Proximity effects on semiconducting mineral surfaces II: Distance dependence of indirect interactions

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Abstract—In a previous study, we described proximity effects on surfaces of the semiconducting minerals galena and pyrite, whereby a chemical reaction at one surface site modifies the reactivity of a remote surface site several Ångstroms or even nanometers away (Becker et al., 2001). The modification of interest does not arise because of a direct “through space” interaction between the two sites, but rather an indirect interaction via the electronic structure of the substrate. Here we investigate the distance and direction dependence of proximity effects using quantum mechanical modeling. The direct and indirect interactions between co-adsorbed oxygen atoms and between adsorbed oxygen atoms and point defects on vacuum-terminated galena (100) surfaces were modeled. Density functional theory cluster and plane wave pseudopotential calculations were used to calculate the modifications to the adsorption energy as a function of separation. Energy-distance plots indicate that the proximity effect energy can become very strong at separations decreasing below about 5 to 6 Å, and persist at increasing separations up to 12 Å in a slowly decaying form. A strong attractive indirect interaction out-competes direct electrostatic repulsion for O-vacancy interactions. An oscillatory asymptotic behavior is found for co-adsorbed O-O indirect interactions, which indicates that the proximity effect energy can vary with surface crystallographic direction. It implies the presence of a strong organizing force on like adatoms that may explain the progressive oxidation of certain sulfide minerals by patchwork growth. These findings begin to pave the way for improved adsorption isotherms and extended surface complexation models that will include the specific influence of semiconductor-type proximity effects. Copyright © 2003 Elsevier Science Ltd

1. INTRODUCTION

Semiconducting minerals have narrow band gaps, giving them electronic characteristics that lead to surface properties that are distinct from insulating minerals. In a recent study, it was shown that these properties could facilitate an electronic interaction between spatially separated sites on galena (PbS) and pyrite (FeS2) surfaces (Becker et al., 2001). More specifically, what was therein termed the proximity effect entails the modification of the reactivity of a remote surface site in response to a reaction occurring at a site several Ångstroms or even nanometers away. The modification of interest does not arise because of a direct “through space” interaction between the two sites, but rather an indirect interaction through the electronic structure of the substrate. For example, in Becker et al. (2001), it was shown that oxidized surface Fe sites on pyrite (100) arising from exposure to O2 alter the electronic structure and therefore the reactivity of unoxidized neighboring Fe sites. With respect to continued oxidation, this indirect interaction creates a distinction between the behavior of unoxidized Fe sites near oxidized areas of the surface and those further away.

The broad-brush implication is that a local-site treatment of surface reactivity, for example in surface complexation theory, for these types of minerals can be incomplete and perhaps even misleading without taking proximity effects into account. Because of the ubiquity of semiconducting minerals and their important role as electron sources and sinks at the sediment-water interface (Luther et al., 1992; Calmano et al., 1994; Nimick and Moore, 1994), a potentially wide range of specific geochemical implications hinges on a better understanding, and preferably quantification or generalization of this effect. Yet the nature of this interaction and even more so to what extent it is amenable to generalization is currently poorly understood.

Therefore, we explore the matter further in this study. Here we apply quantum mechanical modeling to probe some fundamental proximity effect behavior on galena (100) surfaces, where modeling already suggests such effects can operate (Becker et al., 2001). We examine proximity effects occurring in the context of galena oxidation by oxygen, a process of known importance in acid mine drainage and the mobilization of lead in the environment (Durn et al., 1999; Zhang and Ryan, 1999; Younger, 2000), mineral separation technologies (Maier et al., 1997; Woods, 2000; O’Dea et al., 2001), and potentially important in precious metal deposition (Bakken et al., 1989; Starling et al., 1989). Previous experimental and theoretical studies have suggested or implied that the chemisorption of O2 on the surface is dissociative and that this dissociation is a step that precedes the oxidation of surface S atoms in air or under controlled exposures of O2 (Grandke and Cardona, 1980; Becker and Hochella, 1996; Eggleston, 1997). Our model system examines some possible indirect interactions involving chemisorbed O atoms occurring after dissociation of O2. We utilize vacuum conditions to simplify the interpretation of the modeling predictions and to increase the computational efficiency. Thus, our calculations have a narrow focus with respect...
to the overall oxidation process. The significance the current proximity effect findings may have in the overall oxidation process is not critically assessed at this time. Rather, our goal is simply to provide initial determinations of 1) how strong proximity effects can be; 2) whether they are attractive, repulsive, or both; 3) the length scales over which proximity effects are important; 4) if there is a dependence on the type of surface species involved; and 5) if there is a dependence on surface crystallographic direction. To address these issues, we calculate the distance and direction dependence of the proximity energy gains/losses ($E_{\text{prox}}$) which accompany the indirect electronic interaction of adsorbed $O$ atoms with surface $Pb$ vacancies, and the indirect interaction between co-adsorbed $O$ atoms. In the discussion of our results, we use as a backdrop what little is already known about indirect interactions between adsorbates at metal surfaces, recently reviewed by an (Becker et al., 1997).

In this way, we begin to progress towards a long-term goal of assessing the significance of proximity effects at the macroscopic scale of observation for the geochemically important process of sulfide mineral oxidation.

2. THEORETICAL METHODS

2.1. Cluster Calculations

A “$6 \times 4 \times 2$” PbS cluster (24 Pb and 24 S atoms, two atomic planes thick) was used to model the (100) surface. This was the largest computationally feasible cluster for our purposes. Geometry optimizations were performed at the Hartree-Fock and density functional theory (DFT) levels of theory using Gaussian98 (Frisch et al., 1998). The latter treatment was formulated using Becke’s three parameter hybrid DFT method (UB3LYP) (Becke, 1993), which includes both Hartree-Fock and DFT exchange, and the Lee-Yang-Parr correlation functional (Lee et al., 1988). Hay and Wadt type pseudopotentials have been applied for Pb and S with either a minimal basis set (LANL2MB) or a double-zeta valence basis set (LANL2DZ) (Hay and Wadt, 1985b; Hay and Wadt, 1985a; Wadt and Hay, 1985). The minimal basis set used for O was STO-3G (Hehre et al., 1969) and the double-zeta basis set used for O was the Dunning/Huzinaga type (Dunning and Hay, 1976). As mentioned later, the results using the minimal basis sets paralleled those using the double-zeta basis set, but we report only the results for the latter because it is well established that they are more accurate. Results using the minimal basis sets were used to preoptimize the geometry of the surface and of the adsorbates for the double-zeta basis set calculations. Various spin configurations were tested using the unrestricted HF and B3LYP methods, but diamagnetic configurations were found to be energetically favored, consistent with previous calculations on similar clusters (Becker and Hochella, 1996).

The vacuum terminations at the surfaces of the cluster other than the one of interest usually lead to unwanted edge effects which penetrate the cluster to some degree. Previous work has shown that edge effects in these calculations should only penetrate by 2 to 3 Å which means only the outermost edge atoms are significantly modified (Becker et al., 1997). Therefore, in this study, we avoid using the outermost edge atoms as adsorption sites. We also reduced edge effects by embedding the cluster in an array of point charges arranged on lattice positions surrounding the cluster (Becker et al., 1997). In the first layer around the PbS cluster, point charges were derived such that the electrostatic potential in and around the cluster is the same as for an infinite periodic slab. The method to derive these charges is described in (Becker et al., 1997). The point charges further away from the cluster were partial charges based on the computed Mulliken charges of the atoms in the interior of the cluster. Additionally, the adsorption sites for $O$ on clusters with and without a Pb vacancy were kept the same to help neutralize any remaining influence of edge effects by using a cancellation of errors strategy.

For geometry optimizations, while the position of adsorbed $O$ was optimized, surface atoms of the cluster were both allowed to relax and fixed in separate parallel runs to qualitatively determine if the energy gains due to the proximity effect are coupled to elastic deformation of the lattice. The proximity effect energy ($E_{\text{prox}}$) was defined using the following equations:

\[ E (\text{cluster} + \text{vacancy} + O) - [E (\text{cluster} + \text{vacancy}) + E (O)] = E_{\text{ads}} + E_{\text{Coul}} + E_{\text{prox}} \]  

\[ E (\text{cluster} + O) - [E (\text{cluster}) + E (O)] = E_{\text{ads}} \]  

where $E_{\text{ads}}$ is the adsorption energy of an O atom to the PbS surface without proximity effects. Subtracting the second quantity ($E_{\text{ads}}$) from the first gives the magnitude of the energy modification to the O adsorption energy due to direct electrostatic ($E_{\text{Coul}}$) interaction and indirect interaction through the substrate ($E_{\text{prox}}$) with the vacancy. We calculate the direct interaction $E_{\text{Coul}}$ by summing the pair-wise Coulombic interactions over all atoms in the cluster, using the Mulliken charges computed for the optimized clusters. We used the Mulliken charges to maintain consistency with charges directly obtainable for the periodic calculations using CASTEP, described below. On actual surfaces, charge transfer from the surface to the adsorbates leads to the development of dipole moments, which constitutes an additional form of direct interaction. It has been shown that the dipole-dipole interaction energy on metal surfaces should vary as $r^{-3}$ where $r$ is the separation (Kohn and Lau, 1976). In the final analysis, we found no basis for such behavior and have therefore chosen to neglect it. Furthermore, on actual surfaces, direct interactions can also derive from the polarizabilities of atoms leading to some of the van der Waals or dispersion interaction types (dipole-instantaneous dipole interactions, instantaneous dipole-instantaneous dipole interactions) (Einstein, 1996). However, because neither Hartree-Fock nor density functional theory include instantaneous dipole terms in their Hamiltonians (e.g., Wu et al., 2001), these kinds of direct interactions can be safely ignored in the interpretation of our modeling results. However, this does not imply that these kinds of interactions cannot be important components of the direct interactions possible in the real system.

2.2. Calculations using Periodic Boundary Conditions

Periodic bulk and surface structures were optimized at the gradient-corrected DFT level using the plane wave pseudopotential code CASTEP (Payne et al., 1992). The generalized gradient-corrected local spin density approximation (GGS) was
formulated using the Perdew and Wang (1992) parameterization of the exchange-correlation functional (Perdew and Wang, 1992), modified to work with plane wave calculations (White and Bird, 1994). We used the CASTEP parameterization of ultra-soft pseudopotentials (Vanderbilt, 1990) without core corrections. Pseudopotentials were generated using the local spin density approximation (LSDA) which means that the screening effect of the core electrons was modeled using LSDA whereas the screening effect of the valence electrons was modeled using GGS. This approach has been validated previously (Garcia et al., 1992). Optimizations were performed using a cutoff energy of 170 eV, which was facilitated by the use of ultra-soft pseudopotentials, and a conjugate gradient electronic minimizer using the density mixing scheme (Kresse and Furthmuller, 1996). We restricted the number of k-points at which to integrate over the Brillouin zone to the gamma point to make these calculations computationally manageable, a strategy which is routinely employed and typically successful for calculations with relatively large unit cells such as the surface slabs discussed below (e.g., Bridgeman et al., 1996; Chatterjee et al., 2000).

The atomic coordinates and cell parameters of bulk galena were optimized simultaneously in the absence of symmetry restrictions (i.e., in the P1 space group). The calculated bulk lattice spacing was 5.980 Å, a value in reasonable agreement with the experimental value of 5.914 Å (Noda et al., 1987). Slabs were then cut from optimized bulk structures and all atoms were allowed to relax using fixed optimal lattice parameters. The slabs were 1 × 4 bulk lattice spacings in lateral dimensions and two atomic layers thick. Plane wave pseudopotential calculations are periodic in three dimensions so slab models are generated by building in a vacuum layer along one dimension across which interaction between slab atoms is negligible or cancels (e.g., Rosso, 2001). It is well established that relaxation of the (100) surface structure involves only a slight vertical contraction of the uppermost atomic plane (<5% of the bulk lattice spacing) with minor rumpling of the Pb and S sublattices (relative offset ~ 1 to 2% of the bulk lattice spacing) (see review and references in Rosso, 2001). Optimization of all atomic coordinates in our slab models reproduces this behavior, suggesting that the two atomic layers in our models are sufficient to describe the majority of the relaxed surface structure. This is also evidence that the computational conditions (GGS, Ultra-soft pseudopotentials, 170 eV cutoff energy, etc.) are adequate to properly model this surface. Slabs were designed so that they would be similar for co-adsorbed O-O and O-vacancy calculations. The requirement for charge neutrality in the model, the desire to generate surface vacancies, and the computational limitations in slab size forced us to use non-centrosymmetric slab models. There is no net dipole moment for the slab model before O adsorption. Small dipole moments perpendicular to the slab may be present for models with a vacancy (a stoichiometric PbS unit) and/or adsorbed O. We use a vacuum layer approximately 10 Å thick.

We cannot rule out interactions across the vacuum layer, but, as was done for the clusters, a cancellation of errors strategy was used in calculation of \( E_{\text{Prox}} \) to negate any such effects. Because of the periodic treatment, the addition of adsorbed O or the creation of a vacancy in the slab cell creates rows of like features parallel to the short surface repeat dimension. There can be interactions within the rows, but because the spacing of features within a row is kept constant as the features are moved along the longer dimension, these interactions are not expected to affect the estimation of \( E_{\text{Prox}} \).

Calculation of \( E_{\text{Prox}} \) was performed similar to the method described above for the cluster case. For example, for the co-adsorbed O-O cases we used:

\[
E(\text{slab} + O_a + O_b) - [E(\text{slab}) + E(O_a)] = 2E_{\text{Adv}} + E_{\text{Coul}} + E_{\text{Prox}}
\]

\[
E(\text{slab} + O) - [E(\text{slab}) + E(O)] = E_{\text{Adv}}
\]

\( E_{\text{Coul}} \) is calculated by 3D Ewald sums using the Mulliken charges on the atoms. As mentioned previously, we used Mulliken charges to maintain consistency with the cluster calculations described above. To isolate the contribution of O-O or O-vacancy interactions to \( E_{\text{Coul}} \), we calculate the difference between \( E_{\text{Coul}} \) for the slab with and without adsorbed O’s, for example:

\[
E_{\text{Coul}}(\text{slab} + O + O) - E_{\text{Coul}}(\text{slab}) = E_{\text{Coul}}
\]

Small non-zero net charges on the unit cells were sometimes encountered in the sum of the Mulliken charges due to rounding errors, which had subtle effects on \( E_{\text{Coul}} \) and therefore introduced a rigid shift to \( E_{\text{Prox}} \). However, in the final analysis, because \( E_{\text{Prox}} \) was found to generally converge to zero at large distances, we normalized \( E_{\text{Prox}} \) to the \( E_{\text{Prox}} \) at the largest separations, all of which are greater than 10 Å.

3. RESULTS AND DISCUSSION

3.1. Cluster Calculations

A ball-and-stick model of the atomic arrangement used for the cluster calculations is shown in Figure 1. The bare stoichiometric cluster has a net neutral charge, which is modified to −2 by removal of a Pb atom to create a vacancy. The adsorbate O is added as a neutral atom with no unpaired spins (i.e., to mimic an initial product of dissociatively adsorbed \( O_2 \)). The position of the O atom was energy optimized at four different starting separations from a Pb vacancy (labeled \( v_1 \) to \( v_4 \)). Avoiding the outermost atoms because the possibility of edge effects, the cluster setup limited the maximum separation to ~ 9 Å.

![Fig. 1. A ball-and-stick model of the “6 × 4 × 2” PbS cluster used in the cluster calculations, showing one position of an O atom (black ball) and the Pb\(^{2+}\) vacancy. Pb atoms are dark gray and S atoms are light gray balls.](image)
Optimized O positions are shown in Figure 2. The O atom finds various local minima depending on the particular surface “hollow” adsorption site in which it initially starts. In each hollow, the optimized O takes on a bridging configuration between Pb and S atoms (Fig. 2), similar to previous theoretical predictions (Becker and Hochella, 1996).

The drive to fill the O octet is matched by a relative ease of removing electrons from this reducing surface, leading to electron transfer to the adsorbed O and oxidation of S atoms in the cluster. The reducing power of the PbS cluster is enhanced somewhat by the absence of a Pb$^{2+}$ surface ion which leaves atoms around the vacancy (hereafter referred to as simply the vacancy) negatively charged (formally $-2$) and imparts an electron excess in the cluster. The balance of electron affinity of the O atom and the S atoms in the cluster yields a net negative charge on the O atom that is approximately $-0.70$ (HF)/$-0.92$ (B3LYP) without the vacancy by the Mulliken method. With the vacancy, the O charge varies with distance from $-0.92$ (HF)/$-0.72$ (B3LYP) at the smallest separations to $-0.71$ (HF)/$-0.66$ (B3LYP) at the longest separations. For the cases with the vacancy, most of this charge derives from S atoms surrounding the Pb vacancy. This charge transfer from the S atoms around the vacancy to the O causes the strong chemisorption of the O atom to the surface.

The principle challenge in these calculations is to isolate the O-vacancy indirect interaction energy that is mediated by the substrate ($E_{\text{Prox}}$). The indirect interactions are typically accompanied and potentially masked by direct interactions, especially where adsorption is accompanied by charge transfer. All possible direct interactions must be accounted for properly before the indirect interactions can be accurately assessed. Because both the adsorbed O atoms and the vacancy are negatively charged, direct electrostatic repulsion between the two ($E_{\text{Coul}}$) is superimposed on the indirect interaction energy (Fig. 3). In our calculations, the direct Coulombic interaction is taken as the only direct interaction of consequence (see Methods section). Therefore we are forced to estimate $E_{\text{Coul}}$ (see Methods section), which differs from the available calculations reported elsewhere because in those cases the systems considered do not involve nearly as much charge transfer from the surface to sorbates (Lau and Kohn, 1978; Feibelman, 1989; Gumhalter and Brenig, 1995; March, 1995; Bagehorn et al., 1996).

Optimized O-vacancy separations and relevant energies are listed in Table 1. The HF and DFT predictions show similar trends in many respects, but because of the inclusion of electron correlation effects in the latter, the DFT results are favored in the remaining analysis. The DFT energy-distance relationships

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Table 1. Calculated distance-energy data for the O-vacancy interaction using cluster calculations at the Hartree-Fock and density functional levels of theory with a double-zeta pseudopotential basis set.

<table>
<thead>
<tr>
<th>Run</th>
<th>Separation (Å)</th>
<th>Total Energy (eV)</th>
<th>$E_{\text{Ads}}$ (eV)</th>
<th>$E_{\text{Coul}}$ (eV)</th>
<th>$E_{\text{Prox}}$ (eV)</th>
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<td>HF</td>
<td></td>
<td></td>
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<tr>
<td>$cv_1$</td>
<td>4.40</td>
<td>$-391.256$</td>
<td>$-2.48$</td>
<td>$-0.65$</td>
<td>$-0.29$</td>
</tr>
<tr>
<td>$cv_2$</td>
<td>5.85</td>
<td>$-391.220$</td>
<td>$-1.51$</td>
<td>$1.05$</td>
<td>$-0.98$</td>
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<tr>
<td>$cv_3$</td>
<td>7.72</td>
<td>$-391.230$</td>
<td>$-1.78$</td>
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<td>$-0.38$</td>
</tr>
<tr>
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<td>$-391.224$</td>
<td>$-1.61$</td>
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<td>B3LYP</td>
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<tr>
<td>$cv_1$</td>
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<td>$cv_2$</td>
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<td>$-3.81$</td>
<td>$0.20$</td>
<td>$-0.17$</td>
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</table>
are plotted in Figure 4. We chose the convention that a negative (positive) sign on $E_{\text{Coul}}$ or $E_{\text{Prox}}$ indicates the O-vacancy interaction yields a net energy decrease (increase) and is therefore attractive (repulsive). $E_{\text{Coul}}$ is found to be continually higher in energy than $E_{\text{Prox}}$, and therefore $E_{\text{Prox}}$ must be negative in sign and an attractive interaction (Fig. 4a). $E_{\text{Coul}}$ is increasingly repulsive as the O-vacancy separation is decreased, until the smallest separation upon which $E_{\text{Coul}}$ becomes slightly attractive. Remarkably, the magnitude of $E_{\text{Prox}}$ is significant enough to overcome $E_{\text{Coul}}$ repulsion even at large separations. $E_{\text{Prox}}$ is found to be largest at the smallest O-vacancy separations, and decays to smaller values with increasing distance (Fig. 4b). This indirect interaction is also found to be quite long range, spanning further than 1.5 surface lattice constants ($\sim - 9$ Å). We elaborate on these observations further after discussing the results of the periodic calculations. It is interesting to note that $E_{\text{Coul}}$ would be even more repulsive between the negative Pb$^{2+}$ vacancy and the negative adsorbed O if formal charges were used to calculate $E_{\text{Coul}}$. The scheme used here to calculate $E_{\text{Coul}}$ leads to weaker repulsive forces because (1) the Mulliken charges of bulk Pb and S are less than their formal charges and (2) even more so because part of the wavefunction information (and thus, part of the proximity effect) is already contained in the Mulliken charges around the cluster and the adsorption site.

This is another indication of the strong attractive proximity effect in this example.

In our calculations, minimal basis sets were mainly used to preoptimize the geometry of the surface and of the adsorbates for the more accurate double-zeta basis set calculations. The trend for the results of $E_{\text{Prox}}$ calculated using minimal basis sets is similar to the results of double-zeta basis sets but the absolute values of $E_{\text{Prox}}$ are on the order of 20% higher. As described in the Methods section, edge effects penetrate the cluster by only 2 to 3 Å, and edge effects on the calculation of proximity energies are further reduced by comparing the O-vacancy interaction energy with adsorption energies of O at the respective position on the cluster. Therefore, using point charges around the cluster (see Becker et al., 1997) causes a correction of less than 5%. Due to the computational expense of full geometry optimizations of the PbS surface for each possible O position on the surface, we cannot present a complete analysis of $E_{\text{Prox}}$ as a function of surface relaxation. For the calculations that we performed using full geometry optimization, we found that the effect of surface relaxation on the trend of $E_{\text{Prox}}$ is small because surface relaxation is relatively small on PbS (Becker and Hochella, 1996; Becker et al., 2001). In addition, as will be argued below, $E_{\text{Prox}}$ is mainly an electronic effect and, thus, more dependent on the electronic structure.

3.2. Calculations using Periodic Boundary Conditions

The general slab model used in the periodic calculations is shown in Figure 5. The long surface repeat dimension is used as the principal axis for determining the distance dependence of $E_{\text{Prox}}$. The slab models increased the useable separation range to $\sim 12$ Å. The various models were designed to determine 1) the interactions between an adsorbed O atom and a vacancy for comparison with the cluster results; and 2) to determine the interactions between co-adsorbed O atoms on the surface. In the former case (O-vacancy), the vacancy used was a stoichiometric PbS vacancy to maintain a charge neutral cell. This vacancy involves removal of a Pb atom from one surface of the slab and the S atom directly beneath it. The surface of the slab used was that having the missing Pb atom. Two types of O-vacancy series were run (Fig. 6). One series involved later-
ally restricting adsorbed O to an on-top binding configuration over surface Pb sites ($v^*_{1 \text{ to } 4}$), and in the other series adsorbed O was allowed all degrees of freedom during optimization ($v_{1 \text{ to } 4}$). These models provide cases where two different degrees of interaction between surface and adsorbed O atoms are considered because, in the on-top case, the O atom is bound to the surface by just one Pb-O bond and, in the bridging case, the O atom is bound by one Pb-O bond and one S-O bond. For

Fig. 6. Top views of the periodic slab models for O-vacancy interactions showing the optimized positions of adsorbed O atoms in on-top ($v^*_{1 \text{ to } 4}$) and bridging ($v_{1 \text{ to } 4}$) configurations (see Fig. 1 caption for legend). In the on-top configuration, O was confined laterally to surface Pb positions and allowed to optimize in height along the surface normal direction ($v^*_{1 \text{ to } 4}$). As for the cluster optimizations, fully optimized O positions ($v_{1 \text{ to } 4}$) were bridging configurations with two bonds to the surface, one each to a Pb atom and S atom.
the O-O interactions, two different series were also run (Fig. 7). Two lines of surface hollow sites were available along the principal axis. One series involved O-O aligned in a single line, and the in other the O atoms were staggered into the two lines. These two models were designed to elucidate direction dependences in $E_{\text{prox}}$. Collectively, the various models afforded a better basis for interpretation of the proximity effects.

All of the charge transfer processes described for the cluster calculations are operative in each of the periodic calculations. Adsorbed O draws charge from surface S atoms, leading to
negatively charged O atom(s) equivalent to $-0.8$ according to the Mulliken method. For co-adsorbed O-O models, both O atoms are negative and a repulsive direct electrostatic interaction can be expected. The same is true for the O-vacancy models as the part of the vacancy closest to adsorbed O atoms is negatively charged. These direct interactions have to be accounted for so that the energy of indirect interaction can be evaluated. In this regard, the periodic treatment has an advantage over the cluster treatment in that edge effects are not present, but on the other hand, the periodic treatment introduces the possibility for undesirable interactions to accumulate across unit cell boundaries (Fig. 8). We have attempted to eliminate any such effects by adopting a cancellation of errors strategy (see Methods section).

Optimized O-vacancy separations and calculated values for $E_{\text{prox}}$ are listed in Table 2 and the $E_{\text{prox}}$-distance relationships are plotted in Figure 9. Indirect O-vacancy interactions show a uniformly attractive behavior that increases in magnitude as the separation becomes smaller, consistent with the predictions of the cluster calculations (Fig. 9a). In this regard, the periodic and cluster calculations predict very similar behavior for O atoms adsorbed in a bridging surface structural configuration. The periodic treatment improves the development of the distance dependence by adding points at both shorter and longer range. The attractive interaction is non-zero even as far as two surface lattice constants and therefore is remarkably long-ranged ($\sim 12$ Å). Figure 9a also shows that the attractive interaction becomes significantly stronger at close proximities. In fact, surprisingly, the magnitudes of $E_{\text{prox}}$ approach values on the order typical of chemisorption bond strengths at separations less than 4 Å, suggesting the possibility that seemingly dissociated surface adsorbates may be in effect “bonded” to each other through the substrate.

The distance dependence of indirect O-vacancy interaction does appear to depend on how tightly bound the O atom is to the surface (Fig. 9a). For O adsorbed in a relatively weakly bound on-top configuration at surface Pb sites, the distance dependence can be described as shifted out of phase with respect to the behavior for O adsorbed in a more strongly bound bridging configuration. Interestingly, it turns out that the direction of the shift is somewhat counterintuitive, as the more weakly adsorbed O case shows a stronger indirect interaction with the vacancy than does the case where O is more tightly bound to the surface. From this behavior, we conclude that the strength of indirect interaction has little to do with the strength of interaction between adsorbates and surface sites, in this case in terms of number of bonds to the surface, and more to do with specific locations on the surface.

The indirect interactions between co-adsorbed O atoms (models $a_{1\text{-}4}$ and $s_{0\text{-}4}$) show behavior that is similar to O-vacancy interactions on the whole, with an exception that derives from the crystallographic direction dependence of the interaction across the surface (Fig. 9b). For the case where co-adsorbed O atoms are aligned into a single line of surface hollow sites (models $a_{1\text{-}4}$), the distance dependence of $E_{\text{prox}}$ is quite close to that for the bridging O-vacancy indirect interaction. It differs primarily by the fact that $E_{\text{prox}}$ shows a slightly positive region between $\sim 6-10$ Å, equating to a repulsive indirect interaction between co-adsorbed O atoms at long range. But like the bridging O-vacancy interaction, the aligned O-O interaction becomes rapidly attractive as the separation between the interacting constituents decreases. For the staggered O-O interactions, where adsorbed O atoms are offset into
Table 2. Calculated distance-energy data for the O-vacancy and co-adsorbed O-O interaction on galena (100) using plane wave pseudopotential methods and periodic slab models. The aligned O-O interaction refers to O-O configurations which parallel cubic surface directions, whereas the staggered configurations are along different diagonals. The on-top O-vacancy interaction refers to adsorbed O laterally constrained in an on-top configuration on surface Pb sites, whereas the bridging configuration refers to the more energetically favorable binding structure for O on the surface.

<table>
<thead>
<tr>
<th>Run</th>
<th>Separation (Å)</th>
<th>Total Energy (eV)</th>
<th>E_{prox} (eV)</th>
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<tr>
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Collectively, we find that both the cluster and periodic model results highlight several key characteristics of indirect interactions on galena surfaces. The two primary categories of interactions, O-vacancy and O-O indirect interactions, show similar behavior overall, having a very strong attractive energy of interaction as the separation is reduced below ~ 5-6 Å. Except in one instance, the indirect interaction is significantly weaker at distances greater than approximately 6 to 7 Å and the energy modification slowly decays toward zero. There is a strong change in the magnitude of the interaction with surface crystallographic direction, and a relatively subtle change arising from changing the degree of interaction of adsorbed O with the surface.

Indirect interactions through the substrate have three possible origins. The coupling between the interacting species is mediated by either electronic states at the surface, elastic deformation of the lattice, or surface vibrations (Einstein, 1996). In adsorption experiments, determining which coupling processes are operative is non-trivial. In the calculations in this study, we only have to consider the first two because vibrational motions have not been treated in the calculations.

An indirect interaction mediated by elastic deformation of the lattice derives from the possibility that the adsorption of one atom to a surface (or the creation of a vacancy) can deform the nearby surrounding lattice and thereby modify the adsorption energy of subsequent adsorbates in that vicinity. For example, suppose that an adsorbate exerts a net expansion (contraction) of atoms neighboring the adsorption site, causing contraction (expansion) of next nearest neighbor sites. A second like atom adsorbed to a nearest neighbor site will attempt to do the same but will have to undo the contraction (expansion) induced by the former atom at that site. Thus, for like adsorbate atoms, this indirect interaction is always positive and therefore repulsive (Zangwill, 1988). Furthermore, for like adsorbates on metal surfaces, it was shown that the interaction energy arising from elastic coupling varies as $r^{-3}$, where $r$ is the separation between the adsorbates (Lau and Kohn, 1977).

In our periodic surface optimizations, the adsorption of O to the galena surface in a bridging configuration at a surface hollow site is predicted to cause an expansion of the atoms defining the hollow site accompanied by contraction of the next nearest neighbors. In Figure 10, we have plotted the predicted deformations in terms of the series of eight sequential Pb-S
Elastic deformation due to the presence of the vacancy propagates differently than adsorbed O, and therefore we note that the interaction of adsorbed O atoms and vacancies through indirect interactions of the elastic type. However, as argued above, this interaction must be repulsive and precede suggests that it should mimic an $r^{-3}$ distance dependence. Therefore, elastic indirect interactions clearly cannot be the dominant type of interaction leading to the $E_{\text{prox}}$ behavior shown in Figure 9b, especially in the small O-O separation range. For O-vacancy indirect interactions, elastic deformation of the lattice is also a possible coupling mechanism (Fig. 10b). Elastic deformation due to the presence of the vacancy propagates differently than adsorbed O, and therefore we note that the interaction of adsorbed O atoms and vacancies through deformation of the surface is not restricted to be repulsive (Lau and Kohn, 1977). However, it can be seen that while there is a significant difference in the magnitudes of the elastic deformation of Pb-S bond lengths for the bridging O-vacancy and on-top O-vacancy cases (Fig. 10b), there is a disproportionately small difference in the corresponding behaviors of $E_{\text{prox}}$ (Fig. 9a). Based on these arguments and those presented above, we assess elastic coupling as at most a minor mechanism underlying the energy of indirect interaction exhibited in the distance dependence of $E_{\text{prox}}$. We cannot rule out elastic coupling altogether.

Therefore, we deduce that the indirect interactions are primarily mediated by electronic states at the galena surface. Electronic coupling is the most common form of indirect interaction and has been observed routinely for adsorbates on metal surfaces (Einstein, 1996). In the case of metals, indirect electronic interactions between adsorbates are typically observed to have certain characteristics. The interaction energy typically has an oscillatory behavior that asymptotically approaches zero rather slowly with the distance of separation across the surface, usually varying as $r^{-5}$ (Lau and Kohn, 1978; Gumbalter and Brenig, 1995). This behavior has been understood based on the phenomenon known as Freidel oscillations, which are standing wave oscillations in the charge density at the surface in response to the presence of an adsorbate (Zangwill, 1988). Constructive (deconstructive) overlap of Freidel oscillations induced by separate like adsorbates leads to attractive (repulsive) interactions in much the same way as described above for elastic coupling through the substrate. However, in our case, the distance dependence of $E_{\text{prox}}$ shown in Figure 9 does not take on the functional form observed for indirect electronic interaction on metal surfaces. It is similar only in the sense that oscillatory behavior is possible. At the same time, true Freidel oscillations are well-documented only on metal surfaces, whereas galena is a semiconductor with a moderately-sized band gap ($\sim 0.4$ eV). Freidel oscillations on semiconductor surfaces have not been convincingly documented (vanderWielen et al., 1996; de Kort et al., 2001; see also discussion in Ebert, 2001).

Based on the above discussion, we find that although our theoretical results suggest that indirect interactions are mediated by electronic states at the galena surface, when combined with the relatively sparse literature base on indirect interactions on semiconductor surfaces the results are not compelling enough to draw a conclusion on the possible role of Freidel oscillations in this matter. Clearly however, long-range electronic “communication” is being mediated by orbitals at the surface. Examples depicting that this can be so are found by plotting orbital isosurfaces for the “frontier” orbitals (i.e., the highest occupied and lowest unoccupied orbitals) on the periodic slabs (Fig. 11). Such maps show that orbitals associated with adsorbed O and vacancy states on the surface are smeared out over many of the atoms in the repeat cell over long ranges. We hypothesize that the reach of such orbitals between separate interacting species is sufficient to facilitate indirect electronic interactions over nanometer distance scales.

### 4. IMPLICATIONS

The results have many general implications for surface chemistry on semiconducting minerals, with some potentially relevant surface geochemical systems already mentioned in (Becker et al., 2001). These include a host of possible metal adsorption and electron transfer reactions at semiconducting
mineral surfaces. Indirect electronic interaction occurring between spatially separated adsorbates over nanometer scales is a relatively new concept in geochemistry which may lead to improved treatments of surface reaction modeling, site-specific reactivity, and adsorption isotherms on semiconducting mineral surfaces. Here we briefly expand previously reported implications with more specifics.

In particular, we note the importance of the possibility for oscillatory adsorption energy gains/losses with separation during oxidation/reduction of mineral surfaces. The well-established observation that pyrite (100) surfaces initially oxidize in a patchwork manner has not been sufficiently explained (Eggleston et al., 1996; Rosso et al., 1999). An autocatalytic effect was proposed to explain the birth and spread of oxidized Fe$^{3+}$ sites across the surface based on the possibility that oxidation of a surface Fe$^{2+}$ site could be more facile through existing adjacent Fe$^{3+}$ sites (Eggleston et al., 1996). Oxidation of an Fe$^{2+}$ site would then be statistically related to the probability that an oxidant impinging and diffusing on the surface encounters an adjacent Fe$^{3+}$ site. Based on the current study, it seems possible that the observed segregation of oxidation products across the surface could also be explained in part by an attractive proximity effect energy which modifies the probabilities of oxidation of Fe$^{2+}$ sites near Fe$^{3+}$ sites, and possibly even drives adsorbed oxidant species together (see also Becker et al., 2001). Because the magnitude of the attractive force can be on the order of chemisorption bond strengths, presumably it can out-compete the tendency of bonds with the surface to keep the adsorbate fixed during surface diffusion. The differences between these two possible mechanisms of patch formation are subtle and not necessarily mutually exclusive. The proximity effect mechanism relies on a surface physical property as a basis for patch growth, whereas the autocatalytic mechanism relies on a site encounter probability.

The shapes of the patches are also observed to exhibit crystallographic control at their peripheries (Rosso et al., 1999). In this study, we showed that the proximity effect energy is variable with surface direction. In the autocatalytic mechanism, crystallographically controlled patch shape is a result of the possible nearest neighbor complements of Fe$^{3+}$ sites around Fe$^{2+}$ sites in the cubic Fe sublattice. Therefore, both the proximity effect mechanism and autocatalytic mechanism provide possible explanations for the observed shapes of oxidation patches.

A more general implication of proximity effects, especially for the adsorption of redox-active species, is a requirement for appropriate adsorption isotherms to be applied which incorporate indirect interactions in their formulation. Adsorption isotherms that allow for adsorption energy modification arising from adsorbate/adsorbate interactions already exist. For example, direct interactions are incorporated into the Fowler isotherm and indirect interactions are accounted for in the Tempkin isotherm (Adamson, 1990; Masel, 1996). The latter assumes that the adsorption energy is modified linearly with surface coverage due to indirect adsorbate/adsorbate interactions, an untested assumption here. From our results, it is impossible to determine the coverage dependence of the adsorption energy, forming a next logical step for future work in this area. However, it is obvious that a hybrid of the Fowler/Tempkin types may be the most appropriate isotherm for the current system as it will have to include separate terms arising from both direct and indirect interactions.

5. SUMMARY AND CONCLUSIONS

Collectively, the cluster and periodic model calculations have predicted the distance dependence of indirect interactions between spatially separated species on galena (100) mediated by electronic states at the surface. The proximity effect energy can become very strong at separations decreasing below \( \sim 5 \) to \( 6 \) Å, and persist at increasing separations up to \( \sim 12 \) Å in a slowly decaying form. DFT cluster and periodic treatments converged on similar predictions for the distance dependence behavior of the proximity effect energy. An attractive indirect interaction is predicted for both O-vacancy and co-adsorbed O-O surface species, the largest magnitude of which is on the order of chemisorption bonds to the surface. Thus, in a sense, the separated interacting species are in effect bonded to each other through the substrate at small separations. The proximity effect is also predicted to show a dependence on crystallographic direction across a surface and on the nature of the adsorbate-surface bonding interaction. It also implies the pres-
ence of a strong organizing force on like adatoms that may explain the progressive oxidation of certain sulfide minerals by patchwork growth.

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