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Quantum mechanical image potential theory

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We present a quantum-mechanical image-potential theory by determining analytically the Kohn-Sham (KS) exchange-correlation potential $v_{xc}(z)$ in the classically forbidden region of the metal-vacuum interface. The asymptotic structure of the image potential is determined to be $-(\alpha_{KS,x}+1/4)/z$, where $\alpha_{KS,x}$ depends upon the Fermi energy and barrier height of the metal. The structure is obtained from exact expressions derived for $v_{xc}(\mathbf{r})$ in the asymptotic region in terms of the electron self-energy. The KS exchange potential is determined as $v_x(z)\sim-\alpha_{KS,x}/z$, thereby confirming previous work. The correlation part of the self-energy employed is that of the plasmon-pole approximation, and leads to the KS correlation potential $v_c(z)\sim-1/(4z)$. The quantum image potential derived therefore, differs from the commonly accepted classical form of $-1/(4z)$. The import of this result to both the theory of image states and the density-functional theory is also discussed.

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It is well known that in classical physics, the image potential has the form of $-1/(4z)$. In this paper, we derive analytically the quantum-mechanical image-potential structure in the asymptotic classically forbidden region of a metal surface. This structure is of importance in its own right and governs intrinsic metal surface properties such as the image-potential-bound surface states. These image states can be probed experimentally by scanning tunneling miscroscopy,[1] inverse[2,3] and two-photon photoemission,[4] from which there exists data on their binding energy and lifetime.[5] In the theoretical interpretations of such data, the classical image potential structure is usually assumed. We show that the corresponding quantum-mechanical image-potential coefficient is approximately twice as large, and depends explicitly on the Wigner-Seitz radius r_s of the metal.

The quantum image potential is also of importance in Kohn-Sham (KS) theory,[6] which is extensively employed in surface electronic structure calculations. The approximate exchange-correlation (xc) energy functionals commonly used, lead to an asymptotic decay for the potential that is exponential.[7] Thus, the result derived here constitutes a rigorous constraint on the construction of approximate xc energy functionals and potentials.[8,9]

From a quantum-mechanical point of view, the image potential arises from a combination of the external $v(z)$, static Hartree $v_H(z)$, and KS exchange-correlation $v_{xc}(z)$ potentials. In the classically forbidden region, $v(z)+v_H(z)$ decays expotentially, and it is $v_{xc}(z)$ that makes the contribution of $O(1/z)$. We derive $v_{xc}(z)$ at a charge neutral semi-infinite jellium metal surface to be $v_{xc}(z\to\infty)=-\alpha_{KS,xc}/z=-[\alpha_{KS,x}+1/4]/z$, where $\alpha_{KS,x}=[(\beta^2-1)/2\beta^2][1-\ln(\beta^2-1)/\pi(\beta^2-1)^{1/2}]$, $\beta=\sqrt{W/\epsilon_F}$, W is the barrier height, $\epsilon_F=k_F^2/2$ is the bulk Fermi energy, $k_F=1/(\alpha r_s)$ is the Fermi momentum, and $\alpha^{-1}=(9\pi/4)^{1/3}$. The structure is, therefore, different from the commonly accepted conclusion that $v_{xc}(z\to\infty)=-1/(4z)$. With the relationship between β and the Wigner-Seitz radius r_s determined through self-consistent calculations[7] within the local-density approximation (LDA) for the xc energy, we have for metallic densities ($2\leqslant r_s\leqslant 6$) that $0.445\leqslant\alpha_{KS,xc}\leqslant 0.524$. For $\beta=\sqrt{2}$, which corresponds to $r_s\approx 4.1$, for which the approximate r_s value of the jellium metal is stable, $\alpha_{KS,xc}=0.5$. The significance of this different result for both the density-functional theory and the theory of surface states is discussed following the derivation.

In his pioneering paper on the application of Hartree-Fock theory to the metal surface problem (with Coulomb correlations included parametrically), Bardeen[10] assumed the asymptotic structure of each orbital-dependent potential to be the image potential $-1/(4z)$. In the original Lang-Kohn[7] calculation within the LDA for the xc energy, the potential $v_{xc}(z)$ decays exponentially, consistent with the structure of the density. Subsequently these authors[11] introduced an external test charge and obtained its potential to be $-(1/4)/(z-z_0)$, where z_0 is the centroid of the induced charge. Almbladh and von Barth[12] state (without proof) that for macroscopic systems, the exchange potential $v_x(z)$ decays *exponentially*, and thus the asymptotic structure of $v_{xc}(z)$ is a Coulomb correlation or polarization effect. Then determining this polarization *classically*, they obtain the asymptotic structure of $v_{xc}(z)$ to be $-1/(4z)$. The calculation of Sham[13] is based on Rudnick's work[14] on the self-energy, in which approximations such as the use of the free particle Green's function for the inhomogeneous electron system and the infinite barrier model[10] for the metal surface, are employed. Thus, $v_{xc}(z)$ at large z is obtained as $-1/(4z)$ and attributed to Coulomb correlations, while the exchange potential decays as $v_x(z)\sim 1/z^2$ and does not contribute to the leading order.

Harbola and Sahni[15] were the first to show that $v_x(z)$ contributes to $v_{xc}(z)$ by calculating numerically the work done $W_x(z)$ in the field of the dynamic Fermi hole.[16] They next determined[17] $v_x(z)$ numerically for a high density metal via the integral equation of the optimized potential method (OPM), and showed its structure to be image-potential-like, a few Fermi wavelengths from the surface. In the jellium-slab metal, calculations of $v_{xc}(z)$ based on the *GW* approximation to the electron self-energy Σ_{xc}, Eguiluz *et al.*[18] numerically showed that $v_x(z)\sim-1/z^2$ and $v_c(z)\sim-1/(4z)$ asymptotically.

The claim that $v_x(z)$ contributes to the asymptotic structure of $v_{xc}(z)$ was confirmed by Solomatin and Sahni (SS),[19]

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who showed *analytically* via the OPM integral equation that $v_x(z\to\infty)=-\alpha_{KS,x}/z$. They also explained the work of Eguiluz *et al.* by showing *analytically* that for jellium-slab metal, $v_x(z)$ must decay as $-1/z^2$. SS, however, did not consider the asymptotic structure of $v_c(z)$ in their work.

In this paper, we obtain a unified picture of the asymptotic structure of $v_{xc}(z)$ by using exact expressions for $v_{xc}(\mathbf{r})$ in the classically forbidden region derived from the Dyson equation. Employing the most general form of the KS orbitals, whose asymptotic structure is derived from the KS equation, we show analytically that $v_x(z\to\infty)=-\alpha_{KS,x}/z$, confirming the work of SS. Within the same framework, we obtain the KS correlation potential $v_c(z\to\infty)=-1/(4z)$ in the plasmon-pole approximation.

The Dyson equation relating the Green's functions for the real and KS systems is

$$G(\mathbf{r}_1,\mathbf{r}_2;\omega)=G_s(\mathbf{r}_1,\mathbf{r}_2;\omega)+\int G_s(\mathbf{r}_1,\mathbf{r}';\omega)\tilde{\Sigma}(\mathbf{r}',\mathbf{r}'';\omega)\times G(\mathbf{r}'',\mathbf{r}_2;\omega)d\mathbf{r}'d\mathbf{r}'', \tag{1}$$

where $\tilde{\Sigma}(\mathbf{r},\mathbf{r}';\omega)=\Sigma_{xc}(\mathbf{r},\mathbf{r}';\omega)-\delta(\mathbf{r}-\mathbf{r}')v_{xc}(\mathbf{r})$ and $\Sigma_{xc}(\mathbf{r},\mathbf{r}';\omega)$ is the xc part of the self-energy. $G_s(\mathbf{r}_1,\mathbf{r}_2;\omega)$ satisfies the equation of motion, $[\omega-h_s(\mathbf{r}_1)]G_s(\mathbf{r}_1,\mathbf{r}_2;\omega)=\delta(\mathbf{r}_1-\mathbf{r}_2)$, where $h_s(\mathbf{r})=-\frac{1}{2}\nabla^2+v(\mathbf{r})+v_H(\mathbf{r})+v_{xc}(\mathbf{r})$. Operating by $D(\mathbf{r}_1,\mathbf{r}_2)\equiv h_s(\mathbf{r}_1)-h_s(\mathbf{r}_2)$ on Eq. (1) leads to

$$\begin{aligned}D(\mathbf{r}_1,\mathbf{r}_2)[G(\mathbf{r}_1,\mathbf{r}_2;\omega)-G_s(\mathbf{r}_1,\mathbf{r}_2;\omega)]&=-\int\tilde{\Sigma}(\mathbf{r}_1,\mathbf{r}';\omega)G(\mathbf{r}',\mathbf{r}_2;\omega)d\mathbf{r}'\\&\quad+\int G(\mathbf{r}_1,\mathbf{r}';\omega)\tilde{\Sigma}(\mathbf{r}',\mathbf{r}_2;\omega)d\mathbf{r}'.\end{aligned} \tag{2}$$

By carrying through the frequency integration, one obtains from Eq. (2),

$$\begin{aligned}D(\mathbf{r}_1,\mathbf{r}_2)[\gamma(\mathbf{r}_1,\mathbf{r}_2)-\gamma_s(\mathbf{r}_1,\mathbf{r}_2)]&=\frac{1}{\pi i}\int d\omega e^{i\omega\eta}\int[G(\mathbf{r}_1,\mathbf{r}';\omega)\Sigma_{xc}(\mathbf{r}',\mathbf{r}_2;\omega)\\&\quad-\Sigma_{xc}(\mathbf{r}_1,\mathbf{r}';\omega)G(\mathbf{r}',\mathbf{r}_2;\omega)]d\mathbf{r}'\\&\quad+[v_{xc}(\mathbf{r}_1)-v_{xc}(\mathbf{r}_2)]\gamma(\mathbf{r}_1,\mathbf{r}_2),\end{aligned} \tag{3}$$

where $\gamma(\mathbf{r}_1,\mathbf{r}_2)=(1/\pi i)\int_{-\infty}^{\infty}G(\mathbf{r}_1,\mathbf{r}_2;\omega)e^{i\omega\eta}d\omega$, with $\eta=0+$. A similar relation also holds between $\gamma_s(\mathbf{r}_1,\mathbf{r}_2)$ and $G_s(\mathbf{r}_1,\mathbf{r}_2;\omega)$ for the KS system. Since, to leading order, $\gamma(\mathbf{r}_1,\mathbf{r}_2)=\gamma_s(\mathbf{r}_1,\mathbf{r}_2)$ and $\gamma(\mathbf{r}_1,\mathbf{r}_2)-\gamma_s(\mathbf{r}_1,\mathbf{r}_2)\ll\gamma_s(\mathbf{r}_1,\mathbf{r}_2)$ in the classically forbidden region, one has

$$\begin{aligned}D(\mathbf{r}_1,\mathbf{r}_2)[\gamma(\mathbf{r}_1,\mathbf{r}_2)-\gamma_s(\mathbf{r}_1,\mathbf{r}_2)]\\\ll[v_{xc}(\mathbf{r}_1)-v_{xc}(\mathbf{r}_2)]\gamma_s(\mathbf{r}_1,\mathbf{r}_2).\end{aligned} \tag{4}$$

Thus, the term on the left side of Eq. (3) can be dropped. For the same reason, $G(\mathbf{r},\mathbf{r}';\omega)-G_s(\mathbf{r},\mathbf{r}';\omega)\ll G_s(\mathbf{r},\mathbf{r}';\omega)$ for $\mathbf{r}$ in the classically forbidden region. Therefore, one has

$$v_{xc}(\mathbf{r}_1)-v_{xc}(\mathbf{r}_2)=\frac{\Gamma_{xc}(\mathbf{r}_1,\mathbf{r}_2)}{\gamma_s(\mathbf{r}_1,\mathbf{r}_2)}, \tag{5}$$

where $\Gamma_{xc}(\mathbf{r}_1,\mathbf{r}_2)=\Gamma_x(\mathbf{r}_1,\mathbf{r}_2)+\Gamma_c(\mathbf{r}_1,\mathbf{r}_2)$ and $\Gamma_{x,c}(\mathbf{r}_1,\mathbf{r}_2)=\Gamma^{(2)}_{x,c}(\mathbf{r}_1,\mathbf{r}_2)-\Gamma^{(1)}_{x,c}(\mathbf{r}_1,\mathbf{r}_2)$, with

$$\Gamma^{(1)}_{x,c}(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\pi i}\int e^{i\omega\eta}d\omega\int G_s(\mathbf{r}_1,\mathbf{r}';\omega)\times\Sigma_{x,c}(\mathbf{r}',\mathbf{r}_2;\omega)d\mathbf{r}' \tag{6}$$

and

$$\Gamma^{(2)}_{x,c}(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\pi i}\int e^{i\omega\eta}d\omega\int\Sigma_{x,c}(\mathbf{r}_1,\mathbf{r}';\omega)\times G_s(\mathbf{r}',\mathbf{r}_2;\omega)d\mathbf{r}'. \tag{7}$$

Apparently, from Eq. (5), one also has

$$v_{x,c}(\mathbf{r}_1)-v_{x,c}(\mathbf{r}_2)=\frac{\Gamma_{x,c}(\mathbf{r}_1,\mathbf{r}_2)}{\gamma_s(\mathbf{r}_1,\mathbf{r}_2)}. \tag{8}$$

Equations (5) and (8) are, to the leading order, exact results in the classically forbidden region.

We first evaluate $v_x(z)$. The exchange part of the self-energy, $\Sigma_x(\mathbf{r}_1,\mathbf{r}_2,\omega)=-\gamma_s(\mathbf{r}_2,\mathbf{r}_1)/2|\mathbf{r}_1-\mathbf{r}_2|$, can be expressed in terms of KS orbitals via the relation $\gamma_s(\mathbf{r}_1,\mathbf{r}_2)=2\Sigma_{l<\epsilon_F}\phi_l^*(\mathbf{r}_1)\phi_l(\mathbf{r}_2)$. Substituting $\Sigma_x(\mathbf{r}_1,\mathbf{r}_2,\omega)$ into Eq. (6) yields

$$\Gamma^{(1)}_x(\mathbf{r}_1,\mathbf{r}_2)=-2\int\sum_{i,l<\epsilon_F}\frac{1}{|\mathbf{r}_2-\mathbf{r}'|}\times\phi_i(\mathbf{r}_1)\phi_i^*(\mathbf{r}')\phi_l^*(\mathbf{r}_2)\phi_l(\mathbf{r}')d\mathbf{r}'. \tag{9}$$

For both jellium[10] and structureless pseudopotential[20] models of a metal surface, there is translational symmetry in the plane parallel to the surface. Therefore, the KS orbitals are of the form $\phi_{\mathbf{k}}(\mathbf{r})=\sqrt{2/V}e^{i\mathbf{k}_\parallel\cdot\mathbf{x}_\parallel}\phi_k(z)$, where $(\mathbf{k}_\parallel,\mathbf{x}_\parallel)$ are the momentum and position vectors parallel to the surface, and (k,z) are the components perpendicular to it. Employing the KS orbitals in Eq. (9), one obtains

$$\begin{aligned}\Gamma^{(1)}_x(\mathbf{r}_1,\mathbf{r}_2)=&-\frac{1}{4\pi^5}\int_0^{k_F}dk\int_0^{k_F}dk'\,\phi_k(z_1)\phi^*_{k'}(z_2)\\&\times\int_0^{\sqrt{k_F^2-k^2}}d\mathbf{k}_\parallel\int_0^{\sqrt{k_F^2-k'^2}}d\mathbf{k}'_\parallel e^{i\mathbf{k}_\parallel\cdot(\mathbf{x}_{1\parallel}-\mathbf{x}_{2\parallel})}\\&\times\int dz'\,\phi_k(z')^*\phi_{k'}(z')\frac{e^{-q|z_2-z'|}}{q},\end{aligned} \tag{10}$$

where $\mathbf{q}=\mathbf{k}_\parallel-\mathbf{k}'_\parallel$. It is well known[12,15,19] that only $k,k'\sim k_F$ region in the above integral contributes to $\Gamma^{(1)}_x(\mathbf{r}_1,\mathbf{r}_2)$ at large z_1, z_2. Therefore, we can put $\mathbf{x}_{1\parallel}=\mathbf{x}_{2\parallel}$ in Eq. (10) and rewrite it as

$$\Gamma_x^{(1)}(z_1,z_2)=-\frac{1}{4\pi^4}\int_0^{k_F}dk\int_0^{k_F}dk' \times\phi_k(z_1)\phi_{k'}^*(z_2)G(k,k',z_2), \tag{11}$$

where

$$G(k,k',z_2)=2\int dz'\,\phi_k^*(z')\phi_{k'}(z')\int dq e^{-q|z_2-z'|}F(q), \tag{12}$$

with $F(q)=\int d\mathbf{K}\,\theta(\lambda-|\mathbf{K}+\mathbf{q}/2|)\,\theta(\lambda'-|\mathbf{K}-\mathbf{q}/2|)$, $\lambda=\sqrt{k_F^2-k^2}$, $\lambda'=\sqrt{k_F^2-k'^2}$, and $\mathbf{K}=(\mathbf{k}_\parallel+\mathbf{k}_\parallel')/2$. The function $G(k,k',z_2)$ at large z_2 was calculated by SS (Ref. 19) and it was shown that the contribution to $G(k,k',z_2)$ at large z_2 arises only from the deep bulk region of the metal. We now confirm their result by using the most general form of the one-particle orbital at the metal surface,

$$\phi_k(z)=\sin[kz+\delta(k)]\theta(-z-d_1)+f_k(z)[\theta(z+d_1) -\theta(z-d_2)]+D_k z^{\alpha_{KS,xc}/\kappa}e^{-\kappa z}\theta(z-d_2), \tag{13}$$

where $\kappa=\sqrt{2W-k^2}$ and $f_k(z)$ is some finite function of z, whose explicit form is not assumed. In Eq. (13), the orbital is expressed in three regions: bulk region $z\leqslant -d_1$, surface region $-d_1\leqslant z\leqslant d_2$, and asymptotic region $z\geqslant d_2$, with $d_1,d_2\gg 1/k_F$. To derive the asymptotic term of Eq. (13), we have used $v_{xc}(z\to\infty)=-\alpha_{KS,xc}/z$, with the coefficient $\alpha_{KS,xc}$ to be determined. [It is commonly accepted that the asymptotic decay of $v_{xc}(z)$ is $O(1/z)$]. The phase factor $\delta(k)$ and the coefficient D_k are determined by continuity of the wave function at $z=-d_1$ and $z=d_2$. Substitution of Eq. (13) into Eq. (11) leads to

$$\Gamma_x^{(1)}(z_1,z_2)=-\frac{1}{z_2}\alpha_{KS,x}\gamma_s(z_1,z_2), \tag{14}$$

where $\alpha_{KS,x}$ is defined previously and $\gamma_s(z_1,z_2)\equiv\gamma_s(z_1,z_2;\mathbf{x}_{1\parallel}=\mathbf{x}_{2\parallel})$. Similarly, $\Gamma_x^{(2)}(z_1,z_2)=-(1/z_1)\alpha_{KS,x}\gamma_s(z_1,z_2)$. Substituting for $\Gamma_x^{(1)}(z_1,z_2)$ and $\Gamma_x^{(2)}(z_1,z_2)$ into Eq. (8), one obtains

$$v_x(z_1)-v_x(z_2)=-\alpha_{KS,x}\left[\frac{1}{z_1}-\frac{1}{z_2}\right]. \tag{15}$$

The fact that z_1 and z_2 are independent yields the final result that $v_x(z)=-\alpha_{KS,x}/z$. This confirms in an independent manner, the results of SS.

Next, we calculate $v_c(z)$. We make use of the plasmon-pole approximation for the correlation part of the self-energy. It is based on the assumption that the response of the electron system at a metal surface can be described by a frequency-dependent dielectric constant, which has a zero point at ω_s, where ω_s is the surface plasmon frequency. The self-energy under this assumption is $\Sigma_c(\mathbf{r},\mathbf{r}';\omega)=(\omega_s/2|\mathbf{r}-\mathbf{r}_i|)G(\mathbf{r},\mathbf{r}';\omega-\omega_s)$, where $\mathbf{x}_{i\parallel}'=\mathbf{x}_\parallel'$ and $z_i'=-z'$. Substituting $\Sigma_c(\mathbf{r},\mathbf{r}';\omega)$ into Eq. (6), one obtains

$$\Gamma_c^{(1)}(\mathbf{r}_1,\mathbf{r}_2)=\omega_s\left[\sum_{l<k_F}\sum_j-\sum_l\sum_{j<k_F}\right] \times\int d\mathbf{r}'\,\phi_l(\mathbf{r}_1)\phi_l^*(\mathbf{r}')\phi_j^*(\mathbf{r}_2)\phi_j(\mathbf{r}') \times\frac{1}{-\omega_s+\epsilon_l-\epsilon_j}\,\frac{1}{|\mathbf{r}'-\mathbf{r}_{2i}|}. \tag{16}$$

Operating by $D(\mathbf{r}_1,\mathbf{r}_2)$ on Eq. (16) leads to

$$D(\mathbf{r}_1,\mathbf{r}_2)\Gamma_c^{(1)}(\mathbf{r}_1,\mathbf{r}_2) =\omega_s\left[\sum_{l<k_F}\sum_j-\sum_l\sum_{j<k_F}\right] \times\int d\mathbf{r}'\,\phi_l(\mathbf{r}_1)\phi_l^*(\mathbf{r}')\phi_j^*(\mathbf{r}_2)\phi_j(\mathbf{r}') \times\frac{1}{|\mathbf{r}'-\mathbf{r}_{2i}|}+\omega_s\Gamma_c^{(1)}(\mathbf{r}_1,\mathbf{r}_2) +\left[\text{higher order terms with factor }\nabla_1\frac{1}{|\mathbf{r}_1-\mathbf{r}_i'|}\right]. \tag{17}$$

Again the term on the left side of the above equation can be dropped, since $D(\mathbf{r}_1,\mathbf{r}_2)\Gamma_c^{(1)}(\mathbf{r}_1,\mathbf{r}_2)\ll\omega_s\Gamma_c^{(1)}(\mathbf{r}_1,\mathbf{r}_2)$. Therefore,

$$\Gamma_c^{(1)}(\mathbf{r}_1,\mathbf{r}_2)=\left[\sum_{j<k_F}\sum_l-\sum_j\sum_{l<k_F}\right] \times\int d\mathbf{r}'\,\phi_l(\mathbf{r}_1)\phi_l^*(\mathbf{r}')\phi_j^*(\mathbf{r}_2)\phi_j(\mathbf{r}')\frac{1}{|\mathbf{r}'-\mathbf{r}_{2i}|}. \tag{18}$$

By using the closure relation $\Sigma_j\phi_j^*(\mathbf{r}_2)\phi_j(\mathbf{r}')=\delta(\mathbf{r}_2-\mathbf{r}')$, we have

$$\Gamma_c^{(1)}(\mathbf{r}_1,\mathbf{r}_2)=\left[\frac{1}{|\mathbf{r}_1-\mathbf{r}_{2i}|}-\frac{1}{|\mathbf{r}_2-\mathbf{r}_{2i}|}\right]\sum_{j<k_F}\phi_j(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2), \tag{19}$$

which yields

$$\Gamma_c^{(1)}(z_1,z_2)=\frac{1}{2}\left[\frac{1}{z_1+z_2}-\frac{1}{2z_2}\right]\gamma_s(z_1,z_2). \tag{20}$$

Similarly, one obtains

$$\Gamma_c^{(2)}(z_1,z_2)=\frac{1}{2}\left[\frac{1}{z_1+z_2}-\frac{1}{2z_1}\right]\gamma_s(z_1,z_2).$$

We note that no approximation for the one-particle orbital has been made in obtaining these results. Substituting $\Gamma_c^{(1)}(z_1,z_2)$ and $\Gamma_c^{(2)}(z_1,z_2)$ into Eq. (8) then leads to

$$v_c(z_1)-v_c(z_2)=-\frac{1}{4z_1}+\frac{1}{4z_2}, \tag{21}$$

which also means $v_c(z) = -1/4z$. Thus, the final result for the asymptotic structure is $v_{xc}(z) = -\alpha_{KS,xc}/z$, with $\alpha_{KS,xc} = [(\beta^2-1)/2\beta^2][1-\ln(\beta^2-1)/\pi(\beta^2-1)^{1/2}]+1/4$.

The result derived has implications for the construction and interpretation of the approximate xc energy functionals. For example, the nonlocal weighted density approximation[8] (WDA) is known to give an asymptotic structure of $-1/(2z)$, and this has been considered a shortcoming of the approximation. A consequence of modifying[21,22] the WDA so that it gives a $-1/(4z)$ asymptotic structure then leads to unphysical results for the position of the image plane[23] and unreasonable surface energies.[24] Our result explains this discrepancy and shows that the original WDA does yield the essentially exact asymptotic structure at a metal surface. However, as derived, the decay coefficient $\alpha_{KS,xc}(\beta)$ is not constant but depends upon r_s. This then poses a stringent condition on approximate functionals.

The quantum image potential in the classically forbidden region corresponds to an electron that belongs to charge-neutral *N*-electron metal system. For probes that involve external test charges such as ions or positrons, one obtains the classical $-1/(4z)$ image potential as there are no correlations due to the Pauli exclusion principle between these charges and the electrons. However, the quantum image potential is critical to the interpretation of data on image states measured by experiments such as two-photon photoemission[25] and inverse photoemission.[2] The analysis of the existing data on image states to incorporate the result derived is beyond the scope of the present paper and is not considered here. However, the following remarks indicate how the long-range $-Z/z$ structure of the image potential affects the Rydberg states. The basic expression for the energy spectrum is of the general form[5,26,27]

$$E = V_0 + \frac{1}{2}\left(|\mathbf{k}_\parallel|^2 - \frac{Z^2}{\zeta^2}\right), \tag{22}$$

with V_0 the vacuum level, $\zeta = n + \delta_n$, where $n = 1,2,3,\ldots$, and δ_n represents the quantum defect. It is this expression that is usually employed for comparison with experiments. Our new understanding of $Z = \alpha_{KS,xc}(\beta)$ instead of $Z = 1/4$, therefore, modifies the above result. In addition to the coefficient *Z* being different, the Rydberg series is now a function of $r_s: E = E(\beta)$. The localization property as given by the relative probability function $P(z) = |\phi_k(z)|^2/|\phi_k(0)|^2$, where $z = 0$ corresponds to the crystal surface, would also be different for each metal and image state.

In conclusion, we have derived the structure of the quantum-mechanical image potential analytically. This structure depends explicitly on the parameters defining the metal and is different from the commonly accepted classical form of $-1/(4z)$. We have also discussed the consequent implications of this result on both the theory of image states and density-functional theory.

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