Richmol

Release 0.0.1

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Richmol is a collection of nuclear motion programs powered by Python. The package aims at providing simple and efficient platform for simulations of rotational-vibrational energies, spectra, and dynamics in the presence of external electromagnetic fields for general molecule. Richmol uses the Python language to implement most of its features, however the computationally critical parts are implemented with Fortran and C routines.

Chapter 1

An overview of Richmol

Richmol program development was initiated in 2015 as part of ERC Marie Skłodowska-Curie project "Rotationally-Induced Chirality in Molecules", where one of the goals was development of a general variational approach for simulations of time-dependent rotational-vibrational dynamics of molecules in external electric fields.

Initially, Richmol was designed to compute only the solution of the time-dependent Schrödinger equation, starting from field-free rotational-vibrational wave functions calculated externally, for example, using the general-molecule variational approach TROVE. This set down a general layered structure of the model where differen layers represent internal or external field perturbation contributions to the Hamiltonian. The computational modules responsible for different layers are communicating with each other via *Richmol Data Files*.

The package provides a range of tools to support variational calculations of molecular rotational-vibrational energy levels, spectra, field-induced dynamics, and related properties, including the nuclear spin hyperfine effects.

- Interface to TROVE general variational approach for computing field-free rotational-vibrational states of small molecules with high accuracy.
- Interface to DUO general variational approach for computing field-free rotational-vibrational states of diatomic molecules, including the non-adiabatic and spin-orbit coupling effects.

1.1 How to cite

General Richmol bibtex entry:

```
@article{Richmol,
  author       = {Alec Owens and Andrey Yachmenev},
  title        = {{RichMol}: A general variational approach for rovibrational
molecular
                  dynamics in external electric fields},
  year         = 2018,
  volume       = 148,
  number       = 12,
  pages        = 124102,
  journal      = {The Journal of Chemical Physcis}
  doi          = {10.1063/1.5023874},
  url          = {https://doi.org/10.1063/1.5023874},
  archiveprefix= {arXiv},
  eprint       = {1802.07603},
```

```
}
```

Bibtex entries for hyperfine calculations using module `hyfor`:

```
@article{Hyfor1,
  author       = {Andrey Yachmenev and Jochen Küpper},
  title        = {Communication: General variational approach to nuclear-quadrupole
                  coupling in rovibrational spectra of polyatomic molecules},
  journal      = {The Journal of Chemical Physcis},
  volume       = 147,
  year         = 2017,
  number       = 14,
  pages        = 141101,
  doi          = {10.1063/1.5002533},
  url          = {https://doi.org/10.1063/1.5002533},
  archiveprefix= {arXiv},
  eprint       = {1709.08558},
  primaryclass = {physics},
}

@article{Hyfor2,
  author       = {Yachmenev, Andrey and Thesing, Linda V. and Küpper, Jochen},
  title        = {Laser-induced dynamics of molecules with strong nuclear quadrupole
                  coupling},
  journal      = {The Journal of Chemical Physcis},
  volume       = 151,
  year         = 2019,
  number       = 24,
  pages        = 244118,
  doi          = {10.1063/1.5133837},
  url          = {https://doi.org/10.1063/1.5133837},
  archiveprefix= {arXiv},
  eprint       = {1910.13275},
  primaryclass = {physics},
}

@article{Hyfor3,
  author       = {Andrey Yachmenev and Sergey Yurchenko and Guang Yang and Emil Zak
and
                  Jochen Küpper},
  title        = {Theoretical line list for water molecule with hyperfine
resolution},
  journal      = {The Journal of Chemical Physcis},
  volume       = xx,
  year         = 2021,
  number       = xx,
  pages        = xxx,
  doi          = {},
  url          = {},
  archiveprefix= {arXiv},
  eprint       = {},
  primaryclass = {physics},
}
```

1.2 Features

- Calculation of rotational energies and spectra of molecules using the effective-Hamiltonian models, e.g., rigid rotor, Watson A and S Hamiltonians. In principle, arbitrary user-defined Hamiltonian expressed in terms of the angular momentum operators `\hat{J}`, `\hat{J}_z`, `\hat{J}_\pm`, and their powers can be set up.
- Calculation of nuclear spin hyperfine effects, such as nuclear quadrupole, spin-rotational, and spin-spin interactions.
- Calculation of time-dependent wavepacket dynamics of molecules subject to external electric or/and magnetic fields. The type of dynamics here depends on the input field-free basis, which can be the pure rotational states obtained by watie module, the vibrational or rotational-vibrational states, calculated with external variational programs, such as TROVE, or even the hyperfine rotational or rotational-vibrational states, calculated by hyfor module.

1.3 Design

write about the hierarchy of various interactions based on richmol-format files

1.4 Richmol Data Files

Chapter 2

Theoretical background

A basic knowledge of the underlying theory of molecular nuclear motion dynamics is necessary to be able to use Richmol. Here we describe some theoretical aspects and outline mathematical steps behind computing the rotational-vibrational energies, spectra, and field dynamics of molecules.

2.1 Molecular rotations

The molecular rotational Hamiltonian can be set up using the molecular rotational constants `B_x, B_y, B_z` as

```
\hat{H} = B_x\hat{J}_x^2 + B_y\hat{J}_y^2 + B_z\hat{J}_z^2,
```

where the rotational constants can be computed form the equilibrium geometry of the molecule, i.e., Cartesian coordinates of atoms, or, when available, taken from experimental measurements. This form of Hamiltonian assumes that the molecule-fixed frame is oriented in molecule such that the axes `x, y, z` coincide with the moments of inertia `I_x, I_y, I_z`. In other words, the molecular moment of inertia tensor must be diagonal, i.e., `I_{\alpha\beta}=I_\alpha\delta_{\alpha\beta}`.

2.2 Molecule-field interaction

2.3 Time-dependent Schrödinger equation

Version history

1.0 alpha 1	2020-12-31

Chapter 4

Installation

4.1 Manual installation from github repo

Manual installation requires numpy, scipy, h5py, hypothesis, and mendeleev libraries, as well as Fortran (gfortran, Intel Fortran) and C (gcc) compilers. You can download the latest Richmol (or the development branch) from github:

```
$ git clone https://github.com/CFEL-CMI/richmol
$ cd richmol
$ git checkout develop  # optional if you'd like to try out the development branch
```

Build and install the project:

```
$ python3 setup.py build
$ python3 setup.py install --user
```

To ensure the installation is successful, start a Python3 shell, and type:

```
>>> import richmol
```

4.2 Using optimized libraries

The default installation tries to find the mathematical libraries such as BLAS and LAPACK automatically (not yet implemented). You can compile the package with other BLAS and LAPACK vendors, such as, for example the Intel Math kernel Library (MKL):

```
$ need to set this up soon
```

Chapter 5

Watie tutorial

This tutorial shows few examples of typical use cases of watie

5.1 A simple example of rotational states calculation

Here is an example of computing the rotational energies of camphor molecule (S-enantiomer) based on the experimental rotational constants:

```
>>> xxx
>>> xxx
```

Next example shows how one can use the geometry of the molecule (Cartesian coordinates of atoms) for computing the rotational energies:

```
>>>
>>>
```

Alternatively, one can use the kinetic `G`-matrix to build the Hamiltonian and compute the rotational energies:

```
>>>
>>>
```

We can also play with the embedding of the coordinate axes `x, y, z` in the molecule by changing the property frame.

Chapter 6

tdtools tutorial

This tutorial shows few examples of typical use cases of tdtools module. Please note, to run tdtools calculation you need to generate the .. using watie module.

6.1 A simple example of rotational states calculation

Here is an example of computing the rotational energies of camphor molecule (S-enantiomer) based on the experimental rotational constants:

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```

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Alternatively, one can use the kinetic `G`-matrix to build the Hamiltonian and compute the rotational energies:

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>>>
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We can also play with the embedding of the coordinate axes `x, y, z` in the molecule by changing the property frame.

Chapter 7

Richmol for education

Here we provide a suite of computational lab activities suitable for use in classes teaching molecular physcis, rovibrational spectroscopy, or related courses. We aim at increase students' exposure to scientific programming to help students learn molecular physcis through computation.

Here you can also see the PDF version of this manual.