New Methodologies and Applications in Electron Spin Resonance - from Wound Healing to Quantum Computing

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Abstract: Magnetic resonance (MR) is well-known in the world of chemistry, mainly due to its superb analytical capably to decipher the structure of molecules. This method, which can be applied in connection with either certain nuclei or unpaired electrons, originated from basic physics exploration in the 1940's, and has since expanded to address a variety of applications in diverse fields ranging from chemistry to medicine. However, despite its wide commercial and scientific success, MR still suffers from significant limitations of low sensitivity, coarse spatial resolution in imaging, and high complexity and cost of its system. In this short review, I will describe some of the recent efforts in my lab, aimed at overcoming these limitations, which have resulted in unique experimental capabilities, offering ultra-high sensitivity down to the single electron spin level, as well as sub-micron imaging resolution. These capabilities enable one to address unique applications in materials- and life-sciences, ranging from oxygen measurements in cells to basic experiments in quantum computation. In addition, we are developing other systems that are far less complex and costly than the conventional ones, aimed at specific medical applications. This direction, which is only in its infancy, may lead in the near future to a situation where MR technology can serve as a basis for simple and affordable medical instruments, used by physicians and caregivers at the clinic level.

I. Introduction: the pro and cons of magnetic resonance

Magnetic resonance (MR) is one of the most profound scientific observation methods. MR is concerned mainly with nuclear magnetic resonance (NMR) and electron spin resonance (ESR). It has a broad range of applications from chemical structure determination to medical imaging and basic physics. From a scientific standpoint, MR has been at the center of at least seven Nobel prizes in physics[1; 2; 3; 4], chemistry[5; 6], and medicine[7]. From an industrial standpoint, MR is a multibillion industry aimed primarily at a wide range of medical (magnetic resonance imaging, MRI) and chemical (NMR and ESR spectrometers) applications.

Despite the success of MR methodologies, their application is typically limited by sensitivity (the number of species that can be detected), by their coarse spatial resolution in imaging applications, and by the high cost and complexity of MR technology. Overcoming these barriers will pave the way for transformative developments in the experimental sciences. Our group is trying to address all of these issues, ranging over the whole field of magnetic resonance, although currently we are primarily focusing on methodologies and applications related to electron spin resonance. In this short review of activities, we picked some samples of our work related both to basic methodological developments in ESR, and how they can be applied to practical scientific, technological, and medical applications.

As noted above, the most fundamental limitation of magnetic resonance, including ESR, is the low sensitivity. Let us first remind ourselves what ESR is and the origins of its sensitivity problems.

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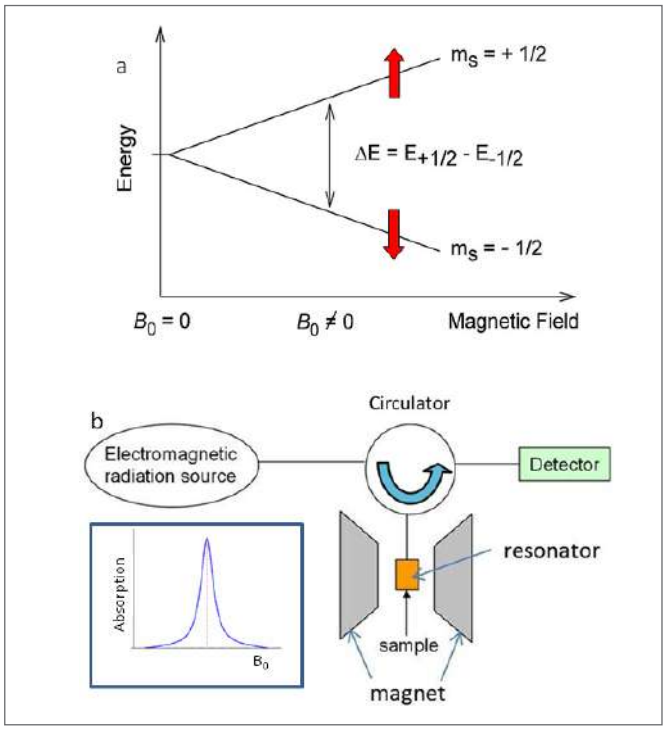

Figure 1: (a) Energy levels of unpaired electron spins as a function of the static magnetic field, showing the so-called Zeeman splitting. **(b)** Simple experimental setup for the detection of unpaired electron spins in a sample. The inset shows the microwave absorption response of the sample as the static field is scanned across the resonance.

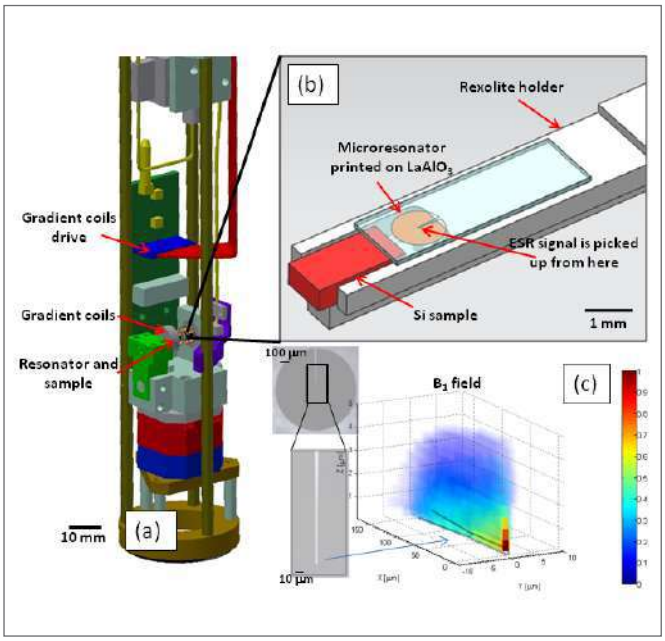

Figure 2: Experimental setup for ultra-high sensitivity and high spatial resolution ESR. **(a)** A drawing of an ESR detection probehead that operates at cryogenic temperatures, showing its main components. **(b)** Zoom-in to the center of the probehead, where a miniature ESR resonator (the "Packman" shaped structure) is located near the sample. **(c)** Microscopic photos of the resonator, showing its details as well as the calculated microwave magnetic field at the center of the resonator, showing that the field is focused in a volume of a few mm3.

Aside from their charge, electrons also carry the magnetic quantum property of spin. Electrons usually team up in pairs with opposite spins, resulting in a zero net spin. However, in many cases, such as free radical molecules, crystal defects, paramagnetic metal ions, and conduction/mobile electrons, the electrons are unpaired and their spin properties can be measured. Spins can be envisioned as small bar magnets which react strongly to the presence of a large external static magnetic field. Being quantum mechanical creatures, these small magnets can be aligned only at selective angles with respect to the external static field, B_0, i.e. either parallel or anti-parallel to it (Fig. 1a). The energy difference, ΔE, between these two states varies linearly with the strength of the external field ($\Delta E \sim 2\mu_B B_0$, where μ_B is a universal constant termed Bohr magneton), but in any case is quite small, in the range of micro-eV to ~ meV at most, for common static fields in the range of ~0.01-10 Tesla. This is one of the prime reasons why it is so hard to detect the presence of these unpaired spins - hard, but not impossible. In practice, detecting the presence of unpaired electron spins in a given sample can be carried out by employing the typical ESR experimental setup as depicted in Fig. 1b (in a schematic manner). The sample is placed in a static magnetic field and is illuminated by an electromagnetic source whose frequency corresponds to the energy difference between the two spin states (based on the well-known Planck formula $\Delta E = h\nu$, where h is the Planck constant and ν is the radiation frequency). For common magnetic fields, this frequency falls within the microwave (MW) region of the electromagnetic spectrum, with a wavelength of ~few centimeters to a few millimeters. An ESR spectrometer usually scans the magnetic field while keeping the MW frequency fixed, and monitors the reflected vs. incident MW power on the sample (through the detector, Fig. 1b). At specific field points, where the resonance condition is met ($2\mu_B B_0 = h\nu$), the sample absorbs a small amount of the incident MW power and this is manifested as a detectable change in the reflected MW power from the resonator arm (see inset in Fig. 1). This is a sign of the existence of unpaired spins in the sample, with the exact resonance field value for a given MW frequency of excitation used as a spectroscopic marker for characterizing the atomic environment of the unpaired spins. The detection of these changes in the reflected MW power is very difficult when a small number of spins is placed inside the resonator, making ESR far less sensitive than other spectroscopic and analytic techniques, such as fluorescence and mass spectrometry. For example, in the most favorable case of a sample having a narrow ESR spectrum, commercial ESR systems require at least 10^9 spins to achieve a measurable signal during 1 s of acquisition time.

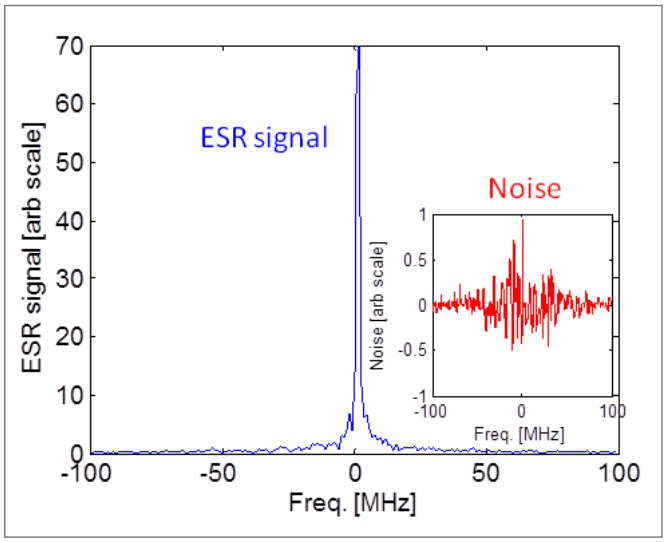

Figure 3: ESR signal and noise in the spectral domain for 28Si:P sample at 10 K, for 1 second of acquisition time[8].

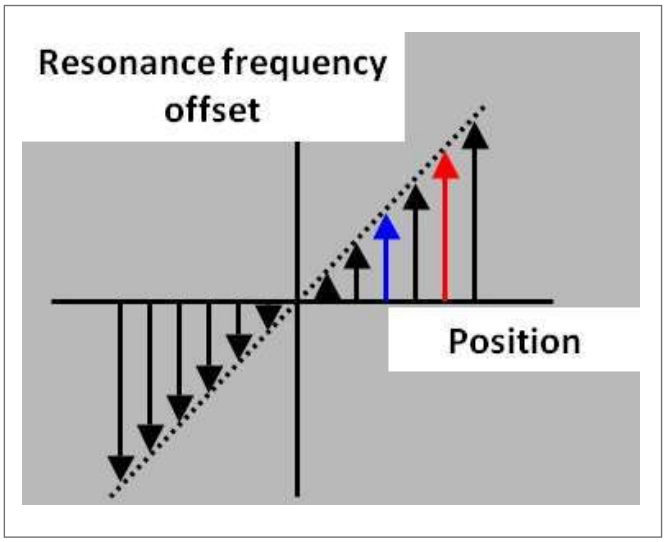

Figure 4: Schematic description of the method for spatial encoding of the sample in magnetic resonance. The resonance frequency of different parts in the sample can be either higher or lower than the resonance frequency of the center of the sample, when a small magnetic field gradient is added to the main static field.

II. Improving the sensitivity

In view of the above, the first challenge that our laboratory had to deal with is to significantly improve the spin sensitivity, aiming at the ultimate sensitivity of a single electron spin. Figure 2 summarizes the approach we took to achieve this goal. It is based on three main pillars. First and foremost, we developed a unique ultra-miniature resonator, which focuses the MW energy to a very small volume, on the mm scale (a highly challenging task since the wavelength of the frequency we work at is ~ 10 mm). This enables us to greatly amplify the response of the MW system to very small changes in the MW properties of a small sample in the resonator (when reaching the resonance condition). The second important point for achieving high sensitivity is that working with such a tiny resonator also enables the use of very low MW power for measuring the sample response, which means that the MW signal coming from the sample can be amplified by very sensitive cryogenic amplifiers that, otherwise, would be damaged by even moderate power MW radiation. This bring us to the last important point in our set up, which includes the use of a cryogenic probehead to enable the measurements at low temperatures where noise level is reduced and also is important for facilitating the use of an ultra-low-noise cryogenic amplifier.

The capabilities of our systems were recently verified by achieving a sensitivity approaching a single electron spin when measuring unpaired spins in phosphorus-doped silicon 28 (^{28}Si:P) wafer (Fig. 3). In this case the sample contained ~ 2×10^6 spins, and analysis of the noise level reveals that a sensitivity of just a single spin can be achieved after a few hours of averaging time[8].

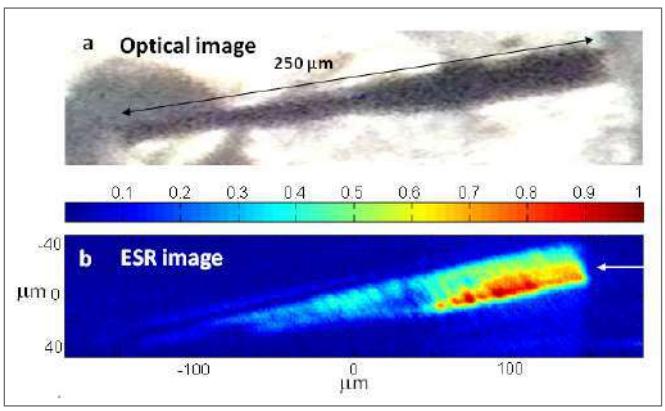

Figure 5: Optical (a) and two-dimensional ESR image (b) of a single paramagnetic Lithium Phthalocyanine crystal. The crystal was positioned with its long axis in the XY plane of the ESR image.

III. Improving the spatial resolution

The second limiting factor for magnetic resonance listed above is the coarse spatial resolution in imaging applications of heterogeneous samples. In order to understand the origins of this limitation, we must first provide a very brief explanation of how magnetic resonance can be used for imaging. The basic idea relies on the linear relation between the resonance frequency and the static field ($\nu = 2\mu_B B_0/h$), as depicted in Fig. 1b. Thus, by placing the sample not in a homogenous static magnetic field, but rather in a field that has a fixed gradient, each position in the sample is encoded

by its resonance frequency (Fig. 4). Namely, different parts of the sample exhibit different resonance frequencies, thereby enabling creation of an image of the sample based on the ESR absorption signal at different frequencies.

Based on this explanation, it is evident that the image resolution depends on the strength of the field gradient employed, meaning the larger the gradient the better the resolution will be. However, as the pixels in the image become finer and finer, there are fewer and fewer spins in each pixel, meaning that at some point their number will be smaller than the minimal detectable number of spins of a given setup, resulting in a complete loss of image contrast in favor of noise. The setup shown in Fig. 2 is aimed at addressing both the gradient strength issue, as well as the sensitivity problem, at the same time. On one hand, it greatly improves the spin sensitivity – as explained above. On the other hand, since the resonator is so small, it enables one to employ miniature coils located around the resonator at very close proximity that generate very powerful magnetic field gradients and also can be switched on/off on a fast - nanosecond time scale (which is another important requirement for high resolution imaging in ESR). Figure 5 provides an example of a high-resolution (better than 1 μm) ESR image of a paramagnetic crystal acquired by our measurement system[9].

IV Applications of High Sensitivity / High resolution ESR

The new capabilities described above can be implemented in a variety of scientific and technological applications. For example, in the field of semiconductor devices, high-resolution ESR imaging enables one to observe diffusion and migration phenomena of point defects in amorphous oxides[10]. Amorphous oxides are key ingredients in electronic and optical devices. Such oxides include a variety of point defects that greatly affect their electrical and optical properties. Many of these defects are paramagnetic and, as such, the best tool to identify them and characterize their structure is ESR. However, due to its limited sensitivity and spatial resolution, traditional ESR could not provide information about the defects' migration properties, which are of crucial importance for device fabrication. Ultra-high-resolution imaging modalities such as transmission electron microscope (TEM), as well as theoretical calculations, are severely limited in amorphous media, resulting in a wide knowledge gap in this field. Our ESR microimaging was applied to examine unique samples that are prepared using e-beam irradiation and have well-defined point defect patterns. This provides a capability to unambiguously identify the defects and at the same time track their migration with high spatial resolution, revealing new information about their properties. Figure 6 shows a typical example of ESR imaging results of amorphous

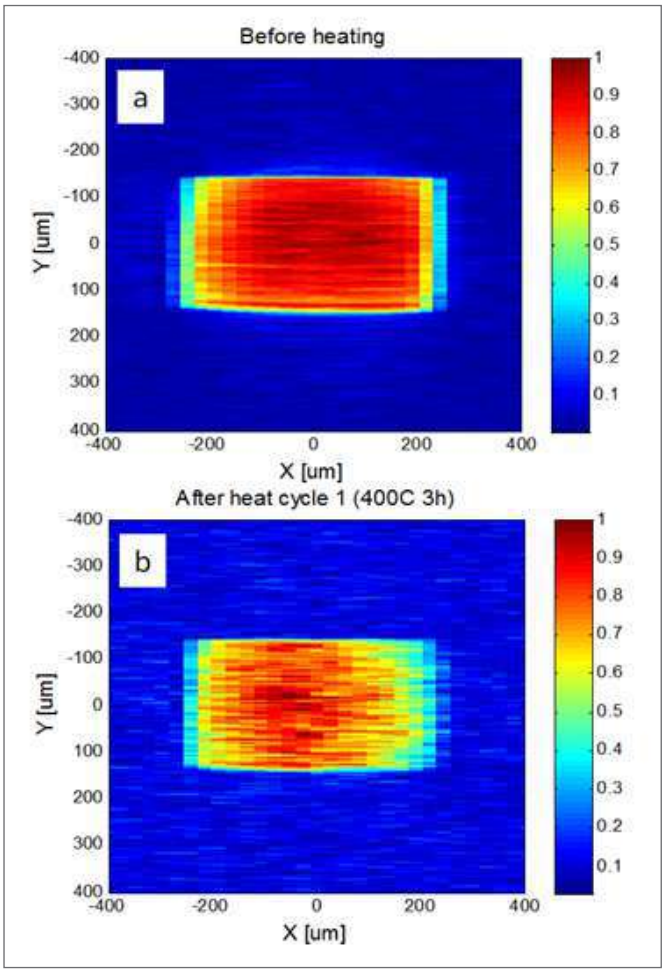

Figure 6: Pulsed ESR 2D images of the irradiated SiO_2 sample before **(a)** and after **(b)** heating cycle at 400 °C for 3 hours. The heat cycle causes some changes in the spatial pattern that can be analyzed to provide information about forces acting on the defects in the SiO_2 and processes they undergo.

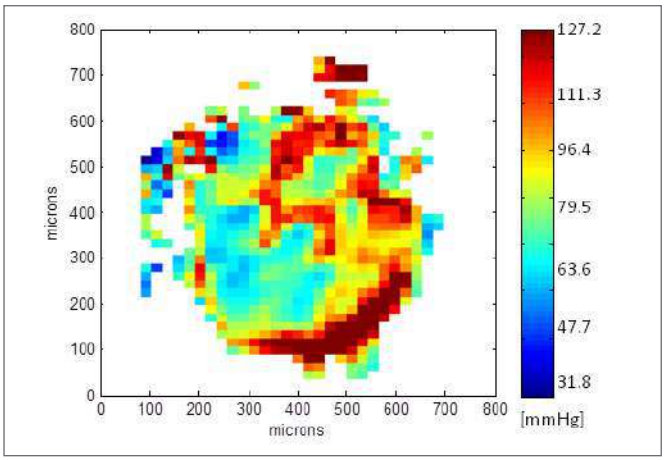

Figure 7: Oxygen map of a spheroid containing LiNc-BuO. The map shows the oxygen concentration in various parts of the spheroid, as derived from their measured spatially-resolved ESR spectrum.

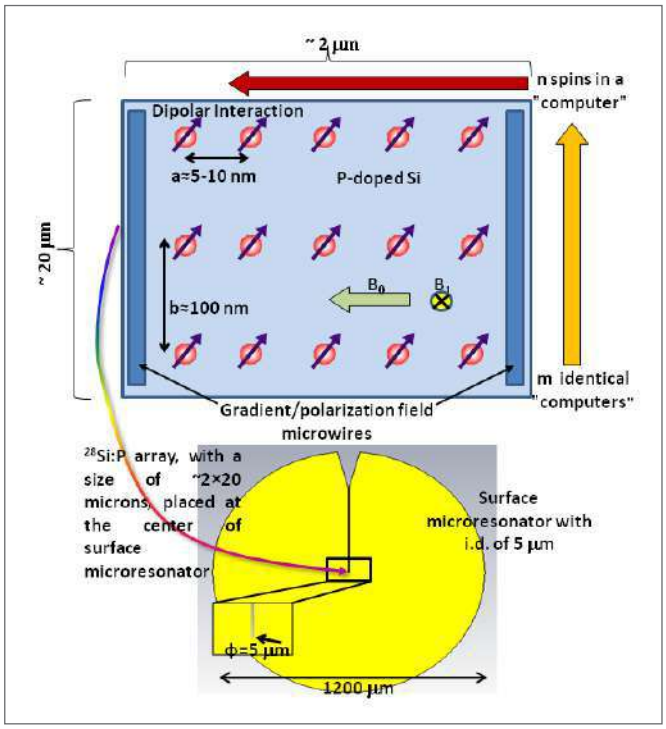

Figure 8: The suggested QC scheme to be used in conjunction with ultra-high sensitivity/high-resolution induction detection[11]. A two-dimensional array of phosphorus atoms is produced inside a pure 28Si single crystal. The crystal is placed upside down on the center of our ultrasensitive surface resonator[16; 17; 18], and operated at cryogenic temperatures. Each phosphorus nucleus in the crystal serves as a logical quantum bit (qubit), while its adjacent electron is the working qubit. The array has two lattice constants: a short one **(a)** that enables electron spins to interact through dipolar couplings along this linear vector (similar to the manner described in ref[19]), and a long one **(b)** that separates many identical copies of the same individual vector computers. Individual spins can be addressed by applying a large magnetic field gradient with DC current into microwires (separating the spins in the frequency domain), and the state of all spins can be read out in parallel via a one-dimensional image along the crystal's x-axis. All parallel identical computer vectors should give the same vector of spin states, thereby increasing the measured signal and also greatly minimizing the need for quantum error correction due to random spin flips, since the measured result averages over ~100-1000 spins per qubit. Information can be swapped between working electron spins and logical nuclear spins through combined radiofrequency (RF) and microwave (MW) pulse sequences, as described in reference[20].

SiO_2 piece on which a rectangular pattern of point defects was created by e-beam irradiation. The piece was imaged immediately after preparation and then following a 3h heat cycle at 400ºC. Changes in the image were analyzed to obtain valuable information about atomic level potentials and forces between point defects in SiO_2[10].

Another example, taken from a completely different field, is focused on the use of ESR micro-imaging for mapping oxygen in sub-mm sized tissues. Oxygen (O_2) plays a central role in most living organisms. The concentration of O_2 is important in physiology and pathology. Despite the importance of accurate knowledge of the O_2 levels, there is very limited capability to measure with micron-scale spatial resolution its distribution in millimeter-scale live biological samples. Many of the current oximetric methods, such as oxygen microelectrodes and fluorescence lifetime imaging, are compromised by O_2 consumption, sample destruction, invasiveness, and difficulty of calibration. In the case of biological samples, ESR imaging requires the incorporation of a suitable stable and inert paramagnetic spin probe into the desired object. In our work, we used microcrystals of a paramagnetic spin probe in a new crystallographic packing form (denoted tg-LiNc-BuO). These paramagnetic species interact with the paramagnetic oxygen molecules, causing spectral line broadening that is linearly proportional to the oxygen concentration. This new oximetry microimaging method addresses all the problems mentioned above. It is noninvasive, sensitive to physiological oxygen levels, and easy to calibrate. Furthermore, in principle, it can be used for repetitive measurements without causing cell damage. The tissue model used in this research was spheroids of Human Colorectal carcinoma cell line (HCT-116) with a typical diameter of ~600 microns. Most studies of the microenvironmental O_2 conditions inside such viable spheroids carried out in the past used microelectrodes, which require invasive puncturing of the spheroid and are also not applicable to 3D O_2 imaging. High-resolution 3D oxygen maps could make it possible to evaluate the relationship between morphological and physiological alterations in the spheroids, which would help in understanding the oxygen metabolism in solid tumors and its correlation with the susceptibility of tumors to various oncologic treatments. Figure 7 shows a typical example of an oxygen map measured for one of the spheroids. It indicates that there is more oxygen on the exterior parts than in the inner parts, as one would expect for such tissues. It also shows the significant heterogeneity such spheroids may possess with respect to their oxygen concentration.

A third emerging application of high resolution/high sensitivity ESR comes from the regime of basic physics, where ESR can be used as a basis for a quantum computer[11]. Quantum computing (QC) is a relatively new concept that aims at significantly improving the capability to calculate some types of high complexity problems by making use of unique hardware and algorithms from the regime of quantum physics. Unlike regular computers that make use of binary bits that can be either 0 or 1, QC employs quantum bits that can be either 0, or 1, or in a superposition of states, being both 0 and 1 at the same time, with some probability. The latter situation is of course only possible for a quantum system and thus electron spins, which can exist in this strange superposition of states, were found to be one of the leading candidates to be used as such quantum bits. However, beyond the basic concept, much practical work is still needed. For example, one must enable

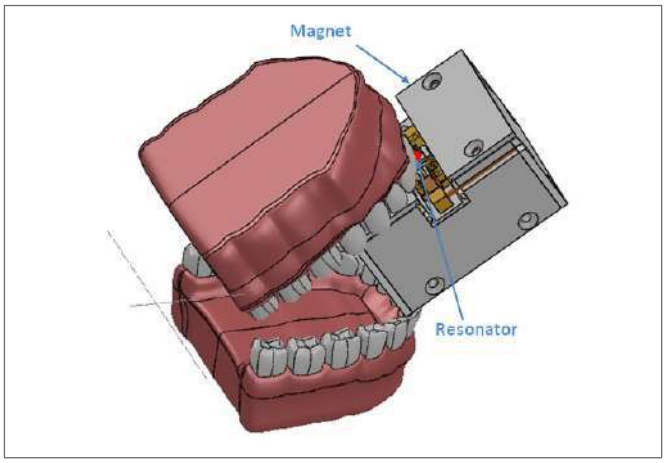

Figure 9: General overview of the compact ESR probehead for ESR measurements of incisor tooth during a projected measurement.

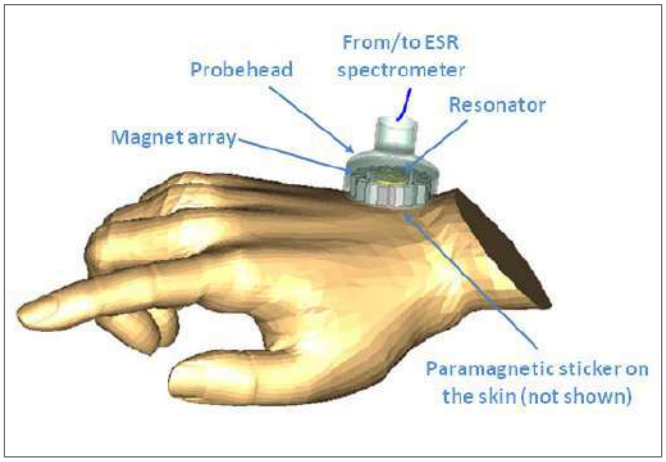

Figure 10: Drawing of the compact skin O_2 ESR probehead, showing the permanent magnet and resonator assembly during a projected in-vivo measurement of skin oxygen level. A special paramagnetic sticker is placed on the skin and the measurement of the relaxation time (T2) of the particles in this sticker provides the oxygen concentration in the skin.

the selective manipulation of these qubits, creating controlled interaction between them to perform calculations, and at the end read out the solution by readout of the state of the electron spins, ideally with single-spin sensitivity and nano-scale spatial resolution. Here is where our high sensitivity/high resolution methodologies come into play in the construction of such unique QC hardware. The basic concept (currently yet only theoretical) is described in Fig. 8[11]. It makes use of an array of multiple identical "computer" vectors of phosphorus-doped silicon where the nuclei serve as logical qubits and the electrons as working qubits. The spins are addressed by a combination of electron spin resonance and nuclear magnetic resonance techniques operating at a field of ~3.3 T and cryogenic temperatures with an ultra-sensitive surface microresonator. Spin initialization to the ground (0) state is invoked by a combination of strong pre-polarization fields and laser pulses. The set of universal quantum gates for this system includes an arbitrary rotation of single qubits and controlled-NOT operation with two qubits. The efficient parallel readout of all the spins in the system is performed by high-sensitivity induction detection of the electron spin resonance signals with one-dimensional imaging.

V. Simple, affordable, and transportable ESR systems

As noted above, the third aspect of magnetic resonance that severely limits its widescale use, is related to the complexity of the systems, their excessive cost and their immobility. Addressing these issues is one of the focal interests of our laboratory, which develops miniature self-contained ESR probes for specific applications, mainly in medicine. However, unlike the cases of sensitivity and resolution improvements, we will not go into the details of the technology behind these devices and simply provide two representative examples that show the scope of our activities in this field.

The first example is a miniature ESR probehead that includes a static field source and a microwave resonator for in-vivo measurement of paramagnetic defects in tooth enamel[12]. These defects are known to be a good marker for quantifying the ionizing radiation dose absorbed in teeth. The probehead has a typical length of just 30 mm and total weight of 220 g. The patient "bites" into the probehead while the measurement procedure is being carried out (Fig. 9). Experimental results with irradiated incisor teeth validated the probehead's sensitivity, being able to detect signals in tooth irradiated by only 2 Gy. Such probe is of importance for fast triage of mass populations that were potentially exposed to ionizing radiation, where a 2 Gy dose serves as a threshold for administrating medical care.

A second example for a compact, simple, and affordable ESR-based measurement system is shown in Fig. 10, which describes a sensor for measuring oxygen content in the skin[13]. Oxygen concentration in the skin is an important clinical indicator for monitoring pathological conditions such as chronic wounds, skin cancer, and peripheral vascular disease. Currently, the only clinically-approved method for acquiring these oxygen levels is based on electrochemical measurements that employ Clarke-type electrodes attached to the skin. This technique has many drawbacks and limitations, making it unattractive for standard medical practice and care. ESR can obtain the oxygen concentration through measurements of the relaxation time (T_2) of paramagnetic species interacting with molecular oxygen and thus provides a possible alternative. However, a traditional ESR setup requires a large homogenous static magnetic field source with a limited gap between the poles and complicated equipment, making it unattractive for clinical

use. Our miniature ESR probehead, which is composed of a specially-designed permanent magnet and a small microwave resonator, can be used for these measurements. The small size of the probehead (36 mm diameter cylinder with a height of 24 mm) enables measurements from virtually any part of the skin. Compared to the electrochemical method, this ESR-based approach may provide faster and more accurate readings of oxygen concentration in the skin, making it highly attractive for future clinical use.

VI. Summary and conclusions

The field of magnetic resonance has enjoyed enormous success, but still suffers from some major limitations in terms of sensitivity, imaging resolution, and affordability, which, if solved could boost its impact even further. Our recent work on ESR, which is an indispensable branch of magnetic resonance, has resulted in significant improvement in spin sensitivity (4-6 orders of magnitude) and image resolution (~2 orders of magnitude), as well as showing how compact, simple, and affordable ESR probes can be constructed to address specific applications (mainly in medicine). These new capabilities have already opened the door to unique applications in wide areas of science and technology. Further work along these lines, which include yet additional improvements in sensitivity, image resolution, and simplification of system architectures, are being pursed in our lab. Some of these efforts make use of conventional resonator-based ESR detection approaches, as discussed in this paper, while others look into advanced and alternative techniques such as electrical and optical detection, which may be useful for additional future applications[14; 15].

VII. Acknowledgments

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