The influence of adsorbate vibration on resonant tunnelling in the STM

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Abstract. We have studied theoretically the influence of adsorbate vibration on the resonant tunnelling current in STM. This study is realized by adapting the Domcke–Cederbaum formalism combined with a tight-binding approximation of the tip–adsorbate–substrate system. We have varied parametrically the bias voltage, the tip–adsorbate–substrate separations, the position of the resonant level relative to the Fermi level of the system and the vibrational energy of the adsorbate. An application to a hydrogenoid system between a tungsten tip and substrate is presented.

1. Introduction

It is definitively established that the scanning tunnelling microscope (STM) is a very powerful tool to obtain local structural information on metallic and semiconducting surfaces. Unfortunately STM use for unambiguous determination of the nature of an adsorbate is still an open problem. It is expected that the vibrational excitation of the chemical bond between the adsorbate and the substrate should provide information for the identification of the specific atoms or molecules adsorbed on surfaces. Until now, efforts to identify changes in the STM current induced through vibrational excitation have not achieved much success.

We consider the tunnelling of electrons from the tip to an adsorbate on a metal surface. The adsorbate is assumed to have an electronic resonance near the Fermi level. This resonance is derived from a localized level on the adsorbate coupled with two continuum energy bands of the substrate and of the tip. By applying a bias voltage, a net tunnel current flows between the surface and the tip through the resonant level of the adsorbate. This resonant tunnelling process can induce vibrational excitation of the adsorbate, and changes are expected to be seen in the tunnelling current.

Persson and Baratoff (1987) pointed out that the tunnelling electrons can induce vibrational excitation of adsorbates also by the dipole scattering mechanism. They showed that resonant tunnelling can give a relative change in the tunnelling conductance which is greater by a factor of 10 than the dipole mechanism change. To prove this fact, they have used (Persson and Baratoff 1987) an Anderson–Newns–Grimley type Hamiltonian and the calculations are made in the limit of the second-order perturbation expansion. Gata and Antoniewicz (1993) have used a Hamiltonian of the same type as Persson and Baratoff (1987) to study the same resonant process. They solved the problem by using the Heinsenberg equations of motion for the operators.

The resonant tunnelling of electrons in the STM is very similar to the inelastic electron scattering from gas-phase vibrating molecules. A well documented gas-phase description of this process was realized by Domcke and Cederbaum (1977).

In this work we use a similar Hamiltonian as Gata and Antoniewicz (1993) and we solve the problem of resonant tunnelling by adapting the Domcke–Cederbaum formalism combined with a tight-binding method of description of the tip–adsorbate–substrate system. We have made detailed studies of the dependence of the tunnelling current and of the conductance, on the bias voltage, vibrational energy of the adsorbate, Fermi level position and tip–adsorbate–substrate separation. Finally an application for a hydrogen-like system placed between a tungsten tip and surface is presented. Our calculations apply for small tip–adsorbate separations, when there is a considerable overlap between the wave functions of the tip and the adsorbate.

2. The Hamiltonian model

We consider the following Hamiltonian that contains the vibration of the adsorbate and the coupling between the adsorbate with the substrate and the STM tip:

$$\hat{H}(z) = \varepsilon_a(z)a^+a + \sum_{k_{L,R}} \varepsilon_{k_{L,R}} a^+_{k_{L,R}} a_{k_{L,R}} + \sum_{k_{L,R}} [\hat{V}_{ak_{L,R}}(z)a^+ a_{k_{L,R}} + \text{HC}] + \omega(b^+b + \tfrac{1}{2}) \qquad (1)$$

$\varepsilon_a(z)$ is the resonance level at a distance z (z associated with the vibrational mode of the adsorbate). ε_{k_L} and ε_{k_R} label the energy levels of the one-particle eigenstate of the metal tip (L) and the metal substrate (R) respectively. V_{ak_L} and V_{ak_R} are the matrix elements for the electron transfer between tip and adsorbate and between adsorbate and substrate. $\varepsilon_a(z)$ and $V_{ak_{L,R}}$ are adiabatically dependent on the nuclear parameter of the adsorbate z:

$$z = \left(\frac{\hbar}{2m\omega}\right)^{1/2} (b^+ + b). \qquad (2)$$

m is the effective mass of adsorbate; $\hbar\omega$ is the vibrational energy. a^+ and a, $a^+_{k_{L,R}}$ and $a_{k_{L,R}}$ and b^+ and b are the creation and annihilation operators for the adsorbate, tip and substrate, and for the vibration mode.

By expanding $\varepsilon_a(z)$ to the first order in z

$$\varepsilon_a(z) \cong \varepsilon^0 + \left(\frac{\partial \varepsilon_a}{\partial z}\right)_{z=0} z \qquad (3)$$

we can rewrite our Hamiltonian (1):

$$\hat{H} = \hat{H}_0 + \hat{V} \qquad (4a)$$

$$\hat{H}_0 = \varepsilon^0 a^+a + \sum_{k_{L,R}} \varepsilon_{k_{L,R}} a^+_{k_{L,R}} a_{k_{L,R}} + \omega(b^+b + \tfrac{1}{2}) \qquad (4b)$$

$$\hat{V} = \sum_{k_{L,R}} (\hat{V}_{ak_{L,R}} a^+ a_{k_{L,R}} + \text{HC}) + k^0 a^+ a(b^+ + b) \qquad (4c)$$

where

$$k^0 = \left(\frac{\hbar}{2m}\right)^{1/2} \left(\frac{\partial \varepsilon_a}{\partial z}\right)_{z=0}.$$

Because of the z dependence, the matrix elements $\hat{V}_{ak_{L,R}}$ are in fact operators in the 'vibration space' and

$$[\hat{V}_{ak_{L,R}}, b] \neq 0.$$

3. The Green function expansion method

To compute the resonant tunnel current we will adapt the Domcke–Cederbaum formalism for gas-phase inelastic collisions. First we need the transition matrix elements from the initial state (described as a direct product between tip states $|k_L\rangle$ and vibrational ground state $|0\rangle$ of the adsorbate) to the final state (a direct product between the substrate state $|k_R\rangle$ and excited state $|m\rangle$ of the adsorbate):

$$\Im(k_R \otimes m, k_L \otimes 0) = \langle k_R \otimes m|\hat{T}|k_L \otimes 0\rangle. \tag{5}$$

The conservation of energy requires that $\varepsilon_{k_R} + m\hbar\omega = \varepsilon_{k_L} \equiv \varepsilon$.

We can use the well known decomposition of the $\hat{T}$ operator:

$$\hat{T} = \hat{V} + \hat{V}\hat{G}\hat{V} \tag{6}$$

with

$$\hat{G} = \frac{1}{\varepsilon - \hat{H} + i\eta}. \tag{7}$$

Because we assume the orthogonality of the states $|k_L\rangle$, $|k_R\rangle$ and $|a\rangle$ among themselves, we have

$$\Im(k_R \otimes m, k_L \otimes 0) = \langle k_R \otimes m|\hat{V}\hat{G}\hat{V}|k_L \otimes 0\rangle = \langle a \otimes m|\hat{V}_{k_R a}\hat{G}V_{ak_L}|a \otimes 0\rangle$$
$$= \langle m|\hat{V}_{k_R a}(\langle a|\hat{G}|a\rangle)V_{ak_L}|0\rangle. \tag{8}$$

For the determination of $\langle a|\hat{G}|a\rangle$ it is useful to perform the next decomposition of the Hamiltonian $\hat{H}$:

$$\hat{H} = \hat{H}_1 + \hat{H}_2 \tag{9}$$

with

$$\hat{H}_1 = \hat{H}_0 + K^0 a^+ a(b^+ + b) \tag{10}$$
$$\hat{H}_2 = \sum_{k_{L,R}}(\hat{V}_{ak_{L,R}}a^+ a_{k_{L,R}} + \text{HC}) \tag{11}$$

and the next expansion of the Green function $\hat{G}$:

$$\hat{G} = \hat{G}_1 + \hat{G}\hat{H}_2\hat{G}_1 = \hat{G}_1 + \hat{G}_1\hat{H}_2\hat{G}_1 + \hat{G}\hat{H}_2\hat{G}_1\hat{H}_2\hat{G}_1. \tag{12}$$

So we write

$$\langle a|\hat{G}_1|a\rangle = \left\langle a\left|\frac{1}{\varepsilon - \hat{H}_1 + i\eta}\right|a\right\rangle = \frac{1}{\varepsilon - [\varepsilon^0 + \omega b^+ b + K^0(b^+ + b)] + i\eta}$$

$$\langle a|\hat{G}_1\hat{H}_2\hat{G}_1|a\rangle = 0$$

$$\langle a|\hat{G}\hat{H}_2\hat{G}_1\hat{H}_2\hat{G}_1|a\rangle = \langle a|\hat{G}|a\rangle\sum_{k_{L,R}}\left(\hat{V}_{ak_{L,R}}\frac{1}{\varepsilon - (\varepsilon_{k_{L,R}} + \omega b^+ b) + i\eta}\hat{V}_{k_{L,R}a}\right)$$

$$\times \frac{1}{\varepsilon - [\varepsilon^0 + \omega b^+ b + K^0(b^+ + b)] + i\eta}.$$

Thus

$$\langle a|\hat{G}|a\rangle = \frac{1}{\varepsilon - [\varepsilon^0 + \omega b^+ b + K^0(b^+ + b)] - \sum_{k_{L,R}}\left(\hat{V}_{ak_{L,R}}\frac{1}{\varepsilon - (\varepsilon_{k_{L,R}} + \omega b^+ b) + i\eta}\hat{V}_{k_{L,R}a}\right)}. \tag{13}$$

By using the notations

$$\Delta(\varepsilon - \omega b^+ b, z) = P \sum_{k_{L,R}} \hat{V}_{ak_{L,R}} \frac{1}{\varepsilon - \varepsilon_{k_{L,R}} - \omega b^+ b} \hat{V}_{k_{L,R}a} \tag{14}$$

$$\Gamma(\varepsilon - \omega b^+ b, z) = 2\pi \sum_{k_{L,R}} \hat{V}_{ak_{L,R}} \delta(\varepsilon - \varepsilon_{k_{L,R}} - \omega b^+ b) \hat{V}_{k_{L,R}a} \tag{15}$$

the transition moment can be rewritten as

$$\Im(k_R \otimes m, k_L \otimes 0) = \left\langle m \left| \hat{V}_{k_R a} \frac{1}{\varepsilon - [\varepsilon^0 + \omega b^+ b + K^0(b^+ + b)] - \Delta - \frac{1}{2}i\Gamma} \hat{V}_{ak_L} \right| 0 \right\rangle. \tag{16}$$

We expand now $\Delta(z), \Gamma(z)$ to first order in z:

$$\Delta \cong \Delta(\varepsilon - \omega b^+ b, 0) + \frac{1}{2} \left[\left(\frac{\partial \Delta}{\partial z} \right)_{z=0} z + z \left(\frac{\partial \Delta}{\partial z} \right)_{z=0} \right] \tag{17}$$

$$\Gamma \cong \Gamma(\varepsilon - \omega b^+ b, 0) + \frac{1}{2} \left[\left(\frac{\partial \Gamma}{\partial z} \right)_{z=0} z + z \left(\frac{\partial \Gamma}{\partial z} \right)_{z=0} \right]. \tag{18}$$

We suppose that

$$\hat{V}_{ak_{L,R}}(z) \approx \hat{V}_{ak_{L,R}}(0) = V_{ak_{L,R}}.$$

With the above assumptions, the transition moments become

$$\Im(k_R \otimes m, k_L \otimes 0) = V_{k_R a}(0) V_{ak_L}(0) \left\langle m \left| \frac{1}{\varepsilon - H} \right| 0 \right\rangle \tag{19}$$

where

$$H = \varepsilon' + \omega b^+ b + K'(b^+ + b) + (b^+ + b)K' + K^0(b^+ + b) \tag{20}$$

with

$$\varepsilon' = \varepsilon^0 + \Delta(\varepsilon - \omega b^+ b, 0) - \tfrac{1}{2}i\Gamma(\varepsilon - \omega b^+ b, 0) \tag{21a}$$

$$K' = \frac{1}{2} \left[\left(\frac{\hbar}{2m\omega} \right)^{1/2} \left(\frac{\partial \Delta}{\partial z} \right)_{z=0} - \frac{i}{2} \left(\frac{\hbar}{2m\omega} \right)^{1/2} \left(\frac{\partial \Gamma}{\partial z} \right)_{z=0} \right]. \tag{21b}$$

We are interested in the probability of tunnelling of an electron having the initial energy ε_{k_L} in a final state with an energy ε_{k_R}:

$$T(\varepsilon_{k_R}, \varepsilon_{k_L}) = \sum_{k'_L} \sum_{k'_R} \sum_{m=0}^{\infty} |\Im(k'_R \otimes m, k'_L \otimes 0)|^2 \delta(\varepsilon_{k'_L} - \varepsilon_{k'_R} - m\hbar\omega) \delta(\varepsilon_{k_L} - \varepsilon_{k'_L}) \delta(\varepsilon_{k_R} - \varepsilon_{k'_R}). \tag{22}$$

Until now we have not considered the influence of the bias voltage V.

We choose the origin of energy at the position of ε_a and the changes in the energy level in the tip and the substrate are

$$\varepsilon_{k_L}^V = \varepsilon_{k_L}^0 + \frac{eV}{2} \tag{23a}$$

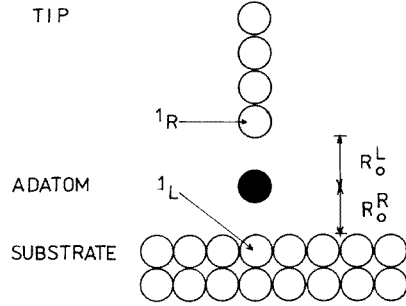$$\varepsilon_{k_R}^V = \varepsilon_{k_R}^0 + \frac{eV}{2}. \tag{23b}$$

Figure 1. A schematic model for the tip–adsorbate–substrate system. $R_0^{L,R}$ are the distances between the adsorbate and the tip and substrate respectively. $1_{L,R}$ denote the orbitals on the tip and substrate which overlap the adsorbate.

The relation (22) becomes

$$T(\varepsilon_{k_R}^V, \varepsilon_{k_L}^V) = \sum_{m=0}^{\infty} \sum_{k_R'} |V_{k_R'a}|^2 \delta \left(\varepsilon_{k_R'}^0 - \varepsilon_{k_R}^V - \frac{eV}{2} \right)$$

$$\times \sum_{k_L'} |V_{ak_L'}|^2 \delta \left(\varepsilon_{k_L'}^0 - \varepsilon_{k_L}^V + \frac{eV}{2} \right) \left| \left\langle m \left| \frac{1}{\varepsilon_{k_L} - H} \right| 0 \right\rangle \right|^2 \delta(\varepsilon_{k_L}^V - \varepsilon_{k_R}^V - m\hbar\omega).$$

(24)

To simplify the notation we will omit in the following the superscript V to denote the energy levels in the presence of the bias.

4. The tunnelling current in STM

We determine the tunnelling current at 0 K.

$$J = \int \mathrm{d}\varepsilon_{k_R} \int \mathrm{d}\varepsilon_{k_L} \, T(\varepsilon_{k_R}, \varepsilon_{k_L}) \left[1 - \Theta_L \left(\varepsilon_F + \frac{eV}{2} \right) \right] \Theta \left(\varepsilon_F - \frac{eV}{2} \right)$$

$$= \sum_{m=0}^{\left[\frac{eV}{\hbar\omega} \right]} \int_{\varepsilon_F + \frac{eV}{2} + m\hbar\omega}^{\varepsilon_F + \frac{eV}{2}} \mathrm{d}\varepsilon \, \Gamma_R \left(\varepsilon + \frac{eV}{2} - m\hbar\omega \right) \Gamma_L \left(\varepsilon - \frac{eV}{2} \right) \left| \left\langle m \left| \frac{1}{\varepsilon - H} \right| 0 \right\rangle \right|^2.$$

(25)

In the above expression Θ is the Fermi distribution function.

We need the explicit evaluation of the functions Δ and Γ.

$$\Delta(\varepsilon) = P \sum_{k_L} \hat{V}_{ak_L} \frac{1}{\varepsilon - (\varepsilon_{k_L}^0 + eV/2)} \hat{V}_{k_L a} + P \sum_{k_R} \hat{V}_{ak_R} \frac{1}{\varepsilon - (\varepsilon_{k_L}^0 - eV/2)} \hat{V}_{k_R a}$$

$$= \Delta_L^0 \left(\varepsilon - \frac{eV}{2} \right) + \Delta_R^0 \left(\varepsilon + \frac{eV}{2} \right).$$

(26)

Similarly we write

$$\Gamma(\varepsilon) = \Gamma_L^0 \left(\varepsilon - \frac{eV}{2} \right) + \Gamma_R^0 \left(\varepsilon + \frac{eV}{2} \right).$$

(27)

In the following we choose a specific geometry for the tip–adsorbate–substrate system. The tip will be modelled as a semi-infinite chain of atoms coupled with an atomic adsorbate

chemisorbed on the top position on the (001) surface of a crystal (see figure 1). For the description of the tip and the substrate we use the tight-binding approximation:

$$|k_{L,R}\rangle = \sum_i c_{k_{L,R}i}|i\rangle \tag{28}$$

where the state $|i\rangle$ describes an atomic orbital centred on the site i. The hopping integrals are nonzero only among the nearest neighbours:

$$\langle a|H|i_{L,R}\rangle = \beta_{L,R}\delta_{1_{L,R}i_{L,R}}. \tag{29}$$

The state $|1_L\rangle$ corresponds to the last orbital of the tip and the orbital $|1_R\rangle$ describes the substrate atom on which is placed the adsorbate (see figure 1).

Then

$$|V_{ak_{L,R}}|^2 = |\beta_{L,R}|^2|c_{k_{L,R}1_{L,R}}|^2 \tag{30}$$

and

$$\Gamma^0_{R,L}(\varepsilon) = 2|\beta_{R,L}|^2 n_{1_{L,R}}(\varepsilon). \tag{31}$$

The density of states n_{1_L} on the tip is (for a semiinfinite chain of atoms) (Desjonquères and Spanjard 1993)

$$n_{1_L}(\varepsilon) = \frac{1}{2\pi}\frac{\sqrt{4\alpha^2 - \varepsilon^2}}{\alpha^2} \tag{32}$$

and the density of states corresponding to a (001) surface (Desjonquères and Spanjard 1993)

$$n_{1_R}(\varepsilon) \equiv n_0(\varepsilon) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\varepsilon x}[J_0^3(2\alpha x) + J_0^2(2\alpha x)J_2(2\alpha x)]\,dx. \tag{33}$$

In the above expressions (31) and (32), α represents the hopping integral between two neighbour atoms.

Δ functions are related to the Γ functions through a Hilbert transformation:

$$\Delta_L^0(\varepsilon) = \begin{cases} |\beta_L|^2\dfrac{\varepsilon + \sqrt{\varepsilon^2 - 4\alpha^2}}{4\alpha^2} & \varepsilon < -2\alpha \\[3mm] |\beta_L|^2\dfrac{\varepsilon}{4\alpha^2} & |\varepsilon| < 2\alpha \\[3mm] |\beta_L|^2\dfrac{\varepsilon - \sqrt{\varepsilon^2 - 4\alpha^2}}{4\alpha^2} & \varepsilon > 2\alpha \end{cases} \tag{34}$$

$$\Delta_R^0(\varepsilon) = |\beta_R|^2\int_0^{\infty}\sin(\varepsilon x)\,2J_0^2(2\alpha x)\left[J_0(2\alpha x) + \frac{1}{2\alpha x}J_1(2\alpha x)\right]dx \tag{35}$$

$$\Gamma_R^0(\varepsilon) = 2|\beta_R|^2\int_0^{\infty}\cos(\varepsilon x)\,2J_0^2(2\alpha x)\left[J_0(2\alpha x) + \frac{1}{2\alpha x}J_1(2\alpha x)\right]dx. \tag{36}$$

The first derivative of the Δ and Γ functions is obtained from the z dependence of the hopping integrals:

$$\langle a|H|1_{L,R}\rangle \equiv \beta_{L,R}(z) = \beta_0\,e^{-q\left(\frac{R_0^{L,R}}{R_0} - 1\right)}. \tag{37}$$

So

$$\left.\frac{\partial\Gamma_{L,R}}{\partial z}\right|_{z=0} = (\pm)\left(-\frac{2q}{R_0}\right)\Gamma_{L,R}(R_0^{L,R}) \tag{38a}$$

$$\left.\frac{\partial\Delta_{L,R}}{\partial z}\right|_{z=0} = (\pm)\left(-\frac{2q}{R_0}\right)\Delta_{L,R}(R_0^{L,R}). \tag{38b}$$

For the significance and the numerical values of the parameters entering (37, 38a, b) see (Forni *et al* 1992).

5. Evaluation of the vibrational transition moments with the continuum fraction method

In the vibrational wave function representation $\{|m\rangle\}$, $\varepsilon - H$ matrix is tridiagonal:

$$\begin{pmatrix} E_0 & -K_0\sqrt{1} & \cdot & \cdot \\ -K_0\sqrt{1} & E_1 & -K_1\sqrt{2} & \cdot \\ \cdot & -K_1\sqrt{2} & E_2 & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{pmatrix} \tag{39}$$

where

$$E_n = \varepsilon - \left[\varepsilon^0 + \Delta(\varepsilon - n\hbar\omega) - \frac{1}{2}\Gamma(\varepsilon - n\hbar\omega) \right] - n\hbar\omega$$

$$K_n = K^0 + \frac{1}{2}\left(\frac{\hbar}{2m\omega}\right)^{1/2}\left\{ \left(\frac{\partial[\Delta(\varepsilon - n\hbar\omega, z) + \Delta(\varepsilon - (n+1)\hbar\omega, z)]}{\partial z}\right)\bigg|_{z=0} \right.$$

$$\left. -\frac{i}{2}\cdot\left(\frac{\partial[\Gamma(\varepsilon - n\hbar\omega, z) + \Gamma(\varepsilon - (n+1)\hbar\omega, z)]}{\partial z}\right)\bigg|_{z=0} \right\}.$$

In consequence

$$\left\langle 0 \left| \frac{1}{\varepsilon - H} \right| 0 \right\rangle = \frac{1}{E_0 - K_0^2/\{E_1 - 2K_1^2/[E_2 - 3K_2^2/(E_3 - \cdots)]\}}. \tag{40}$$

For the evaluation of $R_{n0} = \langle n|1/(\varepsilon - H)|0\rangle$ we use the following recurrence relation (Domcke and Cederbaum 1980):

$$\sqrt{n}K_{n-1}R_{n-10} - E_n R_{n0} + \sqrt{n+1}K_n R_{n+10} = 0 \tag{41}$$

with

$$R_{10} = \frac{E_0 R_{00} - 1}{K_0}.$$

6. Results and discussion

It is difficult to make a complete model for the tip–adsorbate–substrate system which also includes the vibrational degrees of freedom of the components. Any realistic model which considers the essential physics of the problem in appropriate parameters can give useful information on the STM processes, by varying the parameters in a wide range of values.

In the following calculations we choose a hydrogen atom placed between a tungsten tip and substrate. All the parameters entering the hopping integrals and the adsorption distances for H on tungsten are taken from the article by Forni *et al* (1992). For the density of states corresponding to the (100) face of the tungsten we used the relation (33). We also performed the same calculations with a rectangular shape density but the results are not very dependent on this change. The tip is modelled by a linear chain of tungsten atoms with the corresponding density of states, given by the expression (32). The resonant level is taken as the origin for the energy.

Figure 2 shows the energy diagram for our system (a) for an infinitesimal bias voltage between the tip and the substrate and (b) for a finite bias voltage V. In figure 2(a) ε_F denotes the position of the Fermi level of the tip and substrate relative to the resonant level ε_a. In figure 3 we present a tridimensional plot of the tunnelling current dependence (25) for different values of the distance $d = R_0^L = R_0^R$, and the position of the Fermi level relative to the resonant level.
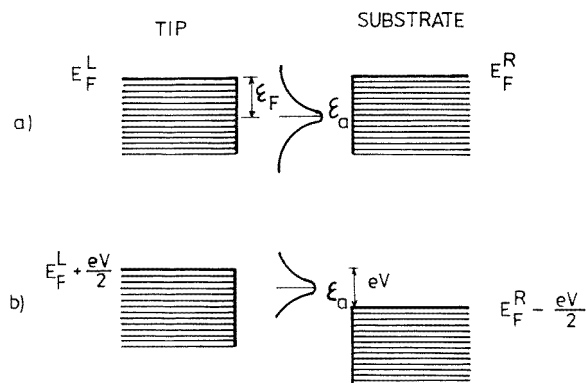
Figure 2. An energy diagram for the tip–absorbate–substrate system, for an infinitesimal bias voltage between the tip and substrate (a) and for a finite bias voltage V (b). In (b) ε_F is the position of the Fermi level relative to the resonant level ε_a of the adsorbate.
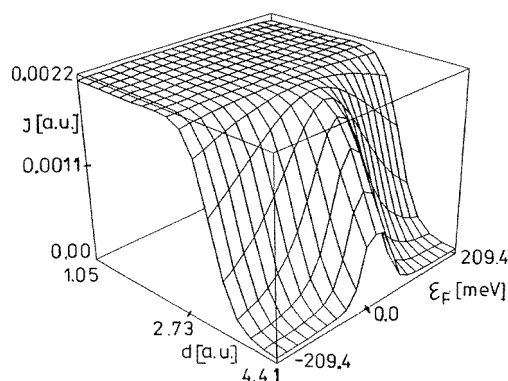

Figure 3. The tunnelling current dependence on the distances $R_0^L = R_0^R = d$ and on the positions of the Fermi levels $\varepsilon_F^{L,R}$ relative to ε_a.

As expected the tunnelling current decreases when the distance between the substrate and the tip grows. This is due to the fact that the projection of the density of states of the adsorbate on the tip decreases exponentially with the distance. The tunnelling current diminishes when the lifetime of the resonant level grows too much. At the same time the current does not change significantly when the distance d is reduced to around 2 au. Even if the projected electronic density of states of the tip on the adsorbate increases, the shift of the resonant level also increases. In these conditions, the electrons tunnel directly between the tip and the substrate and the resonant tunnelling through the adsorbate is ineffective. For a fixed tip–adsorbate–substrate separation, the tunnelling current depends on the Fermi level position ε_F relative to the resonant level position. This level can be situated above (or below) the Fermi level of the substrate and the tip $E_F^L = E_F^R$. In this case, the tunnelling is possible only on the tail of the Lorentzian shape of the resonant level and the tunnelling current is not so high. The maximum of the current is obtained when the resonant level coincides with the Fermi level of the system.

Figure 4 presents the resonant tunnelling current as a function of the bias voltage and the distance between the tip and adsorbate (the distance between adsorbate and substrate is kept constant at 2.1 au).
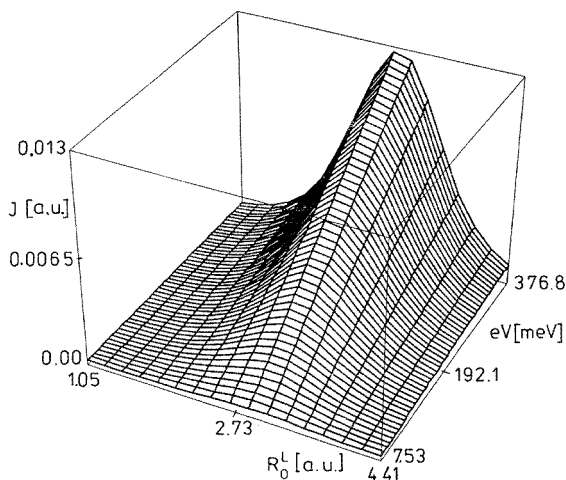
0,013

J [a.u.]

0.0065

0.00
1.05

2.73

R_0^L [a.u.]

4.41   7.53

192.1

eV[meV]

376.8

Figure 4. The tunnelling current dependence on the tip–adsorbate–separation R_0^L and on the applied bias voltage V.

It is very interesting to note that on lowering the distance between the tip and the adsorbate the resonant tunnelling current has a maximum at around 2.5 au. By lowering this distance, the projected electronic density of states of the tip on the adatom grows (the lifetime decreases). At the same time there is a considerable increase of the shift of the resonant level. This last effect is dominant, which explains the decrease of the resonant tunnelling current for low tip–adsorbate separation. To understand the above effects we show in figure 5(a) and (b) the variation of the quantity $|R_{00}|^2$ (which is related to the shift of the resonant level) and the Γ_L (related to the projected density of states) as functions of the tip–adsorbate separation. The resonant current is proportional to the 'product' of the two curves (figure 5(c)), which explains the maximum in figure 4 for $R_0^L = 2.5$ au. This distance between the tip and adsorbate, corresponding to the maximum in the resonant tunnelling, seems to be too short to be seen experimentally, because we are in the region of close contact and the chemical bonding can dominate. The value of 2.5 au corresponds to the specific adsorption system H on W(100). When we consider other atoms or molecules, the maximum occurs at larger separations and such behaviour in the current dependence can present experimental interest.

We stress the fact that the maximum appears only if the adsorbate–substrate distance is nearly constant when the tip approaches the adsorbate. If we change simultaneously the distances R_0^L and R_0^R as in figure 3, our calculations predict a saturation of the resonant current for low separations. This situation can be related to the experimental behaviour observed by Gimzewski and Moller reproduced by Lang (1987, 1989). The calculations performed by Lang to explain the presence of a resistance plateau near the point contact are based on a jellium model of the tip and adsorbate. We consider that the appearance of a maximum or a plateau in the resonant current dependence is determined by the specific system under investigation.
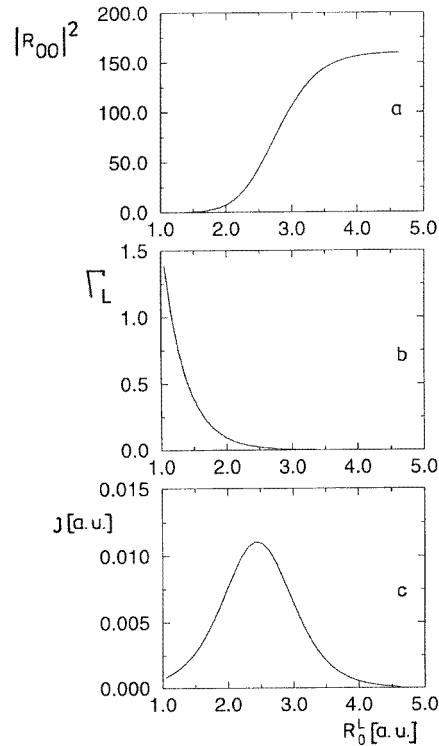
Figure 5. The plots of $|R_{00}|^2$ (a), Γ_L (b) and of the current J (c), as functions of R_0^L (R_0^R is kept constant at 2.1 au).

By approaching the sample with the tip, the potential interaction of an adsorbed atom on the sample can be modelled with a double-well potential. In this work we have considered low tip–sample separations and the adsorbate oscillates in a single-well potential. For larger tip–sample separations quantum coherence oscillations of the adsorbate can appear between the two wells as described by (Grigorescu *et al* 1997) for an Xe atom adsorbed on an Ni surface (the situation of the Xe atom is somewhat different because of physisorption instead of the chemisorption discussed in the present paper).

When we change the bias voltage for a fixed vibrational energy $\hbar\omega$, the tunnelling current presents discontinuities (which signify the opening of the inelastic channels involving phonons). These discontinuities are not visible in the current dependence but can be demonstrated only by studying the first derivative of the current $\partial I/\partial V$ as presented in figure 6. Here we have also changed the vibrational energy of the adsorbate. The conductance of the system $\partial I/\partial V$ presents a discontinuity which correspond to the first inelastic channel ($eV = \hbar\omega$). The next inelastic channels are also present but the amplitudes of the discontinuities decrease so only the first inelastic channel is important. It would be interesting to study the conditions when the next inelastic channels are important. In the calculations of figure 5 we have varied the vibrational energy as a simple parameter without changing the hopping integrals V_{ak}. This assumption is a good approximation for low vibrational energies, but for high vibrational energies the explicit dependence on vibration of these parameters must be included.
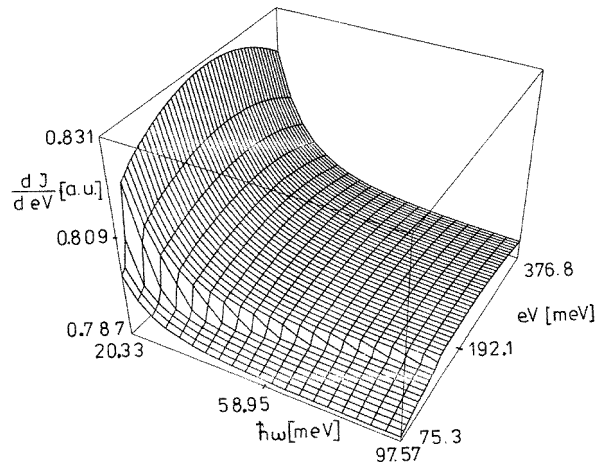
Figure 6. The conductance dependence on the applied bias *V* and on the vibrational energy of the adsorbate.

7. Conclusion

We have presented a theoretical study of the resonant tunnelling current of the STM at small variable tip–adsorbate–sample separations. This regime of close contact between tip and sample in the STM is of high current interest. We have studied the role of the resonant tunnelling and the influence of the adsorbate vibration on the STM current in the adiabatic approximation. A somewhat curious behaviour was demonstrated in the current dependence of the STM for low tip–adsorbate separation, which shows a maximum. This behaviour was explained as a concurrent effect between the decrease of the resonant level lifetime and the increase of the shift relative to the Fermi level. Careful experimental measurements are necessary to demonstrate the discontinuities predicted in the calculations for the STM conductance.

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