VISTA Seminar

Seminar 30

February 2, 2021

10:00 am – 11:30 am EST / 3:00 – 4:30 pm GMT / 4:00 pm – 5:30 pm Paris

TOC:

Sampling general distributions with quasi-regular grids: Application to the calculation of vibrational spectra

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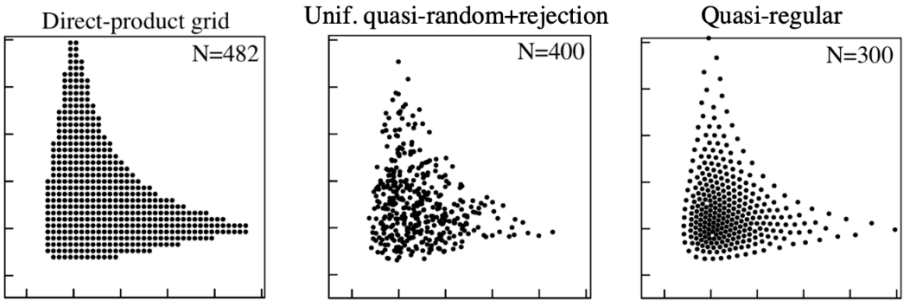

Sampling of a general multi-dimensional distribution function $P(x)$ $(x \in R^d)$ presents a longstanding problem in diverse fields of numerical analysis. One of the closely related problems corresponds to numerical integration. While very efficient in low dimension, quadrature-based methods become unfeasible for computing high-dimensional integrals due to their exponential scaling. High-dimensional integrals are usually computed by Monte Carlo (MC) methods. Yet, due to the presence of "gaps and islands" in an uncorrelated pseudo-random sequence x^i $(i = 1, \dots, N)$, the MC method suffers from relatively slow $\sim 1/\sqrt{N}$ numerical convergence. One potential solution to the slow convergence of MC methods is the use of quasi-random (low discrepancy) sequences. These sequences are designed to be locally uniform in configuration space, thus circumventing the clustering problem and leading to much faster ($\sim$ 1/N) convergence. I will mention application of the quasi-MC method for computing Gaussian integrals in the framework of the Self-Consistent Phonons method.[1] Unfortunately, quasi-random sequences are practical only for distributions that are products of low-dimensional distribution functions, $(x_1, x_2, \dots) = P_1(x_1) \times P_2(x_2) \dots$.

Recently,[2,3] we introduced a new method for sampling a general multi-dimensional distribution function $P(x)$ using a quasi-regular grid (QRG) of points which are locally regular (i.e., form a nearly closed-packed structure) while globally are distributed according to P(x). Such a grid is constructed by minimizing a pairwise functional, $\sum u(x_i, x_j) \rightarrow min$, with a short-range pair pseudo-potential $u(x_i, x_j)$, defined locally according to the underlying distribution $P(x)$.

While QRGs can be useful in many diverse numerical contexts, I will discuss their application to the problem of calculating the eigenenergies and eigenfunctions of a molecular vibrational Hamiltonian in the framework of the collocation method.[4] The particular example involves a 6D vibrational Hamiltonian of the four-atom molecule of formaldehyde.

References

1. S.E. Brown, I. Georgscu and V.A. Mandelshtam, Self-consistent phonons revisited. II. A general and efficient method for computing free energies and vibrational spectra of molecules and clusters J. Chem. Phys. 138, 044317 (2013)

2. S.W. Flynn and V.A. Mandelshtam, Sampling general distributions with quasi-regular grids: Application to the vibrational spectra calculations, J. Chem. Phys., 151, 241105 (2019)

3. S.W. Flynn and V.A. Mandelshtam, Molecular spectra calculations using an optimized quasi-regular Gaussian basis and the collocation method, J. Chem. Theory and Comput. 17 (2021)

4. S. Manzhos and T. Carrington, Using an internal coordinate Gaussian basis and a space-fixed Cartesian coordinate kinetic energy operator to compute a vibrational spectrum with rectangular collocation, J. Chem. Phys. 145, 224110 (2016)

Simulating Photoexcitation with a Laser Pulse beyond the Perturbative Limit

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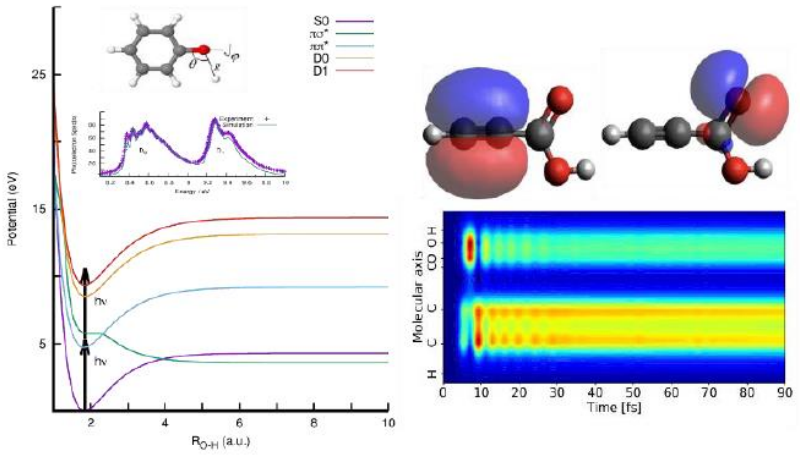

The advent of ultrashort laser pulses in the femtosecond to attosecond regime allows the study of ultrafast molecular dynamics with unprecedented time resolution [1,2]. These powerful modern light sources can result in the ionization of matter and thereby trigger electronic and nuclear dynamics [3,4]. In my talk, I will give an overview of the ongoing research efforts in the Worth group at UCL addressing the following fundamental questions: (i) Can we control photochemical processes by creating/manipulating a quantum superposition state with a laser pulse? (ii) Can we understand the coupled electron-nuclear motion and the associated ultrafast decoherence? (iii) Can we design laser pulses in a simple way to make use of the quantum interference pathways? (iv) Can we simulate an experimental photoelectron spectrum by developing simple theoretical models?

These elementary aspects of laser-matter interactions are governed by quantum mechanics and therefore we solve the time-dependent Schrödinger equation using state-of-the-art quantum dynamics method, MCTDH [5], in combination with vibronic coupling Hamiltonian [6]. This further allows us to deal with the non-adiabatic coupling between the electrons and the nuclei [6]. The ionized electron is modeled explicitly by incorporating the continuum of free-electron states [7]. The QUANTICS suite of programs are used to run the dynamical simulations [8].

References

[1] M. Nisoli, P. Decleva, F. Calegari, A. Palacios and F. Martín, *Chem. Rev.* **117**, 10760 (2017).
[2] H. H. Fielding and G. A. Worth, *Chem. Soc. Rev.* **47**, 309 (2018).
[3] V. Despré, N. V. Golubev and A. I. Kuleff, *Phys. Rev. Lett.* **121**, 203002 (2018).
[4] A. Henley, J. W. Riley, B. Wang and H. H. Fielding, *Faraday Discuss.* **221**, 202 (2020).
[5] M. H. Beck, A. Jäckle, G. A. Worth and H.-D. Meyer, *Phys. Rep.* **324**, 1 (2000).
[6] G. A. Worth and L. S. Cederbaum, *Annu. Rev. Phys. Chem.* **55**, 127 (2004).
[7] M. Seel and W. Domcke, *J. Chem. Phys.* **95**, 7806 (1991).
[8] QUANTICS, http://www2.chem.ucl.ac.uk/quantics/doc/index.html

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Topic: VISTA, Seminar 30
Time: Feb 2, 2022 10:00 AM Eastern Time (US and Canada)

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