Detecting Breather Excitations with Inelastic Tunneling Spectroscopy

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We propose inelastic electron tunneling spectroscopy scanning tunneling microscopy (IETS-STM) as a means of exciting and observing intrinsic localized modes (breathers) in a macromolecule. As a demonstration, inelastic tunneling features of the density of states are calculated for a simple nonlinear elastic Morse chain. The general formalism we have developed for the IETS is applicable to other nonlinear extended objects, such as DNA on a substrate.

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Dynamical localization phenomena have been a subject of intense theoretical research since discrete breathers (or intrinsic localized modes) were proven [1] to be generic solutions of nonlinear spatially discrete systems. These solutions of the underlying equations of coupled nonlinear oscillators are characterized by being temporally periodic and spatially localized [2, 3, 4]. Two particularly important and physically appealing aspects of discrete breathers are 1) that they exist in translationally invariant systems and therefore these excitations are radically different from Anderson localization and other localization effects driven by external disorder or defects, and 2) that they are very robust with respect to changes in the equation of motion. They have been discussed in such diverse systems as spin lattices [5], and dynamics of DNA [6, 7].

The robust localization in the form of discrete breathers occurs because the discreteness of the system provides an effective cutoff for the wavelength of the linear modes (e.g. phonons) that may exist in the system, and this can prohibit phonon resonances with all temporal harmonics of the discrete breather. This effectively eliminates decay mechanisms into extended linear modes. It is the nonlinearity of the systems that makes this possible by admitting frequencies outside the phonon (linear) band.

The field has been dominated by theoretical research, and general methods for direct experimental observation of breathers are lacking, although experiments on localization of light propagation in weakly coupled optical waveguides [8], low-dimensional crystals [9] and Josephson-junction networks [10, 11] have recently been reported.

Here we propose the use of scanning tunneling microscopy (STM) to both excite and observe breathers in an inelastic electron tunneling spectroscopy experiment (IETS). The IETS itself is a well established and powerful tool that allows the measurement of the characteristic energies of local and extended modes. Examples of applications of this technique, among many, include measurements of molecular stretching and vibrational modes in metal-insulator-metal tunnel junctions [12, 13]; observation in tunneling of the local vibrational mode of single atoms or molecules on a surface [14], observation in tunneling of the collective magnetic resonance in the superconducting state of high-$T_c$ materials [15, 16]; and recent IETS-STM of the spin flip of a magnetic atom in a magnetic field [17]. Here we give for the first time a theoretical basis for an IETS-STM observation of the breather mode in an extended system.

The IETS directly measures excitation energies. Electrons scatter off a local (or collective) mode. Due to the scattering, a contribution to the electron self-energy occurs above a corresponding threshold value of the frequency determined by the mode frequency. Thus, in a tunneling experiment, for a voltage bias exceeding the threshold, electrons can excite the mode. This additional scattering channel leads to a step in the density of states and in the tunneling conductance. Low temperatures are required to avoid thermal smearing of the step in the conductance.

The setup we propose is to use STM in a two step process: First we propose to locally excite breathers by...
injecting energetic electrons into the molecule on the substrate. The energy of the injected electrons is taken to be outside the phonon band and able to excite the breather; in the subsequent step we propose to measure the local density of states (LDOS) in the vicinity of the injection point. The first step is a major assumption of this work. There is no detailed microscopic theory for the energy transfer between electrons and breathers. We make the reasonable assumption that the resonance between the energy of the electron and that of the breather will allow efficient energy transfer between electronic degrees of freedom and breathers. At the second stage, the LDOS at a finite bias but with much smaller drive currents will allow measurement of the inelastic processes revealing the existence of the localized breather. Alternatively, one can view our work as addressing what will be the features in LDOS once the breathers are excited. The setup is illustrated in Fig. 1.

In what follows we will use a simple model to demonstrate the possibility of IETS in macromolecules. We consider a translationally invariant long chain with vibrational sites \( n = -N + 1, \ldots, 0, \ldots, N \) with local molecular displacements \( x_n \) at each site, for simplicity taken only along the direction normal to the surface. The role of the surface in this consideration is to provide mechanical support for the chain and to provide conduction electrons whose DOS will ultimately be measured by STM.

Specifically, we consider the following model Hamiltonian:

\[
H = \sum_{n=-N+1}^{N} \left[ \frac{M k_n^2}{2} + V(x_n) + \frac{k}{2}(x_n - x_{n-1})^2 \right] + \sum_k \xi_k c_k^\dagger c_k + H_{\text{int}}.
\]  

(1)

Here the first three terms describes the dynamics for the displacement field in an extended system, the fourth term is the Hamiltonian for uncoupled surface electrons with \( \xi_k = \epsilon_k - \mu \) the energy dispersion measured with respect to the chemical potential, the last term \( H_{\text{int}} = \lambda \sum_{n=-N+1}^{N} x_n \tau_n c_n c_n^\dagger \) is the interaction Hamiltonian that describes a local (Holstein) coupling between the displacement \( x_n \) and local electronic density at a site \( n \). We will ignore spin indices of the fermion operators \( c_n (c_n^\dagger) \), since we are interested in a total electronic density and there is no explicit spin dependence in the Hamiltonian.

We introduce the Matsubara Green’s functions of the electrons on the substrate. The bare Green’s function is given by:

\[
G^0(k, i\omega_n) = \frac{1}{i\omega_n - \xi(k)},
\]

(2)

\[
G^0(r, i\omega_n) = \int \frac{d^d k}{(2\pi)^d} e^{i k \cdot r} G^0(k, i\omega_n),
\]

(3)

where \( \omega_n = (2n + 1)\pi T \) is the Matsubara frequency for electrons. In a two-dimensional (2D) system, assuming that the surface states of the electrons are interacting strongly with the displacements, we have \( G^0(r, i\omega_n) = -i\pi N \delta_{\epsilon_n} J_0(k r r), \) with \( N \) being the density of states of the metal, \( J_0(x) \) the Bessel function of the zeroth order, and \( \delta_{\epsilon_n} \) the sign function. Employing perturbation theory up to second order (in the coupling constant \( \lambda \)) in the presence of the dynamical disorder (discrete breathers) coupled to the electrons, the full Green’s function is

\[
G(r, r'; i\omega_n) = G^0(r, r'; i\omega_n) + \int \int d r_1 d r_2 G^0(r, r_1; i\omega_n) \times \Sigma(r_1, r_2; i\omega_n) G^0(r_2, r'; i\omega_n),
\]

(4)

with self-energy

\[
\Sigma(r_1, r_2; i\omega_n) = \frac{\lambda^2}{\beta} \sum_{i\Omega_m} D^0(r_1, r_2; i\Omega_m) \times G^0(r_1, r_2; i(\omega_n - \Omega_m)) \]

\[= \lambda^2 \int \int d^2 k d\omega \frac{\eta_F(\xi_k) - 1 - n_B(\omega)}{\omega_n - \xi_k - \omega} \times B(r_1, r_2; \omega).
\]

(5)

Here \( D^0(r_1, r_2; i\Omega_m) \) is the Fourier transform of the correlation function \( D^0(r_1, r_2; \tau_1 - \tau_2) = (T_2(x[r_1 \tau_1] x(r_2 \tau_2))), \) \( \Omega_m = 2m\pi T \) is the Matsubara frequency for the bosonic excitations, and the two distribution functions are given by \( n_F,B(E) = 1/[\exp(E/T) \pm 1], \) respectively. Of great importance in Eq. (5) is the generalized spectral function \( B(r_1, r_2; \omega), \) which has not yet been specified and depends on the detailed model for the bosonic excitations. In this sense, Eq. (5) together with Eq. (6) is the most general formalism to describe the effects of the bosonic excitations on the electronic properties.

![FIG. 2: The displacement field in the breather excitation (a), and its Fourier transform b) \( \omega_0 = 0.7, A_n^1 \) - squares, \( A_n^2 \) - circles, \( A_n^3 \) - small circles, \( A_n^4 \) - diamonds, \( A_n^5 \) - pluses.](image)

For the purpose of the present work, we need to identify the spectral function \( B(r_1, r_2; \omega) \) for the breather mode.
Since the dynamics for the breather in [1] is described through a lattice model, we are actually studying the correlation function in discretized space coordinates. In real time and space, the retarded correlation function is given by:

$$D^{0,r}(n,m;t,t') = i\theta(t-t')\langle [\hat{x}_n(t), \hat{x}_m(t')] \rangle \text{,}$$

(6)

where \( n, m \in \text{molecule sites} \), i.e., \( r_n \) and \( r_m \), and \( \hat{x}_n(t) \) is the displacement operator at the site \( n \). We use standard quantized notations:

$$\hat{x}_n(t) = \sum_{\alpha=1}^{\infty} \left[ \hat{b}_\alpha A^\alpha_n e^{-i\omega_\alpha t} + \hat{b}_\alpha^{\dagger} A^\alpha_n^{\dagger} e^{i\omega_\alpha t} \right],$$

(7)

with \( \alpha \) being the eigenvalue index, corresponding to the energy of the mode \( \omega_\alpha = \alpha \omega_0 \) with amplitude \( A^\alpha_n \) and \( \hat{b}_\alpha \) being the mode annihilation operator. We determine the breather solutions as described in [18] and obtain the amplitudes \( A^\alpha_n \) at site \( n \) along the molecule. The coefficients \( A^\alpha_n \) describe the real space amplitude distribution of the breather mode with frequency \( \omega_\alpha \). This is a classical solution that will not decay in time (we ignore weak damping to simplify the calculation). Then

$$D^{0,r}(n,m;t,t') = -i\theta(t-t') \sum_{\alpha=1}^{\infty} \left[ A^\alpha_n A^\alpha_m e^{-i\omega_\alpha (t-t')} - A^\alpha_n A^\alpha_m^{\dagger} e^{i\omega_\alpha (t-t')} \right].$$

(8)

Its Fourier transform is obtained as:

$$D^{0,r}(n,m;\omega) = \sum_{\alpha=1}^{\infty} \frac{A^\alpha_n A^\alpha_m}{\omega + \omega_\alpha + i\delta} - \frac{A^\alpha_n A^\alpha_m^{\dagger}}{\omega - \omega_\alpha + i\delta} \text{,}$$

(9)

with infinitesimal \( \delta \), from which the spectral function follows immediately as

$$B(n,m;\omega) = \sum_{\alpha=1}^{\infty} A^\alpha_n A^\alpha_m \left[ \delta(\omega + \omega_\alpha) - \delta(\omega - \omega_\alpha) \right].$$

(10)

Here, without loss of generality, we have assumed \( A_n^\alpha \) to be real. The electronic self-energy in 2D is then found to be:

$$\Sigma(r_n,r_m;\omega_n) = \Delta^2 N_0 J_0(k_F r_{nm}) \sum_{\alpha=1}^{\infty} A^\alpha_n A^\alpha_m \times \int de \left[ \frac{1-n_F(\epsilon + n_B(\omega_\alpha))}{\omega_\alpha - \epsilon + i\delta} - \frac{1-n_F(\epsilon + n_B(-\omega_\alpha))}{-\omega_\alpha - \epsilon + i\delta} \right].$$

(11)

These formulas are quite general. The only breather-specific features in Eqs. (11) and (10) are that the breather amplitude factors \( A_n^\alpha \) are localized at the position, say \( n = 0 \), where the breather is excited [19].

Once we arrive at the electronic self energy due to the scattering of electrons off the breather mode that resides on the molecule, we are ready to calculate the change in the LDOS of electrons, which is given by:

$$N(r_i,\omega) = -\frac{1}{\pi} \text{Im} G(r_i,r_i,E+i0^+) \text{,}$$

(12)

where the retarded Green’s function is obtained through the analytic continuation from Eq. (11)

$$G(r_i,r_i;E+i0^+) = G^0(0;E+i0^+) + \sum_{n,m} G^0(r_i-r_n;E+i0^+) \Sigma(r_n,r_m;E+i0^+) \times G^0(r_m-r_2,E+i0^+) \text{.}$$

(13)

The LDOS is proportional to the low temperature local tunneling conductance, which can be measured by STM [20].

A little algebra leads to the correction to the LDOS:

$$\frac{\delta N(r,E)}{N_0} = -\pi^2 (\Delta N_0)^2 \sum_{n,m} \sum_{\alpha=1}^{\infty} A^\alpha_n A^\alpha_m \times J_0(k_F r_{1n}) J_0(k_F r_{nm}) J_0(k_F r_{mi}) \times \left[ n_F(E+\omega_\alpha) - n_F(E-\omega_\alpha) + n_B(\omega_\alpha) - n_B(-\omega_\alpha) \right] \text{.}$$

(14)

Equation (14) is the central result of this paper. It allows one to calculate the corrections to the LDOS at any point.

FIG. 3: (Color) The correction of the local density of states calculated at the center of the breather mode (a) and its derivative (b) as a function of electron energy for various temperatures \( T = 0.01 \) (Red), 0.05 (Green), and 0.1 (Blue).
on the surface and quantify the effects of the inelastic tunneling corrections due to coupling to a breather.

For the numerical calculation, we take the parameter values in Eq. (1): The atomic mass \( M = 1 \), the elastic constant \( k = 0.1 \), and a Morse potential \( V(x) = D[1 - \exp(-x^2/\xi_0^2)] \) with \( D = 0.5 \) and \( \xi_0 = 1 \), so that the bottom of the phonon continuum is located at \( \omega_c = 1 \). The lattice constant of the chain molecule is taken to be \( \xi_0 \). Energy is measured in units of \( \omega_c \) and length in units of \( \xi_0 \). We then choose the fundamental frequency of the breather mode \( \omega_0 = 0.7 \), and the dimensionless electron-mode coupling constant \( (\lambda N_0)^2 = 10^{-2} \). As shown in Fig. 2, the breather excitation is localized at some region in the molecule with a length scale of about four lattice constants along the chain direction, in contrast to the vibration mode of a single-atom molecule, which is located on a single site. Moreover, due to the anharmonicity of the Morse potential, the coefficients for higher frequency Fourier modes are finite. All these unique features can be detected by the IETS-STM experiments. Figure 3 illustrates the correction to the LDOS (upper panel) due to the presence to the breather, and the effects on the derivative of the LDOS (lower panel). As expected, there are steps in the LDOS occurring at the energy \( E = \omega_0, 2\omega_0, 3\omega_0, \ldots \). For example the step at \( E = 2\omega_0 \) originates from the inherent anharmonic nature of the breather but has much weaker intensity than the first step. However, corresponding to these steps, the peaks in the derivative of the LDOS are easier to identify. These features are however rapidly smeared out as the temperature is increased. Therefore, to detect the breather excitation, the temperature must be much lower than the mode frequency. Experimentally, the temperature of several Kelvins and a typical value of \( \omega_0 \sim 100\text{meV} \) are easily accessible.

Figure 4 shows the spatial distribution of the derivative of the LDOS correction at energy \( E = \omega_0 \). The strongest intensity occurs at the center of the localized breather core. However, one can also clearly see the spatial extension away from the breather (especially along the chain direction lying horizontally), which can be detected again by the IETS-STM. The ripples in the far field from the breather comes from the rapidly oscillating factors \( J_0(k_r r) \). All these features are observable by the IETS-STM by measuring the local tunneling conductance \( dI/dV \) and its derivative \( d^2I/d^2V \). The strongest signature of the localized lattice excitation is in the vicinity of the breather.

In summary, we have proposed a novel application of STM to perform IETS on extended molecules. Intrinsically localized nonlinear excitations (breathers) can first be excited and subsequently imaged using IETS STM. We find that indeed breathers result in an extremely localized IETS features and may be observed with STM at low temperatures. The formalism we have developed for the IETS of an extended objects is quite general and is applicable to other systems. One of the most interesting extended systems where this experiment could be performed is IETS on DNA.

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