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Comparative LCAO-LAPW study of Cl chemisorption on the Ag(001) surface

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A comparison is made between the results of self-consistent linear-combination-of-atomic-orbitals and linear-augmented-plane-wave calculations for a clean three-layer Ag(001) slab and one with adsorbed Cl in $c(2\times2)$ simple-overlayer and mixed-layer geometries.

In a recent study, Greenside and Hamann[1] have applied a self-consistent Gaussian, linear-combination-of-atomic-orbitals (LCAO) technique to calculate the geometry dependence of the electronic structure for Cl chemisorption on the Ag(001) surface. More recently, one of us (D. R. H.) has completed the development of a self-consistent linear-augumented-plane-wave (LAPW) method[2] for application to bulk[3,4] and surface[5,6] electronic structure studies. It is of some interest to compare the results of these rather different LCAO and LAPW schemes in order to assess their overall accuracy and to establish the relative merits and limitations of the two techniques. A test of the electronic structure results is especially important for this system because the calculated spectrum for the adsorption geometry determined by low-energy-electron-diffraction (LEED) analysis[7] did not agree with ultraviolet-photoemission-spectroscopy (UPS) results.[8] On the other hand, an alternative geometry considered but rejected in the LEED analysis gave a spectrum in good agreement with the UPS data.[1]

For this purpose, we have repeated in part the previous LCAO calculations[1] for the clean Ag(001) surface as well as for the (LEED selected) simple-overlayer[7] and the mixed-layer Cl $c(2\times2)$ geometries using the surface LAPW (SLAPW) technique. In general, the results of the two calculations are in excellent overall agreement. Theoretical work functions are found to agree to within 0.2 – 0.4 eV. Equally impressive agreement is exhibited by total and projected density-of-states (DOS) curves as well as charge-density contours. As expected,[6] the SLAPW charge-density tails in the vacuum region exhibit a much smoother variation than the corresponding LCAO results, where indications of Gibbs oscillations are evident in the outer contours.

As it is applied here, the SLAPW approach utilizes a slab or thin-film geometry with space subdivided into muffin-tin, interstitial, and surface regions. The SLAPW wave function is expanded in terms of numerical radial, plane-wave, and Laue functions in the respective regions. The charge density and potential are expressed in a completely general functional form. They are expanded in lattice harmonics (numerical radial functions multiplied by appropriate linear combinations of spherical harmonics) within the muffin-tin spheres, plane waves in the interstitial region, and parallel plane waves multiplied by numerical normal functions in the surface region. In both calculations, exchange and correlation effects are treated in the local-density approximation using the Wigner interpolation formula.[9].

Both the SLAPW and LCAO calculations apply a frozen-core approximation in which atomic charge densities are used to represent the Ag ($\cdots 3d^{10}4s^{2}4p^{6}$) and Cl($1s^{2}2^{2}2p^{6}$) core states. The SLAPW conduction-band wave functions are expanded in terms of about 40 SLAPW's per atom, which is adequate for convergence in the 0.1-eV range. The SLAPW expansion within the muffin-tin spheres includes spherical harmonics with $l \leq 4$. The sphere radii $R(\mathrm{Ag}) \approx R(\mathrm{Cl}) \approx 1.38$ Å were chosen to produce nearly touching spheres.

Both calculations utilize a three-layer Ag(001) slab to model the semi-infinite solid. The lattice parameter for the slab is set equal to that for bulk Ag, where $a = 4.078$ Å. The bulk value for the interlayer spacing of (001) planes $a/2 = 2.039$ Å is used. In the case of the simple-overlayer model (SOM), the Cl adatoms are assumed to occupy every second fourfold hollow site at a distance 1.88 Å above the Ag surface layer. For the mixed-layer model (MLM), the remaining fourfold hollow sites are filled with Ag atoms.

In the previous LCAO calculations,[1] the Cl and Ag adatoms were situated at different heights (1.66 and 1.91 Å, respectively) above the surface layer for the MLM geometry. These positions gave the best fit to the LEED data that could be obtained for the mixed-layer model.[7] Having the Ag above the Cl in the mixed layer gave a work function decrease [relative to the clean Ag(001) surface] of 1.1 eV, which is easily understood in terms of a partially ionic Ag^+-Cl^- dipole. This is in disagreement with the experimentally observed work function increase of 0.8 eV.[10] To improve upon the MLM geometry, a coplanar Ag-Cl layer has been assumed in the present SLAPW calculations where the mixed layer is placed 1.88 Å above the surface layer, the same height as that for the SOM.

Self-consistent SLAPW calculations were carried out for the thin-film models for the clean Ag(001) surface, SOM, and MLM geometries. The primitive cells contain 3, 8, and 10 atoms, respectively. The charge density was calculated using three special points[11] in the surface Brillouin zone (SBZ), as in the LCAO calculation. Based on this limited sampling of the SBZ, it is expected that calculated work functions will be accurate to about 0.2 eV. Errors of comparable magnitude are expected to arise from the limited thickness of the thin films.

Values for the calculated and measured work functions are summarized in Table I. A comparable range of values is spanned by the experimental and calculated work functions for the clean Ag(001) surface. The SLAPW value for the present three-layer (001) slab is identical to that obtained for a seven-layer slab using the self-consistent-local-orbital method.[14] This work-function value of 4.2 eV is somewhat closer to the experimental range of values than that predicted in the LCAO calculation, which loses some accuracy in surface dipole determination from the charge fit.

Because of its position midway through the Periodic Table, relativistic effects are expected to affect the electronic structure of Ag. For example, Herman and Skillman[15] estimate, using perturbation theory, that the atomic 4*d* and 5*s* levels in Ag are lowered by about 0.5 eV as a result of the Darwin and mass-velocity relativistic effects. A scalar-relativistic procedure[16] for treating these relativistic effects has been incoporated in the SLAPW scheme, and the clean Ag surface results recalculated. A shown in Table I, this yields a slightly increased value for the work function.

The LCAO and SLAPW work-function values for the SOM geometry agree to within 0.2 eV, which is the estimated accuracy of the calculations. The SLAPW calculation gives essentially zero work-function change between the clean surface and the coplanar MLM. As anticipated,[1] this reduces the discrepancy between the calculated LCAO and observed values for the work function. By extrapolation, dropping the Ag half-layer 0.1 Å below the Cl in the MLM should give excellent agreement for the work function. Such a geometry is qualitatively consistent with the difference in ionic radii for Ag^+ and Cl^- (Ref. 1).

A comparison between the LCAO and SLAPW total charge densities for the clean three-layer Ag(001) slab is shown in Fig. 1. Charge-density

TABLE I. Comparison between experimental and theoretical values for the work function (eV).

		Ag(001)	SOM	MLM	Reference
Experiment		4.4	5.2	5.2	10
		4.64			12
		~4.2			13[d]
Theory					
	Local orbital	4.2			14
	LCAO	3.8	6.3	2.7[a]	1
	SLAPW	4.2	6.5	4.1[b]	Present work
	SLAPW(SR)[c]	4.5			Present work

[a] The Cl and Ag adatoms of the mixed layer are at distances of 1.66 and 1.91 Å above the surface, respectively.

[b] The Cl-Ag adlayer is coplanar and located 1.88 Å above the surface.

[c] Involves a scalar-relativistic (SR) treatment that includes Darwin and mass-velocity corrections but neglects spin-orbit coupling.

[d] Estimated by Smith *et al.* (Ref. 14) from photoemission data of Ref. 13.

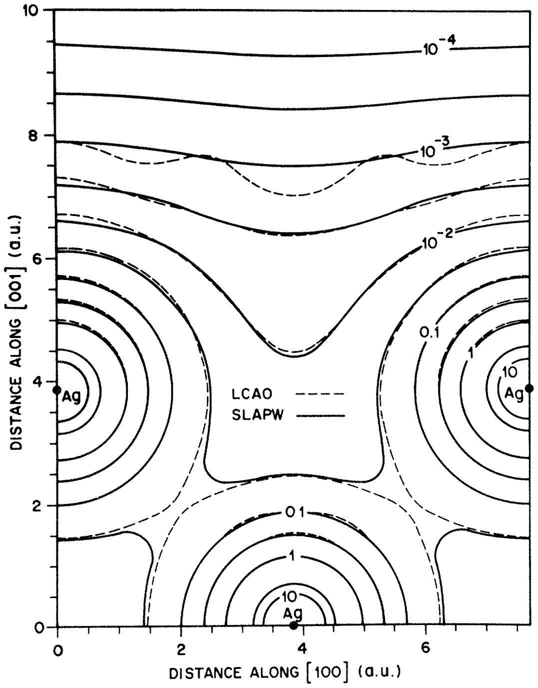

FIG. 1. LCAO and SLAPW total (core plus valence) charge-density contours for Ag in an (010) plane containing surface and central layer Ag atoms. The charge-density units are electrons/a.u.^{3} and adjacent contours differ by factors of $\sqrt{10}$.

contours are plotted here in an (010) plane containing surface- and central-layer Ag atoms. Within the slab, the LCAO and SLAPW charge-density contours are in excellent agreement. The differing connectivity of contours along the nearest-neighbor bond direction indicates a slight additional accumulation of bond charge for the SLAPW result.

More significant discrepancies are found in the vacuum region. As noted previously[1,17] the problem of treating the charge density accurately in this region is a formidable task in the LCAO scheme. The problem is due primarily to the second Gaussian basis introduced to least-squares fit the exact variational charge desnity given by the squares of the occupied wave functions. Even with a carefully chosen basis, one obtains moderate Gibbs-type oscillations in the outermost LCAO charge-density contours. It is a characteristic of a least-squares fit that absolute errors tend to be uniformly distributed. Absolute errors which are negligible in terms of the average charge density within the slab become pronounced relative errors in the exponential tail. By comparison, this surface region is accurately treated by the SLAPW method, where the Laue representation for the wave function is applied.

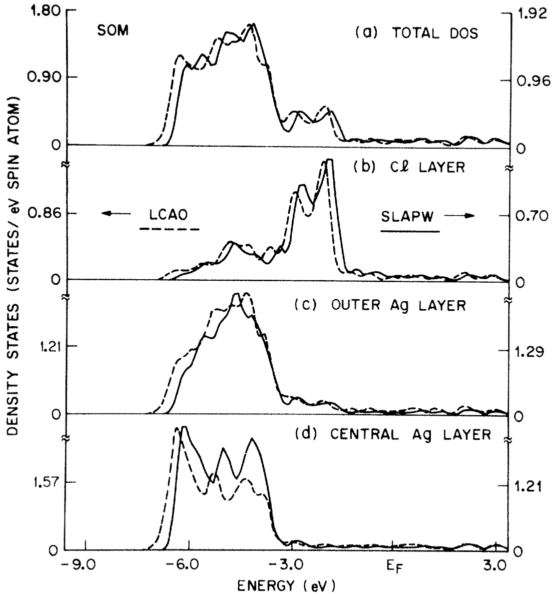

FIG. 2. LCAO and SLAPW total and projected DOS curves for the SOM geometry. The projected SLAPW results include only the integrated charge within the muffin-tin spheres.

Total and layer-projected density-of-states (DOS) curves that are obtained from the LCAO and SLAPW calculations for the SOM, MLM, and clean Ag(001) surfaces are compared in Figs. 2–4, respectively. These were obtained by calculating the electronic-eigenvalue spectrum at 15 special points in the SBZ. The appropriate eigenvalues were sorted to form histograms of width ~0.15 eV and the final DOS curves were obtained by convolution with a Gaussian [FWHM (full width at half maximum) = 0.3 eV].

It is emphasized that a detailed comparison between the LCAO and SLAPW results is meaningful only for the SOM total DOS curves in Fig. 2(a). Here, the same geometry is assumed and both calculations are carried out in the nonrelativistic limit. It is seen that the results of the two calculations are in excellent agreement in regard to overall shape and peak alignment. Discrepancies in the latter correspond to about 0.25 eV, which is primarily a shift of the Fermi level relative to the Ag *d* and Cl features.

Before comparing the layer-projected DOS curves, one must take into account differences in the LCAO and SLAPW schemes. Namely, the LCAO projection is based on atomic orbitals, with overlap charge divided between layers, whereas the SLAPW results include only the charge within the muffin-tin spheres. Despite these differences, the two sets of curves are in good qualitative agree-

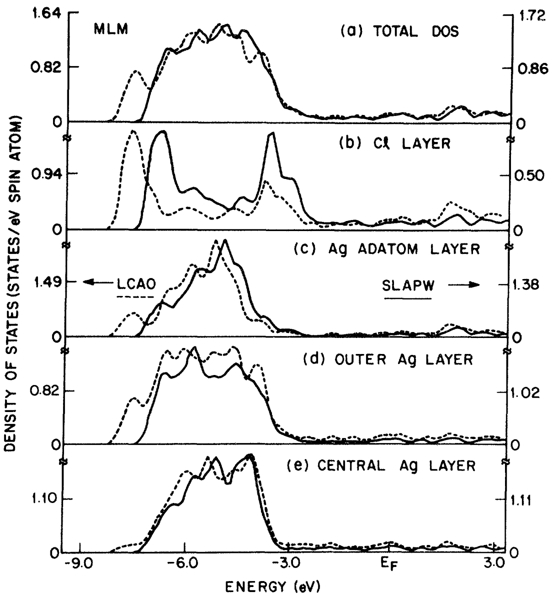

FIG. 3. LCAO and SLAPW total and projected DOS curves for slightly different MLM geometries (see text).

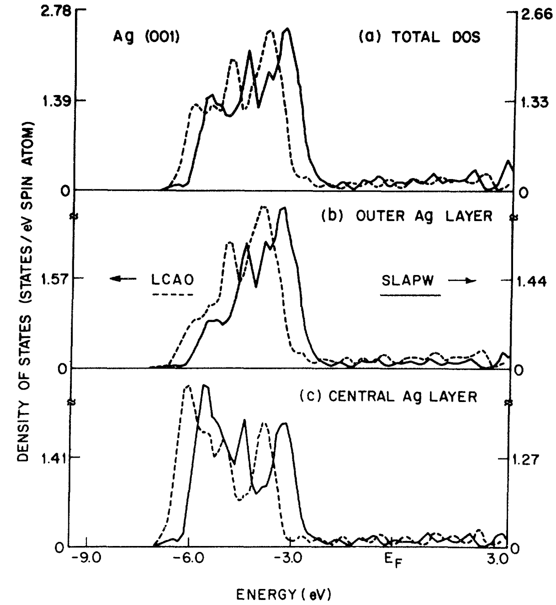

FIG. 4. Nonrelativistic LCAO and scalar-relativistic SLAPW total and projected DOS curves for the clean Ag(001) surface.

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The main differences in the LCAO and SLAPW results in Fig. 3 for the MLM are due to changes in the adlayer geometry. The increased distance of the Cl adlayer from the surface (1.88 Å − 1.66 Å = 0.22 Å) in the SLAPW calculation causes the energy of lower Cl peak to increase by about 1 eV, thereby improving the agreement with the UPS data.[8] The remaining features of the total and layer-projected DOS curves are in qualitative agreement.

Finally, we compare in Fig. 4 the nonrelativistic LCAO and the scalar-relativistic SLAPW DOS curves for the clean Ag(001) slab. Again, the results are in good qualitative agreement. The main effect of the Darwin and mass-velocity relativistic corrections is lower the *s*-*p* bands and E_F relative to the Ag 4*d* bands by about 0.75 eV. Since the Cl features in the MLM spectrum arise from strongly hybridized Ag *d* and Cl *p* states,[1] we expect that including relativistic effects in that model would shift these features with the *d* bands, thereby preserving the agreement with experiment.

In summary, we have presented a detailed comparison of LCAO and SLAPW calculations for a clean Ag(001) surface and one with chemisorbed Cl in $c(2\times2)$ SOM and MLM geometries. The results of the two calculations are in semiquantitative agreement regarding the calculated work functions, DOS, and charge densities. The main advantage of the SLAPW technique is its ability to treat accurately the charge-density tails in the outermost surface regions. The independent verification of the spectra for the two adsorption models narrows the range of issues to be addressed in resolving the serious disagreement between the analyses of the LEED and UPS data.[1,7,8]

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