tion band, at 1.1–1.9 eV for Xe, 1.6–2.1 eV for Kr, and 2.5–3.5 eV for Ar above the bottom of the conduction band. From modified calculations for the EDC's, considering realistic valence bands, one can extract more detailed information about the structure of the conduction bands, which is difficult to get otherwise. Such calculations are in progress.[23]

At energies equal to the sum of the gap energy and the first exciton energy the onset of electron-electron scattering is observed (not shown in Fig. 1). These energies are 17.8 eV for Xe, 21.9 eV for Kr, and 26.3 eV for Ar. The cross section for this process has been studied in detail for Kr and Ar and will be discussed elsewhere.[18,25]

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Self-Consistent Theory of the Chemisorption of H, Li, and O on a Metal Surface

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We report the results of a parameter-free, self-consistent, wave-mechanical calculation of the properties of H, Li, and O chemisorbed on a metal surface. Comparison is made with available experimental results on dipole moments, adsorption energies, and state densities.

We report here the first essentially exact numerical solution of a widely discussed model of chemisorption. The model consists of a semi-infinite uniform distribution of positive charge representing the lattice of substrate metal ions, an atomic nucleus of charge Z, and the gas of interacting electrons. The equilibrium position of the nucleus and the electron density distribution are evaluated self-consistently by use of the Kohn-Sham local-density description of exchange and correlation.[1] From this density distribution, we have calculated the dipole moment, heat of adsorption, and energy density of states.

The uniform-background model for the bare metal surface has been shown to represent accurately the ground-state properties of simple-metal surfaces.[2] We expect this description of the substrate to give good results for chemisorption on surfaces not characterized by either directional bonding or a density of states which varies rapidly with energy in the vicinity of the resonant states associated with the adatom.

The partial differential equations associated with this simple model for chemisorption are difficult to solve; and previous studies[3,4] have introduced approximations which preclude bringing out the full physical and chemical content of the model. These studies, in contrast to the present work, describe the electronic kinetic energy with a finite-gradient expansion, which leads, for example, to qualitatively incorrect values for the dipole moment and the electron density in the vicinity of the nucleus (see below). Our analysis shows in addition that linearizing the response of the metal to the adatom[3] is not an adequate approximation, even for hydrogen chemisorption.

The only input to our calculation is Z and the positive background density of the substrate (specified by r_s). We introduce no adjustable parameters, no linearization, no assumed variational forms for the wave functions (such as Gaussian orbitals), and no assumption of spherical symmetry near the nucleus. The resulting energy spectrum contains both discrete and continuous portions. The wave functions associated with both portions are allowed to polarize freely[5]; this freedom was found essential to give a vanishing electrostatic force on the adatom nucleus at the minimum-energy position (Hellmann-Feynman theorem).

The formalism of Kohn and Sham[1,2] reduces the many-body problem for the ground-state density distribution of an inhomogeneous system of N electrons in a static external potential to the self-consistent solution of a set of Hartree-like equations[6]:

$$\{-\nabla^2+v_{\text{eff}}[n;\vec{r}]\}\Psi_i(\vec{r})=E_i\Psi_i(\vec{r}), \tag{1a}$$

$$n(\vec{r})=\sum_{i=1}^{N}|\Psi_i(\vec{r})|^2, \tag{1b}$$

where v_{eff}, a functional of the electron number density $n(\vec{r})$, is the sum of the electrostatic potential and an effective exchange-correlation potential. The eigenfunctions of Eq. (1a) for the bare model surface (without the adatom) can be written (with use of cylindrical coordinates ρ, φ, z) as

$$\Psi_{Em\kappa}{}^{M}(\vec{r})=e^{im\varphi}J_m(\kappa\rho)u_k{}^{M}(z). \tag{2}$$

(We take the z axis along the surface normal, and label quantities appropriate to the bare surface with an M.) The quantum numbers E, m, and κ reflect the quantities conserved by the symmetry of the bare model surface: energy and the two components of transverse momentum. The $u_k{}^M(z)$, where $k^2=E-\kappa^2-v_{\text{eff}}(\text{bulk})$, are calculated self-consistently.[7] The $\Psi_{Em\kappa}{}^M$ are normalized to $\delta(E-E')\delta_{mm'}\delta(\kappa-\kappa')$.

The fundamental difficulty in the analysis of the combined system (adatom plus surface) is the loss of transverse translational symmetry. Other than azimuthal symmetry, the only major simplicity we can take advantage of is the fact that the metal screens out the effects of the adatom on the charge density and potential (though not on the wave functions) except in the adatom's vicinity. This locality is conveniently exploited by replacing Eq. (1a) for the continuum states by the equivalent Lippmann-Schwinger equation:

$$\Psi_{Em\kappa}(\vec{r})=\Psi_{Em\kappa}{}^{M}(\vec{r})+\int d^3r'\,G_E{}^M(\vec{r},\vec{r}\,')\,\delta v_{\text{eff}}(\vec{r}\,')\Psi_{Em\kappa}(r'), \tag{3}$$

where

$$\delta v_{\text{eff}}(\vec{r})\equiv v_{\text{eff}}[n;\vec{r}]-v_{\text{eff}}[n_M;\vec{r}], \tag{4}$$

and

$$\{\nabla^2+E-v_{\text{eff}}[n_M;\vec{r}]\}G_E{}^M(\vec{r},\vec{r}\,')=\delta(\vec{r}-\vec{r}\,'). \tag{5}$$

While we can use κ to label our scattering solutions, it does not refer to a conserved quantity in the combined system.

In the region surrounding the adatom in which δv_{eff} is nonnegligible, we expand $\Psi_{Em\kappa}$ and $\Psi_{Em\kappa}{}^M$ as

$$\Psi_{Em\kappa}{}^{(M)}(\vec{r})=\sum_{l=m}^{\infty}\alpha_{Em\kappa l}{}^{(M)}\Psi_{Eml}{}^{(M)}(\vec{r}). \tag{6}$$

The Ψ_{Eml} and $\Psi_{Eml}{}^M$ were obtained by direct numerical integration of Eq. (1a)[5] outward from the origin (the position of the adatom nucleus). They differ from their κ counterparts only in the boundary conditions they satisfy:

$$\lim_{r\to 0}r^{-l}\int d\Omega\,Y_{lm}(\Omega)\Psi_{Eml'}{}^{(M)}(\vec{r})=\delta_{ll'}. \tag{7}$$

TABLE I. Calculated values of the dipole moment and atomic binding energy, compared with low-adatom-coverage experimental results. d in the second column is the calculated equilibrium separation in atomic units (bohrs). The computed values of μ and ΔE_a are not inordinately sensitive to d. (For example, a change of d for oxygen by 20% changes μ by less than 15% and ΔE_a by less than 5%.) The available experimental data are for transition-metal substrates: H (Ref. 9); Li (Ref. 10); O [Refs. 11 (μ) and 12 (ΔE_a)]. The < sign in the table refers to the fact that even at low coverages, H and O atoms cluster into islands, making the true zero-coverage limit of μ more negative than the measured low-coverage value (see Ref. 13).

		Theory		Experiment	
	d (a.u.)	μ (D)	ΔE_a (eV)	μ (D)	ΔE_a (eV)
H	1.1	-0.5	1.5	<-0.15	3
Li	2.5	2.6	1.3	~ 1.5–3	~ 2.5–3
O	1.1	-1.7	5.4	<-0.4	5–6

When expansions (6) are substituted into the $r \to 0$ limit of Eq. (3), a linear matrix equation[8] relating the properly normalized $\alpha_{Em\kappa l}$ to the known $\alpha_{Em\kappa l}{}^M$ results. The required $r \to 0$ limit of the metal Green's function was constructed by combining the two sets of independent solutions of Eq. (1a) (with potential $v_{\rm eff}[n_M; \vec{r}]$): those which increase exponentially in the vacuum and those which decay. Our particular treatment of the $\vec{r}$ dependence of Eq. (3) reduces complications stemming from the fact that the atom is most naturally described in spherical coordinates while the metal is naturally described in cylindrical or rectangular coordinates.

We introduce a quantity $\delta n(E, \vec{r})$ defined as twice (for spins) $|\Psi_{Em\kappa}(\vec{r})|^2 - |\Psi_{Em\kappa}{}^M(\vec{r})|^2$ summed over m and κ, plus twice the squares of the discrete-state wave functions (multiplied by energy delta functions). Integration of $\delta n(E, \vec{r})$ over E up to the Fermi level yields the change in electron density $\delta n(\vec{r})$. Integration of $\delta n(E, \vec{r})$ over $\vec{r}$ yields the change in state density $\delta n(E)$.

We now briefly discuss the results of our calculations for H, Li, and O chemisorbed on a high-density metallic substrate ($r_s = 2$). The predicted nucleus-positive-background separations d are given in Table I; these separations are physically realistic.[14] The energy, and the various components of the electrostatic force on the nucleus,[15] are shown for the case of oxygen in Fig. 1.

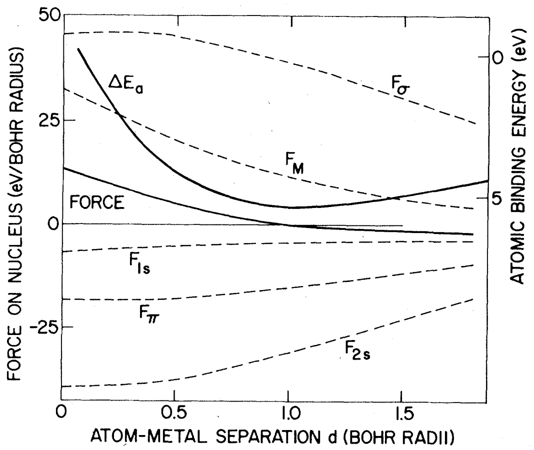

FIG. 1. Energy and forces as functions of d for oxygen chemisorption. The "force" curve gives the total electrostatic force on the adatom nucleus. The different contributions to this force are shown as dashed curves. F_M is the force due to the bare metal. The remaining contributions are due to the various components of the electron density $\delta n(\vec{r})$: F_{1s} and F_{2s} arise from electrons in the 1s and 2s discrete states; F_σ and F_π arise from electrons in continuum states characterized by $m = 0$ and $m \geq 1$ (mostly $m = 1$), respectively. The magnitudes and directions of these force components are similar to those found for the oxygen molecule (see Ref. 15).

Figure 2 gives the state-density changes $\delta n(E)$. Both H and O show resonances in the filled part of the metal band. Unfortunately, the available experimental data are almost entirely for chemisorption on transition-metal or semiconductor substrates, which our model is not primarily in-

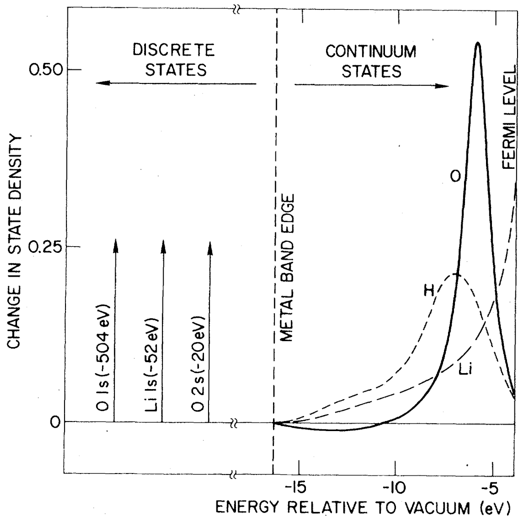

FIG. 2. Changes in state density $\delta n(E)$. The continuum portions are normalized to unity.

tended to describe. For this reason, and also because of the importance of relaxation effects,[16,17] a comparison of these $\delta n(E)$ curves with photoemission difference spectra (at low coverages) can be only qualitative. As examples, peaks in the measured spectra having widths and positions (relative to the vacuum) roughly similar to those of the resonances in Fig. 2 have been reported by Ibach and Rowe[18] (H/Si) and Menzel[19] (O/Ag).

Table I gives the computed dipole moments μ[20-22] and atomic binding energies ΔE_a.[23] Even though the experimental data are again for chemisorption on transition metals,[9-13] the calculated values agree with the data both in sign and in trend with atomic number.

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[20] μ is defined as $-\int d^3r\, z\, \delta n(\vec{r})$ ($z=0$ at nucleus; $z=+\infty$ in vacuum). Thus $\mu < 0$ implies an increase in substrate work function.

[21] We note several differences between the wave-mechanically computed μ values and those obtained in the linearized, gradient-expansion treatment of Ref. 3. [The effect of a finite gradient expansion for the kinetic energy was tested by using the wave-mechanical calculation at Z values for which the other approximation of Ref. 3 (linear response) is not in question, i.e., $Z \ll 1$.] In the range $d=0$ to $d=1.5$ a.u., for example, the value of μ/Z in Ref. 3 varies between -0.02 and $+0.05$ D. The wave-mechanical treatment (with $Z \ll 1$), by contrast, yields a value that increases monotonically over this range from zero to $+0.85$ D (this one result is for $r_s = 1.5$, the substrate r_s used in Ref. 3). With regard to nonlinearity, μ/Z, a quantity which is constant if linear response is valid, changes (at $d=1$ a.u. for example) in the present calculation from $+0.7$ D for $Z \ll 1$ to -0.5 D for $Z=1$.

[22] An important conclusion of Ref. 3 is that chemisorption reduces the electron density at the hydrogen nucleus to $\sim\frac{1}{3}$ its atomic value. Our calculations (for $Z=1$), by contrast, show this quantity to be slightly enhanced by chemisorption.

[23] ΔE_a is the difference in total energy between the metal plus the separated atom, and the metal with the atom chemisorbed on its surface. Energies of isolated Li and O atoms found by J. F. Janak (private communication) in a spin-polarized Kohn-Sham calculation were used.