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Quantum-mechanical origin of the asymptotic effective potential at metal surfaces

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In recent work we interpreted the exchange-correlation potential of density-functional theory to be the work done by an electron against the electric field of its Fermi-Coulomb hole charge distribution. A consequence of this interpretation is that the asymptotic structure of the effective potential of interacting nonuniform electronic systems is due to Pauli correlations. In this paper we show the asymptotic structure of the work required against the field of the delocalized Fermi hole at metallic surfaces to be the image potential.

The classical image potential at a metal surface is derived as the work done against the electric field due to the charge induced at the surface by an *external* point charge. From a quantum-mechanical viewpoint, however, the metal electrons in the classically forbidden region outside the surface constitute part of the nonuniform electron gas system at the metal-vacuum interface. What then is the quantum-mechanical origin and structure of the local effective potential in which these surface electrons move? In this paper we show that the *asymptotic* structure of the effective potential at metallic surfaces is the image potential and that it is due to the electron's Fermi hole charge distribution.

In a recent paper[1] we interpreted the exchange-correlation potential of Hohenberg-Kohn-Sham density-functional theory[2] as the work done against the electric field of the Fermi-Coulomb hole charge distribution. This potential was also shown[1] to satisfy the virial theorem. A consequence of this interpretation is that the quantum-mechanical origin of the *asymptotic* structure of the effective potential of interacting inhomogeneous electron gas systems is the same and due entirely to correlations which arise as a result of the Pauli exclusion principle. We confirmed[1] this for the case of atoms by showing that the asymptotic structure of the work required against the field of the *localized*[3] Fermi hole was $-1/r$. In the present paper we show the asymptotic structure of the effective potential at metallic surfaces as determined from the *delocalized*[4] Fermi hole to be the image potential $-1/4x$. Thus, when viewed within the context of density-functional quantum theory, the image potential asymptotically far from the metal surface is a consequence of Pauli correlations between the electrons. Furthermore, the fact that the same physics leads to the correct asymptotic structure for both few-electron atomic and many-electron surface systems also demonstrates the inherent consistency of the theory.

According to density-functional theory,[2] the ground-state energy of a system of interacting electrons in some external potential may be written as a universal functional of the electronic density $\rho(\mathbf{r})$. In addition, the interacting inhomogeneous system may be replaced by one of noninteracting *quasielectrons* moving in a *local* effective potential $v_{\text{eff}}(\mathbf{r})$. Thus, the Kohn-Sham differential equation to be solved for each quasielectron of momentum $\mathbf{k}$ is

$$[-\tfrac{1}{2}\nabla^2+v_{\text{eff}}(\mathbf{r})]\Psi_{\mathbf{k}}(\mathbf{r})=\epsilon_{\mathbf{k}}\Psi_{\mathbf{k}}(\mathbf{r}),$$

where $\rho(\mathbf{r})=2\Sigma_{\mathbf{k}}|\psi_{\mathbf{k}}(\mathbf{r})|^2$. The effective potential is a sum of the Hartree electrostatic and exchange-correlation potentials. The exchange-correlation potential $\mu_{xc}(\mathbf{r})=\delta E_{xc}[\rho]/\delta\rho$ is the functional derivative of the exchange-correlation energy functional $E_{xc}[\rho]$. This functional, in which all the many-body effects are incorporated, is unknown and, therefore, so is the corresponding potential. Furthermore, although the exchange-correlation energy functional has a physical interpretation,[5] the potential is understood only in terms of its mathematical definition. Thus, the principal approach to the application of Kohn-Sham theory has been via approximations to $E_{xc}[\rho]$ such that its functional derivative is readily determined. As a consequence, in contrast with classical electrostatics where the physical origin of the image potential is understood, the effective potential of density-functional theory at metallic surfaces can only be determined in an approximate manner.

With the physical interpretation provided by us[1] the exchange-correlation potential may be determined *directly* from the Fermi-Coulomb hole charge distribution of an electron and its asymptotic structure obtained *exactly*. The Fermi-Coulomb hole about each electron is a consequence of the reduction in probability of electrons approaching each other due to Coulomb repulsion and the Pauli exclusion principle. Thus, all the many-body effects of the interacting electron gas are represented in the structure of the Fermi-Coulomb hole. In a homogeneous electronic system this charge distribution is *dynamic*[3,4] and changes as a function of electron position. The potential of the electron is, therefore, the work done in bringing it from infinity to its final position against the electric field of this charge distribution. Thus, the exchange-correlation potential $W_{xc}(\mathbf{r})$ is

$$W_{xc}(\mathbf{r})=-\int_{\infty}^{\mathbf{r}}\mathcal{E}_{xc}\cdot d\mathbf{l},$$

where the electric field $\mathcal{E}_{xc}(\mathbf{r})$ due to the Fermi-Coulomb hole charge density $\rho_{xc}(\mathbf{r},\mathbf{r}')$ at $\mathbf{r}'$ for an electron at $\mathbf{r}$ is

given by Coulomb's law as

$$\mathcal{E}_{xc}(\mathbf{r}) = \int \frac{\rho_{xc}(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}' .$$

The above interpretation of the potential seen by the electrons is consistent with our understanding[5] of the exchange-correlation energy being the energy of interaction between an electron and its Fermi-Coulomb hole. If the Fermi-Coulomb charge were static, then the potential would be $V_{xc}(\mathbf{r}) = \int d\mathbf{r}' \rho_{xc}(\mathbf{r},\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$.

Now since we may write the exchange-correlation energy $E_{xc}[\rho]$ as a sum of its exchange $E_x[\rho]$ and correlation $E_c[\rho]$ energy components, we may similarly consider the Fermi-Coulomb hole as being comprised of its Fermi and Coulomb hole distributions. As a consequence of the fact[5,6] that the total charge of both the Fermi-Coulomb and Fermi holes is unity, it follows that the total Coulomb hole charge is zero. Thus, the contribution of the Coulomb hole charge to the electric field and potential for electron positions asymptotically far from the system must vanish. Therefore, the asymptotic structure of the potential $W_{xc}(\mathbf{r})$ as $\mathbf{r} \to \infty$ is that of W_x, the work done against the force field of the Fermi hole charge distribution. However, the potential W_x can be determined exactly since the Fermi hole is known[6] explicitly in terms of the electronic wave functions as $\rho_x(\mathbf{r},\mathbf{r}') = |\gamma(\mathbf{r},\mathbf{r}')|^2/2\rho(\mathbf{r})$, where $\gamma(\mathbf{r},\mathbf{r}') = 2\Sigma_{\mathbf{k}} \Psi_{\mathbf{k}}^*(\mathbf{r}')\Psi_{\mathbf{k}}(\mathbf{r})$ is the single-particle density matrix. Thus, the asymptotic structure of the potential of any nonuniform electronic system is due to Pauli correlation and it can be determined exactly by solution of the Kohn-Sham equation in the exchange-only approximation[7] with μ_x replaced by the work W_x. (Note that $\mu_x = \delta E_x[\rho]/\delta\rho$ also cannot be evaluated since the functional dependence of $\rho_x(\mathbf{r},\mathbf{r}')$ on $\rho(\mathbf{r})$ is unknown.)

We perform our calculations in the jellium model approximation of a metal surface in which the uniform charge background of density $\rho_+(x) = \bar{\rho}\Theta(-x+a)$ begins at the surface at $x=a$. Here $\bar{\rho} = k_F^3/3\pi^2$ is the bulk density, $k_F = 1/\alpha r_s$ $[\alpha^{-1} = (9\pi/4)^{1/3}]$ is the Fermi momentum and r_s the Wigner-Seitz radius. Because of translational invariance in the plane parallel to the surface, the electronic wave functions are of the form $\Psi_{\mathbf{k}}(\mathbf{r}) = -\sqrt{2/V}\varphi_k(x)\exp[i(\mathbf{k}_\parallel \cdot \mathbf{x}_\parallel)]$ where $\varphi_k(x)$ is the component of the wave function in the direction perpendicular to the surface, k and x the momentum and position vectors in that direction, and $\mathbf{k}_\parallel$ and $\mathbf{x}_\parallel$ the corresponding components in the plane of the surface. In terms of the variables $y = k_F x$, $y' = k_F x'$, $\mathbf{y}_\parallel = k_F \mathbf{x}_\parallel$, $\mathbf{y}_\parallel' = k_F \mathbf{x}_\parallel'$, $R = |\mathbf{y}_\parallel|$, $q = k/k_F$, $q' = k'/k_F$, and $Q = (1-q^2)^{1/2}$, the electric field normal to the surface at the position of the electron is

$$\frac{\mathcal{E}_x(y)}{(3k_F^2/2\pi)} = -\frac{8}{\rho_n(y)} \int_{-\infty}^{\infty} dy' \int_0^{\infty} dR \frac{R(y-y')g(y,y',R)}{[(y-y')^2+R^2]^{3/2}},$$

where

$$g(y,y',R) = \left| \int_0^1 dq\, \phi_q^*(y)\phi_q(y')QJ_1(QR)/R \right|^2 ,$$

$J_1(z)$ is the first-order Bessel function and $\rho_n(y)$ is the electronic density normalized with respect to the bulk value $\bar{\rho}$. The corresponding work done is then

$$\frac{W_x(y)}{(3k_F/2\pi)} = 8\int_{\infty}^{y} \frac{dy'}{\rho_n(y')} \int_{-\infty}^{\infty} dy'' \int_0^{\infty} dR \frac{R(y-y')g(y',y'',R)}{[(y'-y'')^2+R^2]^{3/2}} .$$

Since the wave functions and electronic density decay exponentially in the vacuum region, so does the electrostatic potential. Therefore, the asymptotic structure of the effective potential is that of the work W_x. Furthermore, for increasing positions of the electron from the metal surface in the vacuum, the electron's Fermi hole spreads[4] deeper into the crystal. Thus, the accurate determination of the potential many Fermi wavelengths outside the surface requires a knowledge of the Fermi hole structure for at least equivalent distances inside the crystal. However, the asymptotic structure of the potential is insensitive to the choice of orbitals: the significant requirements of the wave functions at a metal surface are that they be exponential in the vacuum region and oscillatory in the metal bulk. Consequently, instead of solving the Kohn-Sham equations self-consistently, which would be a numerical tour de force, we determine the asymptotic structure of the work W_x for accurate semianalytical wave functions.[8] For our wave functions $\varphi_k(x)$ we choose solutions of the Kohn-Sham equation generated by the finite linear effective potential model[8] which are

$$\phi_k(x) = \sin[kx+\delta(k)]\Theta(-x) + [B_k \mathrm{Ai}(\zeta) + C_k \mathrm{Bi}(\zeta)] \times [\Theta(x) - \Theta(x-b)] + D_k \exp(-\kappa x)\Theta(x-b) ,$$

where $k = \sqrt{2E}$, $\kappa = \sqrt{2(W-E)}$, $\zeta = (x - E/F)(2F)^{1/3}$, E is the energy, F is the field strength, W the barrier height, and where $\mathrm{Ai}(\zeta)$ and $\mathrm{Bi}(\zeta)$ are the Airy functions. The phase factor $\delta(k)$ and the coefficients B_k, C_k, and D_k are determined by the requirement of continuity of the wave function and its logarithmic derivative at $x=0$ and $x=b$. The field strength and barrier height parameters of this model are defined as $x_F = F/(k_F^2/2)$ and $b = W/F$, respectively. The results presented here are for a metal of density $r_s = 2.0$, and the parameters[9,10] for the calculations are $y_F = k_F x_F = 3.33$, $y_b = k_F b = 4.25$, and $y_a = k_F a = 1.33$. Note that a value of $y = 2\pi$ corresponds to a Fermi wavelength which for $r_s = 2.0$ is 3.46 Å.

In Figs. 1 and 2 we plot the universal function $\mathcal{E}_x(y)/(3k_F^2/2\pi)$ as a function of electron position y. Note (Fig. 1) that the electric field is largest at the surface region, and that it vanishes in an oscillatory fashion for electron positions inside the metal. For electron positions outside the surface the electric field also decays. Its asymptotic structure is shown in Fig. 2 for a distance of up to approximately eight Fermi wavelengths outside the metal. In this figure we also plot the function $1/2y^2$ which translates in terms of the original variables to $(3/4\pi)/x^2 = 0.24/x^2$. Observe that for an electron at about $y = 50$

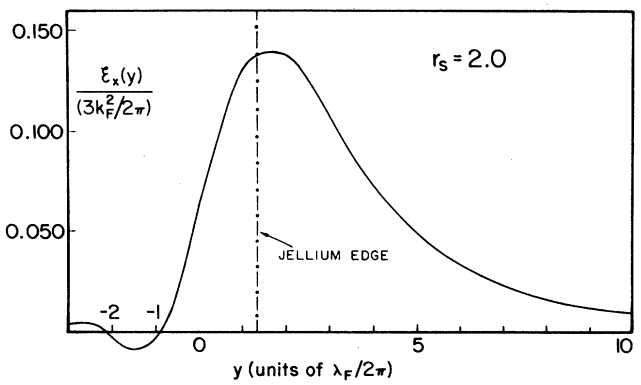

FIG. 1. Variation of the universal function $\mathcal{E}_x(y)/(3k_F^2/2\pi)$, where $\mathcal{E}_x(y)$ is the electric field due to the Fermi hole, vs the electron position y.

the electric field essentially merges with this curve. Thus, the line integral of the electric field which is W_x is then $-1/4x$, the image potential. To demonstrate this explicitly we plot in Fig. 3 the universal function $W_x(y)/(3k_F/2\pi)$ for the same electron positions as in Fig. 2 along with the function $-1/2y(\equiv -0.24/x)$. It is evident that the two curves merge, thereby clearly demonstrating that for asymptotic positions of the electron the potential W_x is the image potential. Thus, asymptotically the image potential is due to the Fermi hole charge distribution which in turn is a consequence of the Pauli exclusion principle.

If the Fermi hole were treated as a static charge distribution, then the corresponding potential is the exact Slater[6] potential

$$V_x^{\text{Slater}}(\mathbf{r}) = \int d\mathbf{r}' \rho_x(\mathbf{r},\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| \, .$$

We have recently determined[9,11] the structure of the Slater potential at metallic surfaces. Asymptotically far from the surface, the Slater potential is also image-potential-like but with a coefficient which is approximately twice as large as the image potential coefficient, i.e., $V_x^{\text{Slater}}(x) \sim -(3/2\pi)/x = -0.48/x$. For comparison we note that the asymptotic structure of the effective potential in the local density approximation[2] for exchange and

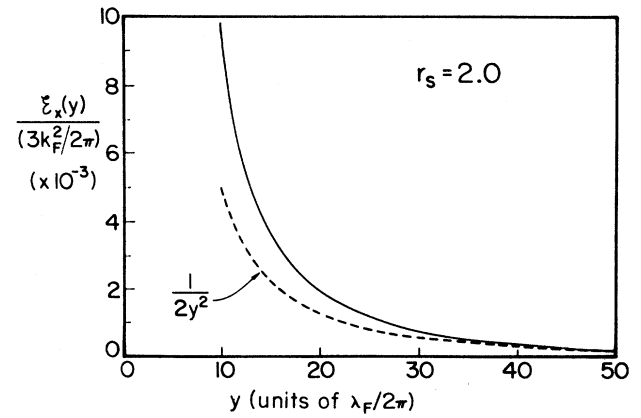

FIG. 2. The figure caption is the same as in Fig. 1.

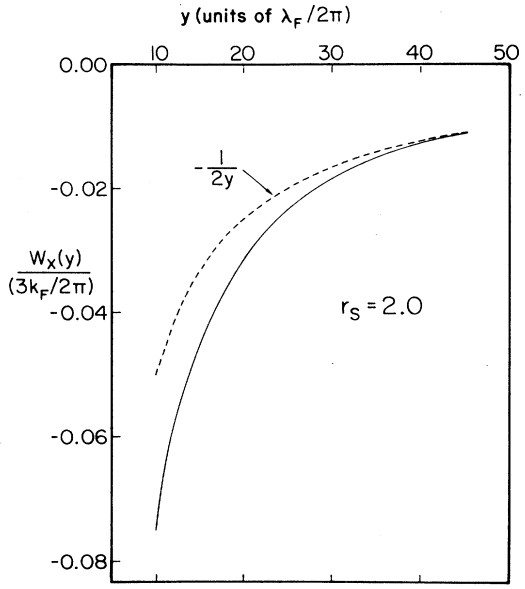

FIG. 3. Variation of the universal function $W_x(y)/(3k_F/2\pi)$, where $W_x(y)$ is the work done against the electric field $\mathcal{E}_x(y)$ due to the Fermi hole, vs the electron position y.

correlation is exponential.[12]

Thus, we see that the quantum-mechanical interpretation of the asymptotic structure of the image potential as due to Pauli correlation effects is consistent with the classical picture of the image potential being a consequence of the Coulomb interaction between a test and its image charge. Classically, the image potential is due to the induced image charge which is the response of the metal surface to the external test charge. For positions asymptotically far from the surface an electron may be considered a distinguishable classical particle and the charge induced by it determined. Thus, treating the electron as an external point charge, Lang and Kohn[12] have calculated the induced charge distribution within linear response theory and shown the energy of interaction to be $-1/4(x-x_0)$, where x_0 is the center of mass of the induced charge. The induced charge has also been shown[12] to have the same structure as the classical image charge in the planes parallel to the surface. The image potential at metallic surfaces has also been derived[13,14] by consideration of the asymptotic structure of the Kohn-Sham exchange-correlation potential $\mu_{xc}(\mathbf{r})$. In these derivations the distant metal electron in the vacuum is also treated as a point charge distinct from the electronic gas of the metal and independent of the inhomogeneity at the surface. On the other hand, from a quantum-mechanical viewpoint this electron is part of the interacting N-fermion system, and is treated as such in the present formalism. The electron is not considered as an external charge and there is, therefore, no induced charge. The Fermi hole of an electron is not an induced charge distribution but rather an intrinsic property of the system itself which contributes to the effective potential. We have determined the effective potential from the electronic wave functions themselves, and shown that quantum

mechanically too its asymptotic structure is the image potential. In quantum theory this structure is a consequence of the Coulomb interaction between an electron and its Fermi hole. The fact that both classical and quantum theories lead to the same asymptotic structure of the potential implies that the interpretations of each formalism are equally valid.

Finally, we note that in accord with exchange-only[2] density-functional theory, our potential (in units of $3k_F/2\pi$) due to the Fermi hole asymptotically goes[1] to a value of $-\frac{2}{3}$ in the metal bulk. (The corresponding value for the Slater potential[1,9] is -1.) Thus, not only does the potential W_x represent the correct asymptotic behavior outside the metal for the fully interacting electron gas, it lowers the electron potential due to exchange by the correct amount inside the metal. With the present quantum-mechanical interpretation of the effective potential, Coulomb correlation effects become significant and contribute to the exchange-correlation potential W_{xc} only for electron positions near the surface. Therefore, to obtain the position of the image plane, the structure of the Coulomb hole and of its contribution to the effective potential need to be determined. Work along these lines within the random-phase approximation is in progress.

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