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Effect of Resonating Paramagnetic Centers on the Current of the Scanning Tunneling Microscope

Rodrigo Prioli and *J.S. Helman*

Centro Brasileiro de Pesquisas Físicas - CBPF
Rua Dr. Xavier Sigaud, 150
22290-180 – Rio de Janeiro, RJ – Brasil

Abstract

We evaluate the amplitude of the Larmor frequency component of the scanning tunneling microscope current induced by a single resonating spin, in a model in which the tunneling barrier is modulated via spin-orbit interaction. From Kramer's theorem follows however, that the barrier height modulation cannot have Larmor components and such components in the current are caused by its non-linear dependence with the barrier height. We obtain an effect which is five orders of magnitude smaller than that reported by Y.Manassen et. al.[Phys.Rev.Lett.,62, 2531,1989].

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1 Introduction

The spin precession of single paramagnetic centers in a constant outside magnetic field can modulate the current of the scanning tunneling microscope (STM) with the Larmor frequency. This has been reported in the case of surfaces of partially oxidized Si(111) [1]. To explain the effect, mechanisms based on the spin-orbit interaction were proposed [2, 3]. Sachal and Manassen [2] proposed a mechanism in which the dangling bond of the paramagnetic center, when excited by the tunneling electrons in the presence of a magnetic field, produces a charge distribution that oscillates with the Larmor frequency. These charge variations induce a time dependent dipole moment, which locally changes the potential barrier between the sample and the tip of the STM, thus modulating the tunneling current. In this paper we evaluate the Larmor frequency component of the tunneling current using a model based on the ideas of Ref.[2]. We show, on the basis of general considerations about time reversal invariance, that the electric dipole moment induced by the resonating electron cannot have Larmor frequency components. As a consequence, in this model, the current modulation with Larmor frequency follows from the non-linear dependence of the current on the barrier height. We obtain a result which is five orders of magnitude smaller than that reported.[1]

2 Model

Following Ref. [2], we consider a paramagnetic center of type P_b [4, 5] constituted by a localized hole at the site of a trivalent Si defect [5], which can be thought as an acceptor, in a crystal field of three other Si atoms. The latter build the basis of a tetrahedron of which the former is the vertex. The z-axis is taken along the axis of the tetrahedron perpendicular to the Si surface. The crystal field has C_{3v} symmetry.

The system is described by the Hamiltonian [2]

$$\mathcal{H} = \Delta + \xi(\vec{L} \cdot \vec{S}) + \mu_B(\vec{L} + g_e\vec{S}) \cdot \vec{H} \tag{1}$$

where $\xi = -0.0017$ eV is the spin-orbit coupling for the 3p orbitals of Si [6], μ_B is the Bohr magneton, and g_e is the free electron gyromagnetic factor. $\vec{S}$ is the hole spin operator, $\vec{L}$ its orbital angular momentum operator and $\vec{H}$ an external magnetic field with direction defined by the angles λ, η :

$$H_x = H_0 \cos(\eta)\sin(\lambda) \tag{2}$$

$$H_y = H_0 \sin(\eta)\sin(\lambda) \tag{3}$$

$$H_z = H_0 \cos(\lambda). \tag{4}$$

The crystal field Δ is taken to be 100ξ [2]. We consider a reduced Hilbert space of eight states which are a representation of the C_{3v} symmetry[2, 7]

$$|0, \alpha\rangle = R(r)(B|S\rangle + A|P_z\rangle)\alpha \tag{5}$$

$$|0, \beta\rangle = R(r)(B|S\rangle + A|P_z\rangle)\beta \tag{6}$$

$$|j,\alpha,(\beta)\rangle = R(r)\frac{1}{\sqrt{3}}(A|S\rangle - B|P_z\rangle + \exp^{i\varphi_j}|P_+\rangle + \exp^{-i\varphi_j}|P_-\rangle)[\alpha,(\beta)] \qquad (7)$$

with $|S\rangle = Y_0^0(\theta,\varphi)$, $|P_z\rangle = Y_0^1(\theta,\varphi)$, $|P_+\rangle = -Y_1^1(\theta,\varphi)$, $|P_-\rangle = Y_1^{-1}(\theta,\varphi)$, where $Y_l^m(\theta,\varphi)$ are the spherical harmonics and $\varphi_1 = 0^0$, $\varphi_2 = 240^0$ and $\varphi_3 = 120^0$. $\alpha(\beta)$ stands for the spin eigenfunction with z component 1/2 (-1/2). θ is measured from the z-axis and φ is the azimuthal angle measured from the x-axis which is taken on the base of the tetrahedron through one Si.

The paramagnetic center is supposed to have a fraction $A^2 = (1 - B^2) = 0.88$ of $|P_z\rangle$ symmetry [5]. The radial part of the wave function is taken to be hydrogenoid, $R(r) = \frac{1}{\sqrt{r_0^3\pi}}e^{-r/r_0}$, with a radius r_0 corresponding to a hole with effective mass m^* belonging to an acceptor in a medium of dielectric constant ϵ [8]. The Hamiltonian (1) was diagonalized in the basis of functions (5-7) for $H_0 = 180$ G, $\eta = 60^0$ and λ from 0^0 to 90^0 in steps of 15^0. The resulting eigenfunctions are denoted by $\Psi_{j,\gamma}$, where $j = 0,\cdots,3$ labels the Kramer doublets, $\gamma = 1,2$ their components and $\hbar\omega_{j,\gamma}$ are the corresponding energies. The energy spectrum and the field dependent g-factors conform with those of Ref.2.

During its scanning, the paramagnetic center is assumed to be somehow perturbed by the tunneling electrons in such a way that the crystal field vanishes [2]. The Hamiltonian (1) was once more diagonalized with $\Delta = 0$ and the corresponding eigenfunctions denoted by $\Psi'_{j,\gamma}$. When the perturbation suddenly ceases, and the crystal field has recovered its initial value $\Delta = 100\xi$, the hole is supposed to be left in a state which is a linear combination of the lowest doublet wave functions

$$\frac{1}{\sqrt{2}}[\Psi'_{0\alpha} + \Psi'_{0\beta}]. \qquad (8)$$

This corresponds to a spin perpendicular to the z-direction. To calculate the subsequent time evolution of the hole initial state, Eq.(8), this is developed in the basis $\Psi_{j,\gamma}$:

$$\frac{1}{\sqrt{2}}[\Psi'_{0\alpha} + \Psi'_{0,\beta}] = \sum_{j,\gamma} A_{j,\gamma}\Psi_{j,\gamma}. \qquad (9)$$

The coefficients $A_{j,\gamma}$ were calculated for the values of $\vec{H}$ mentioned above. The time dependent wave function is given by

$$\Psi(r,t) = \sum_{j,\gamma} A_{j,\gamma}\Psi_{j,\gamma}(r)e^{-i\hbar\omega_{j,\gamma}}. \qquad (10)$$

For simplicity, the potential barrier that determines the tunneling current between the tip and the surface is supposed to have translational symmetry parallel to the surface and to be of square shape, with height

$$V = \frac{(w_t + w_s)}{2} \qquad (11)$$

where w_t and w_s are the work functions of the metallic tip and the Si surface.

The surface density of electric dipole moment

$$D_z(x,y,t) = |e| \int_{-\infty}^{\infty} dz \Psi^*(\vec{r},t) z \Psi(\vec{r},t) \quad (12)$$

induced by the paramagnetic center modifies locally the work function of the Si surface by the amount [9]

$$\Delta w_s(x,y,t) = \frac{|e|}{\epsilon} D_z(x,y,t), \quad (13)$$

here, e is the electron charge.

To further simplify the calculation we replace the local work function variation $\Delta w_s(x,y,t)$ by its average over the area $S = \pi r_0^2$ of the paramagnetic center:

$$\Delta w_s^{ave} = \frac{1}{S} \int_{-\infty}^{\infty} dx dy \Delta w_s(x,y,t) = \frac{e^2}{\pi r_0^2 \epsilon} \frac{3}{2} r_0 G(\eta, \lambda), \quad (14)$$

where $G(\eta,\lambda)$,which is of the order of ξ/Δ, results from the angular integrations. Within the model of an acceptor [8], this can be written in terms of the ionization energy $\Delta E = e^2/2\epsilon r_0 = 0.3eV$ of the hole [5]. Then, the change in the barrier height becomes

$$\Delta V = \frac{\Delta w_s^{ave}}{2} = \frac{3}{2\pi} \Delta E \cdot G(\eta, \lambda). \quad (15)$$

The tunneling current is proportional to $\exp[-\sqrt{2mV/\hbar^2}d]$, where d is the distance between the surface and the tip. For $\Delta V \ll V$ we can write for the relative change of the current

$$\frac{\Delta I}{I_0} = \sqrt{2mV} \frac{d}{\hbar} \frac{\Delta V}{2V} + \frac{1}{2} (2mV) \frac{d^2}{\hbar^2} \left(\frac{\Delta V}{2V} \right)^2 + \cdots . \quad (16)$$

The time dependence of the first term does not contain Larmor frequency components. ΔV is proportional to the matrix elements

$$\int \Psi^*_{j',\gamma'} z \Psi_{j,\gamma} d^3r, \quad (17)$$

which vanish for $j = j'$. This follows from the time reversal symmetry of the electric dipole operator ez and Kramers theorem [10]. Only very large frequencies corresponding to energy differences $\hbar(\omega_{j,\gamma} - \omega_{j',\gamma'})$ for $j \neq j'$, of the order of the spin-orbit splitting, are present in ΔV. Thus the leading terms with Larmor frequency are contained in $(\Delta V)^2$ which involves differences of those large frequencies.

Table 1 shows $\Delta I/I$ for $\eta = 60^0$ and several values of λ. To calculate $\Delta I/I$ we use $\sqrt{2mVd^2/\hbar^2} = 3.6$ which results from the estimated values $V = 4eV$, $d = 3.5\AA$ and m equal to the free electron mass.

3 Conclusions

It is remarkable that the modulation of the tunneling barrier induced by the resonating spin through the spin-orbit interaction has not Larmor components. This is due to

Table 1: Larmor components of the relative tunneling current $\Delta I/I$ for several directions of the magnetic field.

λ	$\Delta I/I$
$0°$	0
$15°$	$9.57 \times 10^{-8}\cos(\omega_L t) - 5.80 \times 10^{-8}\sin(\omega_L t)$
$30°$	$4.01 \times 10^{-7}\cos(\omega_L t) + 5.10 \times 10^{-7}\sin(\omega_L t)$
$45°$	$3.76 \times 10^{-6}\cos(\omega_L t) - 1.93 \times 10^{-6}\sin(\omega_L t)$
$60°$	$3.63 \times 10^{-7}\cos(\omega_L t)$
$75°$	$1.21 \times 10^{-6}\cos(\omega_L t)$
$90°$	0

Kramer's theorem which requires vanishing matrix elements for time reversal invariant operators (like the electric dipole moment) within a Kramer's doublet. $\Delta I/I$ has Larmor components , however, because the current I is a non linear function of the barrier height and frequency differences come into play.

The Larmor component of the ratio $\Delta I/I$ has a maximum at $\lambda = 45^0$ and it vanishes for $\lambda = 0^0$ and $\lambda = 90^0$. Thus, in this model,there is no effect when the field is applied along the axis of the paramagnetic center. It could happen that in the experiment this axis is tilted with respect to the field (which is applied normal to the surface). Even so, the maximum of $\Delta I/I$, at $\lambda = 45°$, is still five orders of magnitude smaller than the experimental value reported for an applied field of $180G$. Thus, in our view an explanation of these STM observations on a center with Kramer's doublets is not possible. In case that the observation is not an experimental artifact, completely different centers which do not have Kramer's degeneracy might be considered.

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