Quantum Mechanics

Exam

First Problem : Absoprtion spectrum of cyanines

Cyanines are organic molecules composed of a long carbon chain bounded by two Nitrogen atoms (Figure 1). The presence of conjugated double bounds delocalizes the lectrons along the chain and gives to these molecules their fluorescence properties. In the problem, we try to understand the dependence of the absorption wavelength given in Fig. 1.

1. Assuming that the electrons are free to move along the carbon chain we can describe their quantum behavior using the Hamiltonian of a 1D particle trapped in a flat potential of length L (the distance between the Nitrogen atoms) and bounded by infinitely high walls. Write Schrödinger's Equation and specify the boundary conditions (m is the mass of the electron). Determine the energy of the n-th level.
2. State Pauli's Principle. How many electrons can occupy a single level ?
3. Consider a cyanine molecule containing $2N + 1$ carbon atomes and assume that each delocalized doublet brings two electrons to the system. Show that $2N + 4$ electrons are delocalized. Deduce the value of n of the last occupied level of the molecule in its ground-state.
4. What is the lowest energy required to bring the molecule in an excited state ? Deduce the value λ_N of the largest wave-length absorbed by the molecule.
5. Note a le length of the C-C and C-N bounds. Express L with N and a. Show that for large N

$$\lambda_N \sim \frac{8\pi m a^2 c}{\hbar} N,$$

   where c is the velocity of light.
6. Comment this result and compare with the data given in Fig. 1.

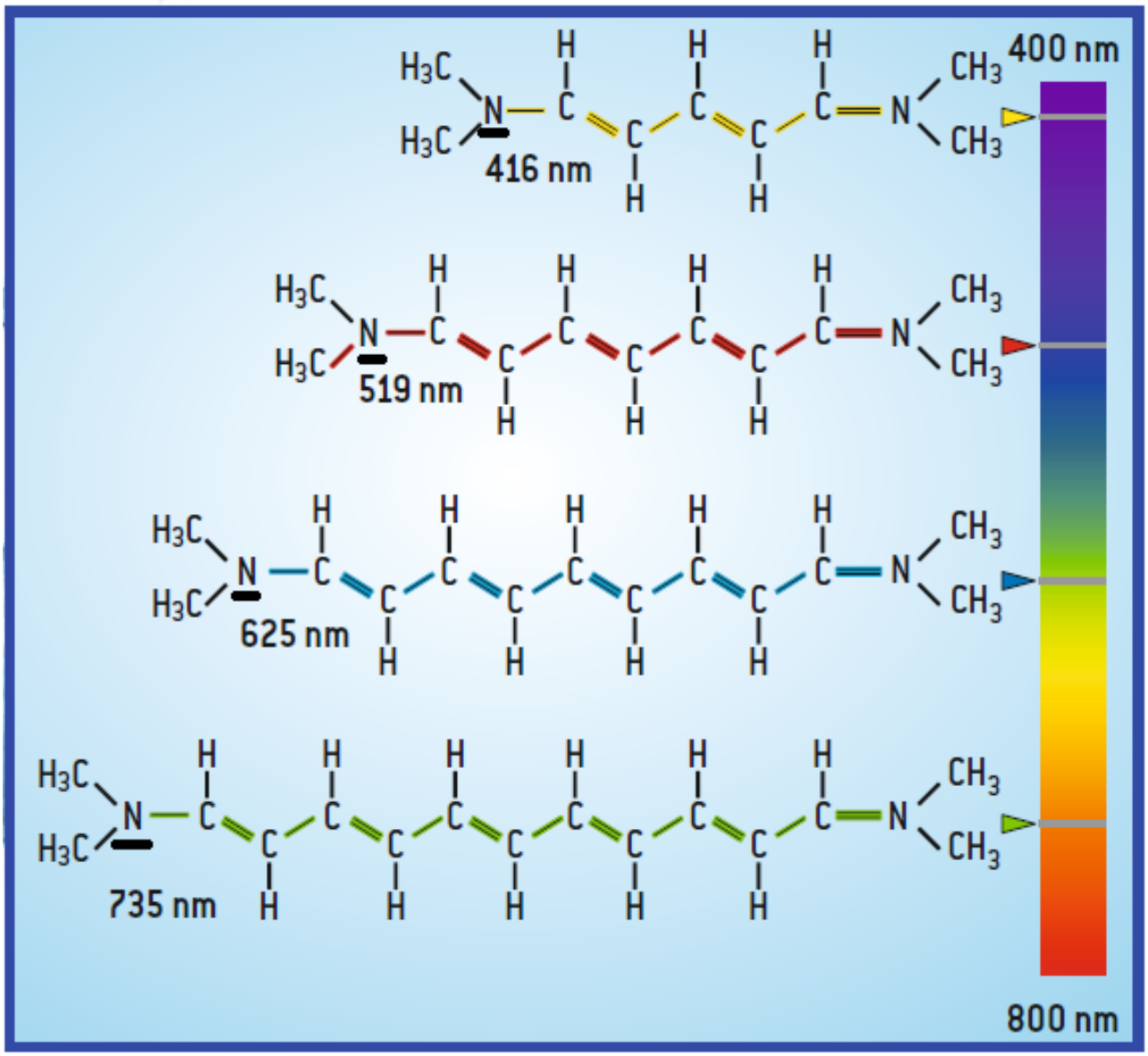

FIGURE 1 – Chemical structure of cyanines and absorption wavelengths. Figure from Pour la Science no 403 p. 96.

Second Problem : structure of the Helium atom

We focus here on the spectrum of the Helium atom. To simplify the problem, we assume that the nucleus is fixed and that the Hamiltonian of the system is given by

$$\widehat{H} = \sum_{i=1}^{2} \left(\frac{\hat{P}_i^2}{2m} - \frac{2e^2}{r_i} \right) + \frac{e^2}{|\hat{\boldsymbol{r}}_1 - \hat{\boldsymbol{r}}_2|}.$$

1. Interpret the different terms of the Hamiltonian.
2. To find the energy of the ground state of the Helium atom, we use a variational method. We take for the wavefunction

   $$\psi(\mathbf{r_1}, \mathbf{r_2}) = \varphi(\mathbf{r_1})\varphi(\mathbf{r_2}),$$

   with $\varphi(r) = Ae^{-r/a}$, and $a \geq 0$ is the variational parameter that os varied to get the value of the ground state energy. Calculate $\int d^3r_1 d^3r_2 |\psi(r_1, r_2)|^2$ and find the value A (assuming it is real and positive).
3. Calculate $E(a) = \langle\psi|\hat{H}|\psi\rangle$. Show that $E(a) = E_{\text{cin}} + E_{\text{pot}} + E_{\text{int}}$, with

   $$\begin{aligned} E_{\text{cin}} &= \frac{\hbar^2}{ma^2} \\ E_{\text{pot}} &= -\frac{4e^2}{a} \\ E_{\text{pot}} &= \frac{Ke^2}{a}, \end{aligned}$$

   where K is a numerical constant defined by a multidimensional integral that you will not try to calculate explicitely.

   Hint : for a spherically symmetric function, $\nabla^2 u(r) = \frac{1}{r}\frac{d^2(ru)}{dr^2}$.
4. Assume that $K = 5/8$. Calculate the value of a (noted a^*) for which E is minimal. Calculate an approximate value E^* of the energy of the ground state of the Helium atom. Is this value an upper or a lower bound of the real value ?
5. The ionization energy of the Helium atom is 78.6 eV. Compare to E^*. Comment.
6. Up to now, we did not take into account the spin and the fermionic nature of the electrons. How does the ket $|\psi\rangle$ describing the system behave after the exchange of the states of the two electrons. Give the spin-state of the system ($|i : \pm\rangle$ will denote the spin state of the electron i).

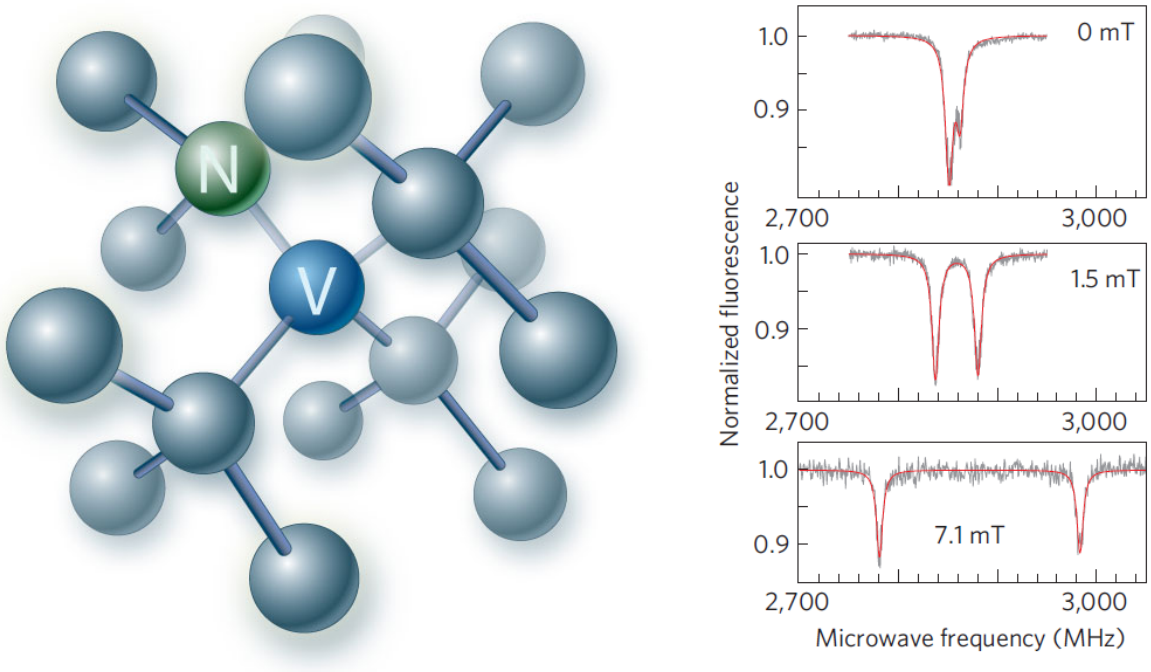

FIGURE 2 – Left : structure of the NV center in diamond. Right : dependence of the absorption spectrum with the magnetic field B_0.

Third Problem : NV centers in diamond

NV centers are defects of diamond in which a crystal vacancy is located nearby a Nitrogen atom (chemical element N). Electrons can be localized in the vacancy and which behaves as an artificial atom of spin $S = 1$.

1. If we consider only the spin degrees of freedom, what is the dimension of the Hilbert space describing the system ?
2. Assume that the interaction between the NV-center and the environment yields the following Hamiltonian

$$\widehat{H} = D\widehat{S}_z^2 + E(\widehat{S}_x^2 - \widehat{S}_y^2).$$

   where D and E are two positive parameters. Express the Hamiltonian using the $\widehat{S}_z$ and $\widehat{S}_\pm$ operators. Give the matrix elements of $\widehat{H}$ in the basis $|S, m_S\rangle$. Calculate the energy spectrum of the system. Give the degeneracy of the different levels for $E = 0$ and $E \neq 0$ respectively.
3. In practice, $E \ll D$. What is the ground-state of the system ?
4. We add a magnetic field B_0 aligned along z. If $\gamma = gq/2/m$ if the gyromagnetic factor of the NV-center, where g is the associated Landé factor, what term should you add in the Hamiltonian to describe the interaction with the NV-center ?
5. Assume that $\mu_B B_0$ is much smaller than $D\hbar^2$. Show that the effect of the magnetic field on the excited state can be calculated within the subspace $|S = 1, m_S = \pm 1\rangle$. Calculate

the spectrum of the NV center excited state in this limit ($E_\pm$ denote the energies of these two states).

We recall that the Bohr magneton is given by $\mu_B = q_e\hbar/2m_e$.

6. What is the effect of the magnetic field on the ground state of the system at first order in perturbation theory.
7. Sketch the energy levels vs magnetic field.
8. From now on, we work in the case where $\mu_B B_0$ is much larger than $E\hbar^2$ but stays smaller than $D\hbar^2$. SHow that in this case, the eigenstates of the system are approximatively the states $|S=1, m_S\rangle$. To simplify, we assume from now on that $E=0$.
9. The system is prepared in its ground state and at $t=0$ we add to B_9 a time-dependent magnetic field $\boldsymbol{b}_1\cos(\omega t)$.
10. Using a symmetry argument, show that if $\boldsymbol{b}_1$ is aligned along z then the system remains in the ground state.
11. Consider now that $\boldsymbol{b}_1$ is along x. Given the expression of the hamiltonien with the operators $\widehat{S}_z$ and $\widehat{S}_\pm$.
12. Take $|\psi(t)\rangle = \sum_{m_S} c_{m_S}(t)|S=1, m_S\rangle$. Give $c_{m_S}(t=0)$.
13. Assuming that $\boldsymbol{b}_1$ can be treated perturbatively, give the expression of the c_{m_S}'s. Interpret the result.
14. We show in Fig. 2 the probability of staying in the ground-state vs the oscillation frequency of $\boldsymbol{b}_1$. Explain the results and give an estimate of the different parameters of the model.