

Noise spectroscopy of surface excitations by scanning tunneling microscopy

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(Submitted 8 October 1992)

Pis'ma Zh. Eksp. Teor. Fiz. **56**, No. 9, 480–484 (10 November 1992)

The spectrum of current fluctuations in a scanning tunneling microscope has a δ -function component at the frequencies of localized surface excitations.

We would like to call attention to the fact that the frequency spectrum of the fluctuations (noise) in a tunneling current can be exploited to determine the frequency of localized surface excitations (e.g., the natural frequencies of adsorbates or the vibrational frequencies of the individual fragments of organic molecules). A scanning tunneling microscope can thus be used as a noise spectrometer to simultaneously determine the frequency of localized excitations and their position on the surface. There are already examples of the successful use of scanning tunneling microscopes as noise spectrometers for detecting the precession of individual spins on a surface.^{1,2}

Let us consider a system consisting of a crystal, the tip of a tunneling microscope, and an excitation which is localized at some site (or at several sites) near the surface of the crystal. We write the Hamiltonian of this system in the form

$$H = H_c + H_t + \sum_{\substack{i,n,\sigma \\ i',n'}} [T_{i'n'\sigma}^{in\sigma} c_{1in\sigma}^+ c_{2i'n'\sigma} + \text{H.a.}]$$

$$+ \sum_n \hbar \omega_n b_n^+ b_n + \sum_{i,n} [\lambda_{in} b_n^+ c_{1in\sigma}^+ c_{1in\sigma} + \text{H.a.}] \quad (1)$$

The first two terms describe the spectra of the noninteracting crystal and the noninteracting tip. The third is responsible for the tunneling between the tip and crystal, with the matrix element $\hat{T} = \{T_{i'n'\sigma}^{in\sigma}\}$. This matrix element describes jumps from the orbital $\varphi_{1n\sigma}(\mathbf{R}-\mathbf{R}_i)$ in the crystal to the orbital $\varphi_{1n'\sigma}(\mathbf{R}-\mathbf{R}_{i'})$ in the tip (n and n' specify the type of orbital, i.e., s , p , or d ; σ is a spin index), and the operators $\hat{c}_{1,2} = \{c_{1,2in\sigma}^+\}$ create electrons (the subscript 1 refers to the crystal, and 2 to the tip). The last two terms describe the energy of the n th localized vibrational mode and its interaction with the electrons at the crystal sites.

Our problem reduces to one of calculating the current-current correlation function, which contains information on the noise spectrum. We find this correlation function in the standard way:

$$(e/\hbar)^2 \langle \hat{I}(t) \hat{I}(t') \rangle = \text{Tr} \langle \hat{\mathbf{T}} \hat{c}_1^+(t) \hat{c}_2(t) - \hat{c}_2^+(t) \hat{c}_1(t) \hat{\mathbf{T}}^+ \rangle \times \langle \hat{\mathbf{T}} \hat{c}_1^+(t') \hat{c}_2(t') - \hat{c}_2^+(t') \hat{c}_1(t') \hat{\mathbf{T}}^+ \rangle, \quad (2)$$

where the Tr is over all the orbital and site indices. All the interactions (the tunneling interaction and the interaction with the local mode) are taken into account in the average over the state of the system. It follows from (2) that the correlation function can be expressed in terms of two-particle Keldysh Green's functions,³

$$\begin{aligned} \hat{\mathbf{K}}_1(t, t') &= \langle T_c(\hat{c}_1^+(t) \hat{c}_2(t) \hat{c}_2^+(t') \hat{c}_1(t')) \rangle, \\ \hat{\mathbf{K}}_2(t, t') &= \langle T_c(\hat{c}_2^+(t) \hat{c}_1(t) \hat{c}_1^+(t') \hat{c}_2(t')) \rangle, \end{aligned} \quad (3)$$

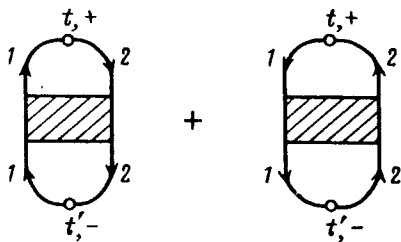
by singling out the components K_1^{+-} and K_2^{+-} [since there is no time-ordering symbol T_c on the time loop in (2)] and by taking the Tr with the tunneling-interaction matrices. This fact can be conveniently expressed in graphical form (Fig. 1a).

The free lines of the two-particle Green's functions are closed through the tunneling-interaction matrix (the circle in Fig. 1a). The hatched rectangle contains all the interactions for the tunneling electrons. In lowest order in the interaction with the local mode, the equation for the two-particle Green's function can be depicted as in Fig. 1b.

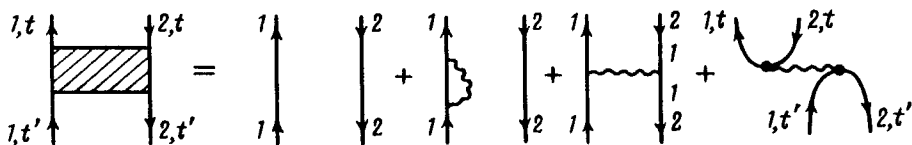
Each line in Fig. 1b is a matrix in terms of Keldysh indices. A wavy line corresponds to the Green's function of a local mode. To find the current-current correlation function we need to single out the components with the $+$ and $-$ external indices on the time loop in these diagrams. Note that each line represents a total Green's function, in the sense that it contains the tunneling interaction in all orders in $\hat{\mathbf{T}}$ (Fig. 1c).

The first diagram in Fig. 1b describes the current fluctuations when the interaction with the local mode is ignored. Of interest for our purposes is the last diagram, which makes a δ -function contribution to the noise spectrum at the frequencies ω_n .

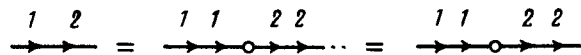
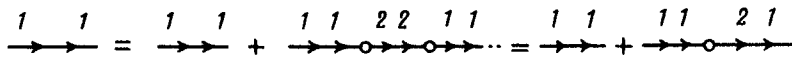
The Keldysh Green's function of the tip and the crystal can be written in the following form, where the tunneling coupling is being taken into account:



a



b



c

FIG. 1.

$$\hat{\mathbf{G}}^{\pm} = \begin{pmatrix} \hat{G}_{11}^{\pm} & \hat{G}_{12}^{\pm} \\ \hat{G}_{21}^{\pm} & \hat{G}_{22}^{\pm} \end{pmatrix} = \frac{\hat{\mathbf{I}}}{\hat{\mathbf{I}} - \hat{\mathbf{g}}^R \hat{\mathbf{T}}} \hat{\mathbf{g}}^{\pm} \frac{\hat{\mathbf{I}}}{\hat{\mathbf{I}} - \hat{\mathbf{T}} + \hat{\mathbf{g}}^A},$$

$$\hat{\mathbf{g}}^{R,A} = \begin{pmatrix} \hat{g}_1^{R,A} & 0 \\ 0 & \hat{g}_2^{R,A} \end{pmatrix}, \quad \hat{g}_{1,2}^{R,A} = \frac{1}{\omega - \hat{H}_{c,t} \pm i0}, \quad \hat{\mathbf{T}} = \begin{pmatrix} 0 & \hat{T} \\ \hat{T}^* & 0 \end{pmatrix}, \quad (4)$$

$$\hat{g}_{1,2}^{\pm}(\omega) = -2\pi i \hat{\rho}_{1,2}^0(\omega) \begin{cases} f_{1,2}(\omega) \\ f_{1,2}(\omega) - 1 \end{cases}, \quad \hat{\rho}_{1,2}^0(\omega) = -\frac{1}{\pi} \text{Im}\{\hat{g}_{1,2}^R(\omega)\}.$$

Here $\hat{\rho}_{1,2}^0(\omega)$ is the matrix of partial densities of states for the noninteracting crystal and the noninteracting tip, and $f_{1,2}$ are the distribution functions for the crystal and the tip, respectively.

Ignoring the interaction with the local mode, and using Fourier transforms, we can write the fluctuation spectrum as follows:

$$\langle \hat{I}\hat{I} \rangle_\omega = - (e/\hbar)^2 \int \text{Tr} \{ \hat{\mathbf{T}}\hat{\mathbf{G}}_{11}^+(\epsilon+\omega)\hat{\mathbf{T}}^+\hat{\mathbf{G}}_{22}^-(\epsilon) + \hat{\mathbf{T}}\hat{\mathbf{G}}_{11}^-(\epsilon+\omega)\hat{\mathbf{T}}^+\hat{\mathbf{G}}_{22}^+(\epsilon) \} d\epsilon/2\pi. \quad (5)$$

In the absence of an applied voltage ($f_1=f_2=f$), expression (5) simplifies:

$$\langle \hat{I}\hat{I} \rangle_\omega = - (e/\hbar)^2 \int \text{Tr} \{ \hat{\mathbf{T}}\hat{\rho}_{11}^+(\epsilon+\omega)\hat{\mathbf{T}}^+\hat{\rho}_{22}^-(\epsilon) \} [2-f(\epsilon)-f(\epsilon+\omega)+f(\epsilon) \times f(\epsilon+\omega)] d\epsilon/2\pi \simeq (e/\hbar)^2 \text{Tr} \{ \hat{\mathbf{T}}\hat{\rho}_{11}^+(\epsilon_F)\hat{\mathbf{T}}^+\hat{\rho}_{22}^-(\epsilon_F) \} \coth(\omega/2T), \quad (6)$$

$$\hat{\rho}_{11,22}(\omega) = -\frac{1}{\pi} \{ \hat{\mathbf{G}}_{11,22}^R(\omega) \},$$

where ϵ_F is the Fermi energy of the system (we assume $\omega \ll \epsilon_F$). When there is an external voltage V , we must make the replacement $f_1(\epsilon) \rightarrow f_1(\epsilon + eV)$ in Eqs. (5) and (6). Expression (6) is essentially the Nyquist formula. The quantity in braces (curly brackets) is the conductance of the tunneling gap.

The contribution of the last diagram (Fig. 1b) to the fluctuation spectrum can be written in the form

$$\delta \langle \hat{I}\hat{I} \rangle_\omega = i(e/\hbar)^2 \text{Tr} \{ 2\hat{\mathbf{T}}\hat{\Pi}_{11,21}^+ [\hat{\mathbf{D}}^+(\omega) + \hat{\mathbf{D}}^-(\omega)] \hat{\mathbf{T}}^+ \hat{\Pi}_{11,21}^+ + 2[\hat{\mathbf{T}}\hat{\Pi}_{11,21}^+ \hat{\mathbf{D}}^+(\omega) \hat{\mathbf{T}}^+ \hat{\Pi}_1 + \hat{\mathbf{T}}\hat{\Pi}_2 \hat{\mathbf{D}}^+(\omega) \hat{\mathbf{T}}^+ \hat{\Pi}_{11,12}^+] + [\hat{\mathbf{T}}\hat{\Pi}_{11,21}^+ \hat{\mathbf{D}}^+(\omega) \hat{\mathbf{T}}^+ \hat{\Pi}_1 - \hat{\mathbf{T}}\hat{\Pi}_2 \hat{\mathbf{D}}^R(\omega) \hat{\mathbf{T}}^+ \hat{\Pi}_{11,12}^+] + \hat{\mathbf{T}}\hat{\Pi}_2 \hat{\mathbf{D}}^+(\omega) \hat{\mathbf{T}}^+ \hat{\Pi}_1 + (\text{substitution } \hat{\Pi}_{11,21} \rightarrow \hat{\Pi}_{21,11}, \hat{\Pi}_{11,12} \rightarrow \hat{\Pi}_{12,11}) \}, \quad (7)$$

where

$$\hat{\Pi}_1 = \hat{\Pi}_{11,21}^+ + \hat{\Pi}_{11,21}^A + \hat{\Pi}_{11,21}^{AR}, \quad \hat{\Pi}_2 = -\hat{\Pi}_{11,12}^+ - \hat{\Pi}_{11,12}^R + \hat{\Pi}_{11,12}^{RA}$$

The polarization operators are defined by

$$\hat{\Pi}_{11,21}^+ = \int \hat{\mathbf{G}}_{11}^+(\epsilon) \hat{\lambda} \hat{\mathbf{G}}_{21}^-(\epsilon+\omega) d\epsilon/2\pi, \quad \hat{\Pi}_{11,12}^{AR} = \int \hat{\mathbf{G}}_{11}^A(\epsilon) \hat{\lambda} \hat{\mathbf{G}}_{12}^R(\epsilon+\omega) d\epsilon/2\pi, \quad \hat{\Pi}_{11,21}^{AR} = \int \hat{\mathbf{G}}_{11}^+(\epsilon) \hat{\lambda} \hat{\mathbf{G}}_{21}^R(\epsilon+\omega) d\epsilon/2\pi. \quad (8)$$

The multiplication in (8) is to be understood as a matrix multiplication. The Keldysh Green's functions of a local excitation are

$$\hat{\mathbf{D}}^+(\omega) = -2\pi i [\hat{\sigma}(\omega)N(\omega) + \hat{\sigma}(-\omega)(N(\omega) + 1)], \quad \hat{\mathbf{D}}^-(\omega) = \hat{\mathbf{D}}^+(-\omega),$$

$$\hat{\sigma}(\omega) = \left\{ \sum_n A_i^n \delta(\omega - \omega_n) A_j^{n*} \right\},$$

$$\hat{D}^{R,A}(\omega) = \frac{1}{2\omega_n} \sum_n A_i^n \left\{ \frac{1}{\omega - \omega_n \pm i0} - \frac{1}{\omega + \omega_n \pm i0} \right\} A_j^{n*}, \quad (9)$$

$$N(\omega) = 1/(\epsilon^{\omega/T} - 1),$$

where $\hat{\sigma}_{ij}(\omega)$ is the spectral density of phonon states, and A_i^n gives the amplitude at site n from the natural mode with frequency ω_n .

The expression for the correction to the correlation function can be put in the final form

$$\delta \langle \hat{I}\hat{I} \rangle_\omega \propto \text{Tr} \{ \hat{T} \hat{\Lambda} \sigma(\omega) \hat{\Lambda}^+ \hat{T}^+ \} \coth(\omega/2T)$$

$$\hat{\Lambda} = \int \hat{\rho}_{11}(\epsilon) \hat{\lambda} \hat{\rho}_{11}(\epsilon + \omega) \hat{T}^+ \hat{\rho}_{22}(\epsilon + \omega) f(\epsilon) [1 - f(\epsilon + \omega)] d\epsilon / 2\pi. \quad (10)$$

The noise spectrum thus has a component proportional to the spectral density of states of the local mode. This increment is proportional to T^4 . It falls off rapidly as the tip is withdrawn from the position at which the vibration is localized on the surface, because of the exponential dependence of the tunneling matrix element on the distance. It also follows from (10) that $\delta \langle \hat{I}\hat{I} \rangle_\omega$ is zero except when the frequency coincides with one of the natural vibrational frequencies of the local mode.

We wish to stress that this increment in the correlation function does not mean that we are going beyond the scope of the fluctuation dissipation theorem.⁴ The reason is that the imaginary part of the response function of the system, incorporating all the interactions, figures in this theorem.

To find a structural feature in the fluctuation spectrum at the frequency of an internal natural mode is not surprising. We might simply recall the classic example of current fluctuations in an oscillator circuit, whose spectrum has a maximum at the resonant frequency of the circuit, $\omega_n = 1/(LC)^{1/2}$.

This contribution to the spectrum of current fluctuations might be called "coherent" and interpreted in the following way. The fluctuations in the current (for definiteness, we assume that the external voltage is $V=0$ and that there is no average current) consist of a tunneling of electrons from the tip into the crystal and also in the opposite direction. The last diagram in Fig. 1b describes the coherent tunneling of a pair of electrons. In the case of tunneling from the tip into the crystal, the electron emits (or absorbs) a phonon. The next electron, as it tunnels from the crystal into the tip, absorbs (or emits) the phonon emitted by the first electron. The tunneling of a pair of electrons is thus correlated through an interaction with the vibrations of the medium. The dynamics of these vibrations is manifested directly as a δ -function contribution to the noise spectrum.

The contribution of these processes should be manifested in the dynamic conductance of the tunneling gap and also during tunneling through quantum wells and

quantum dots (the effect should be stronger in the case of the dots), in which electrons interact with the localized optical phonons.

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Translated by D. Parsons