



Original software publication

Libra: A modular software library for quantum nonadiabatic dynamics

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ABSTRACT

Libra is a versatile open-source software that implements a multitude of community-developed methods and computational workflows for nonadiabatic and quantum dynamics calculations, such as trajectory surface hopping or Ehrenfest dynamics, discrete variable representation or trajectory-guided wavepacket propagation schemes, and more. Through interfaces with electronic structure codes for excited state calculations, Libra enables modeling quantum nonadiabatic processes in extended atomistic systems. Libra can be used as a framework for systematic assessment of various nonadiabatic dynamics methods, a methodology prototyping library, and a fully-fledged suite for applied materials research. In this paper, we briefly overview the Libra package and its impact.

Code metadata

Current code version	V5.3.0
Permanent link to code/repository used for this code version	https://github.com/SoftwareImpacts/SIMPAC-2022-222
Permanent link to reproducible capsule	https://codeocean.com/capsule/4727375/tree/v1
Legal code license	GNU GPL v3.
Code versioning system used	Git
Software code languages, tools and services used	C++, Python, OpenMP
Compilation requirements, operating environments and dependencies	Numpy, matplotlib, scipy, libint2, Eigen3, Boost, Python
If available, link to developer documentation/manual	https://quantum-dynamics-hub.github.io/libra/documentation.html
Support email for questions	alexvakimov@gmail.com

1. Introduction

Understanding the evolution of electrons in manifolds of excited states coupled to the motion of nuclei is a fundamental challenge in photochemistry and in the rational design of solar energy and optoelectronic materials [1–11]. Advances in these fields rely on the ability to reveal mechanisms of excitation energy transfer (EET) and charge transfer (CT), electron–phonon relaxation, electron–electron scattering,

charge carrier trapping, exciton dissociation, intersystem crossing, decoherence, photoinduced isomerization and so on. Computational studies of such processes require software that implements nonadiabatic and quantum dynamics (NA/QD) methodologies that can account for nonadiabatic (NA) transitions, quantum-mechanical branching, quantum decoherence, tunneling, and other quantum effects. In addition, the studies of the NA/QD methodologies themselves constitute an active field of research. Numerous innovative algorithms for quantum,

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semiclassical, and quantum–classical dynamics accounting for NA effects are being proposed and reported regularly, for example [12–29]. The ever-expanding “zoo” of methods can be too difficult to manage, assess, and re-use. The question “which method to choose?” becomes a practical challenge not only to a software “user” (e.g., domain researcher), but often to an expert theorist. This is a consequence of the absence of a comprehensive exploration of the methods’ applicability limits. To test new NA/QD methods, various model Hamiltonians are developed. However, such benchmarks often are not coordinated across the methods. In contrast, the community of electronic structure methods uses well-known standardized benchmark sets [30–32], which are applied to all new methods reported.

In the last decade or two, a wide variety of NA/QD codes have been developed, including Newton-X [33,34], SHARC [35,36], NEXMD [37,38], FIREBALL [39–42], pyUNixMD [43,44], JADE [45], Hefei-NAMD [46], or PYXAID [47,48], to name a few. Despite that codes’ great potential and general availability, they are rather monolithic, highly specialized on particular methodology of strength, and follow rather strictly defined computational workflows, often driven by the standard text-based inputs. Although some of these codes may be well used for methodology development/prototyping purposes, freestyle Python-driven and module-focused execution modes are not generally used, such as those featured in the prototyping-oriented electronic structure codes such as PySCF [49], Psi4NumPy [50], PyQuante [51], or HORTON [52]. Furthermore, the above mentioned NA/QD codes are not meant to be the platforms for methodology assessment and development. Instead, they rely on selected “best practices” or adapt some key methodologies of strength. In contrast, the Libra software reported here is developed as a re-usable library of methodology building blocks, suitable for applied computations in realistic materials, methodology assessment using a wide range of (including the user-defined) model Hamiltonians, and for methodology prototyping.

2. Overview of methodology

The main goal of the NA/QD is to describe the evolution of a system’s electron-nuclear wavefunction, $\Psi(t, \mathbf{r}, \mathbf{R})$, given as $\Psi(t, \mathbf{r}, \mathbf{R}) = \sum_{i=0}^{N-1} c_i(t) \Phi_i(\mathbf{r}; \mathbf{R}(t))$, where $\{\Phi_i(\mathbf{r}; \mathbf{R}(t))\}$ constitutes the basis of electronic states of the system. The wavefunction of the system evolves according to time-dependent Schrodinger equation (TD-SE): $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$, which reduces to $i\hbar \frac{\partial c_i}{\partial t} = \sum_{j=0}^{N-1} H_{ij}^{vib} c_j$, if the basis of stationary states is given. Here, $H_{ij}^{vib} = H_{ij} - i\hbar d_{ij}$, are the matrix elements of the “vibronic” Hamiltonian H_{ij}^{vib} , H_{ij} are the electronic Hamiltonian matrix elements, and $d_{ij} = \langle \Phi_i | \frac{\partial}{\partial t} | \Phi_j \rangle$, is the nonadiabatic coupling (NAC) between states i and j . The latter can be computed numerically, for instance using the Hammes–Schiffer–Tully (HST) finite difference formula, [53] $\langle \psi_a | \frac{\partial}{\partial t} | \psi_j \rangle \approx \frac{\langle \psi_a(t) | \psi_b(t+dt) \rangle - \langle \psi_a(t-dt) | \psi_b(t) \rangle}{2dt}$ or using more advanced interpolation techniques. [54]

Once the TD-SE is solved, the amplitudes, $c_i(t)$, can be used to compute the proposed state hopping probabilities. For instance, in the Tully’s fewest switches surface hopping (FSSH) [55] method they are computed as $P_{i \rightarrow j} = \frac{2d_{ij}c_i c_j^*}{|c_i|^2} dt$. In the original Tully’s FSSH formulation, the proposed hops may be rejected, if the kinetic energy is not sufficient to reach the new state while conserving the total energy of the quantum–classical system. If the hops are successful, the velocity is rescaled along a selected direction, for instance along the derivative nonadiabatic coupling (dNAC) vector, $\langle \Phi_i | \nabla_{\mathbf{R}} | \Phi_j \rangle$. Alternatively, one may accept the surface hops without obeying the energy conservation principle, to ensure the proper energy partitioning between electronic and nuclear subsystems. Furthermore, the nuclear velocities may be left unchanged upon electronic transitions. This neglect of back-reaction approximation has been in a wide use in modeling NA/QD in extended atomistic systems, where the calculations are very time-consuming [46,56–68].

3. Software description

Libra is a powerful general-purpose package suitable for both model testing or methodology validation and for practical studies of atomistic systems. Libra was first released in 2015, and has significantly evolved since then. Libra adopts a hybrid C++/Python design, in which most data types and algorithms are available in C++ but are also exposed to Python via Boost. Python [69–71]. The Python-exposed classes and functions enable a fast prototyping and testing of new methods. The code provides a wide variety of basic building blocks that can be used to construct methodologies for NA quantum–classical and quantum dynamics simulations, including various trajectory surface hopping (TSH) schemes, such as (FSSH) [55], global flux surface hopping (GFSH) [72], or Markov state surface hopping (MSSH) [73], various decoherence methods (DISH [74], mSDM [75,76], EDC [75], A-FSSH [20,77], IDA [78], MF-SD [79,80]), dephasing time calculation schemes, [81,82] approaches for accurate evaluation of NACs, geometric integrators of the TD-SE [48], Ehrenfest dynamics in adiabatic and diabatic representations [83]. Various surface hop acceptance and rejection schemes are implemented. Several options for handling frustrated hops and nuclear velocity rescaling are available. The numerically-exact quantum dynamics split-operator Fourier transform (SOFT) integrator [84] based on the discrete variable representation (DVR) [85] of the wavefunction are available to model closed systems, and the hierarchical equations of motion (HEOM) [86] are implemented to model open systems. In addition, a number of non-equilibrium Fermi-golden rule schemes of Sun and Geva [87–93] are implemented in Libra. The code is equipped with functionality for handling phase correction [83] and state reordering (“state tracking”) [94]. Gaussian wavepacket integrals and data types are implemented to facilitate future developments of the wavepacket-based methods and models, including overlap-based decoherence schemes and local diabatization schemes. Recently, the wavepacket functionality of the code stimulated the implementation of the quantum trajectories guided Gaussians (QTAG) method [95].

In addition, Libra implements a range of computational chemistry methods: molecular dynamics (MD) in various ensembles [96–101], rigid-body MD [101–106], several classical force fields [107–112], Ewald summation for periodic systems [66], charge equilibration scheme for position-dependent partial charges [67], several semiempirical [113–120] methods, and molecular integrals — all the basic components needed to develop and test new algorithms for atomistic simulations of nanoscale, molecular, and condensed-matter systems. Libra implements an original library of intuitive mathematical classes and functions for linear algebra, matrix decompositions, Fourier transforms. Special functions, random numbers generation, and point group symmetry operations are implemented for use in various contexts. Libra implements its own machine learning functionality and classes. At the same time, Libra takes advantage of existing packages such as Eigen 3 [121] (for the time-critical operations such as eigenvalue problem solving) or libint2 (for molecular integrals evaluation). The Python layer of Libra includes an extensive set of predefined workflows (e.g. for applied studies of materials or model problems) and convenience functions for interfacing such workflows with existing electronic structure and classical molecular dynamics packages. To date, interfaces and convenience functions for Quantum Espresso (QE) [122], CP2K [123], DFTB+ [124], GAMESS [125], ErgoSCF [126], ORCA [127,128], OpenMolcas [129,130], LAMMPS [131], VESTA [132], and other packages have been devised within Libra package. The code is designed to facilitate handling ensembles of independent and coupled trajectories. It provides a multithreading support and implements the trivial parallelization over trajectories.

4. Impact

The versatility and modularity of the Libra code have enabled multiple new developments by our group, such as a simple tight-binding

fragment-based NA-MD approach for large-scale systems [133], entangled trajectories Hamiltonian dynamics methodology for capturing nuclear quantum effects [134], the quasi-stochastic Hamiltonian approach (QSH)[135] and the time-domain machine-learning method [136] for extending the timescales accessible in atomistic NA-MD simulations. Libra has enabled multiple comparative studies and assessments of the NA-MD methods [76,137,138], as well as chemistry/material-specific studies [139–142]. With the help of Libra, new schemes for atomistic NA-MD simulation in nanoscale systems have been devised. We have implemented a NAC-free Landau–Zener–Belyaev–Lebedev [143] approach within the NBRA framework [144]. Coupled with the DFTB description of electronic structure of atomistic system, it has enabled inexpensive modeling of “hot” carrier relaxation dynamics in nanometer-size nanoclusters. Recently, the size limit of systems in which NA/QD can be modeled has been extended even further, to systems with 1500+ atoms, in our implementation of the Libra/CP2K workflow that uses the extended tight-binding (xTB) description of electronic states [145]. Such an approach is applicable to both finite and periodic systems of any dimensionality (such as graphitic carbon nitride or metal–organic frameworks). The Libra-based NA/QD workflows enable using many-body description of excited states (e.g. TD-DFT) instead of the commonly-used single-particle (orbital-based) picture. Such an approach qualitatively changes the structure of electronic states coupling and generally accelerates the excited states relaxation processes, as was demonstrated with Si and CdSe quantum dots, 3D metal halide perovskites, and 2D black phosphorus systems [74,146,147]. The Libra workflows have been utilized to study photoinduced charge transfer in organic and inorganic heterointerfaces [140,141]. The interface of Libra with GAMESS code within our Libra-X [148] software allowed us to study CT dynamics in extended prototypical organic photovoltaic materials [137] as well as the photoinduced isomerization dynamics (beyond NBRA) using Δ SCF excited states [149]. With the help of Libra library, we developed the PYXAID2 package [150], which enabled the use of non-collinear wavefunctions (computed with the QE) [122] to account for the effects of spin–orbit couplings (SOC). Such studies demonstrated that SOC can significantly accelerate the nonadiabatic transitions in metal halide perovskites [151]. Libra workflow has been utilized by the Long group in their applied studies of polaron formation and recombination dynamics [152], modeling the role of surface defects [153], and rational design of electron–hole recombination dynamics in various solar energy materials [57,154]. Sanyal group utilized Libra to study the role of defects in determining electron–hole recombination in MoS₂ monolayers [155].

5. Conclusions and outlook

Libra is a versatile and powerful platform for NA/QD methodology development and assessment, as well as for “applied” atomistic material research. It has facilitated and enabled a good body of research, both methodological and material-related. However, given the grand ambition of the code to become a comprehensive and validated community platform for developing, implementing, assessing, and distributing the NA/QD methodologies, there is still a long way to go. Several research groups have actively contributed or are actively contributing to the code, in various ways. We plan to further grow and support the Libra community and we welcome any potential future contributions. Among the nearby future development goals is the incorporation and better testing of new TSH and decoherence schemes, including methods based on coupled trajectories and wavepacket propagation.

CRediT authorship contribution statement

Mohammad Shakiba: Conceptualization, Methodology, Software, Validation, Data curation, Writing – review & editing. **Brendan Smith:** Conceptualization, Methodology, Software, Validation, Data curation, Writing – review & editing. **Wei Li:** Methodology, Software, Validation,

Data curation, Writing – review & editing. **Matthew Dutra:** Methodology, Software, Validation, Data curation, Writing – review & editing. **Amber Jain:** Methodology, Software, Validation, Writing – review & editing, Supervision. **Xiang Sun:** Methodology, Software, Validation, Writing – review & editing, Supervision. **Sophya Garashchuk:** Methodology, Software, Validation, Writing – review & editing, Supervision. **Alexey Akimov:** Conceptualization, Methodology, Software, Validation, Data curation, Writing– original draft, Writing – review & editing, Supervision, Project Administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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