

## Spin-orbit-coupling mechanism for scanning-tunneling-microscopy observation of individual paramagnetic spins

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The observation of the precession frequencies of individual paramagnetic spins with the scanning tunneling microscope is explained here by a spin-orbit-coupling mechanism. The dangling-bond defect is excited into a superposition of eigenstates by the tunneling electrons. The charge density of the dangling bond will therefore be time dependent. Due to the spin-orbit coupling, frequencies close to the precession frequencies will appear in these oscillations, and the tunneling current will have oscillating components that are related to the precession frequency.

The scanning tunneling microscope (STM) is a revolutionary microscopic technique that is capable of atomic resolution.<sup>1,2</sup> The origin of this resolution is the extremely narrow spatial dimension of the measurement probe. The local character of measurement with the STM can be used to measure a variety of physical phenomena with atomic resolution. An example of such a possibility is the observation of the characteristic precession frequencies of individual paramagnetic spins on thermally oxidized Si(111) surfaces.<sup>3</sup>

Such a surface is known to contain isolated paramagnetic Si radicals, as was proved with conventional electron-spin resonance (ESR).<sup>4</sup> These localized dangling-bond defects are known as  $P_b$  centers. The unpaired electron density is 80% localized on the central Si atom. The defect can be charged (to have 0 or 2 electrons) and can become diamagnetic. The charging occurs when bias voltage is applied. The  $0 \rightarrow 1$  electron transition is located 0.3 eV above the silicon valence band, and the  $1 \rightarrow 2$  transition 0.25 eV below the conduction-band minimum.<sup>5</sup>

The localized defect can be described by four  $|SP_3\rangle$  hybridized orbitals. The dangling-bond state  $|SP_3^0\rangle$  is separated from the other three orbitals:  $|SP_3^1\rangle$ ,  $|SP_3^2\rangle$ , and  $|SP_3^3\rangle$  (directed to the three nearest-neighbors atoms) by  $\Delta$ , the energy difference between the molecular orbitals. The defect has a  $C_{3v}$  symmetry. The basis functions are products of the  $|SP_3\rangle$  and the spin wave functions; namely, eight basis functions: twofold- and sixfold-degenerate levels. A more precise description of the system has to incorporate some breaking of the  $C_{3v}$  symmetry (Jahn-Teller distortion) in the system to remove the degeneracy of the sixfold-degenerate level as well as some dehybridization of the  $|SP_3^0\rangle$  orbitals due to the broken symmetry. These modifications, however, should not change the basic behavior which is discussed here and not included. These basis functions are mixed by the spin-orbit coupling. The coupling splits the sixfold-degenerate level into three twofold-degenerate levels with the splittings given by  $\delta_i$ ,  $i=1,2,3$ . An external magnetic field will split the four degenerate Kramers doublets to the corresponding Zeeman levels [Fig. 1(a)]. These orbitals are filled with seven electrons, enabling the treatment of the system as a single-

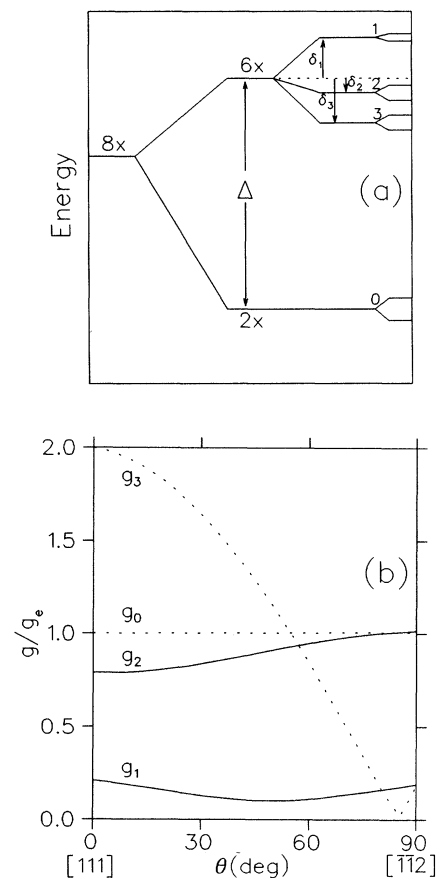


FIG. 1. (a) A scheme of the electronic energy levels as split by the molecular interactions, the spin-orbit coupling, and the magnetic field. These levels are not in scale. The symbols  $8\times$ ,  $6\times$ , and  $2\times$  indicate the degeneracy of the level. (b) The splitting of the four doublets as a function of the orientation of the magnetic field. These splittings are given as a ratio between the particular effective  $g$  value and  $g_e$ .  $g_0$  (which is the splitting of the ground state) is anisotropic, but this anisotropy (1%) is hard to distinguish in the scale required to display the anisotropies of the other splittings.

hole problem. The Hamiltonian for the system is

$$H = \Delta + \xi \mathbf{L} \cdot \mathbf{S} + \beta (\mathbf{L} + g_e \mathbf{S}) \cdot \mathbf{H}, \quad (1)$$

where  $\xi$  is the spin-orbit-coupling constant,  $\mathbf{L}$  and  $\mathbf{S}$  are the orbital and spin angular momenta,  $g_e$  is the isotropic  $g$  factor,  $\beta$  is the Bohr magneton, and  $\mathbf{H}$  is the magnetic field. We use both first-order perturbation theory and numerical calculations to find the eigenvectors  $|u_i\rangle$  and the eigenvalues  $E_i$  of the system. The matrix elements were calculated in the basis  $|SP_3^0\alpha\rangle$ ,  $|SP_3^0\beta\rangle$ ,  $|SP_3^1\alpha\rangle$ ,  $\dots$ ,  $|SP_3^1\beta\rangle$ , from the values of the operators  $\xi \mathbf{L} \cdot \mathbf{S}$ ,  $\mathbf{L}$ , and  $\mathbf{S}$  in the basis of conventional orbital ( $|S\rangle$ ,  $|P\rangle$ ) and spin ( $|\alpha\rangle$ ,  $|\beta\rangle$ ) functions.<sup>6</sup> Perturbation theory is most convenient in the calculation of the frequency of the ground-state Zeeman transition. The spin-orbit term  $\xi \mathbf{L} \cdot \mathbf{S}$  causes mixing between the different basis functions. The mixing coefficients between the unperturbed ground-state functions  $|SP_3^0\alpha\rangle_0$ ,  $|SP_3^0\beta\rangle_0$ , and the other basis functions are calculated by first-order nondegenerate perturbation theory,<sup>6</sup> giving the perturbed eigenfunctions  $|SP_3^0\alpha\rangle_1$  and  $|SP_3^0\beta\rangle_1$ . These coefficients are found to be of the order of magnitude of  $\xi/\Delta$ .

The Zeeman Hamiltonian is applied as a second, smaller perturbation which causes mixing between  $|SP_3^0\alpha\rangle_1$  and  $|SP_3^0\beta\rangle_1$  and removes the degeneracy between these states. The ESR transition that is observed is dependent on the orientation of the magnetic field. This dependence reflects the symmetry of the spin center:  $g_0 = g_e$  when  $\mathbf{H}_x = \mathbf{H}_y = \mathbf{H}_z$  (the magnetic field is parallel to the dangling bond) and  $g_0 = g_e + \xi/\Delta$  when  $\mathbf{H} = \mathbf{H}_x$ ,  $\mathbf{H}_y$ , or  $\mathbf{H}_z$  (the field is parallel to one of the axes). Thus the magnitude of the value of  $\xi/\Delta$  is observed from the  $g$  anisotropy of the ESR line and is 0.01.<sup>4</sup> This value of  $\xi/\Delta$  is assumed in all the calculations. Numerical diagonalization of the Hamiltonian also gives the splittings of the other three Kramers doublets. The dependence of these splittings on the orientation of the magnetic field is given in Fig. 1(b). As expected, these transitions are much more anisotropic than that of the first doublet. This illustrates a general truth: The removal of the degeneracy of different orbitals with the same quantum number (of the orbital angular momentum) results in quenching of the orbital angular momentum. The spin-orbit coupling restores this momentum to an extent which depends on the ratio between  $\xi$  and the splitting which removes the degeneracy ( $\Delta$ ). Since no field (like  $\Delta$ ) is removing the degeneracy between the six excited levels, the contribution of the orbital angular momentum is much larger, giving a much larger anisotropy.

In the STM, the tunneling electrons are capable of inducing very strong local and instantaneous fields at the spin center. These fields may break the symmetry and change the magnitude of the effective crystal fields as well as induce transitions. It is recalled that fluctuating localized energy levels are playing an important role in many dynamic processes at the interface. The size of these fluctuations can be several eV. For example,<sup>7</sup> in a solid-liquid interface, the fluctuations in the polarization field of a polar medium are causing fluctuations in the surface-state energy, resulting in a charge transfer from the solid to the liquid. Such fluctuations also play a role in inelastic tun-

neling processes. It is expected, therefore, that a tunneling electron from the tip which passes in the close vicinity of the spin center is able to cause a significant excitation, namely, to lead to a state  $|\Psi(t_0)\rangle$  which is quite different from the eigenfunctions. The dynamics following such an excitation is calculated by expanding  $|\Psi(t_0)\rangle$ , the excited superposition, in the basis of the eigenfunctions of the system ( $|u_i\rangle$ ):  $|\Psi(t_0)\rangle = \sum_i b_i |u_i\rangle$ , where  $b_i = \langle u_i | \Psi(t_0) \rangle$ . The time evolution of the state will be  $|\Psi(t)\rangle = \sum_i b_i \times \exp[-iE_i(t-t_0)/\hbar] |u_i\rangle$ .

As shown below, if the system is excited into a superposition of states, the charge density of the spin center will be time dependent, with frequency components that are close to the Larmor frequency. This calculation is done as follows. The matrix is diagonalized with different parameters of the Hamiltonian, which are changed by the perturbation. This will give a set of new eigenvectors  $|v_i\rangle$ . An example is assuming a value of  $\xi/\Delta$  much larger than that of the original Hamiltonian. This is possible since both  $\xi$  and  $\Delta$  should be affected by the fluctuating electric field mentioned above. The perturbation is then (suddenly) removed, and the dynamics is calculated with the help of the eigenvectors  $|u_i\rangle$  and the eigenvalues  $E_i$  of the unperturbed Hamiltonian. We choose the excited superposition  $|\Psi(t_0)\rangle = (|v_1\rangle + |v_2\rangle)/\sqrt{2}$ , where  $|v_1\rangle$  and  $|v_2\rangle$  are the ground-state eigenvectors for the perturbed Hamiltonian. This is expanded in the basis of the unperturbed Hamiltonian, and the time evolution of the charge density in the  $|SP_3^0\rangle_0$  orbitals [ $\rho_{|SP_3^0\rangle}(t)$ ] is calculated. In this calculation, a sum of several oscillating components is observed with frequencies which correspond to the energy differences between the eigenenergies. Rearranging this expression gives (only time-dependent and relevant components are included)

$$\begin{aligned} \rho_{|SP_3^0\rangle}(t) = & a_1 \sin(\frac{1}{2} \omega_1 t) \sin(\frac{1}{2} \Omega_1 t) \\ & + a_2 \sin(\frac{1}{2} \omega_2 t) \sin(\frac{1}{2} \Omega_2 t), \end{aligned} \quad (2)$$

where  $\omega_1 = 2(\Delta + \delta_1)/\hbar$ ,  $\omega_2 = 2(\Delta + \delta_2)/\hbar$ , and  $\Omega_1 = g_0\beta H/\hbar$ ,  $\Omega_2 = (g_0 + g_1)\beta H/\hbar$ . These beats are products of "fast" oscillating functions at frequencies corresponding to  $(\Delta + \delta_i)/\hbar$ , and "slow" oscillating functions at frequencies that are related to the Zeeman transitions. In a perfectly linear (Ohmic) device, oscillations at frequencies  $\frac{1}{2}(\omega_1 \pm \Omega_1)$  and  $\frac{1}{2}(\omega_2 \pm \Omega_2)$  could be detected.

However, since the tunneling junction deviates from linearity (as can be seen from an  $I$ - $V$  curve), the slow frequencies  $\Omega_1, \Omega_2$ , which are close to the free-electron ( $g=2$ ) Larmor frequency, as well as the fast frequencies  $\omega_1, \omega_2$ , will be detected. Different excitations (for example, from random fluctuating fields) will lead to a different  $|\Psi(t_0)\rangle$ , but the time evolution will still contain the frequencies  $\Omega_1$  and  $\Omega_2$ . If some symmetry-breaking distortions (Jahn-Teller effect) were included initially in the Hamiltonian, these frequencies would result even closer to the free-electron Larmor frequency. Macroscopic ESR measurements<sup>8</sup> indicated that such distortions do exist and that they can be quite significant. They will split the sixfold-degenerate levels by a factor larger than the spin-orbit coupling. Including these distortions will lead to a better agreement with the frequencies measured experi-

mentally.<sup>3</sup> Measuring such distortions might provide physical information, for example, strain effects. Such a possibility is presently limited by the experimental difficulty of determining the direction of the magnetic field at the microscopic level.

The amplitudes of the modulation ( $a_1$  and  $a_2$ ) are dependent on the initial conditions. These amplitudes are expected to be larger when the deviation of the excited superposition from the eigenfunctions is large. In Fig. 2 the frequencies and the amplitudes are shown in the limit where the initial state  $[\Psi(t_0)] = (|v_1\rangle + |v_2\rangle)/\sqrt{2}$  is such that  $\Delta$  has practically vanished. These parameters were calculated at different directions of the magnetic field. Such an initial state could arise, for example, in cases where an electron was trapped in the  $P_b$  center, and then suddenly departs. Such a sudden departure will lead to an initial state that is similar to the one used in the calculation of the time evolution shown in Fig. 2. The modulation is of the order of magnitude of  $\xi/\Delta$  and will vanish when the size of the spin-orbit coupling is diminished. In addition, when the system is excited to a superposition of states, the electron density in the bonds from the paramagnetic Si atom to the neighboring atoms will have a similar dynamics. Thus the observed charge-density oscillations can affect the tunneling also when the current filament is not precisely above the spin center.

In the previous example, the excited state is formed by changing the size of  $\Delta$ . It is possible, however, that an excited superposition is created in which the different  $\delta_i$  are changed (namely, that the  $C_{3v}$  symmetry of the perturbed system is broken). Such fields can arise when the tunneling current filament is not precisely above the spin center. Our calculations indicated that in this case a much smaller perturbation is sufficient to create a large modulation. In the experiment,<sup>3</sup> the images appeared as two lobes separated by a node. This might be explained by the stronger effect of the symmetry-breaking fields.

It was shown here that the charge density of a localized paramagnetic spin center has time-dependent components (close to the Larmor frequency) when the system is driven out of an eigenstate. There are several ways in which these oscillations can affect the tunneling probability and current: First, such oscillations will modulate all the forces applied on the tunneling electrons as a result of the charge density of the nearby atoms on the surface. They will change the Coulombic interactions as well as the exchange and correlation energies. At distances in which these interactions are of the order of magnitude of electron volts, the time-dependent interactions will be of the order of magnitude of several tens of meV. These oscillations can be directly detected. They can also be detected indirectly by modulating the barrier height and shape, leading to modulations of the tunneling current. Knowing the dependence of the tunneling current on the barrier height, it can be estimated that rf signals of that level are

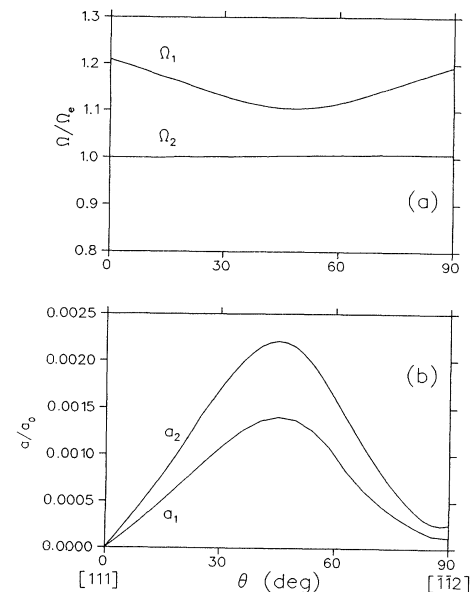


FIG. 2. (a) The frequencies and (b) the relative amplitudes of the slow oscillating components of the charge density [Eq. (2)]. The frequencies are expressed relative to  $\omega_L$ , the Larmor frequency of a free electron. The intensities are expressed relative to  $a_0$ , the time-independent component of the charge density (when the system is in the excited superposition).

above the experimental detection limit (0.1–0.2 nA rf current<sup>3</sup>). In addition, these charge-density oscillations of the localized state must have an effect on the overlap between the tip and the surface wave functions by affecting the surface local density of states.

Fluctuations in the values of  $\xi$  and  $\Delta$  which are a result of the tip motion might also appear. They will result in slow fluctuations of the central frequency. Indeed, such a behavior was observed in the experiment.

There are many further questions regarding this technique, such as the different ways in which the system is excited into a superposition; the effect of the electronic structure (for example, delocalization) of the spin center on this phenomenon; the effect of the size of the spin-orbit coupling, and the effect of the dephasing processes on the signal. These and other questions are being investigated both experimentally and theoretically. The progress that was made in understanding this phenomenon is an important step in providing the STM a new powerful capability: obtaining rich chemical information on individual localized spin centers on the surface.

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