z_0^2 y^2 + (z_0')^2}{1 + \beta_0 z_0 (1+y)}, \quad (3.8)$$

where the above variable change has been made, and z_0' is the r derivative of z_0. If the denominator in (3.8) is expanded into a geometric series, each term will be the product of a y integral and an r integral, both of which are elementary. The resulting series are

$$I'_{\rm gr} = \frac{\pi n_0}{72} \left(8\beta_0 R^2 \sum_{n=2}^{\infty} \frac{(-x)^n}{n(n+1)(n+2)(3n-1)} - \frac{6x}{\beta_0} \sum_{n=1}^{\infty} \frac{(-x)^n}{(n+1)^2(3n+5)} \right), \quad (3.9)$$

where the prime indicates the neglect of an R-independent term in (3.8) and (3.9). Once again, we use a rational approximation to represent these functions,

$$I'_{\rm gr} = \frac{\pi n_0}{72} \left(\tfrac{2}{3} \beta_0 R^2 \frac{0.1x^2 + 0.0244\,x^3}{1 + 0.494\,x + 0.0244\,x^2} + \frac{1}{\beta_0} \frac{0.1875x^2 + 0.0816x^3}{1 + 0.7587x + 0.1024\,x^2} \right) . \quad (3.10)$$

B. Point-Charge-Interaction Terms

Substituting (2.13) into (2.12), we obtain

$$I_{\rm pc} = \tfrac{1}{2} Q^2 R \int_{-\infty}^{\infty} dz \int_0^\infty r\,dr \frac{\mathrm{sech}^2 \beta_0 z}{[r^2 + (z-D)^2]^{1/2} (r^2 + R^3)^{3/2}} . \quad (3.11)$$

The unperturbed electron density produces a potential which is independent of R, but which varies with D and will eventually be added to the image potential. The r integral is elementary after changing to the variable $y = [r^2 + (z-D)^2]^{1/2}$, and

$$I_{\rm pc} = \tfrac{1}{2} Q^2 \textstyle\int_{-\infty}^{\infty} dz\,(\mathrm{sech}^2 \beta_0 z)/(R + |D - z|) . \quad (3.12)$$

This integral depends on two arguments, $\beta_0 R$ and $\beta_0 D$, and is not well represented by a simple formula. However, it converges exponentially and is accurately and quickly computable using a Laguerre-integration scheme.

C. Coulomb Self-Energy

Direct substitution of the perturbing density into (2.4) gives an integral which is nontrivially five dimensional. A more fruitful way to proceed is to use the Fourier transform of the electron density, $\rho(\vec{q})$, in the alternative expression for the Coulomb self-energy,

$$E_{\rm Coul} = \frac{1}{(2\pi)^2} \int d^3\vec{q}\; \frac{|\rho(\vec{q})|^2}{q^2} . \quad (3.13)$$

The Fourier transform of our variational function

$$\rho_1(\vec{q}) = (Q\beta R/2\pi n_0) \textstyle\int d^3\vec{x}\, e^{i\vec{q}\cdot\vec{x}}\, \mathrm{sech}^2 \beta_0 z\, (r^2 + R^2)^{-3/2} \quad (3.14)$$

consists entirely of tabulated integrals provided the angular integration is done first. It turns out to be the rather simple function

$$\rho_1(\vec{q}) = (\pi/2\beta_0 n_0)\, q_z\, \mathrm{csch}(\pi q_z/2\beta)\, e^{-q_r R} . \quad (3.15)$$

When $\rho_1(q_r, q_z)$ is substituted into (3.13), the q_z integral can be performed by contour integration. The infinite semicircle and the real q_z axis enclose a series of poles of csch on the imaginary axis. The contribution from the semicircle does not vanish, but if it passes midway between two poles, its contribution is a tabulated integral. The remaining q_r integral becomes, after the change of variable $t = q_r/2\beta_0$,

$$I_{\rm Coul} = 2Q^2 \beta_0 \textstyle\int_0^\infty dt\, e^{-4\beta_0 R t} [t^2 \psi'(t) - t - \tfrac{1}{2}], \quad (3.16)$$

where ψ' is the trigamma function.

This integral is unpleasant to handle numerically. By expanding the bracketed part of the integrand around $t=0$, an asymptotic series in $1/x$, where $x=4\beta R$, can be developed. For small x, the integral diverges as $\ln x$. By adding and subtracting the leading term in the large-t expansion of the bracket, the coefficient of the ln term and the constant term can be found. A formula can then be devised to fit the leading two terms at large and small x. The result is

$$I_{\mathrm{Coul}}=\frac{Q^2\beta_0}{3}\ln\frac{x^2+5.88x+7.14}{x^2+2.88x}\ . \qquad (3.17)$$

The interpolation formula was checked at $x=1$ by performing the integral numerically, and is accurate there to better than 0.1%.

Having evaluated all the terms in the energy, R is varied to find a minimum of the total energy for a sequence of values of D. A method of successively improved parabolic fits was used to find the minimum from the energy expression itself in preference to computing the derivative analytically and searching for its zero.

IV. EVALUATION OF TWO-PARAMETER VARIATIONAL ENERGY

Evaluating the energy functional for the full variational density (2.3) entails some different procedures than those employed for the restricted function. The local terms are simpler by design. However, the Coulomb terms can be evaluated only by expanding the variational function. $\beta_0 z_0$ measures the extent of the distortion of the charge density, and is the natural expansion parameter. All integrands retain at least second-order terms in $\beta_0 z_0$.

A. Local Terms

The local terms, excepting the gradient, have the form

$$I_{\mathrm{loc}}=(2\pi)\int_0^\infty r\,dr\int_{-\infty}^\infty dz\{\varphi(\beta(r)[z-z_0(r)])-\varphi(\beta_0 z)\}, \qquad (4.1)$$

where φ is some function. To evaluate this integral, we first integrate by parts to obtain an integrand of the form $z\varphi'$. Then the variable change $x=\beta(r)[z-z_0(r)]$ is made in the first term and $x=\beta_0 z$ in the second. The resulting expression is

$$I_{\mathrm{loc}}=(2\pi)\int_0^\infty r\,dr[1/\beta(r)-1/\beta_0]\int_{-\infty}^\infty dx\,x\varphi'(x)\ , \qquad (4.2)$$

where an R-independent term equal to the bulk energy of the added electron density has been dropped. The x integral depends only on n_0. For the kinetic and leading exchange-correlation terms, it is

$$\gamma(\tfrac{1}{2}n_0)^\gamma\int dx\,x\,\mathrm{sech}^2x(1-\tanh x)^{\gamma-1}$$
$$=n_0^\gamma[1/\gamma+\psi(1)-\psi(1+\gamma)], \qquad (4.3)$$

which can be shown from tabulated integrals after making the variable change $y=\tanh x$. ψ is the digamma function and $\gamma=\frac{5}{3}$ or $\frac{4}{3}$. The second term in the exchange-correlation integral depends on n_0 in a more complicated manner and was evaluated numerically. It should be noted that the same coefficients enter in the determination of β_0 because the $1/\beta_0$ term in (4.2) is just the surface energy.

The r integral in (4.2) could be done exactly. However, there is a distinct advantage to expanding $1/\beta(r)$ to second order in cz_0. Since the Coulomb terms will only be carried to second order, this will make the entire energy a second-order polynomial in the variational parameter c, greatly simplifying the minimization. When $1/\beta(r)$ is expanded, the r integrals are just those given in (3.2).

The kinetic-energy-gradient term is more complicated, but may be performed by similar techniques. After the above change of variables, the x integrals are all numerical constants which may be evaluated exactly, and the r integrals are all powers of $\beta(r)$ and $d\beta/dr$. As before, negative powers of β are expanded, and only second-order terms retained. The result is

$$I'_{\mathrm{gr}}=(Q^2/1152R^4)[(3\beta_0/\pi n_0)-(3/\pi n_0\beta_0)c$$
$$+(\pi/4n_0\beta_0^3)c^2]\ , \qquad (4.4)$$

where an R-independent term has been dropped.

B. Point-Charge-Interaction Terms

The expansion of the charge density (2.8) to second order in z_0 is

$$n_0\{\tfrac{1}{2}-\tfrac{1}{2}\tanh[\beta_0+cz_0(r)][z-z_0(r)]\}=\sum_{i=0}^{6}\rho_i+O(z_0^3)\ , \qquad (4.5)$$

where

$$\rho_0=\tfrac{1}{2}n_0(1-\tanh\beta_0 z)\ , \qquad (4.6a)$$

$$\rho_1=\tfrac{1}{2}n_0\beta_0 z_0\,\mathrm{sech}^2\beta_0 z\ , \qquad (4.6b)$$

$$\rho_2=-\tfrac{1}{2}n_0 c z_0 z\,\mathrm{sech}^2\beta_0 z\ , \qquad (4.6c)$$

$$\rho_3=\tfrac{1}{2}n_0 c z_0^2\,\mathrm{sech}^2\beta_0 z\ , \qquad (4.6d)$$

$$\rho_4=\tfrac{1}{2}n_0\beta_0^2 z_0^2\,\mathrm{sech}^2\beta_0 z\tanh\beta_0 z\ , \qquad (4.6e)$$

$$\rho_5=\tfrac{1}{2}n_0 c^2 z_0^2 z^2\,\mathrm{sech}^2\beta_0 z\tanh\beta_0 z\ , \qquad (4.6f)$$

$$\rho_6=-n_0 c\beta_0 z_0^2 z\,\mathrm{sech}^2\beta_0 z\tanh\beta_0 z\ . \qquad (4.6g)$$

In evaluating the interaction of each of these terms with the point charge, the r integral can be done analytically. For ρ_1-ρ_3, it is the same as in Sec. III B, and gives denominators equal to that in (3.12). For ρ_4-ρ_6, the corresponding integral is

$$F_2=\int_0^\infty r\,dr[r^2+(z-D)^2]^{-1/2}(r^2+R^2)^{-3}\ . \qquad (4.7)$$

While this can be evaluated in terms of elementary functions, it is too complicated to be convenient for the subsequent numerical z integration. The fitted interpolating formula

$$F_2\approx(0.587R+0.336|D-z|)/(R+1.161|D-z|)^2 \qquad (4.8)$$

is convenient and accurate to better than 1% over its entire range. All 6 z integrals are done numerically using a Laguerre scheme.

C. Coulomb Self-Energy

There are two distinct types of terms involved in calculating this contribution through second order in Z_0. The first type includes the self-interaction of ρ_1, which was calculated in the one-parameter theory, and the self-interaction of ρ_2. The ρ_1-ρ_2 cross term vanishes from symmetry. The second type includes the interactions of ρ_4 and ρ_5 with ρ_0 and the positive background. Since one charge is uniform in the x-y plane in this case, these terms are much simpler. The corresponding terms with ρ_3 and ρ_6 vanish from symmetry.

The self-interaction of ρ_2 can be evaluated in essentially the same manner as used for ρ_1 in Sec. III C. Since the functional form of ρ_2 is just z times ρ_1, its Fourier transform is just the q_z derivative of (3.15). When this quantity is squared and substituted into (3.13), the q_z integral can be done by contour integration as before, and the q_r integral reduces to

$$I_{\text{Coul}}=\frac{c^2Q^2\pi^2}{4\beta_0^3}\int_0^\infty dt\,e^{-xt}[2(\tfrac{1}{3}t^2-1/\pi^2)\psi^{(1)}(1+t)$$
$$-(2t/\pi^2)\psi^{(2)}(1+t)-(t^2/3\pi^2)\psi^{(3)}(1+t)+\tfrac{1}{3}-\tfrac{2}{3}t], \tag{4.9}$$

where $t=q_r/2\beta_0$, $x=4\beta_0R$, and the $\psi^{(n)}$ are polygamma functions. This exact expression is not convenient, and a useful interpolation formula fit to the large and small x asymptotic series is

$$I_{\text{Coul}}=\frac{c^2Q^2\pi^2}{4\beta_0^3}\,0.0436\ln\left[1+\frac{1}{1.01+0.142x^2}\right]. \tag{4.10}$$

This result can be checked in a completely independent manner as $\beta_0R\to\infty$ by computing the energy per unit area of a similar charge distribution which is uniform in the x-y plane, and then integrating this energy with the appropriate weighting function.

To compute terms of the second type, the cross terms, we start with Poisson's equation for the potential produced by ρ_0 plus the positive background,

$$\frac{d^2v}{dz^2}=4\pi[\rho_0(z)-n_0\theta(-z)]\ . \tag{4.11}$$

The energy is then just

$$I_{0\text{-}i}=2\pi\int_{-\infty}^{\infty}dz\,v(z)\int_0^\infty r\,dr\,\rho_i(r,\ z)\ , \tag{4.12}$$

and the r integrals are straightforward. Since (4.11) can be integrated only once analytically, (4.12) is integrated once by parts. Each resulting z integral is then a power of β_0 times a numerical constant. The results are

$$I_{0\text{-}4}=0.3069(Q^2/8\beta_0R^2)\ , \tag{4.13}$$

$$I_{0\text{-}5}=0.5220(c^2Q^2/8\beta_0^5R^2)\ . \tag{4.14}$$

D. Minimization

All the terms in the variational energy can now be collected and grouped according to their dependence on the parameter c,

$$E(c,\ R)=\alpha(R)c^2+\gamma(R)c+\omega(R)\ . \tag{4.15}$$

It is easily seen that the minimum occurs at

$$c=-\gamma(R)/2\alpha(R)\ , \tag{4.16}$$

and the energy at the minimum is

$$E(R)=\omega(R)-\gamma^2(R)/4\alpha(R)\ . \tag{4.17}$$

This portion of the calculation has the following interpretation: α is essentially a stiffness parameter giving the restoring force with which the surface resists changes in its equilibrium profile. γ is the external driving force, arising largely from the point-charge interaction, but in part from the origin shift (through the kinetic-gradient term). ω is that part of the variational energy arising from the shift alone, and in the limit of a distant or weak charge becomes equivalent to the one-parameter theory. It is clear that as long as the system is stable ($\alpha>0$), the added variational freedom of the present calculation gives additional energy lowering.

The final minimization with respect to R is carried out simply by searching for the minimum as described in Sec. III.

V. RESULTS AND DISCUSSION

We turn first to the results of our one-parameter variational calculation. We have plotted in Fig. 1 the image potential energy E versus distance for metals with $r_s=2$, 5. The solid lines are for point

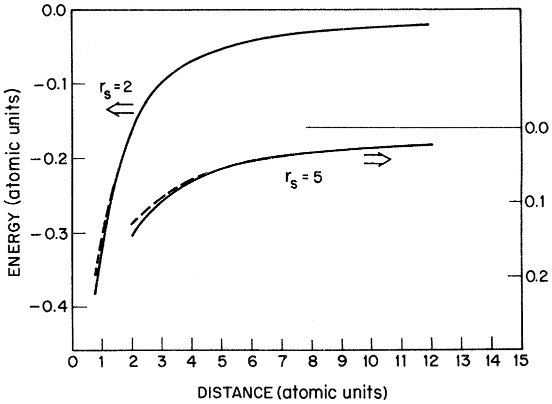

FIG. 1. Total energy as a function of the distance of the point charge from the jellium surface based on the one-parameter variational function. The solid curves are for a positive charge of 1 a.u., and the dashed curves are for a charge of 2 a.u., with the energy scaled by a factor of $\frac{1}{4}$. The energy origins for $r_s=2$ and $r_s=5$ are displaced for clarity.

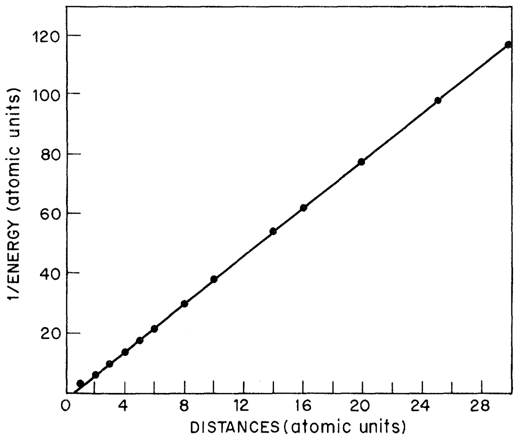

FIG. 2. Reciprocal energy vs distance for the one-parameter theory with $r_s = 2$ and one-unit charge. The quality of the straight-line fit demonstrates how well the classical functional dependence is followed, and the intercept gives the apparent location of the ideal surface.

charges with $Q = 1$, while the dashed curves are for point charges with $Q = 2$. The curves for $Q = 2$ have been scaled by $\frac{1}{4}$. The first thing to notice is that the curves for the two different values of Q are essentially identical except at the smallest distances.

A similar and even more impressive scaling results where one scales from a smaller value of the point charge to one with $Q = 1$. The fact that the image potential is proportional to Q^2 is of course predicted by classical theory as well as any linearized quantum theory. The situation when the point charge is less than 2 a.u. from the surface is by any *a priori* measure, highly nonlinear. For example, the induced charge density produced by the external charge is equal to or greater than that of the background metallic electron density for $D < 2$ and $r_s = 2$. The same statement can be made in comparing the force experienced by a *test* charge at the jellium discontinuity from the unperturbed metallic dipole and that resulting from the point charge and its image. Part of the explanation for the excellent scaling can be found in the fact that the Coulomb terms in the interaction energy scale with Q^2. While these terms do dominate, the remaining quantum terms contribute typically 10% of the energy. Since the scaling of the interaction at $D = 1.5$, $r_s = 2$ is accurate to 1%, one can only conclude that the nonlinear behavior is not strong even in those terms.

A second feature of curves is that they are nearly independent of r_s for $D > 4$. This results from the remarkable independence that β has on r_s. In extracting an analytic form for $E(D)$ we have plotted $1/E$ vs D in Fig. 2. The points with D greater than 3 all lie on a straight line, implying an energy law

$$E(D) = -Q^2/4(D-d) \tag{5.1}$$

for $D > 3$. In other words, we recover the classical image-potential law for distance greater than 3 a.u. if we shift our origin from the jellium discontinuity to a surface $d \approx 0.5$ into the vacuum, a point at which the electron density has fallen to 30% of its bulk value. The radial shape of the induced image charge is determined by R, our variation parameter. We find that for $D > 3$, the range over which (5.1) holds, R is approximately 0.9 a.u. less than D, implying an image charge somewhat more tightly bound than would be predicted by classical electrostatics with the ideal conductive surface at d. For $D < 3$, R tends to saturate, and by $D = 0.75$, $R = 0.72$.

We now move on to consider the results of the two-parameter theory. This theory has certain perturbational aspects with the dimensionless coupling constant proportional to Q/R^2. This restricts the size of our charge and the distance to which we can let the point charge approach the metal surface.

Over a range consistent with these restrictions, we find once again that E scales as Q^2, and that this scaling is much better than would have been predicted from the size of the coupling constant. With this Q^2 scaling rather firmly established, we will use the following ansatz for obtaining $E(D)$ for small D. We will let $Q = 0.01$, which enables us to plot E vs D over almost its entire range, and then scale E up so that it is valid for $Q = 1$.

Once again E vs D appears to obey a classical-image law with a shifted origin. To better reveal this, we have assumed that E obeys Eq. (5.1) with d allowed to vary with D and plotted d vs D for $r_s = 2, 3, 5$ in Fig. 3. We see that d is remarkably constant for $D \gtrsim 3$, after which it begins to drop rapidly. Notice that unlike the one-parameter theory, d is a function of r_s, ranging from ~ 0.5 to

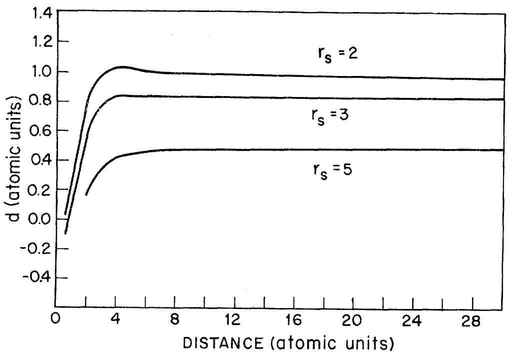

FIG. 3. Apparent ideal-surface location vs point-charge distance for the two-parameter theory and an infinitesimal charge. These plots are obtained by equating the energy to $Q^2/4\,(D-d)$ at each D, and solving for d. Departures of d from constancy correspond to departures of a plot like Fig. 2 from a straight line.

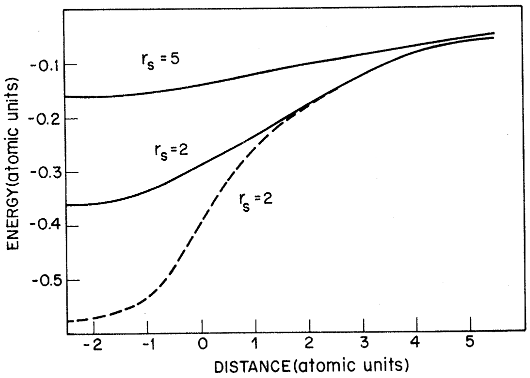

FIG. 4. Solid curves are the effective exchange and correlation potential seen by an electron. They are obtained by interpolating between the local approximation used inside the metal and the image potential calculated outside as explained in the text. For $r_s=2$, the dashed curve shows this plus the Hartree electrostatic potential, and thus represents the total barrier. For $r_s=5$, the Hartree term is so small we have not shown it.

1.0. This arises because of the extra freedom built into the trial density, which allows for polarization of metal through a local change in β. The fact that d increases with decreasing r_s results from an interplay of two factors. For a given change in β, the induced dipole is proportional to the density or r_s^{-3}. The ability of a given applied field to change β is a less sensitive function of r_s (recall that β itself is practically independent of r_s) and the net result is the trend one finds. The value of r is again $\sim D-0.9$ and is independent of metal density. On the other hand, c goes from 0.96 to 0.13 as we let r_s go from 2 to 5.

There exists a fairly substantial theoretical literature on the subject of the image potential. Two of the most recent works are due to Newns[1] and Beck and Celli.[2] Their results are substantially the same. They are both linear dielectric-response theories and adopt infinite-potential-barrier models for the surface potential. The linear treatment they use does not enable them to explore the validity of the Q^2 dependence of the exchange potential or at what distance from the metal surface their predictions break down. They do, however, make a definite prediction concerning the origin one should measure the equivalent classical-image-potential law from.

Since the model they adopt for the surface is different from ours, a precise comparison is not possible. However, they both use jellium models, and using the jellium discontinuity as our common reference for comparison, they find their hypothetical classical surface lies inside this point while we find it outside. Another way of comparing our results would be in terms of electron density. In this case one could say that their surface is situated where the electron density is 60–75% of its bulk value, $r_s=2$–4, where we find a value closer to 15–30%. We feel this discrepancy lies in an inadequacy of the infinite-potential-step model, which inhibits the motion of electron charge into the vacuum. For example, no matter how strong the attractive perturbation might be, electronic charge cannot penetrate beyond the infinite-potential step. Since any improvement in our final density function can only result in an increase of d (by the variational theorem) we expect this conclusion to hold in more refined treatments of the jellium model.

In this connection, there has recently been a study by Lang in which the charge induced by a weak uniform electric field is calculated. Using a jellium model, he carries out a self-consistent quantum-mechanical calculation. One might hope that for a distant point charge the field outside the surface would be sufficiently weak and slowly varying that the z dependence of the induced charge would have the form he has calculated. The induced charge could then be written as a product of a radial function $f(r)$ times Lang's function and an integral equation for f derived from the variational principle. Unfortunately, the kernel for this integral equation would be a complicated multiple convolution of Lang's function, which is only known numerically. Thus application of these results to the image problem would be a formidable undertaking.

If one makes the *ad hoc* assumption that the radial dependence found variationally turns out to be $(r^2+D^2)^{-3/2}$, the "classical result," it is simple to calculate the force on the point charge and show that the origin shift d is proportional to the centroid of the induced charge. For $r_s=2$, this gives $d=0.75$, which is qualitatively similar to our result. However, the changes we find in the radial function can produce comparable shifts, so it is not possible to avoid the self-energy integral if quantitative results are to be extracted.

Within the context of the present calculation we have ignored a number of added complications which we should like to consider now. The first of these is the interaction of the point charge with the undisturbed surface dipole of the metal. This interaction is highly localized, falling off exponentially as $e^{-2\beta_0 D}$ for large D. It is entirely negligible for $D>3$. Its inclusion for both signs of charge is trivial and accounts for the difference between the solid and dashed curves marked $r_s=2$ in Fig. 4. Needless to say, this term depends linearly on Q, and is repulsive for a positive charge.

The second complication concerns our treatment of exchange and correlation when the point charge is an electron. When the electron is in the metal, the exchange and correlation energy represents the energy gained from the formation of an electron deficiency about the electron—the so-called exchange and correlation hole. When the electron leaves the solid, the exchange and correlation hole changes into the image charge. To simply add the exchange and correlation potential to the image potential would be double counting. With this identification in mind, we should now like to consider the interaction energy of a very slow electron incident on a metal surface from infinity. Over most of its path it is essentially a static charge—the image potential we have derived, exhibited in Fig. 1, should be perfectly valid. As the electron approaches closer to the metal surface, it acquires substantial kinetic energy and the static approximation begins to break down. The image energy we calculated is then expected to overestimate the strength of the actual potential.

When the electron has entered the metal, we expect its interaction energy to be better represented by the local approximation to the exchange and correlation potential. As one follows the electron backwards along its trajectory, we expect that the exchange potential will underestimate the interaction energy due to its neglect of nonlocal effects. The actual potential experienced by the electron is expected to be an interpolation between these two limits. Our candidate for such an interpolation is shown in Fig. 4. It is constructed by plotting the exchange and correlation potential as well as the image potential and drawing a common tangent to both curves in an attempt to interpolate smoothly between them. The total potential for $r_s = 2$, including the electrostatic dipole potential, is given by the dashed curve in Fig. 4.

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Statistical Mechanics of Solids

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It is shown that for a solid subjected to external compression or tension, statistical-mechanical calculations lead to inconsistent results unless the Hamiltonian includes terms describing the action of these external forces upon the surface atoms. This requirement is due to the existence of very long-range correlations between atoms of the solid. For liquids or gases not on the verge of a phase transition, the correlations are short ranged and the usual procedures for statistical-mechanical calculations suffice. The question of the characterization and stability of a solid is also discussed.

I. INTRODUCTION

The seemingly straightforward question of how to calculate the thermodynamic properties of a solid subjected either to tension or pressure, using the methods of statistical mechanics, provides a number of surprises. The simplest approach one might propose is to employ the canonical ensemble. Here one only specifies the Hamiltonian describing the atoms comprising the system. In particular, in this approach one completely ignores all interactions between the system and the container "walls." (This is the great beauty of statistical mechanics.) In principle one can calculate the canonical partition function, and from it the Helmholtz free energy $\mathfrak{F}(T, V)$, assuming the system occupies a given volume V. The thermodynamic relation $p = -(\partial \mathfrak{F}/\partial V)_T$ gives the pressure in terms