Electron paramagnetic resonance of individual atoms on a surface

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We combined the high-energy resolution of conventional spin resonance (here ~10 nano–electron volts) with scanning tunneling microscopy to measure electron paramagnetic resonance of individual iron (Fe) atoms placed on a magnesium oxide film. We drove the spin resonance with an oscillating electric field (20 to 30 gigahertz) between tip and sample. The readout of the Fe atom’s quantum state was performed by spin-polarized detection of the atomic-scale tunneling magnetoresistance. We determine an energy relaxation time of $T_1 \approx 100$ microseconds and a phase-coherence time of $T_2 \approx 210$ nanoseconds. The spin resonance signals of different Fe atoms differ by much more than their resonance linewidth; in a traditional ensemble measurement, this difference would appear as inhomogeneous broadening.

Iron atoms adsorb on the oxygen binding site of MgO and have four Mg atoms as second-nearest neighbors, in a $C_{4v}$ symmetry (Fig. 1C). This bonding structure results in a strong easy-axis magnetic anisotropy perpendicular to the surface ($z$ direction), i.e., along the Fe-O bond. Figure 1B and fig. S1 (20) show STM topographic images of the Fe atoms studied. The energy landscape of the lowest five states of the Fe atom (Fig. 1D) consists of low-energy states $|0\rangle$ and $|1\rangle$ that are degenerate states except for the Zeeman splitting, separated by an anisotropy barrier formed by the additional spin states.

A spin-polarized (SP) STM tip was fabricated by transferring one Fe atom from the surface to the nonmagnetic tip apex (20). The SP tip was positioned over the Fe atom under study, and a gigahertz frequency voltage $V_{RF}$ was applied between tip and sample, in addition to the DC bias voltage $V_{DC}$. The RF voltage created a time-dependent electric field between tip and sample (Fig. 1A, blue). This RF electric field drove the resonant transition between states $|0\rangle$ and $|1\rangle$. During EPR measurements, we swept the RF frequency and varied the source power to compensate for the frequency-dependent transmission of the wire, and thereby obtained a constant-amplitude $V_{RF}$ at the tunnel junction (figs. S2 and S3). The DC voltage was used to measure the tunneling magnetoresistance of the tunnel junction with the SP tip, which resulted in a tunnel current that depended on the relative population of states $|0\rangle$ and $|1\rangle$ (14).

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We applied a large static magnetic field, $B = \langle B \rangle$, mostly in the plane of the sample but tilted out by $-2^\circ$, which created a strong in-plane magnetic field, $B_x$, and a small out-of-plane field, $B_z$. The out-of-plane $B_z$ established an energy splitting between states $|0\rangle$ and $|1\rangle$, and the in-plane magnetic field $B_x$ modified the spin components of these two quantum states to strengthen the spin resonance transition between them (see below). We set $B_z$ so that the frequency $\nu_0$ of the RF electric field needed to excite the transition between states $|0\rangle$ and $|1\rangle$ fell at $-25\,\text{GHz} (-100\,\text{meV})$. Given the known magnetic moment 5.2 $\mu_B$ (Bohr magneton) of Fe on MgO (21), this energy spacing was obtained for $B_z = 0.18\,\text{T}$. At the STM operating temperature of 0.6 K and at low tunnel currents, the spin system was mostly (75%) in state $|0\rangle$, except when resonantly excited.

To obtain EPR spectra, we swept the frequency $f$ of the RF electric field and monitored the time-average tunnel current. Figure 2A shows a constant tunnel-current signal over the entire frequency sweep, except for a single EPR peak. The peak position changed linearly with the magnetic field (Fig. 2D). On resonance, the tunnel current increased from the set-point current of 1.0 pA to 1.1 pA. The full-width at half-maximum (FWHM) of the resonance signal was $21 \pm 2\,\text{MHz}$, which is limited here by the strong driving RF field and tip-sample vibrations (20). When a non-spin-polarized tip was used, the EPR signal was absent (Fig. S11), so the contrast observed represented spin-polarized detection. We excited spin resonance in the Fe on the MgO surface, not on the Fe atom on the tip apex, which served only as spin-polarized detector, owing to its subpicosecond excited-state lifetimes (22).

To understand the mechanism of coherent transition, we describe the spin and orbital nature of the magnetic states $|0\rangle$ and $|1\rangle$. Fe on MgO was recently measured with spin excitation spectroscopy and x-ray absorption spectroscopy to determine its low-energy quantum states (22). When bound to MgO, the free-atom’s spin and a large portion of its orbital angular momentum are preserved (21). By using the approximation that the Fe atom is in the $d^8$ configuration and in the lowest Hund’s rule term (orbital moment $L = 2$ and spin $S = 2$), the quantum states determined previously (22) are well approximated by the ligand-field Hamiltonian

$$H_0 = D_L S_z^2 + F_0 (L_x^2 + L_y^2) + \lambda L_z S_z + \mu_B (L \cdot S) - B_0$$

where $D_L = 433\,\text{meV}$ gives the axial (out-of-plane) anisotropy; $F_0 = 2.19\,\text{meV}$ is the tetragonal (fourfold rotational) ligand field that describes the splitting between in-plane orbitals ($d_{xy}$ and $d_{yz}$) that results from the four nearest Mg atoms; $\lambda = 12.6\,\text{meV}$ gives the spin-orbit coupling; and the last term determines the Zeeman energy. Operators $L_x, L_y,$ and $L_z$ refer to the orbital moment’s $z$-axis and ladder operators. The use of this Hamiltonian, rather than an effective-spin Hamiltonian ($I, H, K$), gives richer insight into the effects of electric fields (20).

We propose that the large RF electric field $\vec{E}(t)$, applied mostly along $z$, moves the Fe atom with respect to the MgO lattice. This structural change modifies the ligand field parameters, which results in a time-dependent Hamiltonian $H(t)$ that can drive coherent transitions between states $|0\rangle$ and $|1\rangle$

$$H(t) = H_0(t) \pm \hbar f(t) (L_x^2 + L_y^2)$$

where $H_0(t)$ is the static part of the Hamiltonian.

In the absence of an in-plane magnetic field, the largest terms of the eigenstates of $H_0$ expressed in the basis of $z$-axis orbital and spin quantum numbers $|M_L, M_S\rangle$, are

$$|0\rangle = 0.92|+2, +2\rangle - 0.40|-2, +2\rangle + \ldots$$

$$|1\rangle = 0.92|-2, -2\rangle - 0.40|+2, -2\rangle + \ldots$$

These two states overlap in their orbital components under application of $H(t)$ (both contain $M_L = \pm 2$), but are effectively polarized in their spin component. The absence of overlap in the spin component leads to a nearly vanishing coherent transition rate (i.e., $|H(t)|^2$). In accordance, we did not observe any EPR signals on Fe at $B_z = 0$. When $B_z > 0$, the states $|0\rangle$ and $|1\rangle$ contain other $|M_L, M_S\rangle$ components [see (20)] making the spin component less polarized, thus increasing the coherent transition rate.

We did not observe a spin resonance signal for Co atoms on the MgO surface, even though Co’s magnetic moment is similar to that of Fe (21, 23) (fig. S11). The orbital symmetry of Fe matches the fourfold symmetry of the binding site and leads to resonant transitions, whereas the same binding site symmetry does not lead to resonant transitions in Co because its lowest-energy states are dominantly composed of $M_L = \pm 3$ components. These are not mixed by the fourfold symmetric effect of $(L_x^2 + L_y^2)$, so no
of similar strengths of electric fields were studied. The resistance from the tip to the surface of the Ag substrate was measured using a simple plate capacitor model. The distance available in our STM geometry, we estimated the magnitude of the driving RF field, i.e., the electric field available in our STM geometry, we obtained a value of ~6 × 10^6 V/m. The effects of the driving field on the local environment of each Fe atom (Fig. S1) show no detectable imperfections within ~1 nm of each Fe atom. This comparison demonstrates the importance of single-atom measurement, as the linewidth in the equivalent ensemble measurement would be broadened to ~1 GHz.

To investigate the influence of the tip on the measured EPR spectra, we measured the same set of atoms for a different Fe-terminated tip. The EPR frequency shifted by a constant ~800 MHz for all (except one) atom on the surface (Fig. S8). Thus, differences in resonance frequency remain independent of the tip, and energy differences can be interpreted with high accuracy even though the absolute frequencies are somewhat tip-dependent. A plausible origin of the observed shift is a local magnetic field created by the spin-polarized tip.

A resonantly driven magnetic moment is typically described with three parameters: (i) the energy relaxation time T1; (ii) the quantum phase coherence time T2; and (iii) the strength of the driving field, or equivalently, the rate at which the driving field coherently rotates the quantum system (Rabi rate Ω).

The energy relaxation time T1 describes the time to relax from the excited state |1⟩ to the ground state |0⟩. More precisely, it is the time to relax to a steady-state population, which typically is thermally distributed. We used an electrical pump-probe technique (28) and observed an exponentially decaying tunnel current yielding T1 = 88 ± 20 µs (Fig. 3A) at the tip height and voltage used in the EPR measurements of Fig. 2. A lower bound of the coherence time T2 (20) can be obtained from the resonance peak width of Δf = 3.6 ± 0.4 MHz (Fig. 3B), which gives T2 exceeding 1/πΔf = 100 ns.

The Rabi rate Ω and a more accurate value of T2 can be determined from the EPR signal as a function of RF drive amplitude (Fig. 3C). Simultaneous fits to all five spectra of Fig. 3C yielded a coherence time T2 = 210 ± 50 ns, and a driving strength of Ω = 2.6 ± 0.3 rad/µs for a driving voltage V_{RF} = 8 mV (20). This gives a Rabi flop time, the time needed to reverse the magnetic state coherently, of π/Ω = 1.2 ± 0.1 µs. Despite the flop time exceeding T2 by a factor of ~6, the EPR peaks reached saturation. As is known from traditional EPR, this saturation occurs because of the long T1 time, which allows the spin to perform a random walk consisting of many successive periods of coherent evolution before T1 elapses (1). We did not observe any Rabi oscillations in pulsed EPR experiments; instead, we observed a simple exponential change in polarization because of the small ratio of T2 to Rabi flop time. We cannot increase V_{RF} much further to improve this ratio without exceeding the spin excitation at 14 mV. Thus, we expect that fully coherent reversal of the spin will require further increases in T2—for example, by increasing the MgO thickness.

REFERENCES AND NOTES
QUANTUM OPTICS

Direct sampling of electric-field vacuum fluctuations


The ground state of quantum systems is characterized by zero-point motion. In the form of vacuum fluctuations, it is generally considered to be an elusive phenomenon that manifests itself only indirectly. Here, we report direct detection of the vacuum fluctuations of electromagnetic radiation in free space. The ground-state electric-field variance is inversely proportional to the four-dimensional space-time volume, which we sampled electric-optically with tightly focused laser pulses lasting a few femtoseconds. Subcycle temporal readout and nonlinear coupling far from resonance provide signals from purely virtual photons without amplification. Our findings enable an extreme time-domain approach to quantum physics, with nondestructive access to the quantum state of light. Operating at multiterahertz frequencies, such techniques might also allow time-resolved studies of intrinsic fluctuations of elementary excitations in condensed matter.

Vacuum fluctuations give rise to a variety of phenomena, from spontaneous photon emission (1, 2) and the Lamb shift (3) via the Casimir force (4) to cosmological perturbations (5, 6). Representing the ground state, the quantum vacuum does not possess intensity. However, finite noise amplitudes of electric and magnetic fields should exist because of Heisenberg’s uncertainty principle. These fluctuations are best explained by analogy with a harmonic oscillator of mass \( m \), resonance angular frequency \( \Omega \), and total energy \( H_{\text{HO}} \) (9)

\[
H_{\text{HO}} = \frac{1}{2} m \left( \frac{\partial^2}{\partial x^2} + \Omega^2 x^2 \right)
\]

Quantization results in noncommuting operators for momentum \( p \) and displacement \( x \). The Gaussian wave function of the ground state exhibits a root-mean-square (RMS) standard deviation of \( \Delta x = (h/2m)^{1/2} \) \( \Delta p = (\hbar m)^{1/2} \) (7, 8), where \( h \) is the reduced Planck constant. The total energy of a radiation field of wavevector \( \mathbf{k} \) in free space, with electric and magnetic amplitudes \( E \) and \( B \) (respectively), and vector potential \( \mathbf{A} \) in the Coulomb gauge is (9)

\[
H_{\text{EM}} = \frac{e_0}{2} \left( E^2 + B^2 \right) = \frac{1}{2} \left( A^2 + B^2 \right)
\]

Considering one polarization direction and the transverse character of electromagnetic waves, Eq. 1 maps onto Eq. 2 by replacing \( x \) with \( A \) (amplitude of vector potential \( \mathbf{A} \), \( m \) with \( e_0 V \) (electric vacuum permittivity; \( V \), spatial volume), and \( \Omega \) with \( \Omega \), (c, speed of light; \( k = |\mathbf{k}| \) Instead of \( x \) and \( p \), an uncertainty product now links \( E \) and \( B \) or the amplitudes and phases of \( E, B, \) or \( \mathbf{A} \). An RMS amplitude of vacuum fluctuations \( \Delta A = \sqrt{\langle (\mathbf{A} - 2\mathbf{A}_0)^2 \rangle} \) results. In contrast to the mechanical case where \( \Delta x \) is known, understanding \( \Delta A \) is less straightforward: Outside any cavities, there are no obvious boundaries that define a normalization volume \( V \). This situation raises the question of whether direct measurement of the vacuum field amplitude in free space is physically meaningful and feasible.

The quantum properties of light (10) are typically analyzed either by photon correlation (11–14), homodyning (15–18), or hybrid measurements (19). In those approaches, information is averaged over multiple cycles, and accessing the vacuum state requires amplification. Femtosecond studies still rely on pulse envelopes that vary slowly relative to the carrier frequency (20–23). In our work, we directly probed the vacuum noise of the electric field on a subcycle time scale using laser pulses lasting a few femtoseconds. In ultrabroadband electro-optic sampling (24–27), a horizontally polarized electric-field waveform (red in Fig. 1A) propagates through an electro-optic crystal (EOX), inducing a change \( \Delta n \) of the linear refractive index \( n_\text{EOX} \) that is proportional to its local amplitude \( E_{\text{THz}} \) (Fig. 1A and fig. S1). The geometry is adjusted so that a new index ellipsoid emerges under \( 45° \) to the polarization of \( E_{\text{THz}} \) with \( n_y \) and \( n_x = n_x = \Delta n \). An ultrashort optical probe pulse at a much higher carrier frequency \( v_p \) (green in Fig. 1A); intensity, \( I_p \); electric field, \( E_p \) copropagates with \( E_{\text{THz}} \) at a variable delay time \( t_p \). The envelope of \( I_p \) has to be on the order of half a cycle at the highest frequencies \( \Omega/2\pi \) of \( E_{\text{THz}} \) that are detected. We used probe pulses as short as \( t_p = 5.8 \) fs, corresponding to less than 1.5 optical cycles at \( v_p = 255 \) THz (fig. S2). Upon passage through the EOX, the \( x \)- and \( y \)-components of \( E_p \) acquire a relative phase delay proportional to \( \Delta n \) and \( E_{\text{THz}}(\lambda_\text{EOX}) \). The final polarization state of the probe is analyzed with ellipsometry. The differential photocurrent \( \Delta I/I \) is proportional to the electric field \( E_{\text{THz}}(\lambda_\text{EOX}) \). We used a radio-frequency lock-in amplifier (RFLA) for readout.

We adjusted for optimal conditions to measure the vacuum signal by studying classical multi- terahertz transients, which were synchronized to the probe (8). In Fig. 1B, \( \Delta I/I \) is plotted in red against delay time \( t_p \). Figure 1C shows the amplitude spectrum (red) and phase deviations (blue) within \( \pi \), corroborating calculations (8) of an effective sampling bandwidth of \( \lambda_{\text{eff}} = \Delta \lambda/2\pi = 66 \) THz (figs. S3 and S4) around a center frequency of \( v_c = \Omega/2\pi = 67.5 \) THz (free-space wavelength \( \lambda_c = 4.4 \) mm). The electric-field amplitude \( E_{\text{THz}}(\lambda_\text{EOX}) \) is calibrated using (28–30)

\[
\frac{\Delta I}{I} = \sin \left( \frac{2\pi v_p r_{\text{EOX}} n_\text{THz}^2}{c} \right)
\]

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\]

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**EPR, one atom at a time**
Electron paramagnetic resonance (EPR) usually detects atoms with unpaired electrons as ensemble averages. Baumann *et al.* used a spin-polarized scanning tunneling microscope tip to measure EPR spectra of single iron atoms adsorbed on a magnesium oxide surface at cryogenic temperatures. The measurement depends on the atomic orbital symmetry; no signal was observed for cobalt atoms under the same conditions.*Science*, this issue p. 417