

## An energy functional for surfaces

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We propose a simple way of correcting general gradient and local density approximation surface energies for errors of these approximations intrinsic to surfaces by the appropriate use of reference systems with an exponential surface potential  $v_{\text{eff}}(z) \propto e^{z/a}$ . A test of this approach applied to general gradient and local density approximation surface exchange energies for half jellium systems removes most of the surface-intrinsic errors and yields excellent results. We suggest that the same procedure would also be successful for surface correlation effects. We conclude with some general remarks about future directions of density functional theory. © 2001 American Institute of Physics. [DOI: 10.1063/1.1396649]

In previous publications<sup>1,2</sup> we have pointed out that *a priori* approximations for the exchange correlation energies of density functional theory (DFT),<sup>3</sup> such as the local density approximation (LDA) and various generalized gradient approximations (GGA) cannot be expected to accurately describe electronic surfaces or edges, where the Kohn–Sham wave functions undergo a transition from propagating to evanescent character. The reason is that these approximations have been developed for bulk systems in which there is no evanescence.

As the simplest, parameter-free model we had introduced the Airy gas. However, in applying this model to realistic metal surfaces we found it too simplified. In the present paper we present a new one-parameter model, the exponential model (EM) (similar to, but smoother than, the linear potential model of Ref. 4) in which the Kohn–Sham effective potential is described by a simple exponential in  $z$  (Fig. 1):

$$v_{\text{eff}}(z) = \mu e^{z/a}; \quad \mu = \frac{\hbar^2}{2m} \left( \frac{\gamma}{r_s} \right)^2. \quad (1)$$

Here,  $a$  is the decay length of the exponential,  $\mu$  is the chemical potential, related to the Wigner–Seitz radius  $r_s$ , and  $\gamma \equiv (9\pi/4)^{1/3} = 1.92$ . The dimensionless parameter of this family of potentials is  $\tilde{a} \equiv a/r_s$ . [This potential has two interesting limits: For  $\tilde{a} \rightarrow 0$  ( $\tilde{a} \rightarrow \infty$ ) the surface region approaches that of the hard wall and the Airy gas, respectively.] In this paper we show that the surface-specific corrections to the LDA and GGA exchange energies of the EM are, with appropriate scaling, very accurately transferable to surfaces with other  $v_{\text{eff}}(z)$ .

The solutions of the Schrödinger equation with an exponential potential are known in analytical form. The density

profiles  $\tilde{n}(\tilde{z}) = n(z)/\bar{n}$  [where  $\bar{n} = 3(4\pi r_s^3)^{-1}$  is the electron density in the interior], are given by:

$$\tilde{n}(\tilde{z}) = 3 \int_0^1 dk \left( \frac{2\gamma\tilde{a}k \sinh(2\gamma\tilde{a}\pi k)}{\pi} \right) \times (K_{i2\gamma\tilde{a}k}(2\gamma\tilde{a}e^{\tilde{z}/2\tilde{a}}))^2 (1-k^2), \quad (2)$$

where  $K_\nu(x)$  is a modified Bessel function and  $\tilde{z} = z/r_s$ . They are plotted in Fig. 2.

The first DF calculation of surface energies,<sup>5</sup> using the simplest approximation for bulk systems, the LDA, somewhat surprisingly gave fairly good results. The *ex post facto* explanation was that a very substantial part of the surface exchange- or exchange-correlation-energy comes from inhomogeneous surface regions where, as in the bulk, the Kohn–Sham wave functions are propagating. Therefore, it is also not surprising that bulk-GGAs substantially improved the results for the surface exchange energy.<sup>6</sup> There remains, however, a surface-intrinsic error related to evanescence, whose removal is addressed in the present paper.

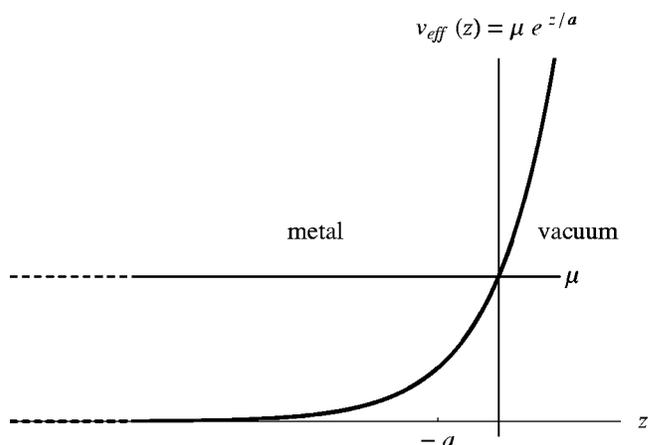


FIG. 1. The exponential surface potential.

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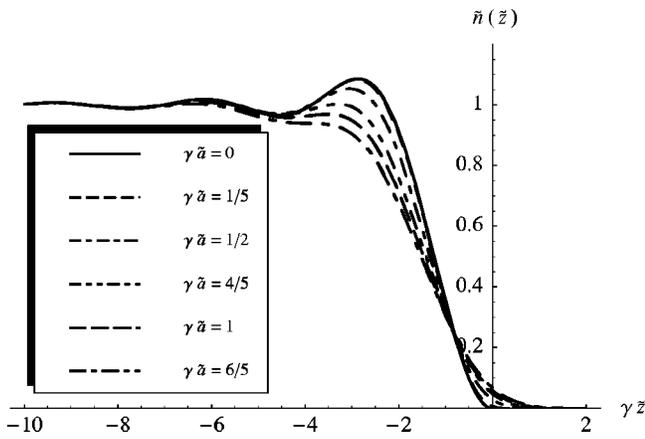


FIG. 2. The exponential surface density profile for  $\gamma\tilde{a}=0, 1/5, 1/2, 4/5, 1,$  and  $6/5$  as a function of  $\tilde{z}$ . Note that the densities for  $\gamma\tilde{a}=0$  and  $1/5$  are almost indistinguishable.

The surface exchange energy is given by

$$\sigma_x = \int_{-\infty}^{\infty} dz n(z) \{ \epsilon_x([n]; z) - \epsilon_x^h(\bar{n}) \} \quad (3)$$

$$= \frac{e^2}{2} \frac{3\bar{n}}{2\pi} \tilde{\sigma}_x, \quad (4)$$

where  $\epsilon_x^h(\bar{n}) = -e^2/2(3\gamma(2\pi r_s)^{-1})$  is the exchange energy density of a homogeneous electron gas with particle density  $\bar{n}$ , and  $\epsilon_x([n]; z)$  is the exchange energy density of the surface in question; and where  $\tilde{\sigma}_x$  is a dimensionless quantity characterizing the surface exchange energy.

We have calculated  $\tilde{\sigma}_x$  for the exponential surface model exactly, as well as within the LDA and the PBE version of GGA<sup>7</sup> for six values of the dimensionless parameter,  $\tilde{a}$ , and tabulated the results in Table I.

Our procedure for calculating the surface exchange energy,  $\sigma_x$ , for a surface system with given  $r_s$  and surface density profile  $n(z)$  is as follows:

- (i) Calculate an approximate surface energy  $\sigma'_x$ , using the LDA or better, a successful GGA.
- (ii) From the density profiles of the exponential surface model, after appropriate rescaling, select the one by least square fitting, which most closely agrees with the given profile.
- (iii) Approximate the remaining surface specific correction,  $\Delta\sigma'_x$ , of the given density profile and given ap-

TABLE I. Calculated dimensionless surface exchange energies,  $\tilde{\sigma}_x$ , for exponential surface systems with various density profiles characterized by  $\gamma\tilde{a}$  ( $\gamma=1.92$ ), (cf., Fig. 2).

$\gamma\tilde{a}$	$\tilde{\sigma}_{x,em}^{exact}$	$\tilde{\sigma}_{x,em}^{PBE}$	$\tilde{\sigma}_{x,em}^{LDA}$
0	0.071 34	0.045 20	0.110 85
1/5	0.0763	0.0509	0.1172
1/2	0.1142	0.0929	0.1566
4/5	0.1715	0.1533	0.2117
1	0.2131	0.1964	0.2514
6/5	0.2557	0.2404	0.2922

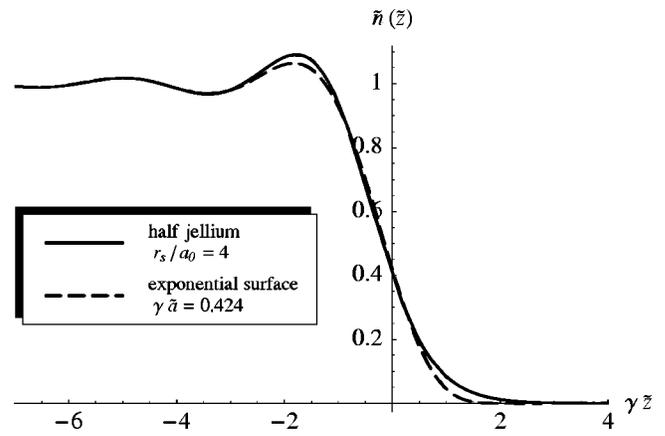


FIG. 3. Fitting of a jellium surface density to an exponential surface density.

proximation (LDA or GGA) with the surface specific correction of the corresponding exponential surface model,  $\Delta\sigma'_{x,em} = \sigma_{x,em}^{exact} - \sigma'_{x,em}$ , i.e.,

$$\sigma_x = \sigma'_x + \Delta\sigma'_{x,em}. \quad (5)$$

We exemplify this procedure for the widely used half jellium model of the surface. Reference 6 provides exact, LDA and PBE values for the exchange energies for different values of  $r_s$ . The authors have also kindly provided us with the corresponding LDA density profiles. Figure 3 shows the density profile for the jellium model for  $r_s/a_0=4$  ( $a_0$  is the Bohr radius) and the best fitting exponential profile ( $\tilde{a}=0.424$ ). Table II compares the exact surface specific corrections of the half jellium model with those calculated from the best fitting exponential potentials. We consider the agreement as very good. Table III refers to the half jellium model and lists exact as well as LDA and GGA surface exchange energies (calculated from the LDA orbitals and densities of Ref. 6), both uncorrected and corrected for surface-intrinsic errors. It is seen that transfers of the surface-intrinsic corrections from the EM to the half jellium model remove almost all the errors from the uncorrected LDA and GGA calculations.

The percentage contribution of the surface-intrinsic energy is an increasing function of  $r_s$  and vanishes in the high density limit,  $r_s=0$ . This is consistent with the numerical examples given in this paper.

Our inclusion of the surface-intrinsic exchange energy has not been self-consistent. However, because of the sta-

TABLE II. Surface-intrinsic corrections to the surface exchange energy for jellium surfaces and for corresponding exponential surfaces, calculated with the LDA and the PBE version of GGA, in units of erg/cm<sup>2</sup>.

$r_s/a_0$	2.00	4.00	6.00
$\Delta\sigma_x^{LDA}$	-413	-65	-21
$\Delta\sigma_{x,em}^{LDA}$	-428	-59	-17
$\Delta\sigma_x^{PBE}$	186	29	10
$\Delta\sigma_{x,em}^{PBE}$	188	31	11

TABLE III. Results for the surface exchange energy of the half jellium system using LDA and PBE, without and with our surface-intrinsic corrections, compared to the exact results (Ref. 8), in units of erg/cm<sup>2</sup>.

$r_s/a_0$	2.00	4.00	6.00
$\sigma_x^{exact}$ (Refs. 6, 8)	2624	157	22
$\sigma_x^{LDA}$ (Ref. 6)	3037	222	43
$\sigma_x^{LDA,corr}$	2609	163	26
$\sigma_x^{PBE}$ (Ref. 6)	2438	128	12
$\sigma_x^{PBE,corr}$	2626	159	23

tionary character of the ground state energy with respect to small density changes we expect that the errors due to non-self-consistency will be extremely small.

We fully expect that our approach, here applied to surface *exchange* energies, applies equally well to surface *correlation* energies, which are typically about one order of magnitude smaller. This would require calculations, e.g., by Monte Carlo methods, of the exact exchange-correlation energies for the series of reference exponential surface systems. We hope that others, more qualified than we, will undertake these.

A remark about the absence of Coulomb tails from our exponential model. For some purposes the tails are very important, e.g., extended excited states of atoms. However, the demonstrated transferability of surface-specific corrections from the EM model to the half jellium model with *radically* different tail behaviors shows that the tail regions, because of the small number of electrons involved and their low density, contribute little to the exchange energy.

This work suggests the following thoughts about future directions of DFT (not including hybrid methods). We see two complimentary ways. One is to continue further with developments of more accurate, local or quasi-local and *uni-*

*versal* approximations, such as the LDA, GGAs, and weighted density approximations, all of which presume an adequate local resemblance to a uniform electron gas. The other is to (a) develop *specific*, non-universal results by some other means (e.g., analytic or Monte Carlo calculations) for the density and energy density for a *portion* of a system in which the universal methods fail in principle (such as the surface region of metals, discussed in this paper) and then (b) repeat, by changing parameters for the entire class of essentially similar systems, such as the  $\tilde{a}$  of the present paper. Finally, (c) relying on the “nearsighted-principle”<sup>9</sup> splice this “bad” portion to the “good” part of the system, for which local or quasi-local methods are sufficiently accurate. Other examples of systems where this approach could be useful are the electron-overlap regions of hydrogen-, ionically or Van der Waals-bonded systems, and internal “surfaces” in vacancy systems<sup>10</sup> and in loosely packed crystal structures.

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