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Atomic, molecular physics and optics
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Problem Set 12: Molecular Spectroscopy II

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Exercise 1: Polyatomic vibrations of H_2O

In this exercise, we investigate the vibrations of the water molecule.

a.) Assume the H_2O molecule lies completely in the yz-plane as shown in Fig. 1. It belongs to the C_{2v} symmetry point group, which includes the identity element E, a 180° degree rotation around the z-axis C_2, and the two mirror planes σ_v and σ_v'. Complete the character table below, showing the four irreducible representations of this symmetry group.

C_{2v}	E	C_2	σ_v	$\sigma_{v'}$
A_1	1	1	1	
A_2	1	1		-1
B_1	1		1	-1
B_2		-1	-1	1

Hint: Use that the rows are orthogonal and normalized(norm$^2 = |C_{2v}| = 4$, where $|C_{2v}|$ is the number of elements in the

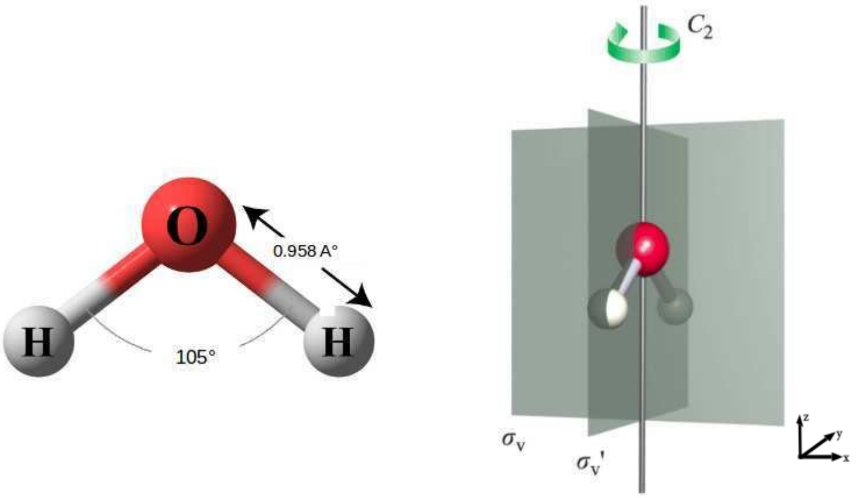

Figure 1: Water molecule and its symmetries.

b.) Following the lecture, define q_i, $i \in 1,..,9$ as the mass weighted diplacement coordinates. More concretely

$$\begin{aligned} q_1 &= m_{H1}^{1/2}(x_{H1} - x_{H1,e}), \quad q_2 = m_{H1}^{1/2}(y_{H1} - y_{H1,e}), \quad q_3 = m_{H1}^{1/2}(z_{H1} - z_{H1,e}), \\ q_4 &= m_{O}^{1/2}(x_{O} - x_{O,e}), \quad q_5 = m_{O}^{1/2}(y_{O} - y_{O,e}), \quad q_6 = m_{O}^{1/2}(z_{O} - z_{O,e}), \\ q_7 &= m_{H2}^{1/2}(x_{H2} - x_{H2,e}), \quad q_8 = m_{H2}^{1/2}(y_{H2} - y_{H2,e}), \quad q_9 = m_{H1}^{1/2}(z_{H2} - z_{H2,e}) \end{aligned}$$

with m_α being the mass of molecule α and $(x_\alpha, y_\alpha, z_\alpha)$ and $(x_{\alpha,e}, y_{\alpha,e}, z_{\alpha,e})$ being its position and equilibrium position respectively.

Write the character table for the physical 9 dimensional representation Γ(H_2O) acting on the q_i.

c.) Divide Γ(H_2O) into irreducible representations.

Hint: Again use that the rows corresponding to the irreducible representations are orthogonal and normalized with resp d.) To which irreducible representation do the translations in x, y, z direction belong.

e.) To which irreducible representation do the rotations around the x, y, z-axes belong.

The remaining three irreducible representations will correspond to the three normal vibrational modes, which we will study next. Departing from general symmetry considerations (which work for any potential energy V) we choose the following explicit potential energy

$$V = \frac{1}{2}k_r(r_1 - r_e)^2 + \frac{1}{2}k_r(r_2 - r_e)^2 + \frac{1}{2}k_\theta(\theta - \theta_e)^2,$$

where $r_1 = |\vec{r}_{H1} - \vec{r}_O|$, $r_2 = |\vec{r}_O - \vec{r}_{H2}|$ and θ is the angle between the H_1O and OH_2 bonds. The interatomic distance r_e as well as the radial and angular force constants k_r and k_θ are assumed to be constant.

f.) Show that the Hessian matrix can be written as

$$H_{ij} := \frac{\partial^2 V}{\partial q_i \partial q_j} = k_r\left(\frac{\partial r_1}{\partial q_i}\frac{\partial r_1}{\partial q_j} + \frac{\partial r_2}{\partial q_i}\frac{\partial r_2}{\partial q_j}\right) + k_\theta \frac{\partial \theta}{\partial q_i}\frac{\partial \theta}{\partial q_j}$$

g.) Numerically determine the Hessian matrix, by using a second order finite difference method for the derivative.

In [ ]:

```
##H20 molecule info
import numpy as np

kr = 450 #kcal/mol/Ang^2
kt = 55  #kcal/mol/rad^2
re = 0.958 #Ang
thetae = 104.5 #degrees
uH = 1 #mass of hydrogen in atomic units
uO = 16 #mass of oxygen in atomic units


#We can leave out the analysis of the x-components. Why?
#dy, dz are used as the WEIGHTED displacment coordinates (to keep the notation simple)

def r1(dyH1, dzH1, dyO, dzO, dyH2, dzH2):
    #takes the weighted displacements as input and outputs r1
    phi = thetae/2/360*2*np.pi #half the opening angle
    yH1 = -np.sin(phi)*re + dyH1/##      #y-coordinate of H1
    zH1 = -np.cos(phi)*re + dzH1/##      #z-coordinate of H1
    yO =  dyO/##                         #y-coordinate of O
    zO =  dzO/##                         #z-coordinate of O
    yH2 = np.sin(phi)*re  +dyH2/##       #y-coordinate of H2
    zH2 = -np.cos(phi)*re +dzH2/##       #z-coordinate of H2
    return np.sqrt((yH1-yO)**2 + (zH1-zO)**2)

def r2(dyH1, dzH1, dyO, dzO, dyH2, dzH2):
    #takes the weighted displacements as input and outputs r2
    phi = thetae/2/360*2*np.pi #half the opening angle
    yH1 = -np.sin(phi)*re + dyH1/##      #y-coordinate of H1
    zH1 = -np.cos(phi)*re + dzH1/##      #z-coordinate of H1
    yO =  dyO/##                         #y-coordinate of O
    zO =  dzO/##                         #z-coordinate of O
    yH2 = np.sin(phi)*re  +dyH2/##       #y-coordinate of H2
    zH2 = -np.cos(phi)*re +dzH2/##       #z-coordinate of H2
    return np.sqrt((yH2-yO)**2 + (zH2-zO)**2)

def theta(dyH1, dzH1, dyO, dzO, dyH2, dzH2):
    #takes the weighted displacements as input and outputs theta
    return


H = np.zeros([6, 6]) #Hessian, we arrange the entries as yH1, zH1, yO, zO, yH2, zH2
delta = 0.01 #Small displacement step for the finite difference method

##Calculate Hessian here
```

h.) Determine the vibrational frequencies (in wavenumber cm^{-1}) for the three vibrational modes.

In [ ]:

```
from scipy.linalg import eigh
evs, evecs = eigh(H)
c = 2.99*10**8
kcal = 4.18*10**6 #kcal/g to J/kg conversion
phl = ## photon wavelength vector, choose the three eigenmodes which correspond to the vibrations
```

```
print('The photon wavelength are', 1/phl ,'cm^{-1}')
```

i.) Sketch the eigenmodes of the hydrogen molecule. Are the corresponding irreducible representations in accordance with exercises c.), d.) and e.)

In [ ]:

```
import matplotlib.pyplot as plt
phi = thetae/2/360*2*np.pi
posy = np.array([-np.sin(phi)*re, 0,np.sin(phi)*re])  #y-positions of the atoms
posz = np.array([-np.cos(phi)*re, 0,-np.cos(phi)*re]) #z-positions of the atoms
sym =[] #Fill the irrep. tag

fig, ax = plt.subplots(1, 3, figsize = (12, 4))
# Create a figure and axis
for i in np.arange(3):
    ax[i].set_title(r'wave number{:.2f} cm$^-$$^1$, irrep. '.format(1/phl[i]*10**(-2)) + sym[i])
    ax[i].scatter(posy[::2], posz[::2], color = 'k', s = 50) #plot hydrogens
    ax[i].scatter(posy[1], posz[1], color = 'r', s = 100) #plot oxygen
    ax[i].plot(posy[0:2], posz[0:2], color = 'k', linestyle= '--')  #HO bond
    ax[i].plot(posy[1:3], posz[1:3], color = 'k', linestyle= '--')  #HO bond

    dy = evecs[::2,##]/4  #displacements y-direction (the division by four is simply to make the arrows smaller)
    dz = evecs[1::2,##]/4 #displacements z-direction (the division by four is simply to make the arrows smaller)

    ax[i].arrow(posy[0], posz[0], dy[0], dz[0], head_width=0.05) #plot the arrows showing the vibrational motion
    ax[i].arrow(posy[2], posz[2], dy[2], dz[2], head_width=0.05) #plot the arrows showing the vibrational motion

plt.show()
```

Exercise 2: Electronic spectroscopy of azulene

In the 1950s, azulene drew significant interest from the scientific community. As one of the first examples, theoretical (computer-assisted) calculations succeeded to quantitatively determine the excited state energies (1956, Pariser) and allowed for a reasonable assignment of the transitions measured by electronic spectroscopy. In this exercise, we'll follow a simplified version of that early research and use the (basic) Hückel model to calculate the electronic states.

a) Using the Hückel model (Serie 7, ex 3), numerically calculate the electronic states and energies of azulene. What is the HOMO-LUMO gap and the corresponding photon wavelength? $\boxed{\text{\newline}}$

Remark: You can use your old code.

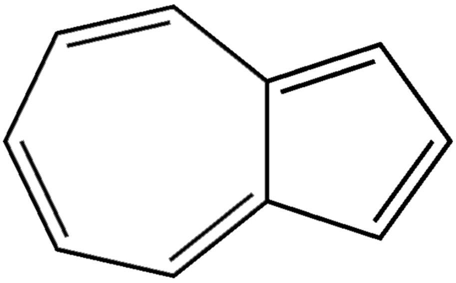

Figure 2: Azulene molecule.

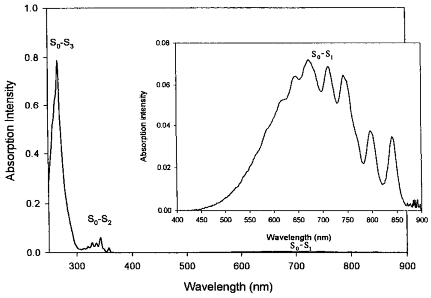

Figure 3: Experimental absorption spectrum of an azulene derivative.

In [1]:

```python
import numpy as np
from scipy.linalg import eigh
import matplotlib.pyplot as plt

ue = 1.602*10**(-19) #unit charge in [C]
hbar = 6.626*10**(-34) #hbar in [Js]
c = 3.0*10**8 #speed of light [m/s]


def azulene():
    #Calculate the spectrum in eV and eigenfunctions
    t = -2.5 # hopping in eV
    mat = np.zeros([10, 10])
    ### Set the hoppings by hand mat[i, j] = t
    evs, evecs = eigh(mat)
    return evs, evecs
```

In [ ]:

```python
evs, evecs = azulene()
Egap = #band gap
lgap = #corresponding wavelength
print('The band gap of azulene is',Egap , 'eV')
print('The corresponding wavelength', lgap, 'nm')
```

b) Use the code below to generate the color corresponding to the photon wavelength. Which color do you think azulene will have? Compare to a quick web search.

The wavelength calculated in a.) is the adsorbed one. The color seen is the transmitted/reflected part of the spectrum th

Remark: For those interested you may look up Lactarius indigo, a surprsingly edible mushroom containing the azulene p

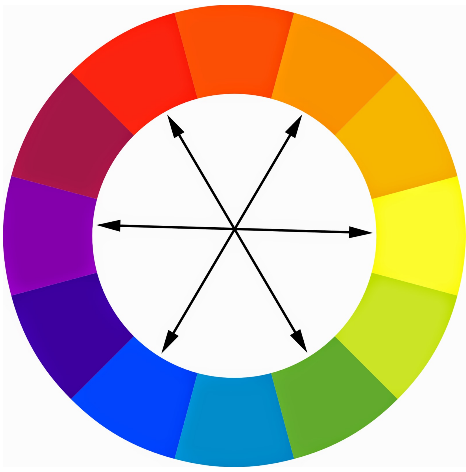

Figure 4: Complementary colors.

In [17]:

```python
import matplotlib.pyplot as plt

def wavelength_to_rgb(wavelength, gamma=0.2):
    ''' taken from http://www.noah.org/wiki/Wavelength_to_RGB_in_Python
    This converts a given wavelength of light to an
    approximate RGB color value. The wavelength must be given
    in nanometers in the range from 380 nm through 750 nm
    (789 THz through 400 THz).

    Based on code by Dan Bruton
    http://www.physics.sfasu.edu/astro/color/spectra.html
    Additionally alpha value set to 0.5 outside range
    '''
    wavelength = float(wavelength)
    if wavelength >= 380 and wavelength <= 750:
        A = 1.
    else:
        A=0.5
    if wavelength < 380:
        wavelength = 380.
    if wavelength >750:
        wavelength = 750.
    if wavelength >= 380 and wavelength <= 440:
        attenuation = 0.3 + 0.7 * (wavelength - 380) / (440 - 380)
        R = ((-(wavelength - 440) / (440 - 380)) * attenuation) ** gamma
        G = 0.0
```

```
        B = (1.0 * attenuation) ** gamma
    elif wavelength >= 440 and wavelength <= 490:
        R = 0.0
        G = ((wavelength - 440) / (490 - 440)) ** gamma
        B = 1.0
    elif wavelength >= 490 and wavelength <= 510:
        R = 0.0
        G = 1.0
        B = (-(wavelength - 510) / (510 - 490)) ** gamma
    elif wavelength >= 510 and wavelength <= 580:
        R = ((wavelength - 510) / (580 - 510)) ** gamma
        G = 1.0
        B = 0.0
    elif wavelength >= 580 and wavelength <= 645:
        R = 1.0
        G = (-(wavelength - 645) / (645 - 580)) ** gamma
        B = 0.0
    elif wavelength >= 645 and wavelength <= 750:
        attenuation = 0.3 + 0.7 * (750 - wavelength) / (750 - 645)
        R = (1.0 * attenuation) ** gamma
        G = 0.0
        B = 0.0
    else:
        R = 0.0
        G = 0.0
        B = 0.0
    return (R,G,B,A)
```

In [ ]:

```
rgb = wavelength_to_rgb(lgap)

fig, ax = plt.subplots()
square = plt.Rectangle((0, 0), 1, 1, color= rgb, label = 'azulene')
ax.add_patch(square)
ax.text(0.5, 0.5, "{:.2f}nm".format(lgap), fontsize=14, ha="center", va="center", color="black")
ax.set_xlim(-0.5, 1.5)
ax.set_ylim(-0.5, 1.5)
ax.set_aspect('equal')

ax.set_xticks([])
ax.set_yticks([])
ax.set_frame_on(False)
plt.legend()
plt.show()
```

c.) The transitions calculated in a.) corresponds to the $S_0 \rightarrow S_1$ (ground state to first excited state) absorption. Find the energy and photon wavelength corresponding to the $S_0 \rightarrow S_2$ absorption.

Hint: The 4 molecular orbitals that normally need to be considered are the two below and two above the Fermi energy. They are named HOMO-1, HOMO, LUMO and LUMO + 1 with ascending energy.
Remark: The actual photon wavelength of the $S_0 \rightarrow S_2$ transition is slightly smaller than calculated (around 350 nm) an

In [ ]:

```
Egap_2 =
lgap_2 =

print('The transition in question is from orbital1 -> orbital2 with energy', Egap_2, 'eV')
print('The wavelength are,' lgap_2, 'nm')
```

In the following we will verify our results using symmetry considerations.

Assume that the azulene molecule lies in the yz-plane, with z pointing along the long axis of the molecule. We first note that the symmetry group of azulene is C_{2v} (see exercise 1) and recall that it consists of four elements id (the identity), C_2 (180° rotation around the z-axis), σ_v (reflection with respect to the xz-plane) and $\sigma_{v'}$ (reflection with respect to the yz plane).

d) To which representation do the molecular orbitals belong, which you obtained using the Hückel model.

e) We know from experiment that the first excited state S_1 has B_2 symmetry, while the second excited stated S_2 has A_1 symmetry. Do you arrive at the same result using the Hückel model?

Hint: Generally the representation of n electrons is given as $\otimes_i \Gamma_i$, where Γ_i are the representations of electron i. The characters of a tensor representation are the products of the characters of the individual representations.

In [ ]: