Contents

1 Introduction

NLOPredict is a program for assissting in the prediction and analysis of nonlinear optical phenomena. The capabilities of the program have been well described elsewhere. [1] It is the purpose of this document to provide additional information about the operation of NLOPredict to both End Users and future developers. Proficiency with UCSF Chimera is assumed. This document was written by Levi Haupert ¡lhaupert@purdue.edu¿ and was last updated 25 May 2009.

2 Configuration Files

NLOPredict stores its state in a Python dictionary data structure. This data structure can be pickled (stored as a persistent Python object) or stored in a plain text format. The pickled storage method was used extensively in older versions of NLOPredict and has been preserved in newer versions for backward compatibility. The plain text option is preferred since they can be used by other programs to prepare or modify configuration files for NLOPredict.

Each line of the configuration text file contains a key/value pair separated by a comma. All names are enclosed in single quotes. Arrays are enclosed in bracketts. Simple numeric values and python boolean values are undecorated.

When NLOPredict imports a configuration file, the program's state dictionary is updated to any key-value pairs found in the configuration file. When writing a configuration file, it is not neccessary to include all possible key-value pairs—only desired key-value pairs are necessary (using all of the key-value pairs for every update can have annoying consequences).

3 Menu

3.1 File

3.1.1 Import

This submenu allows the import of configuration data into the current session of NLOPredict. Either plain text session data files or pickled .cfg files may be imported.

3.1.2 Export

The Export submenu allows NLOPredict to produce various types of persistent data. The Session Data commend produces a plain text file containing NLOPredict's current state. The Contour Matricies command produces a text file containing the values used to construct the current contour plot. The Plot Image command produces a raster graphics file representation of the plot currently displayed in the plot area of NLOPredict. The Tensors command produces a text file containing the current values of the molecular tensor ($\beta^{(2)}$) and select values of the Jones tensor (χ_j) and the Cartesian tensor (χ_c) as well as the combination of

Euler angles that produced them. The .cfg command produces a file containing NLOPredict's pickled state information. This command has been added for legacy purposes only.

Programmer Note: It would be nice to have an automated method for re-importing the exported tensor values from Export Tensors.

3.2 Plot

3.2.1 Single Molecule Mode

When checked, the Single Molecule Mode value directs NLOPredict to apply its tensor information exactly once to the loaded molecule. It should be noted that this behavior is only correct if both the loaded tensor and loaded molecule share a common coordinate system. When not in single molecule mode, NLOPredict applies tensor information to every amide chromophore it detects in the molecule, identified based on sequence assignment from the pdb file. In this mode, NLOPredict determines the orientation of every chromophore and performs a coherent addition to calculate the total tensors.

3.2.2 Total Signal

This command draws two bar plots in the plot window. The top bar graph shows the value of each element of the $\beta^{(2)}$tensor in the current molecular orientation. The bottom plot shows the values of some values of χ_c in the current orientation.

3.2.3 Secondary Structure

This command draws the plots described for Total Signal but shows separate contributions from α helicies and β sheets, based on designations within the pdb file. The Total Signal plot is the sum of all contributions within the Secondary Structure plot. This command functions identically to Total Signal when in Single Molecule Mode.

3.2.4 Contour Plot

The Contour Plot command directs NLOPredict to display contour plots of selected χ_j or χ_c tensor elements, or mathematical combinations thereof, as functions of the θ and ψ Euler angles.

3.3 View

3.3.1 Apply Current Orientation

This command zeroes the Euler angles at the current orientation of the molecule. It is especially important when working with the contour plots and defining local coordinates within a molecule. Changing any other parameters after applying the current orientation will reset the Euler angle zeroes to the original orientation. Changing the Euler angle

zeroes permanently requires exporting structures from UCSF Chimera and Tensors from NLOPredict as new files.

Programmer Note: Loss of applied orientation after adjusting parameters, especially tensor values, is a continued source of consternation for users. Should we find a way to better preserve the applied orientation?

3.3.2 Reset Orientation

This command resets the molecular orientation in UCSF Chimera by returning all of the Euler angles to zero. This command is executed automatically when any of NLOPredict's internal parameters are changed.

3.3.3 Alpha/mu visibility

This submenu provides several options for visualizing important tensors in Chimera. The hidden value (obviously) suppresses visualization of the tensors. Direction draws sagittary representations of $\vec{\mu}$ (yellow vector) and the eigenvalues of α (green double arrows are positive valued while red double arrows are negative valued). The magnitude setting is similar to the Direction setting except that the relative values of the tensor components are considered when drawing the arrows. The surface setting causes a hyperellipsoid representation of $\beta^{(2)}_{ZZZ}$ to be displayed. Red lobes show negative values and blue lobes show positive values.

3.3.4 Tensor Visual Scales

This command opens a dialog box which allows the visual representations of tensors in Chimera to be scaled by arbitrary constants.

3.3.5 Tensor Surface Resolution

The dialog box invoked by this command provides control over how many points are used to represent rotation through the spherical coordinates θ and ϕ when drawing the hyperellipsoid. Entering large values results in a smooth, but computationally expensive hyperellipsoid. Non-integer resolution values will produce strange and startling effects.

3.4 Params

3.4.1 Multiplication Order

While in Full Beta mode, NLOPredict directly uses the values stored in the 'full_beta' line of its configuration for $\beta^{(2)}$. Use this multiplication order if the system if the full molecular tensor with 27 defined elements serves as the input. When in mu*alpha (SHG) or alpha*mu (SFG) multiplication mode, the values stored in 'mu_CO' and 'alpha_CO' are multiplied to create $\beta^{(2)}$. This simplification is only valid near resonance. [2,3] Please note, however, that the lineshape function is not applied to this multiplication in NLOPredict. Multiplication by the lineshape function is still required to generate the complex-valued resonant tensor.

3.4.2 Chi Equation

The δ-function distribution is used for highly ordered systems while the weak orientation limit is used for systems with broad distributions in the θ Euler angle. The weak orientation limit assumes a uniform distribution in the ψ and ϕ Euler angles. A more complete treatment of the Weak Orientation Limit has been elucidated by Gualtieri *et al.* [4].

3.4.3 Tensors

The options in this submenu allow entry of arbritrary values for the $\vec{\mu}$, α, and $\beta^{(2)}$tensors. Only real values are allowed.

3.4.4 Principal Atoms

This menu allows entry of arbitrary coordinates for the principal atoms of the amid chromophore used when not in Single Molecule Mode.

3.4.5 Adjust Y-Limits

This command opens a dialog box for editing the minimum and maximum limits on the Total Signal and Secondary Structure plots (*e.g.* When using confidence limits on experimental observations).

3.4.6 Adjust Contour Plots

This command opens a dialog box allowing access to various contour plot parametaers. Most importatnly, the Upper and Lower Plot entry fields allow selection of which χ values will be displayed. For χ_{ZZZ} enter 'ZZZ' into the field. Allowed χ's are ZZZ, ZXX, XZX, XXZ, XYZ, YZX, ZXY, ppp, pps, psp, pss, spp, sps, and ssp. Python mathematical operators may also be used. For instance 'abs(ppp)**2' will plot the squared magnitude of χ_{ppp}.

3.4.7 Adjust Fresnel Factors

The Fresnel Factor editor allows editing of the three complex-valued Fresnel matrices, which are used to calculate χ_j. Complex values can be entered using standerd Python syntax (*e.g.* `1 + 1j`).

Programmer Note: Only the GUI aspect of the Fresnel Editor is currently implemented and it accepts real and imaginary terms in separate entry fields. The editor needs to edit the Fresnel matrices in the configuration in order to be effective. It would be convenient to have the entry fields accept complex values.

4 Examples

4.1 α-Helix

In this example we will use NLOPredict to separate two exciton states in a typical α-helix. [1] The first step will be getting the desired helix into Chimera for modeling. Enter `open pdbID:2d3e` into the Chimera comand line to import a structure for Tropomyosin from the PDB (connection to the internet is required). The structure is constructed from four helices, but we only need one. Remove all but one of the helices using the command `delete :*.b:*.c:*.d` in the Chimera command line. Rotate the helix into a convenient coordinate system by rotating the molecule in the Chimera window until the helix is orthogonal to the plane of the computer display (long helix axis aligned with the Chimera's Z-axis). Save this orientation by entering `write 0 file_name` into the command line. Close the current session and open file_name and make sure the helix is aligned to Chimera's Z-axis.

Activate the NLOPredict plugin using Chimera's Tool menu. NLOPredict is found under Indiana/Purdue. Once NLOPredict is open, it needs to be configured to analyze the helix. Under the Plot menu, make sure Single Molecule Mode is unchecked. Under the Params menu, make sure the multiplication order is set to mu*alpha (SHG). Make sure the alpha/mu visibility under the View menu is set to Surface. Now, import the provides alpha and mu values for the Amide I vibration. Use the import session data command under the File menu to open `forPDBAmide_I.cfg.txt`. The calculated $\beta^{(2)}$tensor can be exported using export tensors under the File menu in NLOPredict. Export the tensors.

Now it is time to visualize the $\beta^{(2)}$tensors for the two exciton states. All of the molecular tensor elements with z as their first index correspond with the A state. The remaining elements correspond with the B state. Put NLOPredict in single molecule mode using the option under the plot menu. Change the multiplication order under the Params menu to Full Beta. Adjust the $\beta^{(2)}$tensor using the Tensors option under the Params menu. To visualize the A state, copy all the molecular tensor vales with z as the first index from the previously exported molecular tensor into the $\beta^{(2)}$editor and make all other values zero. Applying this tensor will visualize the A state. The B state can then be visualized by setting all of the $\beta^{(2)}$elements with z as the first index to zero and copying the rest of the tensor elements from the previously exported tensor. The results should agree with those presented in J Comput Chem 28: 1996-2002, 2007.

4.2 Thin Film

In this example, we will use NLOPredict to calculate possible orientations of molecules in a thin film by comparing predictions with experimental measurements of the χ_j tensor. In this exercise we will be revisiting the analysis previously performed by Begue *et al.* on disperse yellow-7 (DY7) [5].

The first step in the process is importing the molecule and the configuration data into USCF Chimera and NLOPredict. First, open the structure for planar DY7 (`dy7.mol2`) in USCF Chimera and then open NLOPredict. Make sure NLOPredict is in Single Molecule

Mode and the multiplication order is set to Full Beta. Import the configuration file `dy7beta_config.txt`, which contains the quantum mechanically calculated $\beta^{(2)}$tensor as well as calculated Fresnel Factors for a thin film of DY7 on a glass slide.

We will use NLOPredicts contour plot feature to determine possible orientations of DY7 in the thin film using the experimentally measured ratios $|\frac{\chi_{ppp}}{\chi_{sps}}|$ and $|\frac{\chi_{pss}}{\chi_{sps}}|$. Open the Contour Plot parameter editor and set the upper plot to abs(ppp/sps) and the lower plot to abs(pss/sps). Set the upper plot limits to 2.534 and 2.450 and set the lower plot limits to 1.32 and 1.24 and check the Set Limits box for both plots.

Now that the contour plots are configured, we must place the DY7 molecule and tensors in a coordinate system consistent with the system presented by Begue *et al.* by rotating the molecule in Chimera. The simples way to accomplish this is to set the Euler angles in NLOPredict to $\theta = 90$, $\psi = 180$, and $\phi = 90$. Once the reorientation has been accomplished apply the current orientation. Compare the generated contour plots to those presented by Begue *et al.*—they should be the same.

In order to observe the orientations consistent with the predictions and the experimental results, we need to find places where the upper and lower contour plot traces overlap. Clicking the mouse with the cursor in one of the contour plots immediately shows that orientation in Chimera and places a white dot in both plots. Click and drag the mouse in the upper plot until one the white dot appears over an overlap region. USCF Chimera now displays one orientation of DY7 in the thin film that is consistent with theory and experiment.

5 χ_j Tensor Calculation

The χ_j tensor is calculated in NLOPredict using the folowing equation:

$$\mathbf{J} \cdot \mathbf{F} \cdot \mathbf{Q} \cdot \vec{\beta_c} = \vec{\chi_j}$$

The **J** matrix is a 27 x 8 element matrix which converts Cartesian coordiantes into Jones coordinates. The **F** matrix is a 27 x 27 element matrix which applies Fresnel factor effects. The Fresnel matrix is stored in config files as three 9 element vectors that are multiplied together internally to create the 27 x 27 element matrix. The **Q** is a 27 x 27 element matrix which applies symmetry to $\vec{\beta_c}$, the column vector containing the 27 elements from $\beta^{(2)}$. For a C_∞ system, the **Q** matrix will take appropriate combinations of $\beta^{(2)}$elements to recover the tensor of the ensemble. The **Q** matrix may also be used apply the rotational symmetry operations of crystals. If no transformations are needed, the **Q** matrix may be set to an identity matrix.

References

[1] Moad, A. J., Moad, C. W., Perry, J. M., Wampler, R. D., Goeken, G. S., Begue, N. J., Shen, T., Heiland, R., and Simpson, G. J. *Journal of Computational Chemistry* **28**(12), 1996–2002 September (2007).

[2] Moad, A. J. and Simpson, G. J. *The Journal of Physical Chemistry B* **108**(11), 3548–3562 March (2004).

[3] Moad, A. J. and Simpson, G. J. *The Journal of Physical Chemistry A* **109**(7), 1316–1323 February (2005).

[4] Gualtieri, E. J., Haupert, L. M., and Simpson, G. J. *Chemical Physics Letters* **465**(4-6), 167–174 November (2008).

[5] Begue, N. J., Everly, R. M., Hall, V. J., Haupert, L., and Simpson, G. J. *The Journal of Physical Chemistry C* **XX**(0), ASAP (2009).