Ab initio study of STM-induced vacancy formation on the MoS_2 surface

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Abstract. The *ab initio* projector augmented wave technique has been used to study the STM-induced extraction of single atoms from the surface of MoS$_2$. The STM tip is represented by a cluster of molybdenum atoms and bias effects are introduced by adding a linear external potential (constant electric field) to the total self-consistent potential of the system. It is found that the calculated barriers against extraction of Mo and S atoms from the surface with a tip–sample separation of 8 au (4.2 Å) are too large to explain the reproducibility of atom-extraction experiments on the surface. In fact, from these calculations, local surface temperatures around 1600 K and 5100 K would be required to extract S and Mo atoms respectively at the rates apparent in the experiments. Since it is highly unlikely that such temperatures are achieved, other mechanisms must be contributing to the extraction process and the various possibilities are discussed.

1. Introduction

The invention of the STM by Binnig and Rohrer [1] in the early 1980s has been followed by an explosion of activity focusing on the study of surfaces and the processes which occur at them. Perhaps one of the most exciting abilities imparted by the STM is that to modify a surface on the atomic scale [2–8]. The transition-metal dichalcogenide materials (TX$_2$ where T represents a transition metal from groups IVB, VB or VIB, and X represents one of the chalcogens S, Se or Te) have become popular surfaces upon which to carry out such modification studies [2–5] owing to their useful physical and chemical properties. The TX$_2$ can form in many structures [9], but they all have the same basic form—hexagonal layers of metal atoms sandwiched between two hexagonal layers of chalcogen atoms are stacked vertically in a Van-der-Waals-bonded layered structure. The variety arises from the choice of possible stacking sequence, and the existence of buckled-layer structures, as seen in, e.g., WTe$_2$ [5, 9]. As a result of the layered structure, atomically flat surfaces with very low defect densities can be produced by cleaving.

Heckl *et al* [10] have shown that it is possible to remove single sulphur atoms from the surface of MoS$_2$ by voltage pulsing with the STM tip. In a similar way, Fuchs *et al* [2, 3] have created nanometre scale features such as trimers of peaks and monatomic holes, suspected to be due to monatomic vacancies [11, 12], on the surface of WSe$_2$ and MoS$_2$ [13]. Similar features can also be observed (and presumably created) on the surface of WTe$_2$ [5].

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Hosaka *et al* [4] have gone one step further and have etched nanometre scale characters into the MoS_2 surface by selective removal of S atoms. However, despite the ease with which atoms can be removed from these and other surfaces, the exact nature of the processes occurring during atom extraction is not known.

It is possible to modify conventional field-evaporation theory [14] to include the effect of the STM tip [15] and this can give a reasonable approximation to the critical tip bias required for atom extraction to occur. However, this does not provide great insight into the actual extraction mechanism. Lang [16, 17] has studied the effect of electric field on the transfer of an Al atom between two jellium electrodes and shows that the close proximity of the tip and sample, combined with the electric field, can remove the transfer barrier. Hirose and Tsukada [18] have performed calculations related to the transfer of Al atoms from the Al surface to an Al tip. They found that as the tip–sample bias is increased, the effective barrier to tunnelling electrons reduces, eventually reaching the point where a ballistic current can flow. Again, the atom-transfer barrier is removed when a sufficient bias is applied. Salam *et al* [19] have studied the effect of coherent multiple excitations on the desorption of adsorbates on systems where there is a negative-ion resonance near the Fermi level (as for Xe on Ni(110)). They show that coherent effects are important in the regime where the frequency of tunnelling events is smaller than that of the atomic vibrations (i.e., the low current regime). Avouris *et al* [20] have been using the STM to selectively remove H atoms from the H-passivated Si(100) surface. The dominant mechanism here is argued to be excitation of Si–H σ electrons into the σ^* orbital, in which state the Si–H potential is repulsive, causing the H to dissociate.

It would seem then, that there are a number of potential contributing factors to the extraction process, and that their relative importance is, unsurprisingly, dependent on the system under study. So far, no calculations have been presented related to the STM-induced extraction of atoms from partially ionic surfaces such as the TX_2. The purpose of this article is to report *ab initio* electronic-structure calculations on the MoS_2 surface in the presence of an Mo-cluster tip and an applied external electric field in an attempt to gauge the importance of the tip and field in the atom-extraction process. A preliminary report of this work is already at press [21].

2. Method

The electronic-structure calculations were performed using the *ab initio* projector augmented wave (PAW) technique developed by Blöchl [22]. The PAW technique combines the augmented plane wave and pseudopotential techniques [23] such that the all-electron wavefunctions are calculated (i.e., the self-consistent potential is obtained from the full valence charge, including the core-region oscillations) enabling treatment of traditionally difficult elements such as the transition metals. The current implementation of the PAW method is based on density functional theory (DFT) within the local-density approximation (LDA) [24] and utilizes the Car–Parrinello algorithm [25] for dynamics and relaxation. Ness and Fisher [26] have included the possibility of adding a smooth saw-tooth potential (equivalent to introducing a planar 'capacitor') to the total potential, thereby simulating the effect of a constant external electric field across the simulation cell.

In the calculations, the MoS_2 surface was approximated by a 3×3 cell single slab of material. The single-slab approximation to a surface is justifiable with TX_2 [27] where the interlayer interactions are small, and has been successfully used in other calculations [12, 27, 28]. The tip consisted of a five-atom molybdenum cluster in the geometry obtained by relaxing from the bulk bcc structure subject to the constraint that the four atoms remain
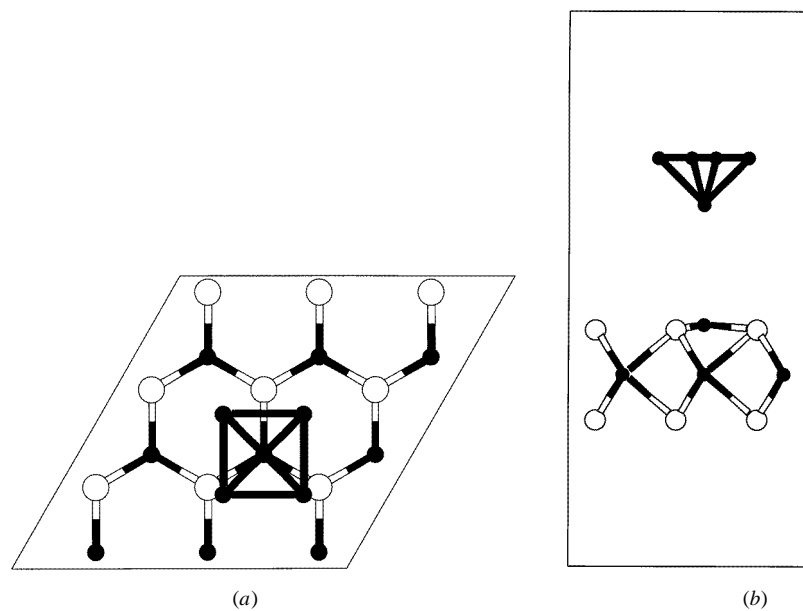
(a)   (b)

Figure 1. The simulation cell used for the atom-extraction calculations from various viewpoints. The tip here is positioned 11 au (5.82 Å) away from the surface Mo plane above an Mo atom which has been moved 3.0 au towards the tip. The position of the tip and atom below the tip will vary depending on the simulation.

in a plane, and was positioned with the apex atom directly over either a surface Mo or S site. Throughout the calculations, the tip and surface were held fixed in their (separate) equilibrium geometries—no further, e.g., tip-induced, atomic relaxation was allowed. The smooth parts of the electron wavefunctions were described by plane waves up to a cutoff of 15 Ryd and only the Γ point of the reciprocal cell was considered.

For all calculations which included an electric field, a field magnitude of 0.015 au (0.772 V Å^{-1}) directed towards the tip (i.e., a tip negative bias to extract preferentially positive ions) was used. For the tip–sample separations considered this gives a nominal tip negative applied bias of around 3.3–4.5 V depending on the points of reference; the bias used in the surface-modification experiments on MoS$_2$ was 5 V (tip negative) [4].

Figure 1 shows the full tip–sample cell with the tip positioned over a Mo site 11 au (5.82 Å) away from the surface Mo plane (the Mo atom below the tip apex has been moved towards the tip—see below). A c dimension of 36 au (19.05 Å) was used in the simulations—figure 2 shows schematically the relative sizes of the slab, tip and the vacuum gaps between them. With the tip apex positioned 11 au from the Mo plane, the distance between the base of the tip and the image-surface sulphur atoms (from periodic boundary conditions) is ∼19 au (10 Å). Also shown is the position of the 'capacitor' used to generate the external field (where applicable).

Atom-extraction barriers were calculated for extraction of both Mo and S atoms from the surface, with and without the external field. In each case, the tip is positioned 11 au above the atom to be extracted (also 10 au for sulphur), and the atom is then moved in steps (of 0.4 or 0.8 au) towards the tip apex in a straight line. No atomic relaxation is allowed in the main calculations, but several support calculations were carried out (e.g., to determine the equilibrium tip–adsorbate separation) which are described where relevant.
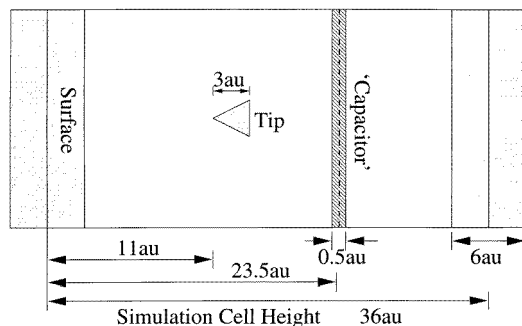
Figure 2. Schematic diagram of the simulation cell showing the sizes of the slab, tip and vacuum gap regions. The dotted line shows the plane of the electric-field cutoff (midway between the tip base and the lower side of the surface). This leaves a distance separating the cutoff from the tip base and the surface of 9.5 au (5.03 Å).

3. Zero-field atom extraction

3.1. Atom extraction barriers

Figure 3 shows the calculated barriers against extraction of single sulphur and molybdenum atoms from the MoS_2 surface. The barriers are obtained from the difference in total energies between the systems in their ground state and the systems with one surface atom displaced towards the tip. 'Ground state' here refers to the electronic ground state with the tip and surface held in their preferred atomic configuration when separated—no further atomic relaxation was allowed in the barrier calculations (actually, full tip and surface relaxation starting from the tip and surface in their separate equilibrium structures resulted in a lowering in energy of only 10^{-4} au). Shown are two extraction barriers for sulphur, one with the tip at 10.0 au and the other with the tip at 11.0 au from the Mo plane, and one barrier for molybdenum extraction with the tip at 11.0 au.

The sulphur-extraction barriers will be considered first. The first thing which becomes apparent is the separation dependence of the barrier. With the tip apex at 11.0 au (i.e., ≈ 8.0 au from the surface sulphur plane) there is a second minimum at 6.8 au associated with the extracted sulphur atom being adsorbed on the tip. In fact, this minimum occurs at the equilibrium tip–sulphur separation (4.17 au (2.21 Å) corresponding to a sulphur position of 6.83 au on the graph) calculated in the absence of the surface assuming the sulphur atom remains on a line perpendicular to the tip through the apex. The barrier prior to the tip-adsorption minimum, which must be overcome for transfer of the S atom from the surface to the tip, has a maximum at an energy of 0.14 au (3.81 eV). However, with the tip positioned one atomic unit closer to the surface (i.e., ≈ 7.0 au from the surface sulphur plane), the barrier has been removed and there is no longer a minimum associated with the atom adsorbed on the tip.

The vanishing of the barrier maximum for the smaller tip–sample separation is a result of the fact that the sulphur is still bound to the surface at the equilibrium tip–sulphur separation and seems to imply that atom extraction could not occur at this tip–sample separation. This conclusion is, however, potentially misleading as it is important to appreciate that figure 3 is really a one-dimensional cut through a three-dimensional potential barrier. A calculation of the full 3D barrier would be extremely costly (both in terms of time and storage) using the PAW technique and, it turns out, largely unnecessary. Support calculations have been
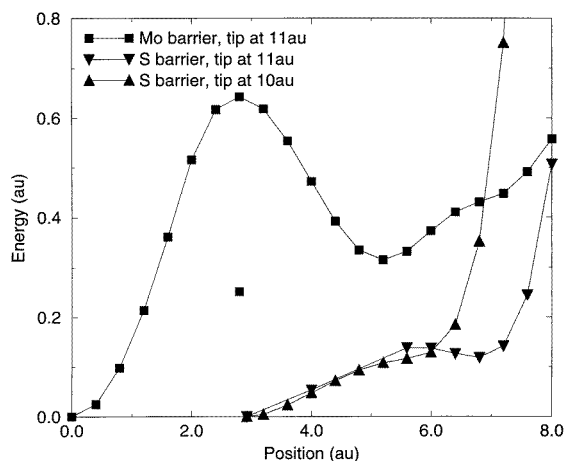
Figure 3. Barriers against extraction of single molybdenum and sulphur atoms from the MoS$_2$ surface in the presence of a tip, but no applied bias. The large peak in the Mo extraction barrier is a result of the lack of atomic relaxation in the simulation. The single point shows the effect of full surface relaxation with the extracted atom at the barrier peak (i.e., in the plane of the surface sulphur atoms)—in this adiabatic limit, the peak disappears. See text for further discussion.

carried out on the tip with a sulphur atom adsorbed on it (i.e., no surface) designed to illuminate the 3D structure of the barrier. These calculations showed that the tip–adsorbate potential is very flat in the plane perpendicular to the tip at the equilibrium tip–sulphur separation. Also, allowing the sulphur atom to relax fully around the fixed tip lowered the system energy by 0.086 au (2.34 eV) relative to the energy at the equilibrium separation on the tip apex. On the other hand, there is almost no surface relaxation about a sulphur vacancy in the absence of a tip. This implies that there is a minimum associated with the extracted atom adsorbed on the tip, but it lies off the chosen line, and that the barrier would not be significantly reduced by allowing surface relaxation. The most likely trajectory of an extracted sulphur atom is along the straight line towards the tip apex up to or near the point of equilibrium separation, whereupon the atom will 'slide' around the side of the tip. Hence it is still possible that sulphur atoms could be extracted even for the lower tip–sample separation with an effective barrier against extraction given approximately by the value of the barrier at the equilibrium tip–sulphur separation, i.e., 0.11 au (3.00 eV).

The molybdenum extraction barrier shown is that with the tip placed at 11.0 au from the Mo plane and has a different form to those for sulphur extraction. The barrier is much higher than that against sulphur extraction (a fact confirmed by experiment [13]), and there is a large peak (height 0.64 au) located at $z = 2.8$ au from the Mo plane, i.e., almost in the plane of the surface sulphur atoms (at 2.92 au). This large peak is a result of the fact that atomic relaxation was not allowed in the calculations and corresponds to the Mo atom 'squeezing' through the surface S layer. A separate calculation involving only the surface with the Mo atom placed 2.8 au away from its equilibrium position, which also allowed atomic relaxation, resulted in a lowering of system energy by 0.339 au (9.24 eV). The single point in figure 3 shows the effect the surface relaxation would have on the barrier—if the Mo atom were extracted adiabatically from the surface (i.e., if the calculation allowed full atomic relaxation), the large barrier would be totally removed.

As the extracted Mo atom approaches the tip, the potential curve starts to resemble that

for extraction of sulphur with the tip placed at 10 au, i.e., there is no minimum associated with the atom being adsorbed on the tip. The equilibrium tip–molybdenum separation was found to be 4.02 au (2.13 Å), which corresponds to a z position of 6.98 au on figure 3. However, as noted above, the lack of a minimum does not necessarily imply that atom extraction is not possible at this separation. Calculations on the tip with a molybdenum adsorbate show that the tip–Mo potential is flat in the plane perpendicular to the tip, through the equilibrium tip–Mo separation. Also, full relaxation of the molybdenum adsorbate around the tip lowered the energy by 0.15 au (4.1 eV) relative to its equilibrium position above the tip. The conclusion, then, is the same as before: it should be possible to extract Mo atoms at this tip–sample separation, and the effective barrier is approximately that at the equilibrium tip–Mo separation, i.e., 0.44 au (12.0 eV).

Table 1 summarizes the barriers against extraction of molybdenum and sulphur atoms with the tip at 11 au from the Mo plane and compares them to the calculated evaporation energies. The presence of the tip has reduced the energy required to extract atoms from the surface by a factor of two.

Table 1. Barrier height against extraction of single Mo and S atoms from the MoS_2 surface in the presence of a tip (apex 11 au from surface Mo plane) compared to the energy required to evaporate a neutral atom from the surface. The tip effectively halves the barrier.

|	Barrier height (au (eV))	Evaporation energy (au (eV))
S	0.14 (3.81)	0.31 (8.45)
Mo	0.44 (12.0)	0.83 (22.6)

Assuming that the atom-extraction process is thermally activated, the equation

$$\kappa = \nu \exp\left(\frac{-\Delta E}{k_B T}\right) \tag{1}$$

can be used to estimate either the extraction probabilities for a given temperature or the temperatures required for a given extraction rate. Here κ is the extraction rate, ν is an assumed effective 'attempt frequency' (but in reality may include other terms such as entropy), ΔE is the barrier height, k_B the Boltzmann constant and T the temperature. The attempt frequency ν is estimated by fitting a parabola to the bottom of the extraction barrier in figure 3. At 300 K the calculated rate of atom extraction is far too low ($\kappa \leqslant e^{-100}$ s^{-1}) for the process to occur in any experiment. Table 2 shows the calculated oscillation frequencies and the local temperatures required to extract atoms at rates of 10^3 and 1 s^{-1}. These temperatures are much higher than those likely to occur on the surface [29] leading to the conclusion that the presence of the tip alone cannot account for the reproducibility of the atom-extraction experiments.

3.2. Bond breaking and gap-state formation

Figure 4 shows the total charge density of the atom-extraction systems, both with the tip and sample in their perfect positions, and with the extracted atom moved to the equilibrium tip–adsorbate separation. The slice is taken in a vertical plane through the tip apex and extracted atom—this plane does not go through any of the base atoms of the tip. The figure shows in a qualitative way how the atoms become detached from the surface and bond to the tip.
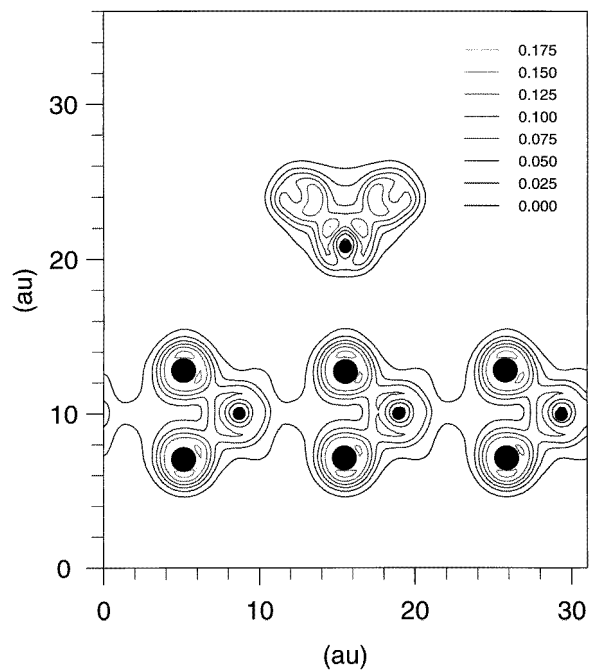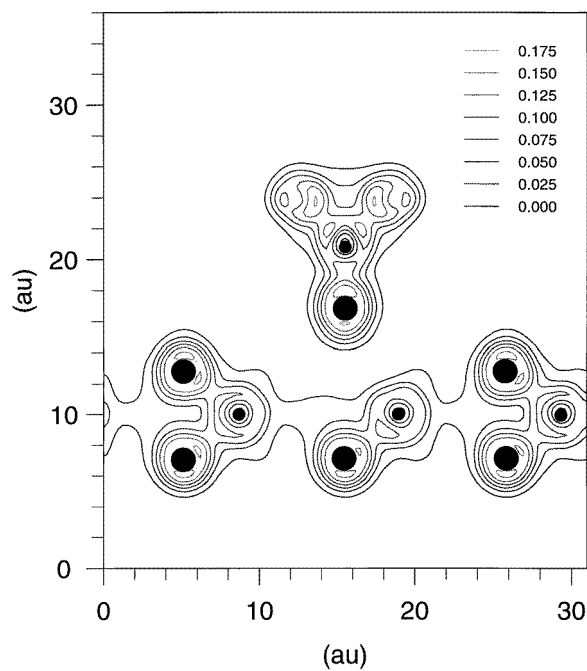
Figure 4. Total charge density in a vertical plane through the tip apex and along the Mo–S bonds for (*a*), (*b*) sulphur extraction, and (*c*), (*d*) molybdenum extraction with the tip at 11 au. Sulphur extraction with the tip at 10 au results in images very similar to those of (*a*) and (*b*).
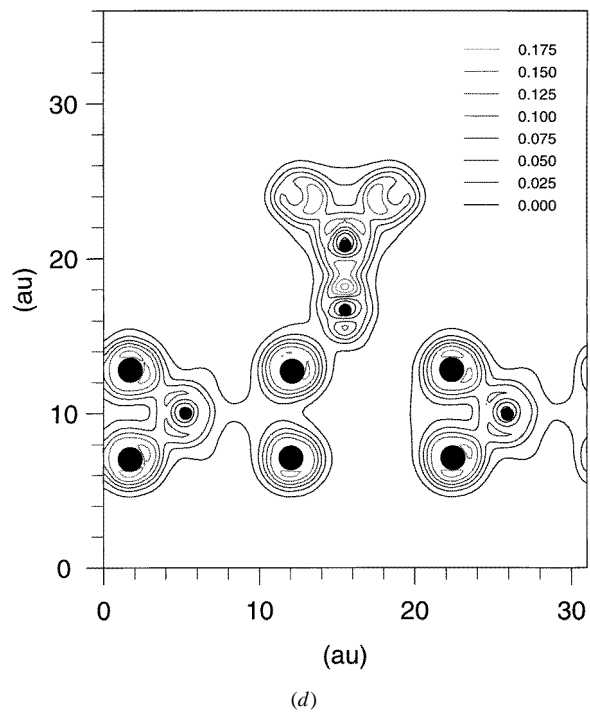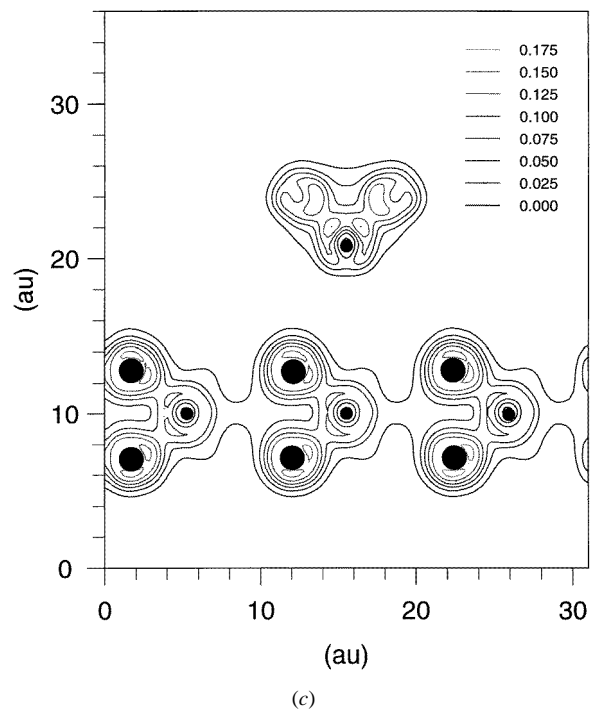
(*c*)

(*d*)

Figure 4. Continued.

Table 2. Local surface temperatures required to extract sulphur and molybdenum atoms from the MoS$_2$ surface based on the zero-field barrier heights in table 1 and the assumption that the atoms oscillate in a harmonic potential with the frequencies given (calculated from the barriers in figure 3).

Atom type	Oscillation frequency ($\times 10^{12}$ Hz)	Extraction rate (s^{-1})	Required surface temperature (K)
Sulphur (tip at 10 au)	9.1	10^3	1500
		1	1200
Sulphur (tip at 11 au)	9.1	10^3	1900
		1	1500
Molybdenum (tip at 11 au)	8.7	10^3	6000
		1	4600

The authors have previously reported PAW simulations on vacancy defects on MoS$_2$ (and MoTe$_2$) [12] and showed that the introduction of a vacancy into the MoS$_2$ surface resulted in electronic states appearing in the surface band-gap which could be associated with the dangling bonds. For the current simulations which include a tip, these states will not necessarily appear in the band-gap (i.e., they may not be the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO respectively)) since the states associated with the metallic tip tend to have higher eigenvalues than those of the surface. However, it is possible to find states which closely resemble the gap-states observed in the surface-only calculations and observe the formation of the 'gap-states' as the atoms are removed (figure 5).

3.3. Electronic potential as a function of tip–sample separation

In section 3.1 it was determined that the close proximity of the tip to the sample has a large effect on the barrier against removal of atoms from the surface. The electron barrier should also be affected in the same way; for example, Hirose and Tsukada [18] have shown that the effective barrier for electrons tunnelling between an aluminium tip and surface vanishes at small tip–sample separations. Figure 6 shows the self-consistent electronic potential in a line along the z axis through the tip and an Mo atom for different tip–sample separations. This potential is not, strictly speaking, that seen by tunnelling electrons as it does not include the image potential and the DFT potential does not necessarily match the actual electronic potential (although it usually does a good job in bulk materials). However, the reduction in the height of the barrier with decreasing tip–sample separation will be similar to the reduction of the tunnelling barrier height under the same circumstances. Figure 6 shows that the barrier height has been reduced by 0.06 au (1.6 eV) by a tip movement of 1.25 au (0.661 Å).

4. Field effects

4.1. Extraction barrier in finite field

Section 3 reported PAW calculations on the extraction of molybdenum and sulphur atoms from the surface of MoS$_2$ and concluded that the atom-extraction process cannot be explained purely in terms of the tip lowering the atom-extraction barrier. Those calculations
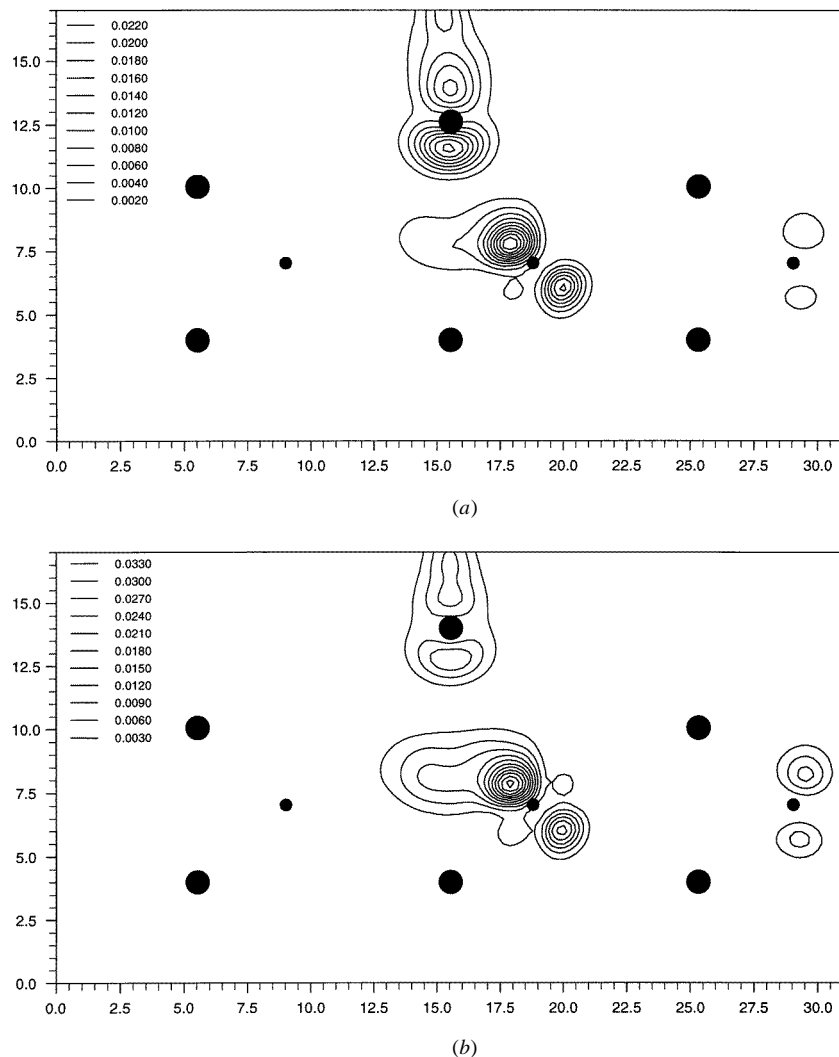
(*a*)

(*b*)

Figure 5. Charge-density contours for selected electronic states as (*a*), (*c*) a sulphur and (*b*), (*d*) a molybdenum atom are extracted from the surface of MoS_2. z_X (X = Mo or S) is the z position of the atom being extracted from the surface (perfect surface positions: $z_S = 2.92$ au and $z_{Mo} = 0.0$ au). As the extracted atom is moved further from the surface, the states start to resemble closely the 'gap-states' in [12]. The slice is in the vertical plane through the vacancy site and the Mo–S bonds.

included a tip, but did not take into account the fact that the tip is held at a different electrostatic potential to the surface. Extraction of sulphur from the MoS_2 surface, for example, is typically carried out by pulsing the tip at -5 V relative to the surface at a tip–sample separation less than or around 5 Å.

The PAW method relies on periodic boundary conditions and is a purely static calculation as far as the electrons are concerned (i.e., there can only be one Fermi level at equilibrium). It is therefore not possible to hold the chemical potential of the tip at a value different to that of the sample. However, it is possible to simulate the effect by applying a constant
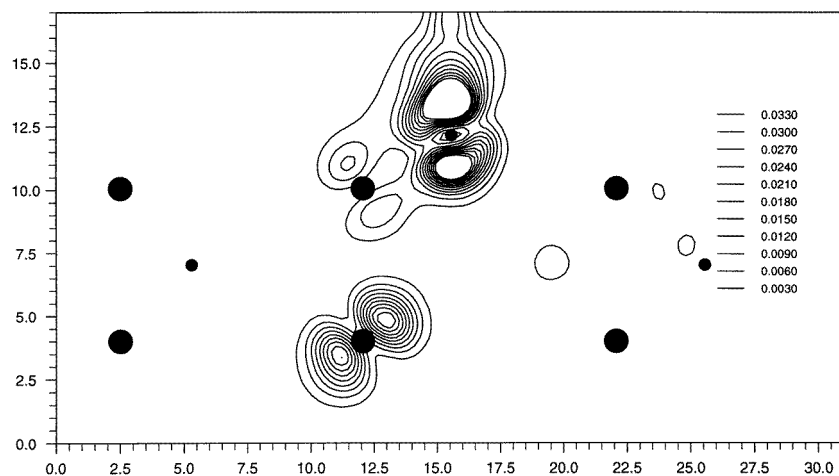
(c)
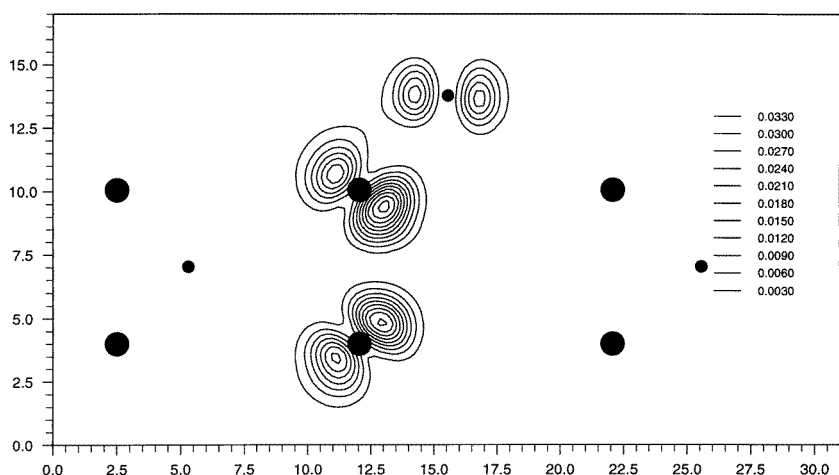
(d)

Figure 5. Continued.

electric field to the system [26]. The system simulated here uses an applied field of 0.015 au (0.77 V Å⁻¹) with the tip apex 11.0 au (5.82 Å) away from the surface molybdenum plane. Taking 8.0 au (4.23 Å, the tip–sulphur separation) as the tip–sample separation, the implied electrostatic potential difference between the tip and sample is −3.3 V (tip negative with respect to surface).

Figure 7 shows the barriers against extraction of Mo and S atoms from the MoS₂ surface with an external applied field of 0.015 au (0.77 V Å⁻¹) in a direction which would attract positive ions to the tip (tip apex at 11.0 au). Also shown for comparison are the zero-field barriers previously shown in figure 3. As before, the single point shows the effect that surface relaxation would have on the zero-field barrier maximum in the Mo-extraction barrier (i.e., for adiabatic atom extraction, the barrier is removed). The figure shows that the application of an external electric field lowers the effective barrier against the extraction
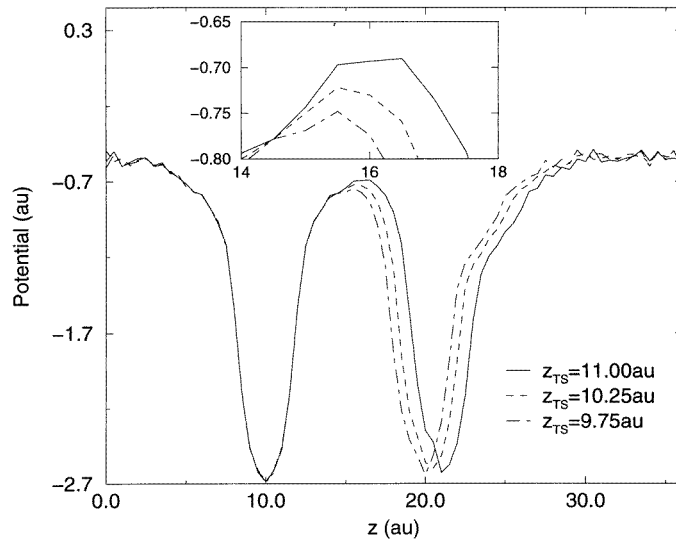
Figure 6. Self-consistent electronic potential in a vertical line through the tip apex and a Mo atom with the tip and surface in their separate equilibrium structures. The inset shows a magnified view of the barrier peak—the barrier height reduces by 0.06 au (1.6 eV) when the tip is moved 1.25 au (0.661 Å).
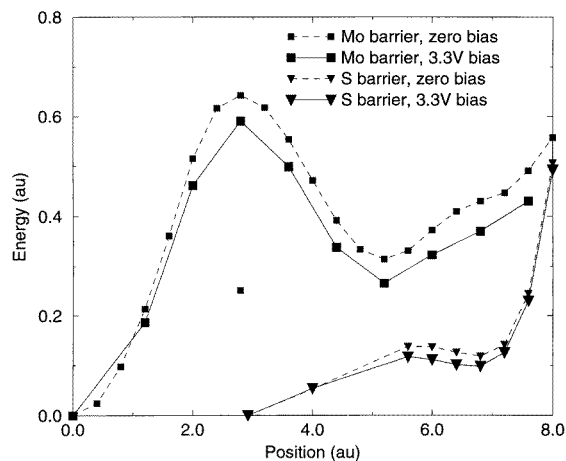

Figure 7. Barriers against extraction of single molybdenum and sulphur atoms in the presence of a 0.015 au (0.77 V Å^{-1}) electric field and tip compared to the barriers without the field. The single point shows the effect of surface relaxation on the zero-field molybdenum-extraction barrier peak at 2.8 au. The tip apex is located at 11.0 au.

of both types of atom from the surface. For the case of sulphur extraction, the barrier is lowered from 0.14 au (3.81 eV) without the field to 0.12 au (3.26 eV) with the field—a reduction of 14%. The effect on the molybdenum extraction barrier (ignoring the initial peak at $z = 2.8$ au) is to lower it by 16% from 0.44 au (12.0 eV) without the field to 0.37 au (10.1 eV) with the field. (See section 3.1 for assumptions about the 3D potential barrier and the effective barrier height.)

Following section 3.1, the temperatures required to extract S and Mo atoms from the surface can be estimated (equation (1)). Table 3 shows the calculated local surface temperatures required to extract S and Mo atoms at rates of 10^3 and 1 s^{-1} in the presence of a 0.77 V Å^{-1} electric field with the oscillation frequencies taken as those assumed in the zero-field calculations (see table 3). Although the electric field has reduced the local temperature required to remove atoms from the surface, the temperatures are still too high to be produced in a typical STM modification experiment. Therefore the atom-extraction process depends on more than just the presence of the tip and the bias-induced electric field effects. Further discussion is deferred to section 5.

Table 3. Local surface temperatures required to extract sulphur and molybdenum atoms from the MoS$_2$ surface for extraction rates of 10^3 and 1 s^{-1} in the presence of an electric field.

| Atom type	Extraction rate (s^{-1})	Required surface temperature (K)
S	10^3	1600
	1	1200
Mo	10^3	5100
	1	3900

4.2. Polarization charge and electric field

The reason behind the application of an electric field to the tip–sample system was to investigate the effects of the relative tip–sample bias on the barrier against atom extraction from the MoS$_2$ surface. The question is, does the system behave in the same way as a real STM tip and sample arrangement under an applied bias? The problem, as already mentioned, is that the PAW method does not allow for the existence of two distinct Fermi levels as in a real system where a net current flows. In the static calculation with a field, the tip and sample, which initially are at different electrostatic potentials owing to the electric field, will exchange charge in such a way that the Fermi levels equalize, removing the electrostatic potential difference.

This feature can be seen in the barriers shown in figure 7: the energy separations between the curves with and without the field for both Mo and S extraction remain constant whilst the atom is within the 'vacuum' region. There are two possible explanations for this phenomenon: either the atom being extracted has no net charge (cf Lang [17] where the net charge on an Al adsorbate atom moved between two closely spaced jellium electrodes attained a maximum value of 0.1 e); or there is no electric field within the gap region (or both may be true). Integrating the charge around the tip and sample (before atom extraction begins) shows that the tip has donated a further 0.8 electrons to the surface as a result of the applied field (to give a net charge transfer of 0.9 e).

Figure 8 shows the polarization charge densities (total charge of the system with the field minus the total charge of the system without the field) for the sulphur and molybdenum extraction systems. Figure 9 shows the difference in electrostatic potentials for the tip–sample systems with and without a field (the gradient of which is the electric field across the cell) for the tip placed above a sulphur and a molybdenum site. These figures show that the tip apex and upper surface are not polarized, and that there is no net electric field in the vacuum gap, as one would expect to occur in the STM under an applied field.

The depolarization and field-screening effects described above are the static-limit
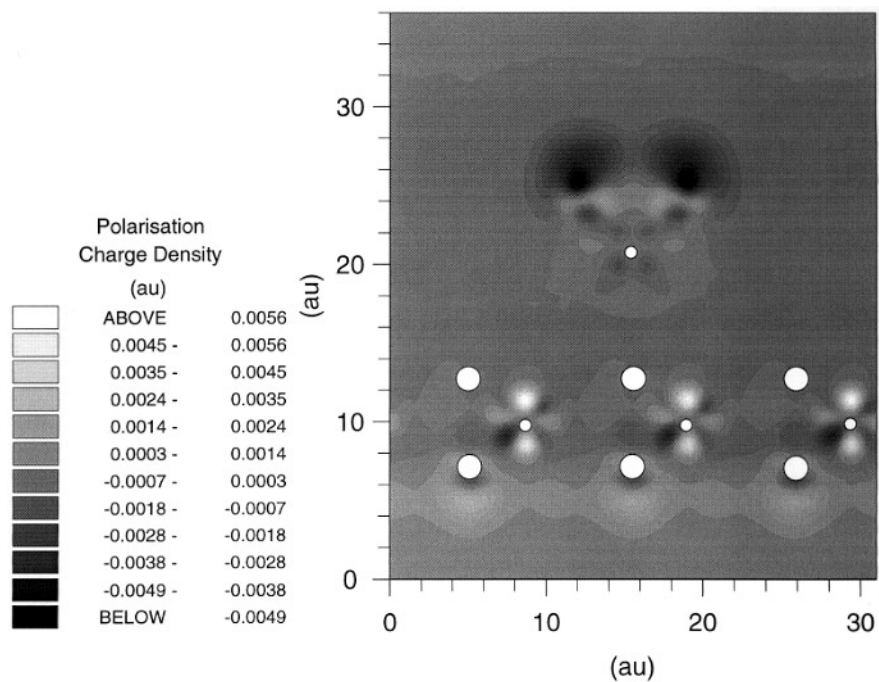
(*a*)
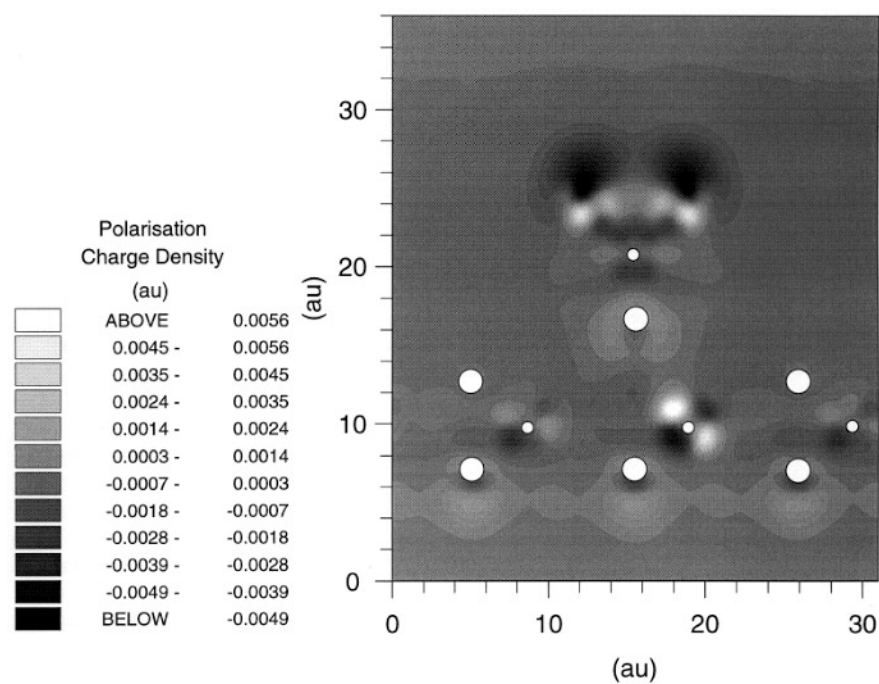
(*b*)

Figure 8. Polarization charge density for MoS_2 in the presence of a Mo tip and an applied field of 0.015 au (0.77 V Å^{-1}) at various stages as sulphur (*a*), (*c*) and molybdenum (*b*), (*d*) atoms are removed from the surface.

Polarisation
Charge Density
(au)

ABOVE	0.0056
0.0045 -	0.0056
0.0035 -	0.0045
0.0024 -	0.0035
0.0014 -	0.0024
0.0003 -	0.0014
-0.0007 -	0.0003
-0.0018 -	-0.0007
-0.0028 -	-0.0018
-0.0039 -	-0.0028
-0.0049 -	-0.0039
BELOW	-0.0049

(c)

Polarisation
Charge Density
(au)

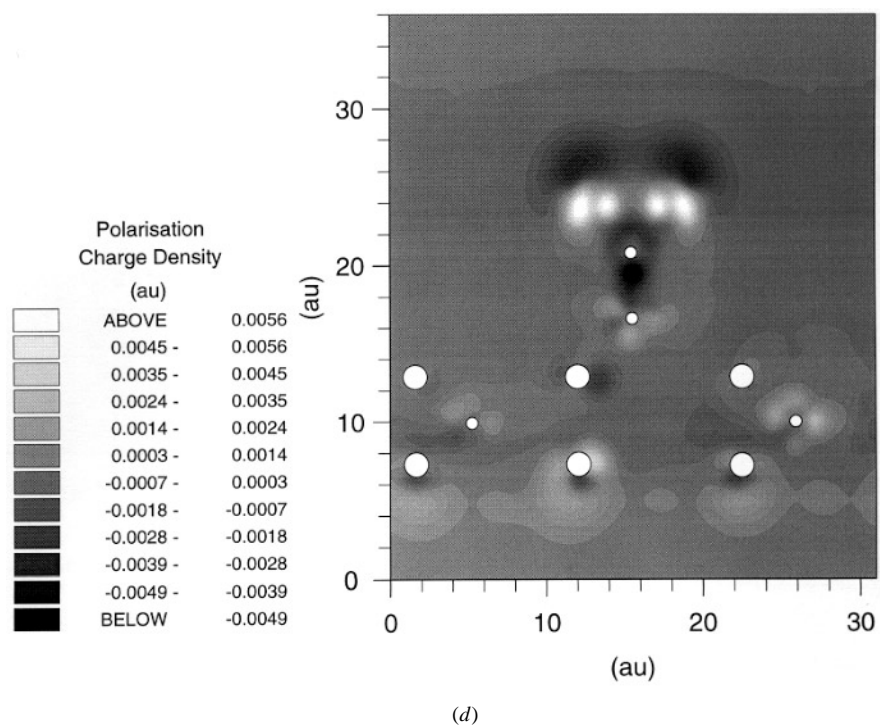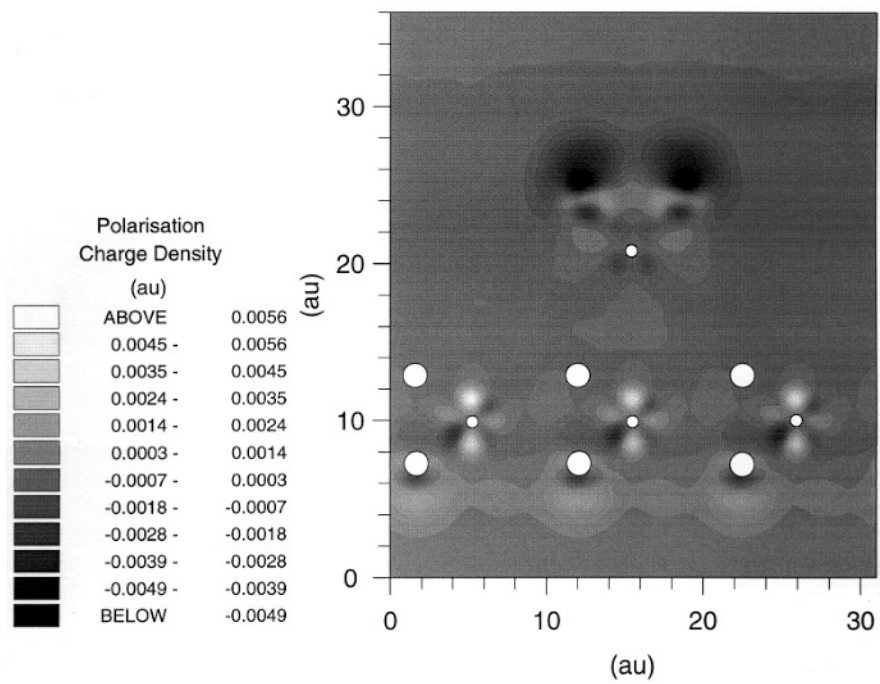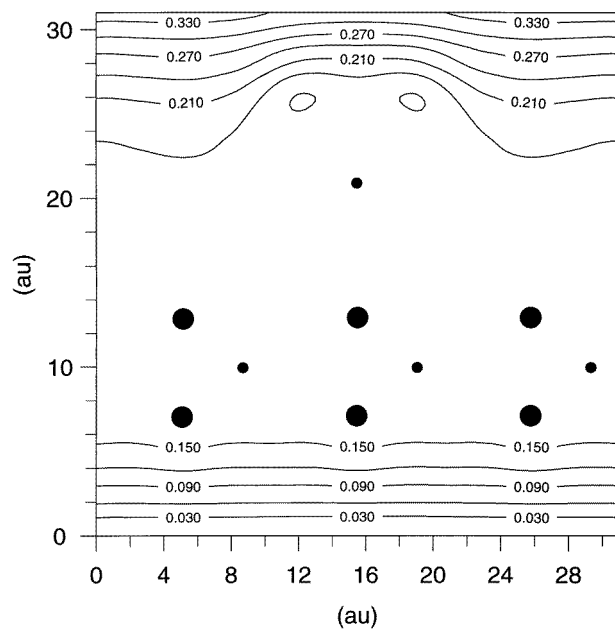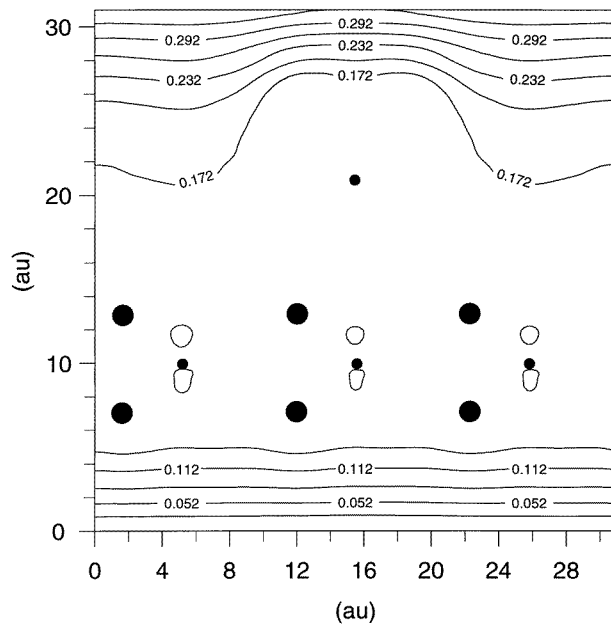|	
ABOVE	0.0056
0.0045 -	0.0056
0.0035 -	0.0045
0.0024 -	0.0035
0.0014 -	0.0024
0.0003 -	0.0014
-0.0007 -	0.0003
-0.0018 -	-0.0007
-0.0028 -	-0.0018
-0.0039 -	-0.0028
-0.0049 -	-0.0039
BELOW	-0.0049

(d)

Figure 8. Continued.

(*a*)

(*b*)

Figure 9. Electrostatic potential difference (see text for definition) for the MoS_2 surface in the presence of an electric field of 0.015 au (0.77 V $\mathring{A}^{-1}$) and an Mo tip located over (*a*) a sulphur site and (*b*) a molybdenum site. Field-induced charge transfer from the tip to the sample effectively screens the electric field in the vacuum gap region.
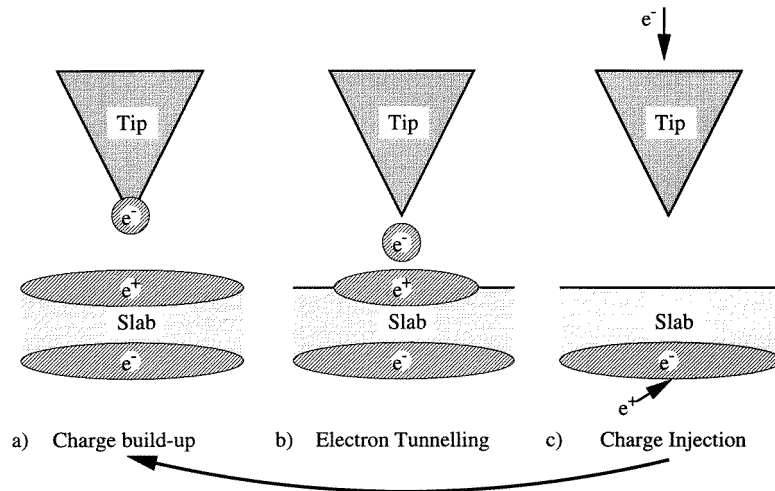
Figure 10. Naive representation of the processes occurring in a dynamic tunnelling current situation. (a) Charge builds up on the tip and the surface polarizes; (b) the electron on the tip tunnels through the barrier into the sample; (c) the tunnelling electron reaches the surface and the polarization in the gap (between the tip and upper sample surface) is reduced or removed. The process then repeats.

approximation to the existence of a tunnelling current (after all, a current is the result of an attempt to equalize the Fermi levels of two electrodes, made impossible by the fact that the Fermi levels at the ends of the electrodes are pinned at different values). A naive description of the processes occurring in a system maintaining a tunnelling current could go as shown in figure 10. First, charge builds up on the tip apex and the surface polarizes owing to the different electrostatic potentials of the two electrodes. Next, the electron on the tip apex will tunnel through the barrier, eventually reaching the surface, reducing the polarization charge at the surface and tip apex. Then, another electron will be injected into the tip, and an electron extracted from the sample, and the process will repeat. Since the tunnelling time ($\sim 10^{-16}$ s) [30] and the time taken for the tip electrons to re-adjust (typically an inverse plasmon frequency, $\tau_{\text{plasmon}} \sim 10^{-16}$ s) are much smaller than the time between tunnelling processes ($e/I \sim 10^{-10}$ s) the system is likely to spend most of its time in the first state (i.e., state (a) in figure 10). So in a dynamic system there will, on average, be an electric field between the tip and sample. Since the shortest time-period in which an atom can transfer from one electrode to the other is of the order of the inverse phonon frequency, $\tau_{\text{phonon}} \sim 10^{-13}$ s for phonons in most materials, the effective barrier against atom transfer will be closer to the barrier in situation (a) than that of situation (c). So, a static calculation with one Fermi level appears to be sampling the wrong end of the tunnelling process. However, further calculations were carried out on the molybdenum-extraction barrier without a tip, but with a charged slab and/or an applied field (removal of the tip was necessary to examine separately the effects of the field and charge transfer). These showed that the surface charging has, energetically speaking, almost the same effect on the extraction barrier as an electric field. Hence the tip and sample calculations including the electric field (which induces the charge transfer) presented here probably provide a reasonably accurate atom-extraction barrier in the presence of a tip and a bias.

5. Conclusions

We have presented *ab initio* simulations in which the barriers against the extraction of single sulphur and molybdenum atoms from MoS_2 were calculated in the presence of a molybdenum tip and an applied electric field. These are believed to be the first calculations in which atom extraction from a partially ionic surface has been considered under such conditions.

A static calculation of a two-electrode system under an applied electric field reacts by transferring charge from one electrode to the other, effectively screening the field between the two. We have argued that the effect of the charge transfer on the barrier is, energetically speaking, similar to that of a net field and is the static-limit approximation to a tunnelling current.

We found that the presence of a tip above the MoS_2 surface significantly reduces the barrier against atom extraction, and that the application of an external field (tip biased negative) reduces the barrier further. However, the calculated extraction barriers are far too high to explain the ease with which the process occurs in experiment and we must conclude that either an important factor is missing from the calculations, or the tip–sample separation is too large. The tip–sample separation was estimated by Hosaka *et al* [4] to be less than or around 5 Å, but it is possible that the actual separation may be less than this as a result of, for example, current-induced thermal expansion of the tip [29]. Reducing the tip–surface separation will certainly reduce the atom-transfer barrier, but at some point the potential well around the side of the tip may disappear. Perhaps the most important feature missing from the calculations is the lack of a dynamic tunnelling current. Inclusion of current (via a multi-Fermi-level simulation) would also inherently include the correct electric field, charge transfer between the tip and sample and current injection into anti-bonding states; it could also, in principle, include effects such as the force on the atoms from the electron current. Inelastic effects have also been shown to be potentially important and some mechanism of including these in the calculations is required for a full description of the atom-extraction processes.

It was also interesting to observe the formation of the filled gap-states associated with the production of a vacancy on the surface, previously reported by the authors [12], as the atoms were moved further away from their perfect-surface positions. In this case, though, the 'gap-states' were not the actual highest occupied states of the simulation as the eigenvalues of some of the states associated with the tip were higher in energy than the surface gap-states.

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