

# Solutions week 11

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November 15, 2024

## 1 Diskusjonsoppgaver

- NMR (Nuclear Magnetic Resonance) spectroscopy works by probing the magnetic properties of certain atomic nuclei to reveal a “fingerprint” of a molecule’s structure. Some nuclei have nonzero spin (such as  $^1H$ ,  $^{13}C$ ). When a sample is placed in a strong static magnetic field ( $B_0$ ), the spins of these nuclei align either with or against the field, leading to a splitting of the energy levels with spacing  $\Delta E$ , which is proportional to  $B_0$ . A radio-frequency field  $B_1$ , applied perpendicular to  $B_0$ , excites some nuclei by matching this energy difference, causing them to flip at a specific resonance, known as the **Larmor frequency**. Each nucleus’s resonance frequency shifts slightly depending on its chemical environment, producing unique **chemical shift** that serve as a molecular fingerprint. Additionally, nearby nuclei interact, causing **couplings**, i.e. small splittings, in the spectrum that give further information about atomic connectivity and spatial properties. This combination of chemical shifts and couplings creates a spectrum that reveals the types and arrangements of atoms, allowing NMR to detail the molecular structure.
- EPR (Electron Paramagnetic Resonance) spectroscopy works similarly to NMR but focuses on **unpaired electrons** rather than nuclei. Molecules with unpaired electrons, such as free radicals or transition metal complexes, contain unpaired electrons with magnetic moments that respond to an external magnetic field. When a sample with unpaired electrons is placed in a magnetic field (often labeled  $B_0$  as in NMR), these electrons align either with or against the field, creating an energy difference ( $\Delta E$ ) between the two orientations. To detect this difference, a second field  $B_1$  is applied at a frequency matching  $\Delta E$ , causing resonance. This energy difference depends on the specific magnetic environment around each electron, giving a characteristic signal. Additionally, if unpaired electrons are near magnetic nuclei, they interact with those nuclei, causing **hyperfine splitting** in the EPR spectrum. This splitting pattern provides structural information, indicating the type and proximity of neighboring atoms and the electron’s local environment. EPR spectroscopy thus offers insights into the presence and behavior of unpaired electrons, making it a powerful tool for studying free radicals, metals, and other paramagnetic species.
- Defining the chemical shift relative to a reference compound standardizes NMR measurements, making them consistent across different instruments and experimental conditions. The absolute resonance frequency of a nucleus depends on the magnetic field strength, which varies between spectrometers. By referencing shifts to a known compound like tetramethylsilane (TMS), we create a fixed baseline, ensuring that chemical shifts are comparable regardless of the equipment. This approach also accounts for minor variations in sample conditions, making shifts reproducible and reliable. As a result, chemists can universally interpret chemical shifts to identify molecular structures and functional groups more accurately.
- In NMR, two magnetic fields are essential: a static field ( $B_0$ ) and a radio-frequency (RF) field ( $B_1$ ). The static field  $B_0$  aligns nuclear spins, creating an energy difference (splitting) between aligned and anti-aligned states. The RF field  $B_1$ , applied at the Larmor frequency, provides energy to flip the spins, creating resonance. For effective excitation,  $B_1$  must be

perpendicular to  $B_0$ ; this orientation satisfies quantum transition rules, allowing the RF field to tip the spins away from alignment with  $B_0$ . This setup lets the spins process, generating a signal used to analyze the molecular structure.

- Hartree-Fock-metoden skalerer som  $O(M^4)$  i antall basisfunksjoner  $M$ . Når du øker antall vannmolekyler fra 1 til 3, vil antallet basisfunksjoner tredobles, siden hvert vannmolekyl bidrar med sitt eget sett av basisfunksjoner.

Hvis vi antar at basisfunksjonsantallet skalerer lineært med antall molekyler, så vil antallet basisfunksjoner for 3 vannmolekyler være  $3M$ . Beregningstiden vil da skales som  $(3M)^4 = 81M^4$ .

Siden én beregning for ett vannmolekyl tar ett sekund, vil beregningen for tre vannmolekyler ta:

$$1 \text{ s} \times 81 = 81 \text{ s.}$$

Altså, det vil ta omtrent 81 sekunder å utføre Hartree-Fock-beregningen for 3 vannmolekyler med samme basis.

- Møller-Plesset perturbasjonsteori (MP) er ikke variasjonell. Dette betyr at energien beregnet med MP ikke nødvendigvis er en øvre grense for den eksakte energien til systemet, som den ville vært i en variasjonell metode. I en variasjonell metode vil energien alltid ligge over den eksakte energien, og jo bedre basissettet eller bølgefunksjonsansatsen er, jo nærmere blir energien den eksakte energien.

Siden MP ikke er variasjonell, kan energien ligge under den eksakte energien, noe som gjør det vanskelig å estimere nøyaktigheten bare basert på energiens verdi. Likevel er MP metoden kjent for å gi bedre svar enn Hartree-Fock, spesielt for systemer i likevekt i mangelektronsystemer. Metoden anses derfor som en forbedring av Hartree-Fock løsningen, selv om den ikke gir en variasjonell garanti.

## 2 Regneoppgaver gjort av meg

- We have that

$$\tanh(x) \approx x + O(x^3) \quad (1)$$

so we get that

$$P(B_0) = \tanh\left(\frac{\gamma \hbar B_0}{2k_b T}\right) \approx \frac{\gamma \hbar B_0}{2k_b T} \quad (2)$$

at room temperature,  $T \approx 298\text{K}$ . We hence get, in SI units,

$$P(B_0) \approx \frac{267.5 \cdot 10^6 \cdot 1.05 \cdot 10^{-34}}{2 \cdot 1.380649 \cdot 10^{-23} \cdot 298} \frac{1}{T} B_0 = 3.4 \cdot 10^{-6} \frac{1}{T}$$

So,  $P(B_0)$  changes by  $\sim 3.4 \cdot 10^{-6}$  per additional Tesla.

- For 1,1,1,2-tetrachloroethane ( $\text{CCl}_3\text{CH}_2\text{Cl}$ ), we can predict the  $^1\text{H}$  NMR spectrum by analyzing the molecule's structure:

**1. Identification of Protons:** The molecule contains a single  $\text{CH}_2$  group with two hydrogen atoms. These hydrogens are attached to a carbon atom bonded to one chlorine atom and a  $\text{CCl}_3$  group.

**2. Chemical Shift:** The two hydrogens on the  $\text{CH}_2$  group are *chemically equivalent* because they are in the same chemical environment. Therefore, they will produce *one unique*  $^1\text{H}$  NMR signal.

**3. Multiplet Splitting (Spin-Spin Coupling):** There are no neighboring hydrogens on adjacent carbons ( $n = 0$ ). According to the  $n + 1$  rule, where  $n$  is the number of neighboring nonequivalent hydrogens, the signal will be a *singlet* ( $0 + 1 = 1$ ). Since there are no other hydrogens to couple with, the peak remains unsplit.

- To predict the hyperfine structure of the EPR spectrum for a radical with two  $^{14}\text{N}$  nuclei and one proton, let's analyze the hyperfine interactions:
  - 1. Nuclear Spins:** Each  $^{14}\text{N}$  nucleus has a nuclear spin  $I = 1$ . The proton has a nuclear spin  $I = \frac{1}{2}$ .
  - 2. Hyperfine Splitting from  $^{14}\text{N}$  Nuclei:** For two equivalent  $^{14}\text{N}$  nuclei, the unpaired electron will interact with both nuclei simultaneously, creating a hyperfine splitting pattern. Since each  $^{14}\text{N}$  has  $I = 1$ , we get  $2I + 1 = 3$  lines per  $^{14}\text{N}$  nucleus. For two equivalent  $^{14}\text{N}$  nuclei, the interaction produces a total of  $2I + 1 = 5$  lines, with relative intensities  $1 : 2 : 3 : 2 : 1$ , due to the binomial distribution of possible spin states.
  - 3. Hyperfine Splitting from the Proton:** The proton (with  $I = \frac{1}{2}$ ) will split each of these 5 lines into 2 lines, resulting in a doublet for each nitrogen pattern. This final splitting results in  $5 \times 2 = 10$  hyperfine lines.