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Scattering of helium from O/Ni(001): Cluster-model studies

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A cluster model has been used to study the interaction of He with O/Ni(001) at $c(2\times2)$ coverage. The $Ni_{11}O_2$ cluster which was used contains two nearest-neighbor O atoms. The self-consistent-field interaction energies of He with this cluster, $Ni_{11}O_2He$, were obtained for several He geometries along the [100] direction between the He directly over an O atom, the on-top site, to He between the two O atoms, the central site. These energies were obtained in the frozen orbital (FO) and relaxed orbital (RO) approximations. The FO and RO corrugation heights between these sites for He distances with repulsive interaction energies of 40, 60, and 100 meV are all near 0.4 Å, very close to the value obtained from experiment. The corrugation curve along [100] at 60 meV was obtained in the FO approximation and has a full width at half maximum of 1.86 Å. The nature and consequence of the charge redistributions associated with the RO interaction were investigated. It is shown that, due to the size of the He atom, it is not possible to equate the variation of the charge-density contours directly to the corrugation as is done when using the Esbjerg and Nørskov approximation which gives the interaction energy as directly proportional to the surface charge density. We show that there are different proportionality constants for different positions of the He atom on the O/Ni(001) surface. A significant conclusion is that there will not be a unique constant when the surface charge density is highly corrugated with respect to the size of the He atom. However, the Esbjerg-Nørskov relation for superimposed atomic charge densities may be adequate for semiquantitative estimates.

I. INTRODUCTION

The use of the diffraction of helium atoms from surfaces to obtain structural information has grown rapidly during the past few years.[1-3] Of particular interest is the knowledge of the helium-surface interaction potential.[4-10] The most widely used helium-surface interaction for the repulsive part of the potential[5] is given in terms of the unperturbed surface charge density,

$$V(x,y,z)=\alpha\rho(x,y,z)\ , \tag{1}$$

where $\rho(x,y,z)$ is the charge density of the free surface and α (Ref. 11) is a proportionality constant. This potential has been successfully used in a number of applications.[6,12-17]

In this paper, we wish to investigate the relation given in Eq. (1) for the highly corrugated surface of oxygen chemisorbed on Ni(001).[18] Our calculations are based on a cluster model description of the O/Ni(001) surface. Hartree-Fock self-consistent-field (SCF) wave functions for the relevant clusters interacting with a helium atom are calculated. Cluster model studies using similar clusters and similar SCF wave functions,[19-21] have yielded valuable information about the electronic state, the adsorption bond distance, and the vibrational frequency of O/Ni(001). Further, there have been cluster model studies of related systems; i.e., O/Si(100),[22] O/Li(001),[23] and the ionic interactions of F/Si(111) (Refs. 24 and 25) and Cl/Cu(001).[26] Based on the successes of these cluster model studies, we have strong reasons to believe that our cluster approach will be valuable for the present study of the interaction of He with O/Ni(001).

One striking conclusion of our study is that although the interaction potential decays exponentially with distance away from the surface, no single unique value of α can be found. In fact, the value of α is about twice as large in an on-top site as compared to a center site. The on-top site refers to a He atom approaching directly above an oxygen atom. The center site has He facing a surface Ni atom. The suggestion has been made that one should not use a free-surface charge density but, instead, take some suitable average weighted with the He charge density; a typical weighting function has been the electrostatic potential due to the helium atom.[9] This produces[16] about a 15% change between the averaged and unaveraged charge density. Such an averaging would not produce the site dependent α that our results predict for O/Ni(001).

Another interesting finding is that the results are somewhat dependent on the level of treatment of the helium atom. By this we mean whether or not there is enough flexibility in the basis sets of the LCAO SCF calculations to permit polarization of the helium charge away from the surface.

A number of calculations in the literature have used the superposition of atomic charge densities to generate the surface charge density. In order to make contact with these calculations, we also construct the cluster charge density in this manner. We find that the corrugation height can be estimated reasonably well in this way. However, the detailed shape of the corrugation function requires a more precise treatment of the charge density.

The organization of the rest of the paper is as follows. In the following section we briefly discuss the *ab initio* cluster model method. In Sec. III, we discuss general features of the He-surface interaction. In Sec. IV, we discuss the applicability of the Esbjerg-Nørskov relation. In Sec. V, we give the interaction results obtained using a superposition of atomic densities. In Sec. VI, we present our results for the full width at half maximum (FWHM) of the corrugation curve. And in Sec. VII, we present our conclusions.

II. COMPUTATIONAL DETAILS

We use a cluster model approach, (see for example, Refs. 27–29), based on SCF (Ref. 30) wave functions to describe He interacting with an oxygen-covered Ni(001) surface at $c(2\times2)$ coverage. The cluster used is a $Ni_{11}O_2$ cluster, see Fig. 1, where there are seven Ni atoms in the top layer and four in the second layer. The Ni-Ni distances are taken from the bulk.[31] The two oxygen atoms are in the fourfold hollow sites at a height of 0.83 Å; this is the equilibrium distance for a $Ni_{25}O$ cluster.[19] The He interaction was considered in detail for two positions, the center position, where the He atom was directly above the central Ni atom and between the two oxygen atoms, and the on-top position, where the He atom was directly above one of the oxygen atoms, see Fig. 1. To model the center position, a He atom was added to the $Ni_{11}O_2$ cluster, $Ni_{11}O_2He$, where the height of the He atom above the central Ni atom was allowed to vary with the positions of the Ni and O atoms kept fixed. Calculations for this cluster were performed in C_{2v} symmetry. To model the on-top site interaction, we used a $Ni_{11}O_2He_2$ cluster for most of the calculations. The two He atoms were directly over the two O atoms and the height of the He atoms above the surface, as defined by the plane of the first layer Ni atoms, was allowed to vary with all other distances remaining fixed. This cluster had the computational advantage of retaining C_{2v} symmetry. At this He-He distance the He-He interaction is negligible, approximately 1×10^{-6} hartrees. To compute the corrugation profile we allowed the symmetry of the $Ni_{11}O_2He$ cluster to drop from C_{2v} to C_s. The He position along the surface was then varied along a line between the on-top site and the central site, the [100] direction. Some calculations for $Ni_{11}O_2He$ in C_s symmetry were performed at the on-top site and gave results very similar to those obtained with $Ni_{11}O_2He_2$.

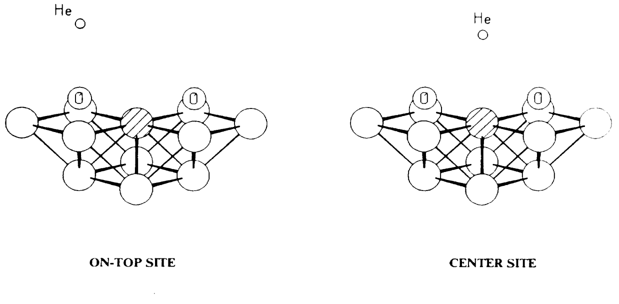

FIG. 1. Cluster model $Ni_{11}(7,4)O_2 + He$ for the on-top and center sites of He interacting with $c(2\times2)$ O/Ni(001). The shaded circle represents the all-electron (AE) Ni atom; the remaining unlabeled circles are the MEP Ni atoms, see text.

The interaction energies were obtained in the frozen-orbital (FO) and relaxed-orbital (RO) approximations. In the FO case the energy for the $Ni_{11}O_2He$ cluster was obtained for the superposed charge densities of $Ni_{11}O_2$ and He; the orbitals of the separated units were not allowed to change. The FO interaction energy represents the interaction of the unperturbed units since the charge distributions of both the surface cluster for O/Ni(001) and the He atom are not allowed to change because of the presence of the other unit. For computational convenience, we have Schmidt-orthogonalized the orbitals of $Ni_{11}O_2$ to those of the He atom because we calculated the expectation value of the energy using an expression which assumes orthogonal orbitals. However, we stress that this orthogonalization does not, in any way, change the antisymmetric determinantal many-electron wave function from that given by using nonorthogonal orbitals. In the RO case, a fully converged SCF energy was obtained for $Ni_{11}O_2He$ or $Ni_{11}O_2He_2$. The cluster calculations were performed using contracted Gaussian-type orbital (CGTO) basis sets. For the central Ni atom, all the electrons were included but for the remaining Ni atoms a pseudopotential was used. For these Ni atoms, the core electrons, $1s$-$3d$, are represented by a modified effective core potential (MEP). All of the electrons are included for the O and He atoms. This mixed-cluster approach, where the atoms directly involved in the He-surface interaction are described at an all-electron level while the environmental atoms are treated with a pseudopotential, has been shown previously,[32,27] to give results very close to an all-electron treatment at a fraction of the computational expense. The all-electron Ni basis set is that of Wachters,[33] with the diffuse p (Ref. 33) (multiplied by 1.5) and the diffuse d of Hay.[34] This basis set is contracted $(12s11p6d/8s6p4d)$. For the pseudopotential Ni atoms, the MEP parameters and valence basis set are taken from Melius *et al.*[35] This basis set is contracted $(4s3p/2s1p)$. The oxygen basis set is that of Dunning and Hay,[36] which includes a diffuse p function necessary to describe O^- and is contracted $(9s6p/4s3p)$. For the He atoms, two different basis sets were used. The first is an s-only basis set of van Duijneveldt,[37] contracted $(9s/3s)$ and the second set, given in Ref. 38, starts with an s basis set of van Duijneveldt and augments it with three p functions, $(10s,3p/5s3p)$. With this second basis set the He atom is able to polarize and become nonspherical.

The state used for $Ni_{11}O_2$ was determined by adding the electrons in steps and filling the lowest virtual orbitals of the cluster ion in each step. For Ni_{11} we found the energy to be relatively insensitive to the symmetry of the d hole on the central, all electron, Ni atom; the spread between states of different symmetry was less than 0.5 eV. We used a d hole in b_2 symmetry; the only lower energy holes were the two in a_1 symmetry, but these were computationally more difficult to treat. The resulting state used for $Ni_{11}O_2$ was

$$(1a_1-12a_1)^2 13a_1^1 (1b_1-8b_1)^2 (1b_2-4b_2)^2 \times 5b_2^1 (1a_2-2a_2)^2 ({}^3B_2) \ . \quad (2)$$

The states used for $Ni_{11}O_2He$ and $Ni_{11}O_2He_2$ were formed by adding one or two closed-shell a_1 orbitals to the state of Eq. (2). For the C_s symmetry calculations the same state was used with the appropriate reductions in symmetry.

III. ON-TOP AND CENTER SITE INTERACTIONS: GENERAL FEATURES

In this section, we consider the properties of the interaction of a He atom at two positions on a $c(2\times2)$ coverage of O/Ni(001). These are (1) He directly above an O atom and, (2) He between the two O atoms along the [100] direction; see Fig. 1. The principal properties of concern are the height of the corrugation along [100] direction, denoted by ζ, and the softness parameter, κ, of the interaction. These properties have been computed at three levels of approximation. First, we superimpose the unperturbed charge densities from the $Ni_{11}O_2$ cluster and the He atom and evaluate the interaction energy from these frozen orbitals. In this approximation, denoted FO, the Esbjerg-Nørskov relation[5] is not used; rather a full account of the Coulomb and exchange terms in the SCF energy expression[30] are taken. Second, using an s basis set only for He, we obtain fully relaxed SCF energies for the $Ni_{11}O_2He$ cluster; these results are denoted RO(s only). At this level of approximation, the $Ni_{11}O_2$ cluster is able to respond to the presence of the He but the He charge distribution remains spherical; it cannot polarize and acquire any induced dipole moment. In the third approximation, denoted RO(s and p), the $Ni_{11}O_2He$ SCF energies are computed using a basis set for He which contains p functions. Here the He charge can polarize and acquire an induced dipole moment. There are significant differences among the FO, RO(s only), and RO(s and p) results which we shall interpret in terms of the nature of the charge redistributions when $Ni_{11}O_2$ and He interact.

The softness parameter, κ, is obtained by a least square fitting of the interaction energy, $E_{\rm int}$, with the exponential form

$$E_{\rm int}=A\exp(-\kappa z) \ , \quad (3)$$

A is a constant and z is the distance of the He atom (nucleus) above the first layer of Ni atoms. $E_{\rm int}$ is defined as the difference of the sum of the energies of He and $Ni_{11}O_2$ and the energy of the cluster, $Ni_{11}O_2He$ (center) or $Ni_{11}O_2He_2$ (on top),

$$Ni_{11}O_2He\text{:}\ \ E_{\rm int}=E(Ni_{11}O_2He)-E(Ni_{11}O_2)-E(He) \ , \quad (4a)$$

$$Ni_{11}O_2He_2\text{:}\ \ E_{\rm int}=[E(Ni_{11}O_2He_2)-E(Ni_{11}O_2) -2E(He)]/2 \ , \quad (4b)$$

$E_{\rm int}>0$ indicates a repulsive interaction. The only difference between the various levels of approximation arise in the evaluation of $E(Ni_{11}O_2He)$. A reasonably good fit to $E_{\rm int}$ can be made with Eq. (3) for z ranging between 4.5 and 8.0 bohrs. At the closest distances, $E_{\rm int}$ is approximately 1 eV; a rather large repulsion. For the on-top position of He, points between $6.25\le z\le 8$ were explicitly used for the least-square fit; for the center position points between $4.5\le z\le 7.0$ were used. The near-linear behavior of $\ln(E_{\rm int})$ can be seen in Fig. 2 where $E_{\rm int}$ is plotted for the center position. It is interesting to note that the RO(s and p) $E_{\rm int}$ departs from this linear behavior at large z; the departure is rather large at $z=7$ bohrs. A similar departure is found for the on-top position of the He atom, see below. The reason for this departure is that there is a weak attractive Van der Waals well at large z. The effect is largest for the RO(s and p) wave functions since the He p basis functions allow the He charge distribution to po-

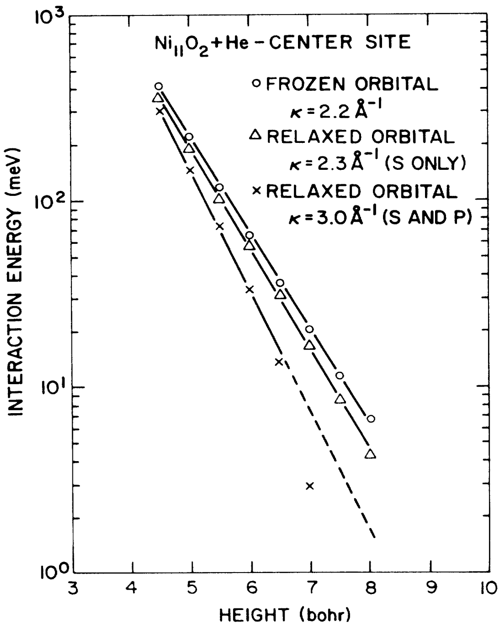

FIG. 2. The log of $E_{\rm int}$ versus the height of the He atom above the surface, z, at the center site is shown for the three levels of calculation, frozen orbital, FO, relaxed orbital with an s-only He basis set, RO(s only), and relaxed orbital with an s and p He basis set, RO(s and p). The deviation from linear for the RO(s and p) values shows the onset of the long-range attractive portion of the potential.

larize, become nonspherical, which leads to a dipole-induced dipole attraction. Below, we discuss the He polarization in more detail in connection with its contribution to the charge rearrangement in the region where the interaction is repulsive.

From Fig. 2, it is also clear that the repulsion is largest with the FO approximation, smaller for RO(s only) and smallest for RO(s and p). This is expected since the variational SCF energy of $Ni_{11}O_2He$ must be lower than the FO value. This energy must be lower (or the same) when the He basis set is larger; i.e., when it contains both s and p functions. Thus the order of E_{int} is

$$E_{\text{int}}(\text{FO}) \geq E_{\text{int}}(\text{RO } (s \text{ only})) \geq E_{\text{int}}(\text{RO } (s \text{ and } p)) \ .$$

The values of κ are given in Table I.

For all the approximations, κ for the on-top position is between 22% and 30% larger than at the center position. This is not surprising since at the on-top position the He is directly approaching an O atom and the surface charge density will vary more rapidly than at the center position where He is approaching the surface between two O atoms. Similar differences in κ have been obtained for different surface positions for He/Cu(110) (Refs. 32 and 39) and He/Ni(110).[39] In the case of He/Cu(110), the κ was 7% larger when He approached directly above an atom than when He approached at a bridge site. The order of these κ's is the same as for He approaching O/Ni(001) and for the same reasons. This site dependence of κ indicates that the corrugation will be energy dependent.

We also note that the interaction becomes harder, less soft, when the charge distributions are allowed to relax, RO, than when they are kept fixed, FO. This is because the relaxation energy for the RO SCF solutions varies as a function of the He-surface distance. The relaxation energy, E_R, is defined as the difference between E_{int}(FO) and E_{int}(RO),

$$E_R = E_{\text{int}}(\text{FO}) - E_{\text{int}}(\text{RO}) \tag{5}$$

and measures the energetic importance of the SCF orbital relaxation. The fact that the RO κ is larger than the FO value means that E_R/E_{int}(FO) becomes smaller as He approaches the surface; i.e., as z becomes smaller. From Fig. 2, we see that both E_R and E_{int}(FO) increase but that E_{int}(FO) increases more rapidly as z decreases. From Fig. 2 and Table I, it is clear that the difference between the FO and RO(s only) κ's is small but that the change is much larger for RO(s and p). In other words, the He polarization which occurs with the s and p basis set is relatively large compared to E_{int}(FO) at large z. We shall examine this in more detail below. Here we point out that the large increase of the RO(s and p) κ indicates a limitation of the softness computed by evaluating E_{int} without allowing the charge distributions, in particular that of He, to relax. This FO procedure for obtaining E_{int} is used with the Esbjerg-Nørskov relation.[5] This strong dependence of κ on allowing the He to polarize may be a special feature of the strongly ionic O adsorption[19,20,40] in that the polarization of He approaching the negatively charged O may be particularly large. The importance of the He polarization may be significantly smaller on clean metal surfaces where the surface charge separation is smaller than for O/Ni(001). In these cases, it is possible that the FO E_{int} will more properly describe the softness of the interaction.[32]

TABLE I. The values of the softness parameter, κ, in Å^{-1}, for the on-top and center He positions are given. The values are obtained from a least-square fit of the interaction energy curves described by three levels of approximation: (1) frozen orbital (FO), (2) relaxed, SCF, with an s-only He basis set [RO(s only)], and (3) relaxed, with an s and p He basis set [RO(s and p)].

	κ(on-top)	κ(center)
FO	2.7	2.2
RO(s only)	2.8	2.3
RO(s and p)	3.9	3.0

For the corrugation, we consider the height above the surface of the classical turning point of the He atom; this is the height for which E_{int} is equal to the z component of the energy of the incident atom. Heights for energies of 40, 60, and 100 meV for the on-top and center positions, z(on-top) and z(center), are considered. These energies correspond to normal incident He atoms with wavelengths $\lambda = 0.72$, 0.59, and 0.49 Å, respectively and are representative of the values used by Rieder.[18] The corrugation ζ along the [100] direction is

$$\zeta = z(\text{on-top}) - z(\text{center}) \ . \tag{6}$$

Values of z and ζ are given in Table II; they have been obtained by interpolation of the E_{int} curves in Fig. 2 and the analogous curves for the on-top He position.

For both the on-top or center positions, the RO turning points lie closer to the surface than the FO values at all three energies. Obviously, this is because the SCF relaxation reduces the repulsion and He can approach closer to the surface before reaching the classical turning point; with the He s and p basis, E_R is larger and z is smaller. Despite the large differences in z(on-top) and z(center) for the FO and RO approximations to E_{int}, the corrugations, ζ, are very similar; within the uncertainties of the interpolation, the values of ζ are essentially the same. This important result shows that a FO approach can give reasonable values for the corrugation.

The ζ does have a weak dependence on the He normal energy; it becomes smaller as E decreases by about the same amount for all the E_{int} approximations. This energy dependence of ζ arises because the softness parameter is different, larger, for the on-top than for the center position. This energy dependence is illustrated in Fig. 3, where the RO(s and p) $\ln(E_{\text{int}})$ curves are plotted for these two positions. Clearly, if κ were the same for these two positions, ζ would not change with the He energy. This is true independent of the softness or hardness of the potential; i.e., whether the value of κ is large or small.

The ζ obtained from Rieder's He diffraction data[16,18] is 0.4 Å for a normal He energy of 37 meV; our values of ζ at this energy are smaller. However, we recall that we have placed the O atom 0.83 Å above the surface; this is the low-coverage equilibrium normal distance, R, computed with SCF wave functions for the $Ni_{25}O$ cluster.[19] This

TABLE II. The values of the classical turning points, z, in Å, for the on-top and center He positions are given for incident He atom energies of 100, 60, and 40 meV. Three levels of approximation are considered, FO, RO(s only), and RO(s and p). Also given are the corrugation heights, ζ, in Å, for the three incident energies. The uncertainties represent deviations in the least-square fitting and interpolation of the interaction energy curves, see Fig. 2.

		z (Å)		
E (meV)	Approximation	z(on-top)	z(center)	ζ (Å)
100	FO	3.40	3.00	0.40±0.02
	RO(s only)	3.30	2.93	0.38±0.01
	RO(s and p)	3.18	2.80	0.38±0.02
60	FO	3.58	3.21	0.37±0.02
	RO(s only)	3.48	3.15	0.33±0.01
	RO(s and p)	3.30	2.96	0.34±0.01
40	FO	3.73	3.40	0.33±0.02
	RO(s only)	3.63	3.32	0.31±0.02
	RO(s and p)	3.41	3.10	0.31±0.01

value is smaller than the surface extended x-ray-absorption fine structure (SEXAFS) (Ref. 41) $R = 0.86 \pm 0.007$ Å and the low-energy electron diffraction (LEED) (Ref. 42) $R = 0.9$ Å. At the on-top position, the He sees essentially only the O charge density, (see Sec. IV). It is reasonable to expect that the classical turning point at this position, z(on-top), will increase by Δ if the O is moved up from $R = 0.83$ Å by an amount Δ. At the center position, the distance of the He atom from the nearest O or Ni atoms does not change significantly when the O distance from the Ni surface is changed by small amounts. We do not expect z(center) to change significantly for small displacement of O. Thus, the corrugation, ζ, is reasonably expected to increase from the computed value by Δ as the O is moved Δ above $R = 0.83$ Å. The RO(s and p) ζ for 40 meV would be 0.34 ± 0.001 Å if the O were placed at $R = 0.86$ Å and 0.38 ± 0.01 Å if O were placed at $R = 0.9$ Å. These values are quite close to the corrugation along the [100] direction obtained from the He diffraction data.[16,18]

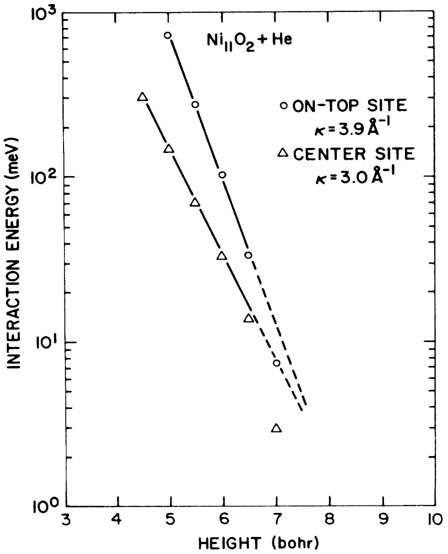

FIG. 3. The log of E_{int} versus the height of the He atom above the surface, z, at the center and on-top sites is shown for the RO(s and p) calculation. At larger heights, the deviation from linear shows the onset of the attractive portion of the interaction potential.

We now consider the nature of the charge rearrangement when the SCF solutions for the $Ni_{11}O_2$-He interactions are obtained. We shall be primarily concerned with the vertical motion of charge which can be measured by changes in the z component, μ_z, of the cluster dipole moment. For the calculation of μ, we assume, for the ten Ni atoms which are treated with a pseudopotential, that the core electrons, $1s$-$3d$, plus the Ni nucleus yield an effective charge of 1 at the position of the nucleus. This is the effective charge that would arise from a spherical distribution of the core electrons. It does not include small effects due to polarization of the core electrons not permitted with the pseudopotential[35] which we have used. For the bare $Ni_{11}(7,4)$ cluster, $\mu_z = +0.402$ a.u. (1 a.u. = 2.54 debyes). Considering the number of atoms in the cluster this value of μ_z indicates a small displacement of the center of electronic charge below the center of nuclear charge by 0.01 bohrs ≈ 0.005 Å. At a Ni surface, the electronic charge extends beyond the nuclear charge[43] and the surface dipole has the opposite sign to that for $Ni_{11}(7,4)$. This is not at all surprising since the cluster is much too small to properly represent the charge distribution of the surface conduction band. The sign of μ_z is a cluster artifact; only the changes in μ_z, as O is added to form $Ni_{11}O_2$ and when the $Ni_{11}O_2$-He interaction takes place, can be expected to have physical significance. For $Ni_{11}O_2$, $\mu_z = -0.639$ a.u. for a change of -1.041 a.u. from bare Ni_{11}. This is in the correct direction of change for the negative ionicity of the adsorbed O and in the correct direction for the 0.3—0.4 eV increase in the Ni work function, Φ, for both $p(2\times2)$ and $c(2\times2)$ coverages of O on Ni(001).[44] The Mulliken population analysis[45] for $Ni_{11}O_2$ gives an O ionicity of $-0.8e$ (electrons); this is only a rough guide to the ionicity since the population analysis involves significant artifacts.[24,46] If we assume that the charge on O is -1, a simple analysis would suggest a much larger change in μ between Ni_{11} and $Ni_{11}O_2$; the change would be $\Delta\mu_z = -2R = -2\times 1.57$ bohrs $= -3.1$ a.u. The actual change is much smaller because of a large polarization of the metal charge down from the surface;[26] this polarization reduces the overlap, and consequent Pauli repulsion of the metal and HO charge distributions and enhances the electrostatic attraction between Ni and O. The main point is that O chemisorbed on Ni(001) has a large negative charge; a reasonable description of its ionicity is O^{-q}, where q is large, $q \approx 1$.

In Table III, we give interaction energies and dipole moments for He approaching at the on-top position for both the *s*-only and *s* and *p* He basis sets. We consider first the *s*-only results. As the He atom is lowered from $z = 7.0$ to 6.0 bohrs, E_R increases from 11 to 46 meV. However, the ratio of $E_R/E_{\text{int}}(\text{RO})$ is approximately constant at ~ 0.3; this is why the FO and RO(*s* only) κ's are nearly the same, see Table I. An important consequence of the charge rearrangements which lead to E_R is given by μ_z; $\Delta\mu_z$ is the difference between the $Ni_{11}O_2He$ and the bare $Ni_{11}O_2$ values for μ_z. The dipole moments for He interacting with the $Ni_{11}O_2$ cluster are larger, less negative, than the bare cluster values. The charge associated with $Ni_{11}O_2$ is polarized away from the He, down below the surface, in order to reduce the overlap between the surface and He charge distributions, and the repulsion which arises from this overlap. With the *s*-only basis, the He charge can only contract radially to reduce the overlap; it cannot polarize. Such a contraction cannot change the dipole moment significantly. The Ni and O charge polarization is larger when He is closer to the surface because the overlap and consequent repulsion, as measured by $E_{\text{int}}(\text{FO})$, is larger. The larger polarization leads to larger E_R as z is made smaller. With the *s* and *p* He basis set, the He plus $Ni_{11}O_2$ μ_z increase less than they do with the *s*-only He basis. For all distances shown in Table III, the difference between the $Ni_{11}O_2He$ μ_z for the two basis sets is nearly constant at 0.013 a.u. This can be interpreted in terms of a polarization of He charge in addition to the polarization of the O/Ni(001) charge. The He charge becomes polarized away from the surface so that He has an effective dipole of -0.013 a.u. This polarization further reduces the overlap repulsion and leads to an electrostatic attraction between O^- and the induced He dipole. Thus E_R(*s* and *p*) is larger than E_R(*s* only). This additional He polarization leads to an increase in E_R which is inversely proportional to the distance of the He above the surface while E_{int} increases exponentially, see Eq. (3); this is the reason that the RO(*s* and *p*) κ is much larger than the RO(*s* only) and FO values.

Analogous results for E_{int}, E_R, μ_z, and $\Delta\mu_z$ for He in the center position are given in Table IV. We note first that, for comparable values of $E_{\text{int}}(\text{RO})$, the relaxation energy, E_R is a factor of 2 smaller than the on-top E_R when the E_{int} values are the same. The $\Delta\mu_z$ values for the *s*-only basis set are also smaller at the center position. Of course, in this geometry the O charge can be polarized along the [100] direction as well as into the surface; however, we have not measured this polarization. The smaller E_R and the smaller He *s*-only basis set $\Delta\mu_z$ both suggest that for He at this position the substrate, O/Ni(001), charge is less polarizable than at the on-top position. The E_R at the center position with the He *s* and *p* basis set is larger than with the *s*-only basis set as for the on-top position. However, the difference in μ_z due to the polarization of the He atom is much smaller than for the on-top position. This is because at the center position the He can be polarized laterally; this lateral polarization is not measured by μ_z. As for the on-top position, the polarization of the substrate charge as measured by the E_R for the *s*-only He basis is roughly a constant fraction of E_{int}; for this position, $E_R \approx 0.15 E_{\text{int}}(\text{RO})$. Thus, κ[RO(*s* only)] $\approx \kappa$(FO). The E_R due to the polarization of the He atom with the *s* and *p* basis depends strongly on the He-surface distance z; this distance dependence leads to a large increase in κ[RO(*s* and *p*)] over κ[RO(*s* only)]. For both He positions, the polarization of the He atom leads to a large increase in the hardness of the interaction over

TABLE III. The interaction energy, E_{int}, relaxation energy, E_R, and the dipole moment, μ_z, are given for SCF calculations, using both the *s*-only and *s* and *p* He basis sets, of He interaction with the $Ni_{11}O_2$ cluster at the on-top site. Also given is the change in the dipole moment, $\Delta\mu_z$, between the bare $Ni_{11}O_2$ cluster and the cluster with He present. Recall that for the on-top site the calculations were performed in C_{2v} symmetry for the cluster $Ni_{11}O_2He_2$ thus, the values of E_{int} given are one-half of the computed values.

He basis	z (bohr)	E_{int}(RO) (meV)	E_R (meV)	μ_z[a] (a.u.)	$\Delta\mu_z$ (a.u.)
s-only	5.5	330.1	104.0	-0.560	$+0.079$
	6.0	144.6	46.1	-0.591	$+0.048$
	6.5	66.6	21.7	-0.612	$+0.027$
	7.0	32.0	10.8	-0.624	$+0.015$
s and *p*	5.5	279.3	154.7	-0.574	$+0.066$
	6.0	103.6	87.2	-0.605	$+0.034$
	6.5	34.7	53.7	-0.653	$+0.014$
	7.0	7.3	35.5	-0.637	$+0.001$

[a] This value is computed as: $\frac{1}{2}[\mu_z(Ni_{11}O_2He_2)-\mu_z(Ni_{11}O_2)]+\mu_z(Ni_{11}O_2)$.

TABLE IV. The interaction energy, E_{int}, relaxation energy, E_R, and the dipole moment, μ_z, are given for SCF calculations, using both the s-only and s and p He basis sets, of He interaction with the $Ni_{11}O_2$ cluster at the center site. Also given is the change in the dipole moment, $\Delta\mu_z$, between the bare $Ni_{11}O_2$ cluster and the cluster with He present.

He basis	z (bohr)	E_{int}(RO) (meV)	E_R (meV)	μ_z (a.u.)	$\Delta\mu_z$ (a.u.)
s-only	5.0	190.2	31.0	−0.596	+0.043
	5.5	103.5	15.3	−0.612	+0.027
	6.0	57.0	8.0	−0.622	+0.017
	6.5	31.2	4.9	−0.629	+0.010
s and p	5.0	149.3	72.0	−0.595	+0.044
	5.5	71.5	47.4	−0.618	+0.021
	6.0	33.3	31.8	−0.633	+0.006
	6.5	13.8	22.5	−0.641	−0.002

the FO value.

IV. LIMITATIONS OF THE ESBJERG-NØRSKOV RELATION

The Esbjerg-Nørskov relation,[5] Eq. (1), is that the repulsive portion of E_{int} is proportional to the unperturbed surface charge density $\rho(x,y,z)$ at the position of the He nucleus, where α is the proportionality constant. It is also possible to consider a $\bar{\rho}$ suitably averaged over the He electrostatic potential[16] rather than the substrate density at the He nucleus. Batra and Baker[16] have shown that the use of ρ or $\bar{\rho}$ leads to small, approximately 15% changes, in E_{int}; this correction has been made[16] for precisely the system of interest here O/Ni(001). The relation of Eq. (1) has been used for virtually all theoretical analyses of He diffraction.[6,12–17] For a clean metal surface, Cu(110), Batra *et al.*[32] have tested this relation with cluster model calculations and have found that it holds reasonably well for this surface for both on-top and bridge positions of He. As we show below, this is not so for the interaction of He with O/Ni(001).

In Table V, we give values of α(FO), α[RO(s only)], and α[RO(s and p)] for both the on-top and center He positions for the same distances which we used for E_R and μ_z in Tables III and IV. The different values of α are those obtained with the appropriate interaction energies, E_{int}(FO), E_{int}[RO(s only)], and E_{int}[RO(s and p)] for α(FO), α[RO(s only)], and α[RO(s and p)], respectively. For either position, the values of α are roughly constant; the α[RO(s and p)] are constant within 10%. The deviation of the α[RO(s and p)] at the largest z in Table V for either He position is because these points are closest to the attractive part of the interaction, see Sec. III. Since the E_{int}[RO(s and p)] are our best estimates of the interaction energy, these results suggest that the Esbjerg-Nørskov relation[5] is, in fact, a reasonable way to obtain the interaction energy. However, there is a very important qualification; the values of α are very different for the two He positions. The value for the on-top position, $\alpha \approx 500$ eV bohr^3, is one-half as large as the center position, $\alpha \approx 1100$ eV bohr^3. The corrugation heights, ζ's, obtained with a single α for both sites would be different from that given with the two values of α.

The different values of α arise because the O/Ni(001) surface charge density contours are strongly corrugated with respect to the size of the He atom. This corrugation can be seen from Fig. 4 which shows the $Ni_{11}O_2$ charge contours; the points at 3.44 Å, on-top position, and 2.91 Å, center position, are the calculated points nearest to

TABLE V. The values of α computed from the Esbjerg-Nørskov relation using the SCF computed values for the interaction energy and charge density are given. The values are given both for the on-top and center sites at the three levels of approximation, FO, RO(s only), and RO(s and p). The He positions are the same as those used in Tables III and IV.

		α (eV bohr^3)		
He position	z (bohr)	α(FO)[a]	α[RO(s only)]	α[RO(s and p)]
on-top	5.5	770	590	500
	6.0	1000	760	540
	6.5	1260	950	490
	7.0	1430	1070	240
center	5.0	1570	1350	1060
	5.5	1950	1700	1170
	6.0	2170	1900	1110
	6.5	2130	1840	810

[a] FO with He s-only basis. Values with larger s and p basis set for He are essentially the same.

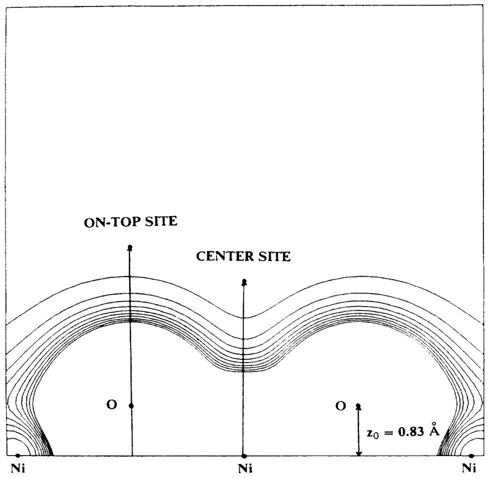

FIG. 4. The charge density contour plot for $Ni_{11}O_2$ is shown. The contours are given for a plane passing through the two oxygen atoms and the three Ni atoms lying along the [100] direction. The contour values are: maximum contour = 0.0095 a.u., minimum contour = 0.0005 a.u., and contour interval = 0.001 a.u., where 1 a.u. = electron/bohr^3. Also indicated are the positions where an incident He atoms would experience 100 meV repulsion for the on-top and center positions.

$E_{\text{int}}[\text{RO}(s \text{ only})] = 100$ meV; at the on-top position $E_{\text{int}} = 67$ meV and at the center position $E_{\text{int}} = 103$ meV. The corrugation is even more dramatically demonstrated in Figs. 5(a) and 5(b) which show the same contours for the $Ni_{11}O_2He$ SCF calculations. These contours have been computed with the He s-only basis set for the heights noted above. At the on-top position, the He charge density overlaps with the density of one O atom only; at the center position, the He charge density overlaps with the substrate densities due to both adsorbed O atoms and to the Ni atoms as well. The extent of the overlap can be estimated by drawing a line connecting the points on each contour where the density is changing from being dominated by He to being dominated by $Ni_{11}O_2$. This is shown as a dotted line in Figs. 5(a) and 5(b). The length of this line is a measure of the extent of the overlap of the He and O/Ni(001) charge distributions. A larger overlap means a larger repulsion. Clearly, the dotted line is considerably longer at the center position than at the on-top position. Thus the density at the He nucleus must be multiplied by a larger α at the center than at the on-top position to give E_{int}.

If a value of $\alpha = 750$ eV bohr^3, roughly the average of the RO(s and p) on-top and center values, is used, a somewhat larger ζ is obtained than with the direct calculation of the interaction energies. The classical turning points, z(on top) and z(center), and ζ for the Esbjerg-Nørskov relation with $\alpha = 750$ are given in Table VI; these should be compared with the directly calculated values which are given in Table II. The z(on top) calculated with this average α is slightly larger than the directly calculated RO(s and p) value; the z(center) is slightly smaller. The overall effect is that the corrugation with the average α is too large by approximately 0.15—0.20 Å. The ζ obtained with

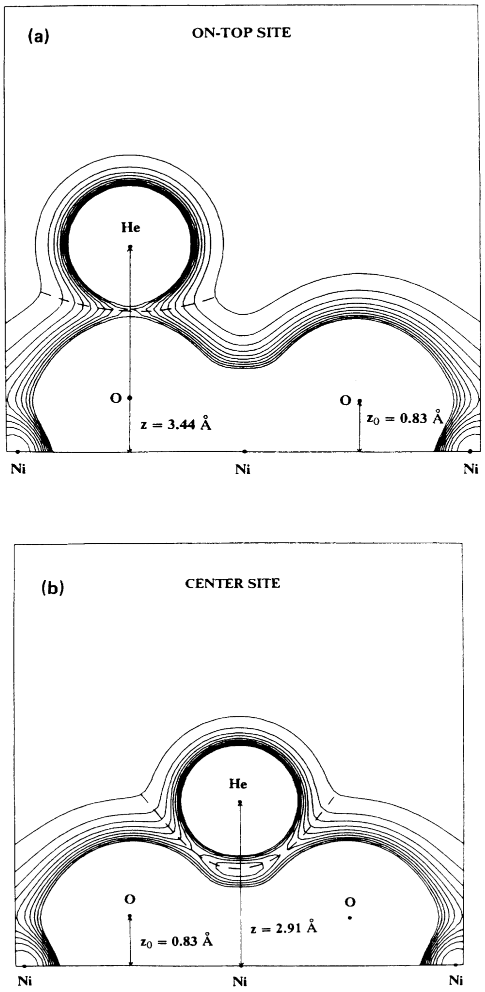

FIG. 5. (a) The charge density contour plot for $Ni_{11}O_2$ plus He at the on-top site is shown. The position of the He atom corresponds to 100 meV repulsion. The dotted line indicates schematically the length over which the He and the surface interact. The He has an s-only basis. See Fig. 4 for a description of the cluster orientation and contour values. (b) The charge density contour plot for $Ni_{11}O_2$ plus He at the center site is shown.

TABLE VI. The values of the classical turning points, z, for the on-top and center He positions are given for incident He atom energies of 100, 60, and 40 meV. The interaction energy is computed using the Esbjerg-Nørskov relation with an α value of 750 eV bohr^3. Also given are the corrugation heights, ζ, for the three incident energies. The uncertainties represent deviations in the least-square fitting and interpolation of the interaction energy curves, see Fig. 2.

	z (Å)		
E (meV)	z(on-top)	z(center)	ζ (Å)
100	3.29	2.68	0.61±0.02
60	3.43	2.86	0.57±0.03
40	3.52	3.00	0.54±0.03

the average α is qualitatively reasonable. Batra and Barker[16] used a single value of α with the Esbjerg-Nørskov relation to study the diffraction from O/Ni(001). They were able to show that the Upton and Goddard[40] proposal that at $c(2\times2)$ coverage the O was 0.25 Å above the surface was not at all consistent with the diffraction data. However, the ζ which we obtain with the average α is 50% larger than when the E_{int} are calculated directly; see Table II. Thus, the Esbjerg-Nørskov relation must be used with great caution for quantitative surface geometries; it probably cannot be used for this purpose when the surface change density is strongly corrugated as is the case for ionic adsorption.

V. COMPARISON WITH ATOMIC SUPERPOSITION

We carried out a number of calculations on various clusters starting with the $Ni_{11}O_2$ cluster used previously, see Fig. 1, using superposition of atomic charge densities to generate the cluster charge density. The basis sets used for constructing the atomic charge densities are the same as used to obtain the $Ni_{11}O_2$ cluster wave functions discussed in the previous sections. We focus on the constant charge density contour $\rho_0=3.4\times10^{-4}$ a.u. Using the Esbjerg-Nørskov relation, Eq. (1), with an α value[16] of 175 eV bohr^3, this contour corresponds to an interaction energy of 59.5 meV. Several conclusions can be drawn from these simple calculations.

First of all we studied the effect of systematically enlarging the cluster size on the corrugation height, ζ, along the [100] direction, beginning first with the $Ni_{11}O_2$ cluster and extending it to a semi-infinite slab. It was found that the corrugation height changed less than 5% between the $Ni_{11}O_2$ cluster and the semi-infinite slab. We also studied the effects of changing the ionicities of the atomic components on the resulting cluster charge density and hence on the corrugation heights. We found that the corrugation height was a sensitive function of the atomic (ionic) configuration chosen to generate the cluster charge density. Using neutral oxygen atom the corrugation was negligible in all cases. Ionic configurations, O(-1) and Ni($+0.5$) produced results closest to the experimental values, and those obtained from the $Ni_{11}O_2$ SCF cluster results.

The computed values of the corrugation height for a constant charge density contour ($\rho_0=3.4\times10^{-4}$) gave values of 0.27 Å for an oxygen height, z_0, of 0.83 Å. This value dropped to approximately 0.1 Å when oxygen atoms were pushed closer to the surface ($z_0=0.25$ Å). Thus even though the absolute value of the corrugation is not in very good agreement with the $Ni_{11}O_2$ SCF cluster results or with the experimental data, the relative change permits one to infer some information about the vertical height of the oxygen atoms above the surface. The softness parameter, κ, calculated using atomic superposition gave values of κ(on-top)$=2.8$ Å^{-1} and κ(center)$=2.2$ Å^{-1}. These values are in close agreement with those calculated above for the frozen orbital case, see Table I.

In Table VII we compare the SCF and atomically superposed charge density for the cluster $Ni_{11}O_2$ at the two different sites which were used for corrugation analysis.

TABLE VII. Cluster SCF and atomically superimposed charge densities for the on-top and center He positions.

z (bohr)	On-top SCF	On-top Atomic superimposed	Center SCF	Center Atomic superimposed
	Charge densities ρ (10^3 a.u.)			
5.0	1.640	1.979	0.141	0.636
5.5	0.561	0.844	0.061	0.360
6.0	0.190	0.375	0.030	0.204
6.5	0.070	0.179	0.017	0.116
7.0	0.030	0.091	0.010	0.065

We note that the SCF charge density above the surface is always below the atomic superposed values even though the decay parameters are quite similar. This is to be expected because the SCF calculations permit bond formation and rehybridization within the cluster; charge is removed from the vacuum region in order to do this. For atomic superposition, the cluster does not hold any preferential position over the vacuum region. Thus, it is not too surprising that the atomic superposition only gives semiquantitative values for the corrugation height and poor results for the corrugation shape.

VI. CORRUGATION CURVE

Finally, we present results for the relative corrugation heights along the [100] direction between the on-top and center sites. At the He positions away from these two high-symmetry points, we have only calculated the E_{int} in the FO approximation using the He s-only basis set; we have not obtained self-consistent solutions at these points. The FO corrugation curve is shown in Fig. 6 for the classical turning point for He atoms incident with 60 meV normal energy. The full width at half maximum (FWHM) of this curve is 1.86 Å. The FWHM of

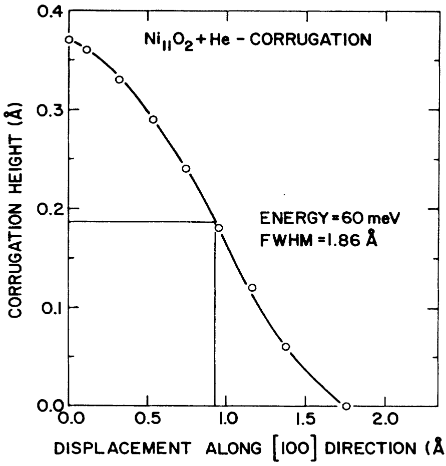

FIG. 6. The corrugation height, ζ, as a function of displacement along the [100] direction for an interaction energy of 60 meV is shown. The results are for a frozen orbital calculation of $Ni_{11}O_2He$ in C_s symmetry.

Rieder's[16] experimental data[18] for He atoms with a normal incident energy of 37 meV is 1.83 Å which is slightly smaller than our value. However, we recall that we have placed the O atom 0.83 Å above the Ni(001) surface which is closer than the experimental values[41,42] by between 0.03—0.07 Å and we have computed the FWHM for 60, not 37, meV. In our earlier discussion, see Sec. III, we noted that raising the O atom to a more correct, higher position, would be expected to lead to larger increases in the height of the classical turning point for He positions near the on-top site and smaller increases for positions near the bridge site. The effects of these changes should be a small decrease in the FWHM of the corrugation curve. We note that the charge contours about the O atoms shown in Fig. 4 have a reasonably circular shape. Thus, we find that there is no need to propose a prolate O charge distribution, as has been suggested by others,[16,18] in order to obtain reasonable agreement with experiment for the FWHM.

VII. CONCLUSIONS

In conclusion, we find that the FO interaction of He with a $Ni_{11}O_2$ cluster gives a very reasonable representation of the corrugation along the [100] direction for $c(2\times2)$ O/Ni(001). A RO, SCF, calculation leads to slightly smaller values for the corrugation height, ζ, with both the FO and RO results being in good agreement with experiment. We also find that the charge contours for $Ni_{11}O_2$ do not provide a good description of the magnitude or shape of the corrugation. The He atom is large with respect to variations of these charge contours. This has important consequences for the applicability of the Esbjerg-Nørskov relation. For a highly corrugated system such as O/Ni(001), we find that a single value of α cannot be used to accurately describe the interaction at different sites on the surface; i.e., between the on-top and center sites the value of α needs to differ by a factor of 2. We do find however, that if a single value of α is used in combination with a charge density constructed from a superposition of atomic charge densities, reasonably good values can be obtained for the corrugation height but not for the corrugation shape.

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