Quantum mechanics and spectroscopy exam 12.4.2021

*The response time is **four and a half hours**, from which the last half an hour should be reserved for the submission of the solutions. Return the solutions to the return box in the Exam subsection in the 2021 Quantum Mechanics and Spectroscopy MyCourses page. **Save all your solutions as a single PDF-file!** I will be available throughout the exam via email at lauri.partanen@aalto.fi*

1. Molecules like 1,4-diphenyl-1,3-butediene are used as commercial dyes. In these molecules, the conjugated π-electrons can be approximately modeled as particles in a box. The 1,4-diphenyl-1,3-butediene system under investigation has four such π-electrons, because the phenol groups do not participate in the conjugated network.

   a) Sketch the energy level diagram for the conjugated π-electron system. Include the electrons in your diagram. What are the quantum numbers for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)?

   b) From computational chemistry, the length of the conjugated π-electron system is known to be 695 pm. What is the longest wavelength photon that the system can absorb? Draw the corresponding transition on your sketch for part a).

   c) Sketch the wavefunction and the probability density for the HOMO and LUMO electrons. Discuss the correspondence principle in light of your drawings.

   d) What is meant by the expectation value of an operator? Determine the expectation value of position based on your sketch for part c)? Check your reasoning by calculating the expectation value of position with the integral
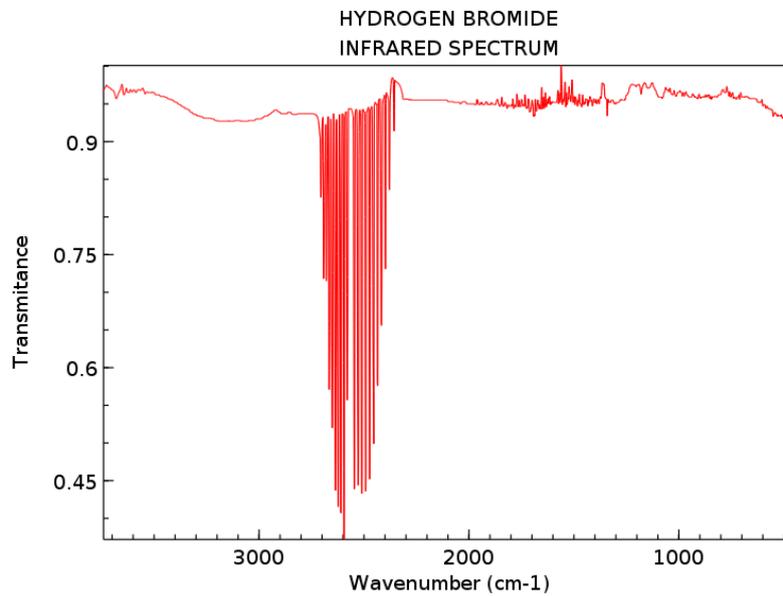
   $$\int_0^b x \sin^2(ax)\mathrm{d}x = \frac{b^2}{4} + \frac{1 - \cos(2ab)}{8a^2} - \frac{b\sin(2ab)}{4a},$$

   where a and b are constants.

   e) Compare how the energies or the wafefunctions of the 1,4-diphenyl-1,3-butediene system would change if the system was treated with a finite instead of an infinitely deep box.

2. The picture below shows a part of the $^1\mathrm{H}^{81}\mathrm{Br}$:n IR-spectrum. If this molecule is modeled as a Morse oscillator, its energy levels (in wavenumber) have the form

   $$\tilde{E}_v = \left(v + \frac{1}{2}\right)\tilde{\nu}_\mathrm{e} - \left(v + \frac{1}{2}\right)^2 x_\mathrm{e}\tilde{\nu}_\mathrm{e}.$$

   a) Explain carefully why do we observe a band of peaks as shown in the figure, instead of just a solitary peak. Justify also the intensities of the observed band.

   b) Based on the figure, estimate the wavenumber for the fundamental vibrational transition for $^1\mathrm{H}^{81}\mathrm{Br}$.

   c) The hot transition $v(2 \leftarrow 1)$ in $^1\mathrm{H}^{81}\mathrm{Br}$ has the wavenumber 2468,83 cm^{-1}. Based on a), estimate the anharmonicity constant x_e, the harmonic vibrational wavenumber $\tilde{\nu}_\mathrm{e}$ and the wavenumber for the first overtone $v(2 \leftarrow 0)$.

   d) What can you say about the intensity of the overtone $v(2 \leftarrow 0)$?

HYDROGEN BROMIDE
INFRARED SPECTRUM

NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)

Vetybromidin IR-spektri

3. Let's investigate the simultaneous determination of position and energy in a He^+-ion:

   a) Write out the Hamiltonian operators for He^+-ion and He, and give a physical interpretation of the different terms in them. In which case is the Schrödinger equation easier to solve and why?

   b) Define the concept of a commutator. What physical significance does it have in quantum mechanics?

   c) The 1s orbital for He^+ has the form $\psi_{1s} = \left(\frac{8}{\pi a_0^3}\right)^{\frac{1}{2}} e^{-\frac{2r}{a_0}}$, where r is the distance from the nucleus. Sketch the probability density as a function of r and calculate the expectation value for $\hat{r}$. Use the integral

   $$\int_0^\infty x^n e^{-bx} \mathrm{d}x = \frac{n!}{b^{n+1}},$$

   where $b > 0$ in your calculation. Interpret the calculated expectation value physically.

   d) Based on your sketch in part c), is it possible to measure the location of the electron in an 1s orbital with arbitrary accuracy? What can you conclude about $[\hat{H}, \hat{r}]$?

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