Simple Spectrum Simulation

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General Idea:

This small python program has a purpose to simulate simple spectrum. By giving a list of vertical excitation energies E_{0i}^{v} and oscillation strengths f_{0i}, a spectrum can be obtained by solving this equation:

$$\sigma(E) = 0.619n \sum_i \frac{f_{i0}}{\Gamma_i} e^{-\left(E - E_i^v + \delta_i\right)^2 / \Gamma_i^2} \quad (1)$$

Where n is the refractive index,Γ_i is the width of band i, δ_i is the energy shift between the vertical excitation and the band maximum.
E is the domain of values, where Emin is a minimum value of E, Emax is a maximum value of E and dE is a size of the interval, as shown in fig.1.

Each parameter has a default value in the program as shown, used in some cases:

Parameters	Unit	Default value
gamma	eV	0.4
delta	eV	0.0
n	-	1.0
Emin	eV	2.0
Emax	eV	10.0
dE	eV	0.1

After execution of the program, a spectrum is obtained by plotting energies (E) given in (eV) x $\sigma(E)$ with units of absorption cross section $\text{Å}^2.\text{mol}^{-1}$.

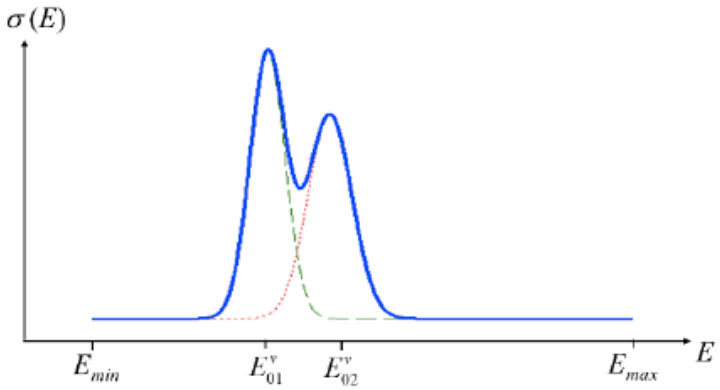

Fig.1

Theory:

Experimentally, the oscillator strength of an absorption band ε_i is given as:

$$f_{0i}= \frac{10^3 ln(10) mc}{\pi N_A e^2 n} \int \varepsilon_i(\nu) d(\nu)$$

Where m_e is the mass of the electron, *c* is the speed of the light, ε_0 is the vacuum permittivity, N_A is the Avogadro's number, and *e* is the electron charge (CGS units) and ε_i is the molar absorbance.
Integrating over the absorption frequency ν and supposing that the band has a gaussian shape with maximum ε_i^{max} at ν_i^{max} and width γ_i, the integral gives:

$$\int \varepsilon_i(\nu) d(\nu) = \int \varepsilon_i^{max}\, e^{-\left(\upsilon - \nu_i^{max}\right)^2/\gamma_i^2} = \sqrt{\pi}\, \varepsilon_i^{max} \gamma_i$$

Thus, the oscillator strength is

$$f_{0i}= \frac{10^3 ln(10) mc}{\pi N_A e^2 n}\, \varepsilon_i^{max} \gamma_i$$

Following these definitions, the total simulated spectrum can be written as the sum of all bands

$$\varepsilon(\nu) = \sum_i \varepsilon_i(\nu)$$

$$= \sum_i \varepsilon_i^{max}\, e^{-\left(\upsilon - \nu_i^{max}\right)^2/\gamma_i^2}$$

$$= \frac{\sqrt{\pi} N_A e^2 n}{10^3 ln(10) mc} \sum_i \frac{f_{0i}}{\gamma_i}\, e^{-\left(\upsilon - \nu_i^{max}\right)^2/\gamma_i^2}$$

The absorption cross section is given by

$$\sigma(\upsilon) = \ln(10) \frac{10^3}{N_A} \varepsilon(\nu)$$

$$= \frac{\sqrt{\pi} e^2 n}{mc} \sum_i \frac{f_{0i}}{\gamma_i}\, e^{-\left(\upsilon - \nu_i^{max}\right)^2/\gamma_i^2}$$

It is convenient to express the absorption cross section in terms of the absorption energy

$$\sigma(E)=\frac{2\pi^{2/3}\hbar e^2 n}{mc}\ \sum_i \frac{f_{0i}}{\Gamma_i} e^{-\left(E-E_i^{max}\right)^2/\Gamma_i^2} \quad (2)$$

where Γ_i is the energy width of the band, E_i^{max} its energy maximum and $\hbar$ is the reduce Planck constant

Usually, the energy of the band maximum E_i^{max} is red-shifted in relation to the vertical excitation E_i^v. Thus, an energy-shift parameter δ_i is added to account for its effect expressed as:

$$E_i^{max} = E_i^v - \delta_i$$

Replacing this equation in Eq (2) gives (in CGS unit):

$$\sigma(E)=\frac{2\pi^{2/3}\hbar e^2 n}{mc}\ \sum_i \frac{f_{0i}}{\Gamma_i} e^{-\left(E-E_i^{max}+\delta_i\right)^2/\Gamma_i^2}$$

For energies in eV and absorption cross section in $Å^2.mol^{-1}$, it gives the main equation (1)

How to run it?

Input:

To run the program, the following files are needed:

1. spectra_simulation.py : file containing the code
2. inp.dat : file containing the parameters and their values
3. energies_forces.dat : file containing the excitation energies and oscillation strengths (to be modified by the user)
4. gamma.dat : file containing values of gamma, which will be used in some cases (the values should be modified by the user)
5. delta.dat : file containing values of delta, which will be used in some cases (the values should be modified by the user)

All the files are prepared and given, only the values should be modified

1. The file called "inp.dat" contains the parameters (gamma, delta, n, Emin, Emax, dE). These parameters can be modified according to the case as presented below.

Each parameter has a default value as shown:

Parameters	Allowed values	Unit	Default value
Gamma	>0 – use this value as Γ_i for all bands 0 – read Γ_i from a file named gamma.dat	eV	0.4
delta	≥0 – use this value as δ_i for all bands 0 – read δ_i from a file named delta.dat	eV	0.0
n	>0 – refractive index n	-	1.0
Emin	>0 – minimum value of E	eV	2.0
Emax	>0 – maximum value of E	eV	10.0
dE	>0 – interval size of E	eV	0.1

Where the parameters are explained above.

Two conditions are applied for all parameter:

a. If the parameter exists in the inp.dat file, its value is used for all the excitation energies.
b. If the parameter does not exist (deleted) in the file, the default value is used.

For gamma:

a. If the parameter exists and the given value > 0, this value is used for all the bands
b. If the parameter exists and the given value = 0, gamma will be read from a "gamma.dat" file where it should contain a list of values corresponding to each excitation energy.

For delta:

a. If the parameter exists and the given value > or = 0, its value is used for all the bands
b. If the parameter exists and the given value = -1, delta be read from a "delta.dat" file where it should contain a list of values corresponding to each excitation energy.

2. The file called "energies_forces.dat" contains two columns, E_i^{ν} (excitation energies) and f_i (oscillation strengths). The values should be modified by the user.

3. To be able to run the code, numpy library is needed.

4. To plot σ(E) x E:
   a. Using matplotlib, install the library, uncomment the plotting part (the last four lines in the code) and the first line in the code
   b. Or simply using a graphical program as gnuplot or Excel, leave the commenting part.

5. Run the program by: python spectra_simulation.py

Output:

1. After execution , a file called "Output.dat" is created containing four columns:
   (E(eV) λ(nm) σ($Å^2$.mol^{-1}) ε($M^{-1}cm^{-1}$))

Where:
λ is the wavenumber corresponding to (1240/E)
ε is the molar absorbance or extinction coefficient (ε = σ/3.82353x10^{-5})

2. After every execution of the program, the Output.dat file in overwritten. It is recommended to rename the output file for each execution