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Tip Induced Localized States in Scanning Tunneling Microscopy*

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Abstract

We have investigated the Scanning Tunneling Microscopy (STM) of graphite with varying tip-to-surface distance. Using an LCAO type approach we showed that at small separations states are localized between the tip and the surface. The energies and the characters of these Tip Induced Localized States (TILS) depend on the height and the lateral position of the tip. These states play a significant role in the tunneling process and influence the STM corrugations predicted from the local density of states. We have developed a current expression, which includes these local interactions, but differs significantly from earlier theories.

1. Introduction

The Scanning Tunneling Microscopy (STM) has proven to be one of the most powerful tools of surface structure studies [1, 2]. Because of the real-space imaging it has found a wide range of applications especially for non-periodic structures and defective surfaces. While the applications of the STM have advanced tremendously, there are still some important theoretical problems to be addressed.

The initial aim of designing STM was tracing the atomic charge densities and thus deducing the surface geometry. Using Bardeen's tunneling formalism [3] Tersoff and Hamann [4] found that the current in STM is proportional to the local density of states at the Fermi level, $\rho(\mathbf{r}, E_F)$. For many metals with extended Fermi surface the total charge density, $\rho_s(\mathbf{r})$ is reminiscent of the local density of states at the Fermi level [5]. Nonetheless, there are cases for which these two quantities i.e., $\rho_s(\mathbf{r})$ and $\rho(\mathbf{r}, E_F)$ are totally different [5], hence the STM line scans may not provide direct information about the atomic positions [6].

In this paper we will analyze one of these structures, i.e., the graphite surface. It is known that experimental studies of this surface result in corrugations much higher than that one normally obtains from the total charge density [7–10]. In fact, a theoretical study using the local density of states approach predicts an infinite corrugation for a graphite monolayer (ML) [5]. It is clear that this special structure deserves a more careful treatment.

In the STM theories which are based on Bardeen's tunneling formalism [3], the tunneling current is calculated by using time-dependent perturbation theory applied to many-particle wave functions of two electrodes. In the STM applications many-particle wave functions are replaced by frozen wave functions [4]. These functions are solutions of the one-particle Hamiltonians of infinitely separated electrodes and do not include the interaction between the tip and the surface.

Although the frozen wave function scheme may be valid

for large tip-surface separations, h , significant interaction with the surface wave functions is inevitable as the tip gets closer to the surface [11]. It was argued that at small tip-to-surface distances the tunneling barrier may break down, which influences the tunneling phenomenon [12]. As a matter of fact, recent STM studies were carried out with a tip-to-surface distance so small as to lead to elastic deformations on the graphite surface [10].

In this study we have focused our attention on small tip-to-surface distances and on the interactions arising therefrom. We have developed a formalism for the tunneling current including significant revisions in the earlier description based on the $\rho(\mathbf{r}, E_F)$.

We have found that the interactions on the atomic scale lead to Tip Induced Localized States (TILS) in the vicinity of the tip. These states are shown to play a significant role in the tunneling process, and influence the corrugations predicted from $\rho(\mathbf{r}, E_F)$.

2. Method

In view of the localized nature of the interactions the use of localized orbitals to represent the electronic states is convenient. Although the Wannier functions seem to provide an appropriate representation, we rather use a Linear Combination of Atomic Orbitals (LCAO) basis set to circumvent computational difficulties. Therefore, we consider Bloch wave functions constructed from the localized, non-overlapping atomic-like orbitals. Since the potential barrier is expected to be low, the tip and the graphite surface are treated by a Hamiltonian:

$$H = H_T + H_S + H_{TS} \quad (1)$$

where H_T and H_S denote non-interacting Hamiltonians of the tip and the surface, respectively. The interaction term H_{TS} is negligible for large h , whereby the use of the frozen wave functions is justified. On the other hand, H_{TS} becomes significant when h is comparable with the nearest neighbor distance of the graphite surface.

For the sake of computational ease we use a periodic tip model [13]. To hinder the intertip interactions, the tips are arranged on a lattice, the unit cell of which is (2×2) times larger than the unit cell of the graphite surface. The tip is simulated by a single carbon atom. In actual experiments the tip is produced in an uncontrollable and unreproducible manner [1, 2], and the microstructure of the tip is not known exactly. Here we are concerned mainly with the localized interaction at small h , and thus the microscopic character of the tip, where the outermost atoms of the tip determine the local electronic structure. Moreover, we assume that the tip

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atom is imbedded in a jellium-like, macroscopic tip. Accordingly we take the orbital energies of the tip atom (except the s -type states far below the Fermi level) to be equal to the Fermi level. Since we are investigating the constant voltage — constant current mode of STM, with infinitesimal bias, the tip and graphite are assumed to have the same Fermi level.

It is known that the bulk graphite has a layered structure parallel to the (0001) planes with a weak interlayer interaction [14, 15]. While the unsupported graphite monolayer has a sixfold rotation symmetry with zero charge density at the center of the hexagon, and with the Fermi surface collapsed to a single point at the K point of the Brillouin Zone (BZ), this symmetry is lowered when the interlayer interactions are included. Owing to the shift of atomic positions in the consecutive layers, such that only three atoms of a surface hexagon have carbon atoms directly below, the sixfold symmetry changes into a threefold rotation symmetry, and the Fermi surface becomes small pockets rather than single points. As shown earlier this symmetry lowering of the interlayer interaction can be resolved by STM [16]. However, since we are concerned with the TILS, discussion is mainly based on the monolayer which happens to be quite appropriate for the purpose of the present study. Nevertheless, we also carried out calculations on a three layer slab to investigate the confinement of TILS at the close proximity of the surface.

In summary, we calculate the electronic states of a system which has a super unit cell consisting of one tip atom over the (2×2) graphite surface unit cell, with different lateral and vertical tip positions. Two lateral positions, i.e., the on-top site and the hollow site positions, are of common interest.

We use explicit atomic-like localized orbitals, and obtain the matrix elements of the Hamiltonian by fitting the band structure of graphite calculated by using more elaborate techniques [14]. One set of parameters represent the on-site interactions of an orbital with itself, which we call orbital energy. The second set incorporates the parameters for interaction between orbitals of different atoms, which we call interaction parameters.

Bands calculated using the fitted parameters are shown in Fig. 1. Apparently, the fitted bands are sufficiently reliable, especially near the K -corner of the BZ, which is relevant for the study of the STM.

One crucial aspect of the empirical LCAO calculations is the determination of the tip-surface interaction terms for varying h . The interaction parameters are taken equal to the fitted values of the bulk when the distance between the tip and surface atoms, d , is equal to the nearest neighbor distance, a_0 , in graphite. For d differing from a_0 the corresponding interaction parameters are scaled by a factor $e^{-\mu \cdot (d-a_0)}$ where μ denotes the exponent of the atomic function for the tip, ($E_t = -\hbar^2 \mu^2 / 2m$). This approximate wave function was used in an earlier study [17].

3. Results

Bands calculated by using the method described above are shown in Fig. 2. Illustrated bands are calculated for a tip height $c/4$ (where c is twice the interlayer separation for bulk graphite) which is equal to 1.675 Å. Owing to the (2×2) graphite unit cell used in our calculations, the BZ of the surface is folded into a new zone having half of the size of the parent (1×1) zone. The Fermi level occurs at $K_{2 \times 2}$ point (at

Fig. 1. Electronic band structure of the graphite monolayer calculated by using an empirical LCAO method. Squares indicate the band points calculated by Tatar and Rabii (Ref. [14]). π -, π^* -bands and sp^2 -bands are shown with dashed and full lines, respectively. Inset is the Brillouin Zone of the graphite surface with hatched irreducible part.

the corner of the new zone), which will be denoted as K hereafter.

In Fig. 2(a) bands for the on-top site position of the tip are shown. At the K -point π -, π^* -bands of the graphite and the

Fig. 2. Bands of the carbon tip atom and the graphite monolayer corresponding to the tip location at the on-top site (a) and the hollow site (b). The tip-to-surface distance, h is equal to $c/4$ (1.675 Å). Bands between -5.0 and -11.0 eV are shown. Insets indicate the atomic configurations.

p_z -orbital state of the tip become degenerate when the tip-surface interaction is neglected (which corresponds to large h). However, all the states around the Fermi level change their characters near the K point when the tip-surface interaction becomes significant at small h .

TS_1 is the tip-to-surface bonding state at -8.05 eV with 82% orbital contribution from the tip p_z and 15% from the surface s - and p_z -orbitals. This state becomes an intrinsic graphite state at the K -point, for which there is no contribution from the tip. This state pins the Fermi level for the tip + graphite system at -7.85 eV. States labeled TS_2 and TS_3 are again mixed states at about -6.5 eV with a dispersion of ~ 0.5 eV. They are formed mainly from the tip orbitals (75% tip p_x - and p_y -contribution, and the rest from the graphite). Bands labeled $T + \pi$ and $T + \pi^*$ are mixed states formed from the tip orbitals and the graphite π - and π^* - states near the K -point, respectively. While the $T + \pi$ states display a bonding character at -8.34 eV, the $T + \pi^*$ states have an antibonding character at -7.7 eV. The tip p_z -orbital contribution to these states ranges from 40% to 50%. These states are identified as TILS. However, away from the K -point the tip contribution is reduced (less than 5%). The energies of TILS relative to E_F depends on the tip-to-surface separation. These states are normally broadened and overlap with the Fermi level for a realistic tip.

In Fig. 2(b) bands for the hollow-site position of the tip are shown, the tip-to-surface distance being the same as that of the on-top site ($h = c/4$). For the sake of comparison we used the same labeling. As it is seen these bands are quite different from those of the on-top case. First of all, the mixing of the tip and graphite states is much smaller as compared to the on-top position. For example, the contribution of the tip is already less than 1% for the $T + \pi$ and $T + \pi^*$ states around the K -point. At the K -point these bands become degenerate as in the free ML case, and thus they determine the Fermi level. Also the TS_1 , TS_2 and TS_3 bands are closer to the Fermi level and all three originate mainly from the p -orbitals of the tip (orbital contribution being larger than 95%).

From this analysis it appears that owing to the relatively larger atomic separations and symmetry of the system, the mixing between tip and graphite states is practically negligible, and therefore no strong localized interaction is expected at the hollow site position. Consequently, the effect of the local interaction can be totally neglected.

The character and the location of TILS is evident in Fig. 3, where the contour plots of the charge density $T + \pi$ state are illustrated. The charge density is calculated using the atomic orbitals (Slater type orbitals with decay constants given by Clementi and Raimondi [18]), and is localized in the barrier region and in the close proximity of the tip. These contour plots give also some idea about how the substrate states are affected from the local interaction of the tip.

Finally, there are two points that deserve detailed consideration. The first one is about the localization of TILS. We used larger unit cells for the band calculations to prevent intertip interaction. Also we carried out calculations for a multilayer graphite slab. We found that TILS are confined at the outermost layer and around three rings of nearest neighbors at the proximity of the tip. The second point is the dependence of TILS on the tip-to-surface separation. We found that for distances larger than $\sim c/2$ even the mixing

Fig. 3. Local Density of States (LDOS) of $T + \pi$ in Fig. 2(a) at the $K_{2 \times 2}$ -point. Contour plots in a vertical plane passing through the tip atom and two nearest neighbor atoms on the surface (a), and a horizontal plane (parallel to the surface) $0.25 \text{ \AA}$ above the graphite surface (b). Full and open circles represent graphite and tip atoms (projected positions in b), respectively. Charge density increases in the direction of arrows.

between the tip and graphite states, and thus the local interaction is negligible for the on-top site position.

Although we are interested in the constant voltage-constant current mode of the STM with an infinitesimal bias, we also calculated electronic states for nonzero biases. States near the K point show almost no change in their character for biases on the order of ± 0.1 V, and the shift of the tip-surface mixed states is less than the half of the bias voltage. It is concluded that our discussions based on the zero bias are not affected in any essential manner when the bias is small. However, for large biases special emphasis must be placed on the BZ points where states of graphite approach the Fermi level of the biased tip.

4. Tunneling current at small tip-to-surface distance

From the previous discussion it appears that TILS between the tip and the surface may act as a channel to enhance the tunneling current. In what follows we will show that this is really the case, and the tunneling current is modified strongly because of the tip-surface interaction.

Using the model described in Section 2, so far we were able to consider only the outermost tip atom engaged in a strong interaction with the graphite surface leading to TILS. To calculate the total current one has to use, however, the total Hamiltonian corresponding to a realistic tip (with quasi-continuous, propagating states, and TILS), and the graphite substrate together. Although we are not able to perform a detailed computation with a realistic, extended tip, we never-

theless attempt to get an approximate expression for the current.

To this end we use a simple model, in which the strong interaction between the tip and the graphite surface for small $\hbar$ is taken into account by TILS. The rest of the states participating in the tunneling process can be considered by an approach similar to that of Bardeen [3]. These are jellium-like tip states (Ψ_T) and graphite states (Ψ_S), which are solutions of the Hamiltonians H_T and H_S , respectively. Following Bardeen and neglecting the interaction between Ψ_T and Ψ_S (orthogonality, etc.), these states are the solutions of the total Hamiltonian (tip and substrate together) in a domain of limited extend.

$$H\Psi_T = E_T\Psi_T \quad (\text{for } \mathbf{r} \in \mathbb{R}_T) \quad (2a)$$

$$H\Psi_S = E_S\Psi_S \quad (\text{for } \mathbf{r} \in \mathbb{R}_S) \quad (2b)$$

$$H\Psi_{\text{TILS}} = E_{\text{TILS}}\Psi_{\text{TILS}} \quad (\text{for } \mathbf{r} \in \mathbb{R}_{\text{TILS}}) \quad (2c)$$

where $\mathbb{R}_T$ and $\mathbb{R}_S$ are domains, wherein Ψ_T and Ψ_S , respectively, are solutions of the total Hamiltonian. Similarly, $\mathbb{R}_{\text{TILS}}$ indicates a domain in the potential barrier between the tip and the graphite surface.

Note that owing to the extended tip assumed here, the total Hamiltonian differs from that used in Section 2. Also since Ψ_T , Ψ_S and Ψ_{TILS} are not solutions of the same Hamiltonian they are not orthogonal. This way extended tip as well as localized states of the electrodes are incorporated in the formalism. The series of approximations used here seems to be an oversimplification of the problem, but as will be seen it is physically meaningful in describing the physical aspects of the problem.

The applied bias voltage is assumed to result in a Fermi-Dirac distribution, in which the graphite states near E_F and TILS are partially empty and the tip states are partially occupied. Physically two different types of tunneling process is possible. The first one is the direct tunneling to the graphite states, which was treated previously [4]. The second process is indirect, in which electrons first hop to TILS before they leave the tip totally. This second process has not been considered in previous theories [4, 13], and becomes important when the tip gets closer to the surface. Tunneling currents in the presence of TILS can be calculated to the first order using a time-dependent perturbation approach. Effects of the filled TILS are only second order contributions, and therefore are neglected.

The total wave function describing the dynamic nature of the process can be written as:

$$\begin{aligned} \Psi(\mathbf{r}, t) = & a_T(t)e^{-iE_T t/\hbar}\Psi_T(\mathbf{r}) + a_S(t)e^{-iE_S t/\hbar}\Psi_S(\mathbf{r}) \\ & + a_{\text{TILS}}(t)e^{-iE_{\text{TILS}} t/\hbar}\Psi_{\text{TILS}}(\mathbf{r}) \end{aligned} \quad (3)$$

Using this wave function in the time-dependent Schrodinger equation for the total Hamiltonian, we get an equation for a_i 's. Since we are concerned with small currents, we can approximate the overall transition with the first order term only.

Taking $a_T \cong 1$, a_S and $a_{\text{TILS}} \cong 0$, $da_T/dt \cong 0$ (assuming that there is a bias that fills the tip state and discharges the graphite state and TILS continuously) the tunneling current

can be easily calculated as:

$$I = \frac{2\pi e^2 V}{\hbar(1 - |S|^2)} |M_{T-S} - S^* M_{T-\text{TILS}}|^2 \quad (4)$$

where S is the overlap of the graphite state and TILS:

$$S = \int d^3r \Psi_{\text{TILS}}^* \Psi_S \quad (5)$$

and M represents the transition matrix elements from tip state to TILS or graphite state:

$$M_{T-\text{TILS}} = \int d^3r \Psi_{\text{TILS}}^* (H - E) \Psi_T \quad (6a)$$

$$M_{T-S} = \int d^3r \Psi_S^* (H - E) \Psi_T \quad (6b)$$

Following Bardeen's arguments we find:

$$M_{T-\alpha} = - \frac{\hbar^2}{2m} \int dS \cdot (\Psi_\alpha^* \nabla \Psi_T - \Psi_T^* \nabla \Psi_\alpha) \quad (7)$$

We can further simplify this current expression using Tersoff's local density of states expression for tunneling current. Also note that M_{T-S} is a real number, whereas $M_{T-\text{TILS}}$ is purely imaginary.

Defining:

$$I_{\text{LDOS}} = \frac{2\pi e^2 V}{\hbar} |M_{T-S}|^2 \delta(E_T - E_S) \quad (8a)$$

$$I_{T-\text{TILS}} = \frac{2\pi e^2 V}{\hbar} |M_{T-\text{TILS}}|^2 \delta(E_T - E_{\text{TILS}}) \quad (8b)$$

$$\cong \frac{2\pi e^2 V}{\hbar} D \left| i \frac{\hbar k_T}{m} 4\pi c_T \right|^2 \delta(E_T - E_{\text{TILS}}) \quad (8c)$$

where c_T is the orbital contribution of tip atom in the TILS and D is the density of jellium states at the tip atom position. Then the final form of the current expression for real S and M 's becomes:

$$I = \frac{1}{(1 - S^2)} |(I_{\text{LDOS}})^{1/2} - i S (I_{T-\text{TILS}})^{1/2}|^2 \quad (9a)$$

$$= \frac{1}{(1 - S^2)^2} \{I_{\text{LDOS}} + S^2 I_{T-\text{TILS}}\} \quad (9b)$$

This expression verifies our argument about the role of TILS in the tunneling. It is seen that the overlap of the TILS with the graphite ML state is the characteristics measure of the tip-surface interaction. In spite of the fact that I_{LDOS} is a crucial quantity in the tunneling process, the tunneling current can not be obtained from only I_{LDOS} as S attains finite values.

Note that for $I_{T-\text{TILS}} = 0$ (when no electrons are injected in the TILS) the tunneling current is still larger than that predicted by the local density of states approach. This is a result of the orthogonality constraint for the solutions of total Hamiltonian. As $\hbar$ decreases, and thus the potential barrier is lowered, the substrate wave functions will differ from Ψ_S , obtained with no TILS present. Apart from the direct contribution of TILS, this effect is accounted by the factor $(1 - S^2)^{-2}$ in front of the current expression.

Developing the current formalism we can analyze the effects of the tip-surface interaction on the tunneling for the structures analyzed in Sec. 3. For the on-top site position, $T + \pi$ and $T + \pi^*$ states have $S \cong 0.5$, thus $T + \pi^*$ state will have a significant contribution to current. Since $T + \pi$ state lies below the Fermi energy, its effect will be second

order and can be neglected. TS_1 state has no tip orbital contribution and its effect is included in the I_{LDOS} term for frozen wave functions. TS_2 and TS_3 states are orthogonal to graphite ML states, therefore have no tunneling contribution.

For the hollow site position of the tip states for the localized interactions come out to be nearly orthogonal to the ML states around Fermi level and thus can not enhance the current very much. Therefore we can conclude that states for the total tip + surface system do not affect the current as it was for the on-top site.

At large h (large bias) the STM line scans has to reflect $\varrho(\mathbf{r}, E_F)$, whereas at small bias the tip has to be lowered toward the surface. For a graphite substrate of finite thickness, $\varrho(\mathbf{r}, E_F)$ at the hollow side is small but is nonzero. Based on the above discussion the effect of the local electronic interaction is negligible, and the current is proportional to $\varrho(\mathbf{r}, E_F)$. However, the situation is quite different as the tip approaches to the on-top site, where TILS are produced, and enhance the current. To keep the current fixed, the tip is retracted. As a result the vertical displacement between these two positions has to be larger than the corrugation predicted from $\varrho(\mathbf{r}, E_F)$.

5. Conclusion

It emerges from the present study that the interaction between the tip and the substrate surface becomes significant when their separation is small. Owing to this interaction a state localized in the barrier may form, and also the substrate states participating in the tunneling process depart from those corresponding to the infinitely separated electrodes. In this case, the current expression, which was derived from $\varrho(\mathbf{r}, E_F)$ of the substrate fails to describe the tunneling. In this study we first showed that the Tip Induced Localized States exist for a system at hand. Using a simple model we developed an expression for the tunneling current, in which those effects arising from small h are incorporated. In this new

expression, while the current obtained from $\varrho(\mathbf{r}, E_F)$ is modified, an additional current due to TILS is included. In view of these findings it is concluded that the STM images obtained at small h do not provide a direct information about the surface atomic positions, or $\varrho(\mathbf{r}, E_F)$ as well.

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