

Theory of resonant spectroscopy of adsorbates with the help of a scanning tunneling microscope

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Tunneling through an adsorbate molecule excited by external laser light in a scanning tunneling microscope is analyzed. The photoinduced tunneling current in this case is derived.

New modifications of scanning tunneling microscopy are adding to the capabilities of this method: In addition to measuring surface relief, one can now investigate atomic forces at a surface,¹ the local thermoelectric power,² the emission of photons,³ and ionic conductivity.⁴ One can furthermore obtain information on the local density of states⁵ at a surface and on adsorbates⁶ on a surface. One can study individual paramagnetic centers at an atomic sensitivity.⁷ In a new working regime of a scanning tunneling microscope which was recently demonstrated,⁸ the tunneling gap is illuminated with laser light, and the induced tunneling photocurrent is measured (the “rectified” steady-state current in the absence of an external voltage). It turns out that the tunneling photocurrent is sensitive to the surface structure at the atomic level.⁸ This working regime presents some interesting new possibilities. By carrying out measurements with light at various frequencies, one can study resonant vibrations associated with adsorbates or other optically active excitations. Such resonant vibrations can be localized on a surface with an atomic resolution. Below we derive an expression for the tunneling photocurrent in the case in which the tunneling occurs through an optically excited adsorbate.

We will use a tunneling-Hamiltonian method to describe the tunneling between two subsystems, the first being the crystal plus the adsorbate, and the second being the tip.

The tunneling photocurrent can be written in the strong-coupling basis as follows:

$$\hat{H}_t = \sum_{\substack{n, \\ i,}} \sum_{\substack{n', \\ i'}} \left\{ \left[T_{ii'}^{nn'} + \frac{eE(t)}{\hbar\omega} d_{ii'} T_{ii'}^{nn'} + \tilde{u}_i(t) \frac{dT_{ii'}^{nn'}}{d\vec{R}} \right] c_{i'n'}^\dagger c_{i'n} + \text{H.a.} \right\}. \quad (1)$$

The first term describes jumps of electrons from the $\varphi_n(\vec{r} - \vec{R}_i)$ orbital in the crystal to the $\varphi_{n'}(\vec{r} - \vec{R}_{i'})$ orbital in the tip (n specifies the type of orbital, i.e., s, p, d, \dots). The second term corresponds to an interaction of the electrons with an electric field of frequency ω in the tunneling gap. The third term is responsible for a change in the tunneling matrix element during a mixing of the adsorbate atoms (near resonance, these atoms dominate the situation). In practice, the wavelength of the field is much

larger than the tunneling gap, so the field can be assumed to be uniform. In (1) we have introduced

$$d_{ii'} = \int_{\vec{R}_i}^{\vec{R}_{i'}} \vec{E}_0 d\vec{l} / |\vec{E}_0|,$$

$$T_{ii'}^{nn'} = \frac{i\hbar^2}{2m} \int \{ \varphi_n(\vec{r} - \vec{R}_i) \frac{d}{d\vec{r}} \varphi_{n'}^*(\vec{r} - \vec{R}_{i'}) - \varphi_{n'}^*(\vec{r} - \vec{R}_{i'}) \frac{d}{d\vec{r}} \varphi_n(\vec{r} - \vec{R}_i) \} ds. \quad (2)$$

In this one-particle approach we are ignoring the effect of the tunneling electron on the state of the adsorbate. Analysis of the experimental results shows that this approximation is valid for layers of adsorbate and large molecules,⁶ but in principle it may not be totally valid for small molecules such as CO.

The forced vibrations of the adsorbate atoms caused by the electric field are described by the standard equations

$$M_s \ddot{\vec{u}}_s(t) + \gamma_s \dot{\vec{u}}_s(t) = - \sum_{s'} \vec{G}_{ss'} \vec{u}_{s'}(t) + e_s E_0 \sin(\omega t). \quad (3)$$

Here $\vec{G}_{ss'}$ is the elastic-constant matrix, e_s and M_s are the effective charge and the mass of the ion, and γ_s is a phenomenological decay constant of the decay caused by the interaction with other modes. Near resonant frequencies we can ignore the displacements of the other atoms on the surface far from the needle tip and the molecule. The displacement amplitudes can be written as follows with the help of (3):

$$\vec{u}_s(t) = \vec{u}_s^0(\omega) e^{i\omega t} + \text{c.c.}$$

$$= \frac{\sum \Delta_{ss'} e_{s'}}{\det \{ M_s \omega^2 - i\gamma_s \omega + G_{ii'}^{nn'} \}} E_0 e^{i\omega t} + \text{c.c.} = \hat{\alpha}(\omega) \vec{E}_0 e^{i\omega t} + \text{c.c.}, \quad (4)$$

where $\hat{\alpha}(\omega)$ is the polarizability matrix, which has singularities at resonant frequencies (at the zeros of the det).

The tunneling current can be expressed in terms of Keldysh Green's functions:⁹

$$I(t) = \frac{e}{\hbar} \text{Sp} \{ (\hat{T} + \hat{E}(t) + \hat{U}(t)) \hat{G}_{ct}^+(t, t) - \hat{G}_{tc}^+(t, t) (\hat{T} + \hat{E}(t) + \hat{U}(t))^+ \}. \quad (5)$$

The trace (Sp) is evaluated over the orbital and spatial indices. The indices c and t refer to the crystal and the tip. We introduce

$$\hat{T} = \{ T_{ii'}^{nn'} \}, \quad \hat{E}(t) = \hat{E}_0 e^{i\omega t} + \text{c.c.} = \left\{ \frac{2eE_0}{i\hbar\omega} T_{ii'}^{nn'} d_{ii'} \right\} e^{i\omega t} + \text{c.c.},$$

$$\hat{U}(t) = \hat{U}_0(\omega) e^{i\omega t} + \text{c.c.} = \left\{ -2i\vec{u}_i^0(\omega) \frac{dT_{ii'}^{nn'}}{d\vec{R}_{i'}} \right\} e^{i\omega t} + \text{c.c.} \quad (6)$$

Using a quasienergy representation for the Green's function,

$$\hat{G}(t, t') = \sum_{n=-\infty}^{\infty} \hat{G}_n(t-t') e^{i\omega n(t+t')/2}, \quad (7)$$

we find the following expression for the steady-state tunneling photocurrent as a function of the frequency of the external field, in second order in \hat{H}_I :

$$\begin{aligned} I_{\Phi}(\omega) = & \frac{2\pi e}{\hbar} \text{Sp} \int \{ [\hat{U}_0(\omega) + \hat{E}_0] \hat{\rho}_c(\Omega + \frac{\omega}{2}) [\hat{U}_0(\omega) + \hat{E}_0]^+ \hat{\rho}_t(\Omega - \frac{\omega}{2}) \\ & \times [n_c(\Omega + \frac{\omega}{2}) - n_t(\Omega - \frac{\omega}{2})] \\ & - [\hat{U}_0(\omega) + \hat{E}_0] \hat{\rho}_c(\Omega - \frac{\omega}{2}) [\hat{U}_0(\omega) + \hat{E}_0]^+ \hat{\rho}_t(\Omega + \frac{\omega}{2}) \\ & \times [n_t(\Omega + \frac{\omega}{2}) - n_c(\Omega - \frac{\omega}{2})] \} d\Omega. \end{aligned} \quad (8)$$

Here $n_{c,t}$ are one-particle distribution functions, and $\hat{\rho}_{c,t}$ are density matrices of the states of the crystal (plus adsorbate) and the tip, respectively. These matrices are given by

$$\hat{\rho}_{c,t}(\Omega) = \{ \rho_{ii'}^{n,n'}(\Omega) \} = \{ \sum_{\mu} A_{in}^{\mu} A_{i'n}^{\mu*} \delta(\Omega - \epsilon_{\mu}) \}, \quad (9)$$

where ϵ_{μ} is an eigenvalue of the energy spectrum, and A_{in}^{μ} are the coefficients of an expansion of the eigenfunction of level ϵ_{μ} in localized orbitals $\varphi_n(\vec{r} - \vec{R}_i)$. All the information on the electronic and atomic structure of the crystal (plus adsorbate) and of the tip is embodied in the coefficients A_{in}^{μ} .

The onset of a photocurrent can be explained at a qualitative level as follows. The tunneling current is the difference between two fluxes: that out of the crystal into the tip and that out of the tip into the crystal. In the absence of light and in the absence of an external voltage, these two fluxes are equal. When the tunneling gap is illuminated (and no voltage is applied), an electron tunneling out of the crystal into the tip may absorb a photon of energy ω and go into an energy state in the tip which is shifted by an amount ω from its original energy. The inverse process also occurs: An electron tunneling out of the tip into the crystal can also absorb a photon of energy ω . The difference between the two fluxes gives us the resultant tunneling photocurrent, which is described by (8).

Near the resonant frequency ω_s [i.e., under the condition $M_s(\omega^2 - \omega_s^2)l^2/\hbar\omega \ll 1$, where l is a length scale of the tunneling gap] we can ignore \hat{E}_0 in (8). For the steady-state tunneling photocurrent in the absence of an external voltage we have ($T \ll \omega, \epsilon_F$, where T and ϵ_F are the temperature and Fermi energy in the tip)

$$I_{\Phi}(\omega) \propto \frac{2\pi e\omega^2}{\hbar} \text{Sp} \left\{ \frac{d}{d\epsilon} [(\hat{\alpha}(\omega)\nabla\hat{T})\hat{E}_0\hat{\rho}_c(\epsilon)(\hat{\alpha}(\omega)\nabla\hat{T})^+\hat{E}_0\hat{\rho}_t(\epsilon)]|_{\epsilon=\epsilon_F} \right\} \quad (10)$$

$$\nabla \hat{T} = \left\{ \frac{dT_{ii'}^{nn'}}{d\vec{R}_{i'}} \right\}.$$

Near the resonant frequency, the tunneling photocurrent is proportional to the squared polarizability of the adsorbate molecule.

In the absence of an applied voltage, the tunneling photocurrent arises from a modulation of the effective size of the asymmetric tunneling gap between the crystal (plus adsorbate) and the tip. Because of the adsorbate, the amplitude of the modulation of this gap itself depends on the field frequency. In the case of a symmetric transition, there is no effect, as follows from (8).

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