Week 7

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7.1 EPR Spectroscopy

• Today: EPR Spectroscopy.

• Thursday: XAS and EXAFS (guest lecturer with great experience in the field).

• As an official policy and a cautionary note, don't use ChatGPT to solve this course's homework.

• Benefits of EPR.

    – Allows you to look at electronic spin flips.

    – Allows you to look at paramagnetic complexes (the class complementary to those you can observe with NMR).

• Most of today: Doublets.

• Electron spin.

    – An electron can be either spin up or spin down.

    – These states are degenerate in the absence of a magnetic field.

    – However, a magnetic field induces a Zeeman[1] splitting described as follows.

• The intrinsic electron spin has a magnetic moment defined as

$$\mu_z = g\beta M_s$$

    – g is the gyromagnetic ratio for an *electron* (= 2.0023219278; we usually just treat it as 2; can deviate depending on SOC).

    – $M_s = \pm 1/2$ is our spin quantum number.

    – $\beta = e\hbar/2m_e$ is our Bohr magneton.

• It follows that
$$E = -\mu \cdot \vec{H} = -\mu H \cos\left(\vec{\mu} \cdot \vec{H}\right) = -\mu_z H = g\beta H M_s = \pm\frac{1}{2}g\beta H$$

    – This Zeeman splitting is pretty easy to visualize (see Figure 6.2a).

    – Thus, the energy to flip an electron is going to be $g\beta H$.

        ■ This is also known as the **resonance condition**.

• Aside: Be familiar with ENDOR spectroscopy, a combination of nuclear and electronic.

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[1]ZAY-mon.

- In an EPR experiment, we apply radiation to stimulate a spin flip.

  - $E = h\nu = g\beta H$.
  - This energy is in the microwave region.
  - Microwaves are much higher in energy than radio waves, thus are more difficult to handle for technical reasons.
  - Thus, we cannot run complex, pulsed experiments analogous to in NMR; we just run more simple scans.
  - Indeed, herein we *fix* the microwave frequency and vary the magnetic domain.
  - Takeaway: EPR is much cruder than NMR in many ways (for technical reasons).

- The frequency domain ν can vary based on the spectrometer from 1-285 GHz.

  - X-band (9.6 GHz) spectrometers are the most common.
  - More rarely, Q-band (35 GHz) and W-band (95 GHz) are used.
  - Milwaukee has an S-band EPR at 2 GHz.
  - High frequencies give you worse splitting (opposite of NMR) but better signal-to-noise.

- **Continuous wave EPR**: EPR experiments run under a fixed frequency domain and variable magnetic domain. *Also known as* **CW EPR**.

  - All of the setups described above constitute CW EPR.

- We scan across our magnetic field and observe (fairly broad) Gaussian lineshapes. Thus, we usually plot the first derivative.
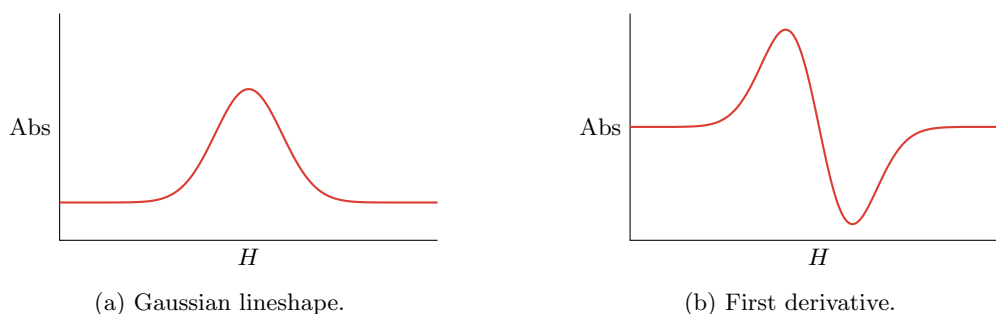

(a) Gaussian lineshape. (b) First derivative.

Figure 7.1: EPR spectra are plotted as the first derivative.

- There are two main types of EPR line broadening.

  1. **Secular broadening**. This comes from processes that vary the local magnetic field. Two sub-classes.
     (a) *Dynamic broadening.* A homogeneous broadening obtained by adding a paramagnetic ion to a solution of a free radical. This gives Lorentzian lineshapes.
     (b) *Static broadening.* This is effectively the same, but induced by frozen solution and hence no longer homogeneous. This gives Gaussian lineshapes.

2. **Lifetime broadening**. This occurs when the excited state lifetime is too short. It mathematically originates from the Heisenberg uncertainty principle. In particular, we have that

$$\Delta E \Delta t = \frac{h}{2\pi} \qquad\qquad \Delta h\nu = \Delta E = g\beta H = g\beta \Delta H$$

$$\Delta h\nu \Delta t = \frac{h}{2\pi} \qquad\qquad \Delta \nu = \frac{g\beta}{h}\Delta H$$

$$\Delta \nu = \frac{1}{2\pi \Delta t} \qquad\qquad \Delta H = \frac{h}{g\beta}\Delta \nu$$

so, combining the above two expressions, the FWHM ΔH is given by

$$\Delta H = \frac{h}{2\pi}\frac{1}{g\beta \Delta t}$$

Essentially, as Δt gets really small, everything else starts to blow up since its in the denominator in the last term.

- We typically do EPR experiments in a frozen solution.

- Two flavors of EPR we really care about.

- **Spin-lattice relaxation**: The interaction of spin with the surroundings. *Denoted by T_1. Given by*

$$\Delta H = \frac{\hbar}{g\beta}\frac{1}{2T_1}$$

  – In other words, if some spin is oriented away from H, how much time does it take to "reparallelize?"

- **Spin-spin relaxation**. *Denoted by T_2. Given by*

$$\Delta H = \frac{\hbar}{g\beta}\frac{1}{T_2}$$

- Combining the two gives the total homogeneous line width T_2':

$$\frac{1}{T_2'} = \frac{1}{T_2} + \frac{1}{2T_1}$$

- Result: We need to go to low temperatures for EPR spectroscopy both for the lifetime reason and for technical reasons.

  – We need to go to helium temperatures in many cases.

  – Low spins may be observable at "high" temperatures like $77\,\mathrm{K}$ or even room temperature in some cases.

- g-values.

  – The g-value is sort of like a ppm shift value for the EPR signal.

  – Recall that g is determined by the resonant frequency H_r at which we observe the excitation.

$$\Delta E = \Delta E$$
$$g\beta H_r = h\nu$$
$$g = \frac{h\nu}{\beta H_r}$$

  – Organic radicals almost always exist at $g = 2$ and are isotropic. Deviation might be 1/10,000. This is because organic compounds are composed of light atoms that just don't have much SOC.

– For TM's (and lanthanides), g varies widely. Fortunately, it varies in a way that we can understand with orbitals.

■ Again, we visualize "ring currents."

■ One that opposes the magnetic field induces $g < 2$.

➢ Think of a lone electron in a set of 5 degenerate d-orbitals.

■ If a hole "hops" through and generates a ring current as in d^9 Cu^{2+}, we have a ring current that reinforces the magnetic field and hence $g > 2$.

■ Essentially, there are three scenarios that determine the value of g.

➢ If the d-orbitals are less than 1/2 filled, $g < 2$.

➢ If $>$ half filled, $g > 2$.

➢ At a perfectly half-filled shell, we should have $g \approx 2$.

■ This gives us sign. For magnitude...

➢ The magnitude of the deviation is related to the magnitude of the SOC.

➢ To a first approximation, this will relate to symmetry and the degeneracy of orbitals.

■ Trust the half-filled value, not the hole: When you have d^2 in an octahedral field, for instance, the t_{2g} set is less than half-filled, so $g < 2$; it's not that you have one hole rotating so $g > 2$.

■ It is the possibility of orbital angular momentum coupling with the spin angular momentum that allows g to change.

• Anisotropy: Thus far, we've only considered the effect of isotropic transitions. But both the magnetic field and spin are tensors with x, y, z-components.

– An isotropic magnetic field is described by

$$\hat{H}_{\text{iso}} = g\beta\hat{H} \cdot \hat{S}$$

■ You spin your samples to try to average this out in solid-state NMR, but it's not perfect so you do need to take axes into account.

– An anisotropic magnetic field is described by

$$\hat{H}_{\text{aniso}} = \beta\hat{H} \cdot \hat{g} \cdot \hat{S} = \beta(H_x, H_y, H_z) \begin{pmatrix} g_x & 0 & 0 \\ 0 & g_y & 0 \\ 0 & 0 & g_z \end{pmatrix} = \beta H_x g_x S_x + \beta H_y g_y S_y + \beta H_z g_z S_z$$

– If a molecule has very high symmetry (e.g., T_d, O, I_h, etc.), then $g_x = g_y = g_z$. In this case, we get back to our nice isotropic, one peak picture (Figure 7.1a).

■ Molecular geometry is *related* to g variations, but they're not the same thing. Don't make the mistake of looking at a highly symmetric molecule and thinking you know what the EPR spectra should be! You have to consider orbitals.

– EPR is often done on frozen solutions (sometimes powders) so that we don't have rapid solution-phase tumbling to average out the g-values but have everything stuck in some orientation. In particular, g-values will be inequivalent in frozen solutions!

• Anisotropic spectra.
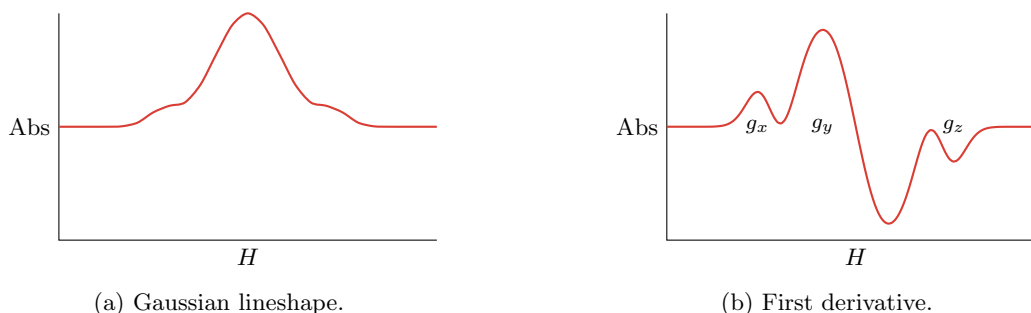

(a) Gaussian lineshape.

(b) First derivative.

Figure 7.2: Rhombic anisotroic EPR spectra.

- – Note that we don't know anything about Cartesian coordinates from the spectrum, so Anderson prefers g_1, g_2, g_3.
  - – This is a rhombic spectrum, meaning that $g_x \neq g_y \neq g_z$.
  - – Axial spectra are often referred to as $g_\parallel$ and $g_\perp$. This corresponds to $g_x \approx g_y \neq g_z$.
    - ■ We typically have a small $g_\parallel$ peak downfield of a big $g_\perp$ peak (picture in notes).
    - ■ You see spectra like this for when your molecules have a clear symmetry axis; decreasing the symmetry further will tend to introduce some more rhombicity.
  - – Anisotropy only occurs via coupling into orbital angular momentum. Thus, it is observed for TMs but typically not for organic radicals.

- We now discuss fine structure for a while.

- Fine structure basics.

  - – The electron spin can also interact with nuclear spin in **hyperfine interactions** and **superhyperfine interactions**.
    - ■ These lead to additional signals and structure.
    - ■ Be aware of the differences between hyperfine and superhyperfine, but only hyperfine interactions will be analyzed for the remainder of the time.
  - – The quantum-mechanical basis for fine structure involves the following Hamiltonian.

  $$\hat{H} = g\beta \vec{H} \cdot \hat{S} + a\hat{I} \cdot \hat{S} = g\beta H \cdot \hat{S}_z + a\hat{I}_z \cdot \hat{S}_z$$

  - ■ $\hat{I}$ is the nuclear spin operator.
  - ■ $\hat{S}$ is the electron spin operator.
  - ■ z is the component along H.
  - ■ a is the hyperfine coupling constant.
  - – Energies: Found by calculating eigenvalues.

  $$E = \pm\frac{1}{2}g\beta H + \frac{a}{4} = \frac{1}{2}g\beta H \pm \frac{a}{4}$$

- **Hyperfine interaction**: An interaction with the direct nucleus which bears the radical.

- **Superhyperfine interaction**: An interaction involving additional coupling to other nuclei via delocalization.

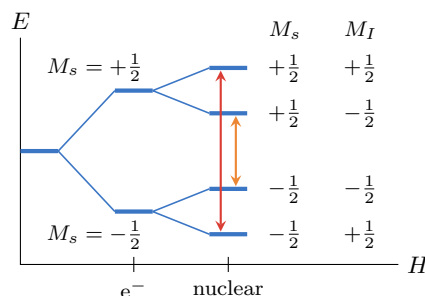- Hyperfine Zeeman splitting diagram.

Figure 7.3: Hyperfine splitting.

- – We first have our electron splitting.
- – Then if we turn on nuclear splitting, that happens next, yielding four distinct states.

- Hyperfine election rules.

  - Thus far, we have implicitly used $\Delta M_s = \pm 1$.
  - We must have $\Delta M_I = 0$ as well! We can have an electron spin flip, but we can't do a nuclear spin flip at the same time, which may make some intuitive sense as well since the probability that these two unlikely events would happen simultaneously is very low.
  - Thus, we have two allowed transitions in Figure 7.3.

- Hyperfine EPR spectrum.

  - The peak splitting is A, which is related to the actual hyperfine coupling constant a as we'll talk about shortly.
  - A lot of the time, you don't see y-axis labels in EPR spectra because "the first derivative of absorbance" is not a particularly helpful unit.

- A few final notes on hyperfine coupling.

  1. The hyperfine coupling constant a is field independent.
     - Zeeman splitting is the only thing that is field dependent.
  2. a is a scalar HF constant and
     $$a = g\beta A$$
     - A is measured in Gauss; it is the *experimental* HF constant.
  3. a can also be anisotropic.
     - Each of the values g_x, g_y, g_z can have an a.
     - a can be 0 for some g_i and not others.
  4. M_I can have many values.
     - Just like with NMR, a nuclear spin with $M_I > 1/2$ can give multiline patterns.
     - Examples.
       - ^{14}N has $M_I > 1/2$.
       - TMs can go up to 7/2 or 9/2, leading to very complicated multiline coupling patterns very quickly.
  5. M_I sums the contribution from other neighboring nuclei.
     - Multiple nuclei can also give multiline patterns, notably with $2nI + 1$ lines.
  6. If a spin active nucleus is not 100% abundant, we get a superposition.
     - Cool example: $\text{Mo(CN)}_8{}^{3-}$.
       - This is a d^1 $S = 1/2$ compound.
       - $I = 0$ is 75% abundant, but ^{97}Mo is 25% abundant with $I = 5/2$.
       - Thus, an amount of intensity equivalent to 1/3 of the central signal gets divided among 6 smaller neighboring peaks that are all evenly spaced apart (see notes for image).

- We now get move on to higher spin species.

  - This is a further level of complication.
  - However, these species may have more accessible EPR transitions.
  - We usually have larger splitting for higher M_s values.

- **Kramer's theorem**: Ions with an odd number of electrons will always have as their lowest energy level at least a doublet that will split in an applied magnetic field and give rise to an EPR signal.

- **Kramer's doublet**: The doublet predicted by Kramer's theorem.

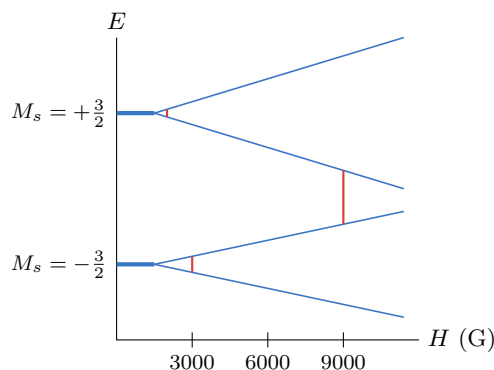- Example: Transitions predicted to be visible for a quartet ($S = 3/2$).

Figure 7.4: Quartet EPR signals.

  - Something lower around $2000\,\text{G}$, higher around $3000\,\text{G}$ and, if our spectrometer is powerful enough, something around $9000\,\text{G}$.
  - Recall $\Delta M_s = \pm 1$.

- Example: Transitions predicted to be visible for a triplet ($S = 1$).

  - Triplets are very difficult to see because the lower state takes a long time to drop low enough to see the ground state.

- Treating spin-orbit coupling.

  - We have that $\vec{\mu} = g\beta\vec{J}$.
  - It follows that
  $$g = \frac{J(J+1) \cdot S(S+1) - L(L+1)}{2J(J+1)} + 1$$
  - What people tend to do is look at the spectrum.

- That's it for higher spin species.

- A few practical points on EPR spectroscopy.

  1. Use a microwave cavity, a fixed frequency, and vary the field.
  2. Avoid solvents that strongly absorb microwaves (e.g., water, other polar solvents). This can sometimes be ok if the sample is frozen.
  3. Usually quote g-values.
     - Do we report values as H or g??
  4. You can double integrate vs. a standard to quantity $\pm 20\%$.

- We now move on to advanced EPR techniques.

  - These are analogous to some of the fancy things you can do with NMR.
  - Essentially, they are alternate ways of getting data out of an EPR machine besides straight-up absorption spectra.

- In particular, we will focus on **ENDOR** and **ESEEM** spectroscopy.

- **Electron spin echo envelope modulation** (spectroscopy). *Also known as* **ESEEM**.

- **Electron nuclear double resonance** (spectroscopy). *Also known as* **ENDOR**.

- Background.

  - Most EPR spectroscopy compared to NMR is pretty rudimentary.

    ■ In NMR, every carbon spectrum you take is proton-decoupled (we'll talk about this later).
    ■ Radiofrequency is really nice to control.

  - However, these are both 2D experiments between EPR and NMR.

    ■ They allow us to see spin-active nuclei that are close to the paramagnetic center.
    ■ 2D EPR can give you a ton of information about paramagnetic compounds; the most useful are those that couple electron transitions with nuclear transitions.

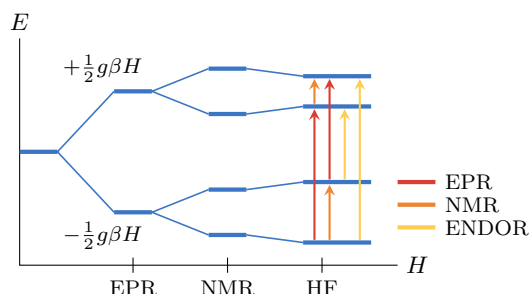 - These are super powerful techniques.

- ENDOR spectroscopy.

Figure 7.5: ENDOR splitting.

  - The quantum-mechanical basis for ENDOR involves the following Hamiltonian.

  $$\hat{H} = \underbrace{g\beta\hat{H} \cdot \hat{S}}_{\text{EPR}} - \underbrace{g_N\beta_N\hat{H} \cdot \hat{I}}_{\text{NMR}} + \underbrace{ha\hat{I} \cdot \hat{S}}_{\text{HF}}$$

  - Three levels of splitting: EPR, NMR, and HF.

    ■ The last one doesn't actually induce splitting; it's just coupling between the first two that affects energy levels.

  - EPR has $\Delta M_s = \pm 1$, $\Delta M_I = 0$.
  - Here, we turn on semi-forbidden transitions, i.e., those with $\Delta M_s = \pm 1$ and $\Delta M_I = \pm 1$.
  - $1 \rightarrow 3$ and $2 \rightarrow 4$ are EPR allowed.
  - $1 \rightarrow 2$ and $3 \rightarrow 4$ are NMR allowed.
  - ENDOR transitions (which we're turning on in this experiment) are $2 \rightarrow 3$ and $1 \rightarrow 4$.
  - ENDOR spectra tend to look like look like a big messy hunk corresponding to the nucleus, and then distinct ones further out which correspond to the NMR transitions.

- Possibly a bit more ENDOR on Friday.

- We now move on to ESEEM.

  - Do we need to know this??