Correlated-basis-functions theory of metal surfaces. Preliminary results

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We report here a variational method for calculating surface energies and electronic density profiles using correlated wave functions. Preliminary results are given for the whole range of densities corresponding to simple metals. Our method provides an alternative to the density-functional method. In addition, it furnishes a basis for obtaining many-body wave functions for metal surfaces.

The density-functional formalism (DFF) has dominated metal surface calculations that include many-body effects for more than a decade. Starting with the original work of Lang and Kohn,[1] discussions have centered about the importance of correlation effects, the accuracy of the local-density approximation (LDA), and the validity of using first-order perturbation theory to calculate lattice corrections. Improvements have been made in at least four directions: gradient expansion for the exchange-correlation energy functional,[2] wave-vector corrections on LDA,[3] inclusion of the ion lattice by means of pseudopotentials in the Hamiltonian (but not in the single-particle equation) for a variational calculation,[4] and three-dimensional band calculations that account for exchange and correlation only in low orders.[5]

We would like to present an alternative to DFF, using the formalism of correlated basis functions (CBF).[6] One purpose is to develop a method that treats correlations in the bulk and in the surface region using the same scheme. Another is to provide many-body wave functions for metal surfaces that are needed, e.g., for the evaluation of matrix elements that couple adsorbed atoms and molecules to surface excitations. Previously, we have developed CBF for electron liquids without using cluster expansions,[7] and have applied the method to systems with relatively small density variations, such as metallic hydrogen.[8] We have also calculated leading terms for the metal surface problem using the simplest variational wave functions.[9]

In this paper we describe a full CBF calculation of metal surface energies and electronic density profiles. We first consider the electrons to be moving in a uniform positive charge background occupying the space $Z < Z_G$, Z_G being the Gibbs surface for the electrons. The Hamiltonian has the form

$$\mathcal{K} = \sum_{\substack{i \\ \text{electrons}}} \frac{p_i^2}{2m} + V_{\text{electron-electron}} + V_{\text{electron-ion}} + V_{\text{ion-ion}} .$$

Central to our method is the construction of a correlated wave function:

$$\Psi(1, 2, \ldots, N) = F(1, 2, \ldots, N)D[\varphi] ,$$

where

$$F(1, 2, \ldots, N) = \sum_{i < j} \exp[\tfrac{1}{2} u(r_{ij})]$$

is a multiparticle correlation factor taken from a previous bulk electron liquid calculation.[7] The function $u(r)$ has the form $u(r) = -(a/r)(1 - e^{-br})$, where $a = 2e^2/\hbar\omega_p$ with $\omega_p^2 = 4\pi ne^2/m$, and b denotes a parameter determined variationally for every r_s. $D[\varphi]$ is a determinant of single-particle orbitals $\{\varphi_j(\vec{r})\}$ for an electron moving in a suitable model potential $V(\vec{r})$; thus

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \right]\varphi_j(\vec{r}) = \epsilon_j \varphi_j(\vec{r}) . \qquad (1)$$

Since F is a known function, Ψ is totally determined by the choice of $V(\vec{r})$. Formally, the variational problem reduces to minimizing $E = \langle \Psi | \mathcal{K} | \Psi \rangle / \langle \Psi | \Psi \rangle$ with respect to $V(\vec{r})$. For this calculation, we choose a two-parameter potential that resembles the potential an electron might experience in a semi-infinite metal:

$$V(\vec{r}) \equiv V(z) = \begin{cases} -S\dfrac{\hbar^2 k_F^2}{2m} & \text{for } z < z_0 \equiv \dfrac{\alpha}{2Sa_0 k_F^2} \\[2mm] -\dfrac{\alpha e^2}{4z} & \text{for } z \geq z_0 , \end{cases} \qquad (2)$$

where S and α are variational parameters. It should be noted, however, that $V(\vec{r})$ bears no resemblance to the effective self-consistent field in DFF. It is a variational function. Using the form of Ψ given earlier we can write the energy as follows:

$$E = T + T' + V_c + V_{es} , \qquad (3)$$

$$T = \sum_i \epsilon_i - \int p(\vec{r})V(\vec{r})d\vec{r} , \qquad (4)$$

$$T' = \frac{\hbar^2}{8m} \left[\int p(\vec{r}_1, \vec{r}_2)[\nabla_1 u(r_{12})]^2 d\vec{r}_1 d\vec{r}_2 + \int p(\vec{r}_1, \vec{r}_2, \vec{r}_3)[\vec{\nabla}_1 u(r_{12}) \cdot \vec{\nabla} u(r_{13})] d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \right] , \quad (5)$$

$$V_c = \frac{e^2}{2} \int \frac{p(\vec{r}_1, \vec{r}_2) - p(\vec{r}_1)p(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 , \quad (6)$$

$$V_{es} = \frac{e^2}{2} \int \frac{[p(\vec{r}_1) - \rho_+(\vec{r}_1)][p(\vec{r}_2) - \rho_+(\vec{r}_2)]}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 . \quad (7)$$

In the above equations, $p(\vec{r}_1, \ldots, \vec{r}_n)$ is the n-particle distribution function. Exchange and correlation are seen to contribute to the energy through the terms T' and V_c, and also by their effects on the shape of the profile. We make simplifying approximations (explained below) on $p(\vec{r}_1, \vec{r}_2)$ and $p(\vec{r}_1, \vec{r}_2, \vec{r}_3)$. E can be evaluated once the single-particle distribution function, or density profile $p(z)$, is available. To calculate the surface energy, we subtract the energy for the bulk metal from that of the semi-infinite system.

We now state how $p(z)$ is obtained for a given $V(z)$. First, we define

$$\Psi(\lambda) \equiv \left[\sum_{i<j} \exp\left[\frac{\lambda}{2} u(r_{ij}) \right] \right] D[\varphi] , \quad (8)$$

and denote the corresponding generalized density profile by $p(z|\lambda)$. For a system of independent particles, $\lambda = 0$, $\Psi = D[\varphi]$, and thus $p(z|0) = \sum_j |\varphi_j|^2$. So the "uncorrelated" density profile can be easily calculated after we solve Eq. (1) for $\{\varphi_j(\vec{r})\}$. For a system of fully interacting particles, $\lambda = 1$, and $p(z|1) = p(z)$, the desired density profile. $p(z|\lambda)$ is related to $p(z|0)$ through the equation[8,9]

$$\ln p(z_1|\lambda) = \ln p(z_1|0) + \int_0^\lambda d\lambda' \int d\vec{r}_2 p(z_2|\lambda') u(r_{12}) g(1,2|\lambda')$$

$$+ \frac{1}{2} \int_0^\lambda d\lambda' \int d\vec{r}_2 \int d\vec{r}_3 p(z_2|\lambda') p(z_3|\lambda') u(r_{23})[g(1,2,3|\lambda') - g(2,3|\lambda')] , \quad (9)$$

where

$$g(1,2|\lambda) \equiv p(\vec{r}_1, \vec{r}_2|\lambda)/p(z_1|\lambda)p(z_2|\lambda)$$

and

$$g(1,2,3|\lambda) \equiv p(\vec{r}_1, \vec{r}_2, \vec{r}_3|\lambda)/p(z_1|\lambda)p(z_2|\lambda)p(z_3|\lambda)$$

denote generalized pair and triplet correlation functions. Under the convolution approximation,

$$g(1,2,3|\lambda) - g(2,3|\lambda) \approx h_{12} + h_{13} + h_{12}h_{13} + h_{12}h_{23} + h_{13}h_{23} + \int p(z_4|\lambda)h_{14}h_{24}h_{34} d\vec{r}_4 ,$$

where $h_{12} \equiv g(1,2|\lambda) - 1$ satisfies the normalization condition $\int d\vec{r}_1 p(z_1|\lambda)h_{12} = -1$. We further make the approximation

$$g(1,2|\lambda) \approx g_{bulk}(r_{12}|\lambda) \approx g_{bulk}(r_{12})$$

and take it from Ref. 7. These same approximations are used in simplifying the energy terms. Some of the resulting integrals in Eq. (9) are divergent, but we have proven that the divergences are spurious, and can be removed by properly ordering the limits in which the three length scales: size of the system, distance between the cleaved surfaces, and the range of the Coulomb force, are taken to infinity. Details will be given in another publication.

We solve Eq. (9) iteratively, and use the result in the variational energy. For the ion lattice model, we choose our Hamiltonian as containing pseudopotentials, and make corrections to the jellium calculation given above in much the same manner as Lang and Kohn.[1] The difference is that we do not carry out a first-order perturbation calculation. We vary the
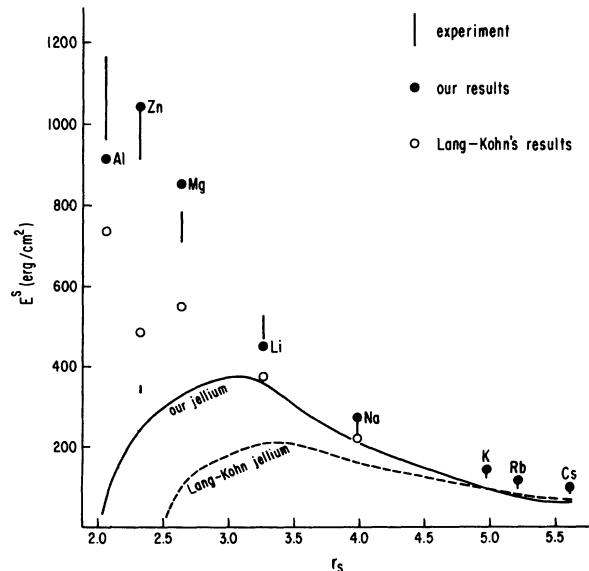

FIG. 1. Surface energy.

TABLE I. Surface energies of simple metals (in units of ergs/cm^2).

Metal	r_s	Face	S	α	Present work Jellium model	Ion lattice model	Experiment	DDF Lang-Kohn	DDF Monnier-Perdew
Al (fcc)	2.07	(111)	2.3	1.2	102	915	1143,[a] 1170,[b] 965[c]	730	795
Zn (hcp)	2.30	(0001)	3.5	1.4	278	1040	913,[a] 1040,[b] 350[d]	480	590
Pb (fcc)	2.30	(100)	3.5	1.4	277	624	690,[b] 593[a]	1140	456
		(111)			277	−270			
Mg (hcp)	2.66	(0001)	4.0	1.7	309	859	785,[a] 712[e]	546	619
Li (bcc)	3.28	(110)	4.4	1.8	363	445	522,[a] 470[e]	380	392
Na (bcc)	3.99	(110)	4.7	1.9	204	277	261,[a] 275,[b] 220[f]	230	247
K (bcc)	4.96	(110)	8.0	2.0	94	139	145,[a] 135,[b] 125[f]	140	148
Rb (bcc)	5.23	(110)	8.3	2.0	76	121	117,[a] 95[f]	120	117
Cs (bcc)	5.65	(110)	8.5	2.1	62	99	95,[a] 80[f]	102	93

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parameters S and α in evaluating the expectation value for the *full* Hamiltonian. It turns out that the energy minimum shifts very slightly, indicating that the first-order perturbation theory is valid at least from the point of view of a variational calculation using our rather restricted class of trial wave functions.

Table I and Fig. 1 give pertinent results for metals with r_s ranging from 2.07 (Al) to 5.65 (Cs). On account of the bulk approximation for $g(1,2|\lambda)$, these results should be regarded as preliminary. We are encouraged that they have the right order of magnitude. Ongoing work makes elaborate improvements

on $g(1,2|\lambda)$, and will be reported elsewhere.

Note added in proof. Calculations without using the bulk approximation for $g(1,2|\lambda)$ are now complete. Results are similar to those reported here except for small r_s, and will be published in detail elsewhere.

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