

A general simulated annealing approach to extracting nuclear dynamics from ultrafast x-ray scattering data

Thomas Northey

November 24, 2022

Abstract

abst

1 Introduction

1m structure method [7]

Some references [8, 7, 5, 6, 1, 3, 2]

1.1 Simulated annealing

Simulated annealing is a type of Metropolis algorithm, in that it always takes a downhill step while sometimes taking an uphill step [4].

It is a powerful tool in combinatorial minimisation, where the space over the which the function is defined is a discrete but very large configuration space. The size of the configurational space is factorially large, so that it cannot be explored exhaustively. Furthermore, since the set is discrete, we are deprived of any notion of continuing downhill in a favourable direction. The concept of direction may not have any meaning in the configuration space. A classic example of this is the travelling salesman problem.(taken from [4])

The x-ray scattering signal is predominantly governed by the set of interatomic distances in any given molecule, as we know from the Debye model (independent atom model). The molecule itself moves along a continuous potential energy surface.

2 Method

2.1 Simulated Annealing for molecules

2.1.1 Theory

The molecular coordinates move iteratively according to,

$$\mathbf{R}_{i+1} = \mathbf{R}_i + T_i \sum_{k=0}^{\text{modes}} a_k \hat{d}_k$$

for temperature T_i at iteration i , step-size Δs , displacement unit vectors \hat{d}_k , and wavenumbers ω_k for each normal mode. The factors a_k are obtained from a uniform random distribution with range $\Delta s_k[-1, 1]$ to allow the molecule unconstrained movement along all its degrees of freedom. The motions are ω -damped by the factor,

$$w_k = \frac{\omega_0}{\omega_k}$$

or

$$w_k = \exp\left(\frac{\omega_0}{\omega_k}\right)$$

for mode wavenumbers $\{\omega_0, \omega_1, \dots, \omega_n\}$, to avoid oversampling large motions of high frequency modes.

The temperature decreases linearly at iteration i as,

$$T_i = T_0(1 - i/N)$$

for starting temperature $T_0 \in (0, 1]$, and total iterations N .

After each iteration, if the error function χ^2 decreases the iteration is accepted

$$i \rightarrow i + 1$$

If not, the iteration can still be accepted with probability,

$$P = T_i$$

which allows the molecule to sometimes travel uphill on the χ^2 surface, thus escape local minima.

$$\chi^2 = (x - y)^2$$

If using multiple target and predicted data sources,

$$\chi^2 = \sum_k A_k (x_k - y_k)^2$$

2.1.2 Algorithm

Current working strategy.

- Low step-size (e.g. $\Delta s = 0.03$), large number of steps, multiple restarts (e.g. 10), last restart is a stochastic descent ($T_0 = 0$; greedy algorithm) starting from χ_{best}^2 .

This usually finds very good starting time-steps, because the low step-size combined with large N is very good at finding structures nearby to the starting geometry. That is, when the ring is starting to open.

- Subsequent runs with varying step-sizes (usually larger to find further away structures, $\Delta s = 0.05, 0.1, 0.2$) that load data from the previous run, and accept time-steps with $\chi^2 < \beta$, for e.g. $\beta = 10^{-5}$ or 10^{-6} (how low you can set the target depends on noise of data, in practice set it slightly lower than the best χ^2 values of the first run). It will re-run time-steps starting from the previous ‘good’ structures at earlier time.

Assumption: the next best fit is ‘nearby’ the previous step.

- Start at $\mathbf{R}(t_0)$, e.g. the optimised ground state geometry
 - Start at $\mathbf{R}(t_j)$ and search for $\mathbf{R}(t_{j+1})$
 - Perform N temperature cycles ($T = T_0$), to allow a large search space around $\mathbf{R}(t_j)$
 - * Start at the end point of each cycle \mathbf{R}_i to find the next cycle end point \mathbf{R}_{i+1}
 - * Save \mathbf{R}_{best} , the geometry with the lowest value of χ^2

3 Results

3.1 CHD ring-opening example

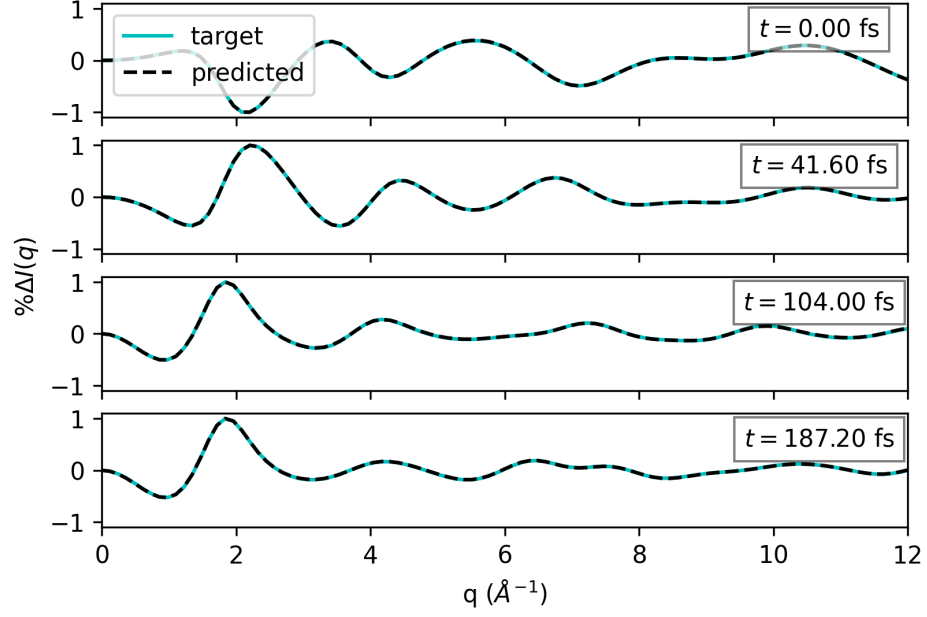
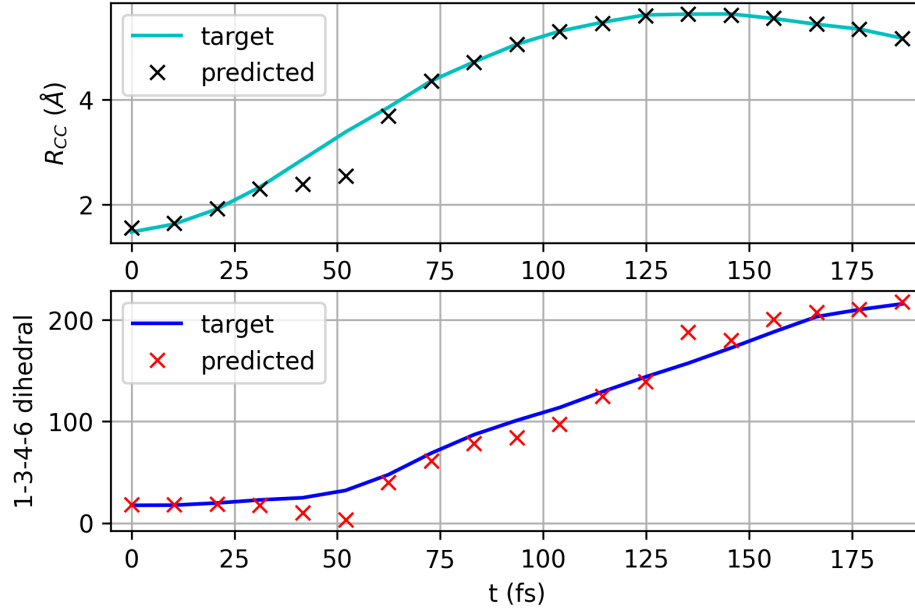
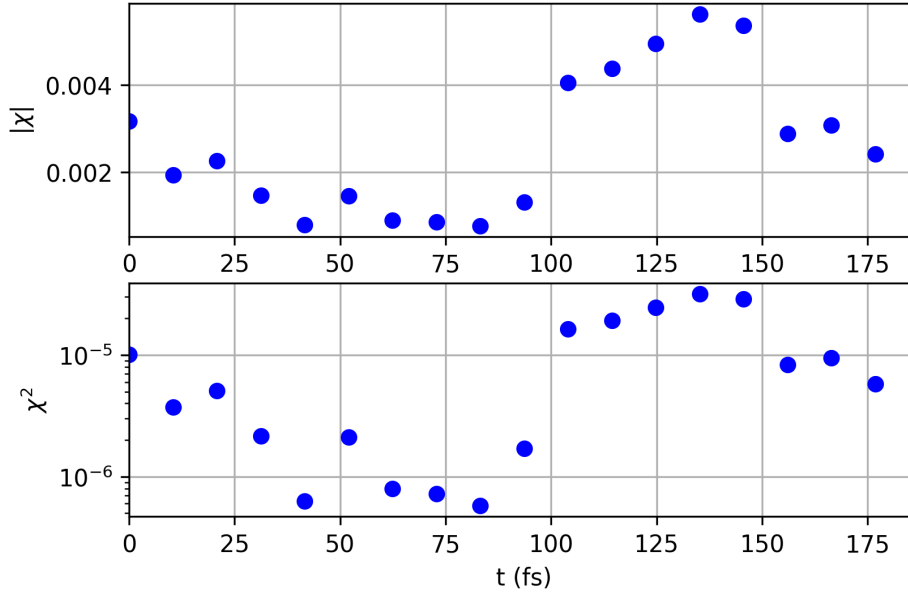


Figure 1: CHD x-ray scattering lineouts.

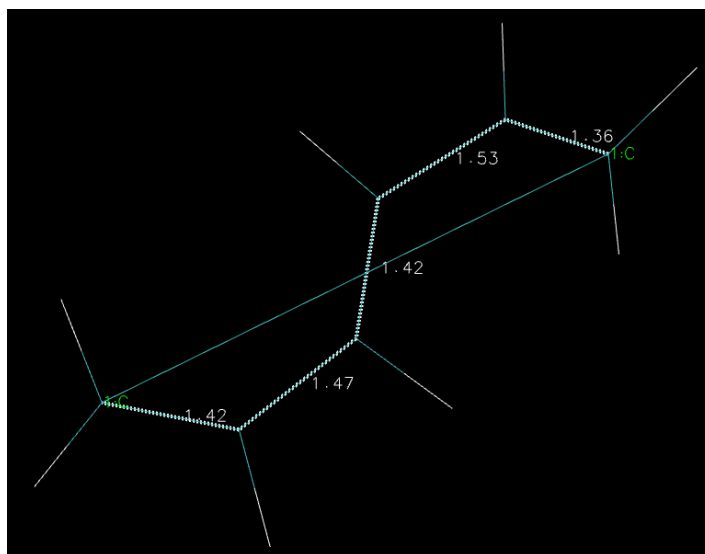


(a) Bond-opening C-C distance, and 1-3-4-6 dihedral angle.

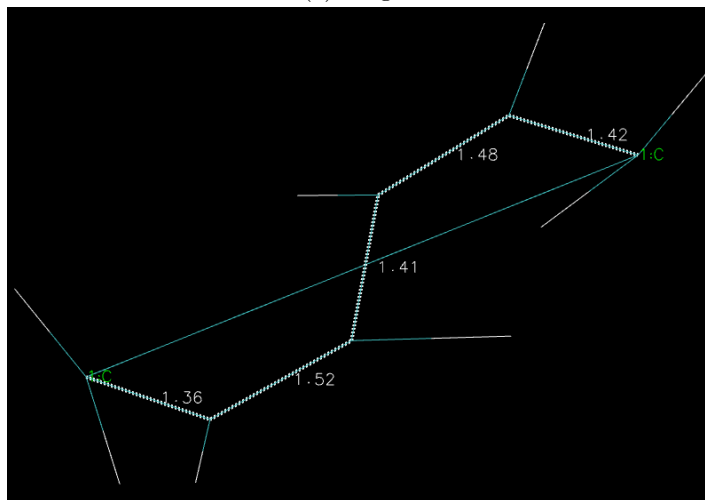


(b) $|\chi|$ and χ^2 values for each time-point.

Figure 2: CHD ring-opening C-C distance, R_{CC} . The target is from a surface hopping trajectory. Predictions are using $q_{\max} = 12.0 \text{ \AA}^{-1}$.



(a) Target.



(b) Predicted.

Figure 3: CHD target and predicted, showing all C-C bond-lengths.

3.2 Reproduce NMM trajectory from experiment data

References

- [1] Andrés Moreno Carrascosa, Haiwang Yong, Deborah L Crittenden, Peter M Weber, and Adam Kirrander. Ab initio calculation of total x-ray scattering from molecules. *Journal of Chemical Theory and Computation*, 15(5):2836–2846, 2019.
- [2] Thomas Northey, Andrés Moreno Carrascosa, Steffen Schäfer, and Adam Kirrander. Elastic x-ray scattering from state-selected molecules. *The Journal of Chemical Physics*, 145(15):154304, 2016.
- [3] Thomas Northey, Nikola Zotev, and Adam Kirrander. Ab initio calculation of molecular diffraction. *Journal of Chemical Theory and Computation*, 10(11):4911–4920, 2014.

- [4] William H Press, Saul A Teukolsky, William T Vetterling, and Brian P Flannery. *Numerical recipes 3rd edition: The art of scientific computing*. Cambridge university press, 2007.
- [5] Brian Stankus, Haiwang Yong, Nikola Zotev, Jennifer M Ruddock, Darren Bellshaw, Thomas J Lane, Mengning Liang, Sébastien Boutet, Sergio Carbajo, Joseph S Robinson, et al. Ultrafast x-ray scattering reveals vibrational coherence following rydberg excitation. *Nature chemistry*, 11(8):716–721, 2019.
- [6] Thomas JA Wolf, David M Sanchez, J Yang, RM Parrish, JPF Nunes, M Centurion, R Coffee, JP Cryan, Markus Gühr, Kareem Hegazy, et al. The photochemical ring-opening of 1, 3-cyclohexadiene imaged by ultrafast electron diffraction. *Nature chemistry*, 11(6):504–509, 2019.
- [7] Haiwang Yong, Andrés Moreno Carrascosa, Lingyu Ma, Brian Stankus, Michael P Minitti, Adam Kirrander, and Peter M Weber. Determination of excited state molecular structures from time-resolved gas-phase x-ray scattering. *Faraday Discussions*, 228:104–122, 2021.
- [8] Haiwang Yong, Jennifer M Ruddock, Brian Stankus, Lingyu Ma, Wenpeng Du, Nathan Goff, Yu Chang, Nikola Zotev, Darren Bellshaw, Sébastien Boutet, et al. Scattering off molecules far from equilibrium. *The Journal of Chemical Physics*, 151(8):084301, 2019.