

# **Richmol**

***Release 0.0.1***

**Andrey Yachmenev and CMI**

Oct 11, 2020



<b>1</b>	<b>An overview of Richmol</b>	<b>3</b>
1.1	How to cite . . . . .	3
1.2	Features . . . . .	5
1.3	Design . . . . .	5
1.4	Richmol Data Files . . . . .	5
<b>2</b>	<b>Theoretical backgrounds</b>	<b>7</b>
2.1	Molecular rotations. . . . .	7
2.2	Molecule-field interaction . . . . .	9
2.3	Time-dependent Schrödinger equation . . . . .	9
<b>3</b>	<b>Version history</b>	<b>11</b>
<b>4</b>	<b>Installation</b>	<b>13</b>
4.1	Manual installation from github repo. . . . .	13
4.2	Using optimized libraries. . . . .	13
<b>5</b>	<b>Watie tutorial</b>	<b>15</b>
<b>6</b>	<b>Tdtools tutorial</b>	<b>17</b>
<b>7</b>	<b>Hyfor tutorial</b>	<b>19</b>
<b>8</b>	<b>Richmol molecular database</b>	<b>21</b>
<b>9</b>	<b>Richmol for education</b>	<b>23</b>



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.



## 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, using as a basis field-free rotational-vibrational wave functions calculated externally, for example, with the general-molecule variational approach [TROVE](#). This initial setting determined the current structure of the program, which consists of different modules each providing a solution for a specific  $H_0 + H'$  problem in the basis of  $H_0$  eigenstates. For example, `hyfor` module adds the nuclear spin hyperfine Hamiltonian ( $H' = H_{\text{hf}}$ ) to the rotational-vibrational Hamiltonian ( $H_0 = H_{\text{rv}}$ ) and expands hyperfine wave functions in the basis of rotational-vibrational state functions. `tdtools` module in turn can combine a time-dependent field-induced potential  $H'(t)$  with the total hyperfine Hamiltonian ( $H_0 \rightarrow H_{\text{rv}} + H_{\text{hf}}$ ) and expand time-dependent wave function in the basis of hyperfine state functions. Different modules are communicating 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 Phycis}
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 Phycis},
  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 Phycis},
  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 Phycis},
  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

## 1.4 Richmol Data Files



---

## Theoretical backgrounds

---

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 rotational energy levels, wave functions, spectra, and matrix elements of multipole-moment Cartesian tensor operators (e.g., dipole moment, polarizability, quadrupole moment, etc.) are computed by the module `watie`.

#### 2.1.1 Principal axes system

The molecular rotational Hamiltonian can be set up from the molecular rotational constants  $B_x$ ,  $B_y$ ,  $B_z$  as

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

The rotational constants can be computed from 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 within molecule such that the axes  $x$ ,  $y$ ,  $z$  coincide with the moments of inertia  $I_x$ ,  $I_y$ ,  $I_z$ . Put differently, the molecular inertia tensor is diagonal, i.e.,  $I_{\alpha\beta} = I_{\alpha\delta} \delta_{\alpha\beta}(\alpha, \beta = x, y, z)$ . Such coordinate system is called the Principal Axes System (PAS).

In order to change the molecular coordinate system to PAS, one computes and diagonalizes the moment of inertia tensor  $\mathbf{I}$ , i.e.,

$$\mathbf{I} = \mathbf{V} \mathbf{I}^{\text{diag}} \mathbf{V}^{-1},$$

and rotates with the eigenvector matrix  $\mathbf{V}^{-1}$  all Cartesian vectors, which include Cartesian coordinates of atoms  $\mathbf{r}_{\text{atom}}$  and all molecular Cartesian tensors, such as, for example, dipole moment  $\boldsymbol{\mu}$  or polarizability  $\boldsymbol{\alpha}$ , i.e.,

$$\begin{aligned} \mathbf{r}_{\text{atom}}^{\text{PAS}} &= \mathbf{V}^{-1} \mathbf{r}_{\text{atom}} \\ \boldsymbol{\mu}^{\text{PAS}} &= \mathbf{V}^{-1} \boldsymbol{\mu} \\ \boldsymbol{\alpha}^{\text{PAS}} &= \mathbf{V}^{-1} \boldsymbol{\alpha} \mathbf{V} \end{aligned}$$

The rotational constants are computed as

$$B_{\alpha} = \frac{\hbar^2}{2hc I_{\alpha}^{\text{diag}}}(\alpha = x, y, z).$$

**Note** The *rotation* of all Cartesian quantities in `watie` module is done automatically following the user's choice of molecular frame, which is done by setting `watie.RigidMolecule.frame()` to "pas", for example. There is no need to do the above rotations of Cartesian coordinates and tensors manually (in place).

---

## 2.1.2 Quantization axis

The eigenvalues of inertia tensor after diagonalization are sorted such that  $I_x^{\text{diag}} \leq I_y^{\text{diag}} \leq I_z^{\text{diag}}$ , accordingly  $B_x \geq B_y \geq B_z$ . In spectroscopic literature rotational constants sorted in descending order are labelled as  $A \geq B \geq C$  and the corresponding PAS axes as  $a, b, c$ .

One is free to permute the  $x, y, z$  axes without any effect on the final results, such as energies, wave functions, or time-evolution dynamics in fields. However, a particular choice of the axes can change complexity of the rotational wave functions and as a result their spectroscopic assignments. Sometimes it is beneficial to choose certain PAS axis as the  $z$  axis in order to simplify calculations of observables, such as, for example, expectation values of  $\cos^2\theta$  (where  $\theta$  is the Euler angle between the laboratory  $Z$  and molecular  $z$  axes).

---

**Note** Computed observables, such as energies, spectra, and time-evolution dynamics must not depend on the choice of the coordinate system, i.e., the orientation of  $x, y, z$  axes in molecule as well as the choice of quantization axis, i.e., whether the Hamiltonian is  $\hat{H} = A\hat{J}_x^2 + B\hat{J}_y^2 + C\hat{J}_z^2$ , or  $\hat{H} = C\hat{J}_x^2 + A\hat{J}_y^2 + B\hat{J}_z^2$ , or  $\hat{H} = B\hat{J}_x^2 + C\hat{J}_y^2 + A\hat{J}_z^2$ , etc.

---

There are few special types of molecules with two out of three or all three rotational constants being equal, i.e., *spherical top* molecules with  $A=B=C$ , *prolate symmetric top* molecules with  $A>B=C$ , and *oblate symmetric top* molecules with  $A=B>C$ . Linear molecules have only two rotational constants  $A=B$ . For these special cases the Schrödinger equation with rotational Hamiltonian can be solved exactly provided the  $x, y, z$  axes are chosen in a certain way. For *prolate symmetric top* molecules the  $z$  axis must be aligned along the smallest inertia  $a$  axis. For *oblate symmetric top* molecules the  $z$  axis must be aligned along the largest inertia  $c$  axis.

The solutions of *spherical top* and *symmetric top* problems are symmetric-top functions  $|J, k, m\rangle$ . For more general problem of rotation of *asymmetric top* molecules (molecules with all three rotational constants different  $A>B>C$ ) the wave function is build as a linear combination of symmetric-top functions, so the choice of the  $x, y, z$  axes in an *asymmetric top* molecule will affect the linear combination coefficients, however not the energies. When a molecule is close to either of the special types, i.e., being *near prolate top* with  $A>B \approx C$  or *near oblate top* with  $A \approx B>C$ , it might be beneficial, mainly for the state assignment purposes, to choose the  $z$  in accord with the corresponding type of *symmetric top*. To tell which of *symmetric top* types a given molecule is close to, one can compute the so-called asymmetry parameter  $\kappa = (2B - A - C) / (A - C)$ , which is equal to  $-1$  for a *prolate symmetric top* and  $+1$  for an *oblate symmetric top*.

---

**Note** A standard spectroscopic convention is the following: when  $\kappa \simeq -1$ , permute the  $x, y, z$  axes such that  $B_z$  becomes the largest rotational constant, and when  $\kappa \simeq +1$ , permute the  $x, y, z$  such that  $B_z$  becomes the smallest rotational constant. The Hamiltonian is  $\hat{H} = B_x\hat{J}_x^2 + B_y\hat{J}_y^2 + B_z\hat{J}_z^2$ . In `watie` the axes permutations can be set by a user using the molecular frame function `watie.RigidMolecule.frame()`.

---

### 2.1.3 Other choices of axes

Another popular choice of the molecular axes is along the principal moments of molecular polarizability tensor. In general, one follows the same procedure as for the PAS, with the molecular polarizability tensor put in place of the moment of inertia tensor. The rotational Hamiltonian is then constructed as

$$\hat{H} = \frac{1}{2} \sum_{\alpha, \beta=x,y,z} G_{\alpha\beta} \hat{J}_{\alpha} \hat{J}_{\beta},$$

where  $G_{\alpha\beta}$  is the rotational kinetic energy matrix.

## 2.2 Molecule-field interaction

## 2.3 Time-dependent Schrödinger equation



---

## Version history

---

1.0 alpha 1	2020-12-31
-------------	------------





---

## 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 (*automatic configuration is 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
```



---

## Watie tutorial

---

This tutorial shows few examples of typical use cases of `watie` module.



---

## Tdtools tutorial

---

This tutorial shows few examples of typical use cases of `tdtools` module.



---

**Hyfor tutorial**





---

## Richmol molecular database

---

The database contains precomputed Richmol files for various molecules and multipole moment tensor operators.



---

## Richmol for education

---

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

*... Add excercises from Modern Molecular Physics course in UHH*

Here you can also see the [PDF version](#) of this manual.





