The electron possesses a magnetic dipole moment, and the magnitude of its z-component given by $\mu_z = \frac{1}{2} g_e \mu_B$ where the g_e is the electron *g-factor* and $\mu_B = \frac{e\hbar}{2m_e} = 9.27401 \times 10^{-24}$ J/T is the *Bohr magneton*. The g-factor is a dimensionless number that gives the ratio of a particle's magnetic dipole moment to its spin angular momentum. The g-factor would be 1 for a classical sphere of spinning charge with a constant mass to charge ratio. The fact that fundamental particles have a g-factor different from 1 shows quantum effects. In this lab you will determine an experimental value for g_e and compare it to the accepted value of $g_e = 2.0023$.

When placed in a magnetic field along the z-axis, the electron will have a potential energy of $-|\mu_z B|$ if the magnetic moment is aligned parallel to the magnetic field or $+|\mu_z B|$ if it is aligned anti-parallel. If an electron in a magnetic field is exposed to electromagnetic radiation (typically in the microwave range) whose energy quantum equals the energy difference ($hf = 2|\mu_z B|$) the electron can absorb a photon and transition from the lower energy level (aligned with the field) to the higher energy level (aligned opposite the field). This process is called either *electron spin resonance* or *electron paramagnetic resonance*.

Insert the TCNQ sample through one side of the Helmholtz magnet. Try to center the sample in the middle of the coils. Gently insert the NMR & ESR probe head through the other side of Helmholtz magnet until it is all the way in. We want to make our first measurements in an orientation where the Earth's magnetic field is not substantially changing the applied field. Therefore orient so that the bore of the Helmholtz magnet is along the East-West axis; this means that the probehead and sample will be oriented along the North-South axis. Go to the folder *C:/NMR and ESR/Continuous Wave NMR and ESR Lab/CWS/CWS 12-50 ser086/Software/cws*. Start the cwne2 program. Under the Spectrometer tab, hover over Communication Port; it should be set to COM2. If not change it to COM2. Under the Spectrometer tab, select Connect. Make sure that the Mode is set for 'ESR'. Start with the gain set at 200 and the Phase set at 15°. Under Modulation, select Field Sweep and set the 2nd Mod Amplitude to 0.05 Gs (gauss). Note: 1 Gs=10^{-4} T. Start with a quick sweep to obtain the ESR signal: set the Field Sweep range to 5 Gs, the Sweep Time to 1 min, and press start. The ESR signal is the derivative of the absorption, so the resonance occurs where the signal crosses zero between the two lobes. The x-axis gives the magnetic field strength as the difference from B0. Once you find the signal you'll want a better scan. Adjust the gain so that the signal covers about half of the vertical range. You can also adjust the phase if you want. Center the window near the resonance (by adjusting B0) and gradually decreases the scan range and speed until you have a 2 min long scan

with a 2 or 3 Gs range (do this in steps because the resonance position will shift as you slow the speed). An example of a good scan is shown below. Notice that in this scan B0 is set to 17.76 Gs, but when we move the vertical purple cursor to the point where the signal cross zero it occurs at -0.03 Gs (as shown in the box in the upper left corner). Therefore this run has a resonance frequency of 17.73 Gs = 1.773 mT. Oddly, sometimes the program will appear to display nothing. If this happens go to the pass display option at the top and set it to 1.

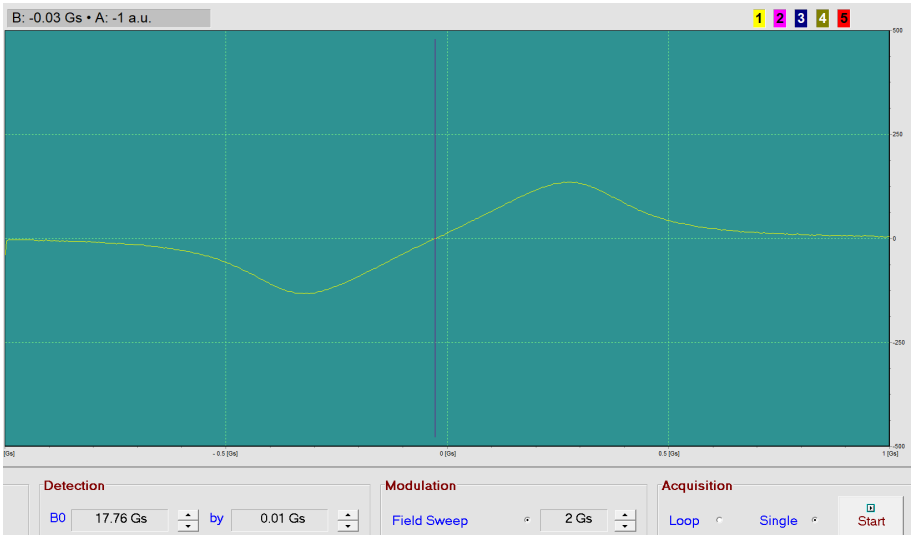


FIG. 1: Example ESR signal for a TCNQ sample.

Once you have a repeatable good scan you will save a scan in a text file. Find the Tools tab, then choose File Location. For both the Acquisition directory and the Data output directory, put your cursor in the box and then choose Browse. Change the location to a place you can easily find, such as `C:\Users\(your alfa)\Desktop`. Enter the file name you want in the 'Store in file' box under Acquisition box and run. Go to File→Save Data As. Then go to Tools→Data Processing. Open your file. Then choose Export to Ascii to save your file in a format you can use later. Check to make sure that this created a .txt file with the same name as you used to title your file. If you can't find or get at a .txt file let me know; we might need to change to data path to save things in a folder that does not need Admin privileges to access. This is your data for TCNQ (7,7,8,8-tetracyanoquinodimethane). This compound contains electrons that are essentially free.

Part 1: Electron g-factor

Determine the electron g-factor. Your data so far gives you the magnetic field for resonance (B0 plus the graph position where the signal crosses zero) at the default

frequency (likely 50000 kHz). Repeat the measurement at roughly 10 different frequencies and determine the resonance field at each. (Depending on your window size you may need to adjust B0 to keep the signal in the window.) The allowed frequency range for the instrument is 49000 kHz to 51000 kHz. Make a plot of the resonance field as a function of frequency. Fit your graph to a line (preferably with the y-intercept fixed to 0) and determine its slope with an uncertainty in the slope. I usually suggest keeping at least two significant figures in the uncertainty and enough significant figures in the value so that its last digit matches the last digit in the uncertainty; your uncertainty may be very small which might require increasing the number of displayed significant digits. Use this to determine g_e with an uncertainty. Compare this to the accepted value by stating how many σ (standard deviations or error bars) your answer is from the accepted value. I'll note that for this to be accurate, any constants you use in the calculation (h and μ_B) will need to be accurate to at least as many significant figures as your value; this could very well require looking them up to more precision than you are used to.

Part 2: Magnetic field of the Earth

Return to the default frequency. Place the magnet coils and probe head on the compass printed on the table. Carefully, orient them along the 0° direction. Repeat your scan and determine the resonance field. Carefully rotate the coils and probe head to be along the 20° direction. Repeat the measurement and again record the resonance field. Do this in 20° steps from 0° to 360°. Make a plot that shows the resonance field as a function of angle. Fit this graph to a sine curve. (Fixing the period of the sinusoid to be 360° might improve the fit.) The amplitude of this fit gives the Earth's magnetic field. The idea behind this graph is that the actual resonance field is fixed, but as you rotate the Helmholtz coil the Earth's magnetic field will align or antialign the magnetic field created by the Helmholtz coil.

Part 3: Excitation lifetimes

Remove the TCNQ sample and replace it with the DPPH (2,2-diphenyl-1-picrylhydrazyl) sample. Repeat your measurement. This signal will be broader, so you will need a larger scan range; perhaps a 7.5 Gs range. It might also be weaker. I used a 2^{nd} Mod Amplitude of 0.35 Gs, a gain of 220, and a phase of 55°. Save the scan, open in in Data Processing, and save it as an ascii.

Open both data sets (TCNQ and DPPH) in spreadsheets (opening as space delimited should give the field and signal data in separate columns). The ESR signal is the derivative of absorption, so we will want to integrate your data in order to

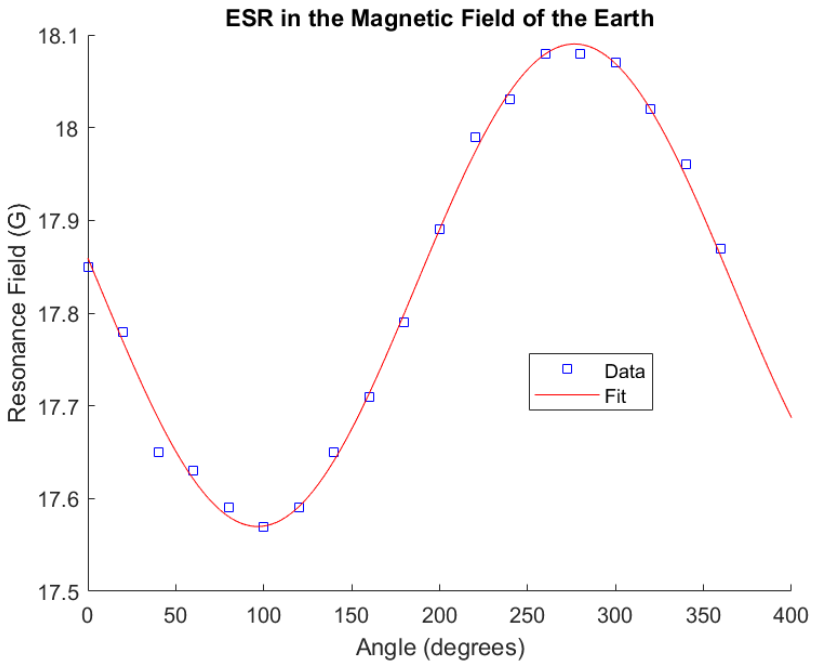


FIG. 2: ESR resonance field for a TCNQ sample plotted as a function of angle, fit to a sinusoid.

obtain the absorption data. Manually integrate the data in the spreadsheet (you can treat each step size as equal). Depending on phase your absorption peak might be negative: if so multiply by -1 to make it positive. For both TCNQ and DPPH fit the absorption data to a Lorentzian function:

$$f(x) = \frac{A}{\pi} \cdot \frac{\Gamma}{(x - x_0)^2 + \Gamma^2}$$

where Γ is the half-width at half-maximum. You might be able to improve the fit by allowing for a sloped background as well (to account for an offset from the real zero in the signal). I was successful in using LoggerPro for these fits. I found that the DPPH data fit fairly well to a Lorentzian, but the TCNQ data did not fit quite as well. Your data will likely fit better than my example here because you used a smaller 2^{nd} Mod Amplitude. Likely, some of the width of the signal in the TCNQ data is coming from the instrumental resolution. Ideally, we would try to fit this data to a Voigt profile, which is a convolution of a Gaussian function (representing the instrumental resolution) and a Lorentzian function (representing the intrinsic signal). We will just accept the Lorentzian fit and use the width fit parameter as a upper bound on the intrinsic width. The DPPH signal is significantly broader than the instrumental resolution, so it is well fit by a Lorentzian.

Determine Γ with an uncertainty for both TCNQ and DPPH. This is a reasonable value to describe ΔB, the uncertainty (or spread) in the resonance field. Therefore

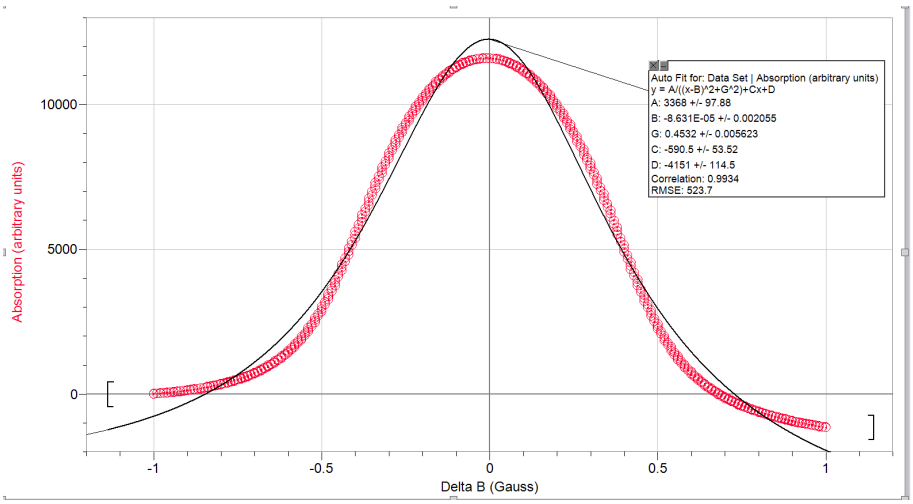


FIG. 3: TCNQ absorption data (integrated signal) plotted against ΔB and fit to a Lorentzian plus a sloped background.

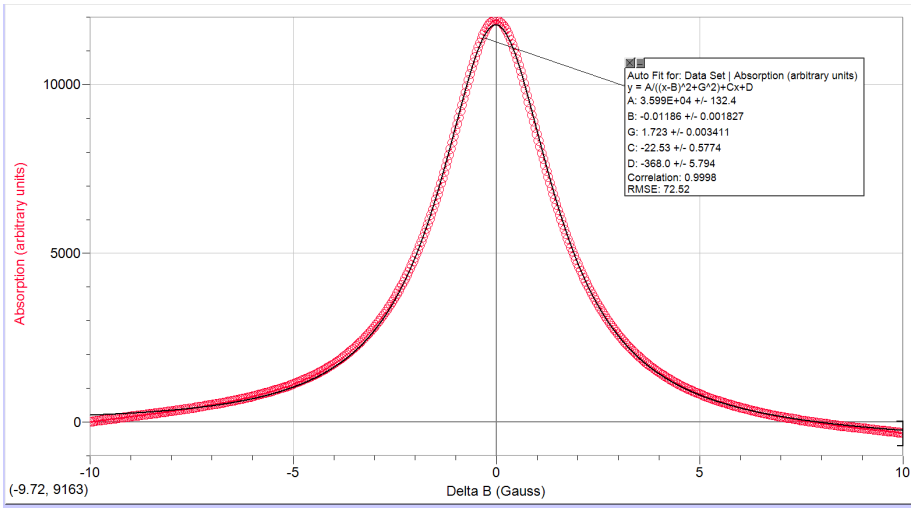


FIG. 4: DPPH absorption data (integrated signal) plotted against ΔB and fit to a Lorentzian plus a sloped background.

$\Delta E = \frac{1}{2} g_e \mu_B \Gamma$ can be used to represent the uncertainty in energy. Determine ΔE with an uncertainty for both TCNQ and DPPH (use the accepted value of $g_e = 2.0023$ for this calculation.) The energy-time uncertainty principle tells us that $\Delta E \, \Delta t \geq \frac{\hbar}{2}$. For our purposes let's just assume that $\Delta E \, \Delta t = \hbar$. Determine Δt with an uncertainty for both TCNQ and DPPH. This gives the excitation lifetime: the average time that an electron excited to the higher energy state will stay there before decaying back to the ground state.

Electron Spin Resonance

1. Using LoggerPro, provide a graph showing the ESR signal vs magnetic field for a single nice scan. Provide a figure showing the resonance field as a function of frequency. This should be fit to $y = Ax$. This fit parameter should be

visible; adjust the display so that two significant figure are displayed in the uncertainty in the slope and that enough significant figures are displayed in the value to match the last decimal place displayed in the uncertainty. Provide the slope and its uncertainty with appropriate units. Use this to determine an experimental value of the electron g-factor with its uncertainty and appropriate units. Compare this to the actual value by giving the number of error bars (uncertainties) your value is away from the actual value. All axes should be appropriately labelled with units.

2. Using LoggerPro, provide a graph showing the measured resonance field as a function of angle as you rotate the Helmholtz coil around in a circle. Axes should be labelled with appropriate units. Fit the data to a sinusoid and give the amplitude with units and uncertainty. (Keep two significant figure in the uncertainty and enough significant figures in the value to match the last decimal place in the uncertainty.)

3. Using LoggerPro, provide a graph showing the absorption (integral of the ESR signal) as a function of magnetic field for a scan of the TCNQ sample. The data should be fit to a Lorentzian function (likely with a sloped background needing to be added in). The Lorentzian width fit parameter should be visible; adjust the display so that two significant figure are displayed in the uncertainty in the slope and that enough significant figures are displayed in the value to match the last decimal place displayed in the uncertainty. The width fit parameter should be provided with an uncertainty and units. This should be used to determine the excitation lifetime with an uncertainty and units. All axes should be appropriately labelled with units.

4. Using LoggerPro, provide a graph showing the absorption (integral of the ESR signal) as a function of magnetic field for a scan of the DPPH sample. The data should be fit to a Lorentzian function (likley with a sloped background needing to be added in). The Lorentzian width fit parameter should be visible; adjust the display so that two significant figure are displayed in the uncertainty in the slope and that enough significant figures are displayed in the value to match the last decimal place displayed in the uncertainty. The width fit parameter should be provided with an uncertainty and units. This should be used to determine the excitation lifetime with an uncertainty and units. All axes should be appropriately labelled with units.