A Modern-Fortran Program for Chemical Kinetics on Top of Anharmonic Vibrational Calculations

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Abstract. We discuss the design and implementation of StarRate, a modern-Fortran program for the calculation of chemical kinetics coupled to anharmonic vibrational perturbative treatments. The program is written in the F language, a carefully crafted subset of Fortran 95, and is conceived in an object-based programming paradigm, i.e. the set of object-oriented programming features supported by Fortran 90/95. StarRate is made up of three main modules handling the involved molecular species, the elementary reaction steps, and the whole reaction scheme. Input data are accessed through an XML interface based on a cross-code hierarchical data format granting interoperability with popular electronic-structure packages and with the graphical interface of the Virtual Multifrequency Spectrometer developed in our group. Data parsing is performed through versatile Python scripts. Test calculations on the isomerization reaction of C-cyanomethanimine using anharmonic densities of states obtained with a development version of Gaussian are reported together with an account of ongoing developments.

Keywords: Object-based programming · Modern Fortran · Chemical kinetics · Anharmonic perturbative models · Reaction rates

1 Introduction

The concept of object-oriented programming (OOP), as opposed to procedural programming, originated as early as the Sixties [1] and has since influenced many programming languages. Nowadays, several flexible and powerful languages have emerged combining both the object-oriented and procedural

The research leading to these results has received funding from Scuola Normale Superiore through project "DIVE: Development of Immersive approaches for the analysis of chemical bonding through Virtual-reality Environments" (SNS18_B_RAMPINO) and program "Finanziamento a supporto della ricerca di base" (SNS_RB_RAMPINO). The authors are grateful to Dr. Daniele Licari (Scuola Normale Superiore) for fruitful discussions.

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S. Misra et al. (Eds.): ICCSA 2019, LNCS 11624, pp. 401–412, 2019.
https://doi.org/10.1007/978-3-030-24311-1_29

programming paradigm, with Python and Ruby being the most popular languages among the scientific community, whereas Java is most widely used in commercial platforms.

Although these recent high-level, (semi-)interpreted programming languages are good at writing easy-readable codes, Fortran is the most widely adopted language in many branches of computational chemistry and physics. This is partly due to historical reasons (for instance, some of the first molecular electronic structure packages that are still universally used, such as the Gaussian package [2], were written and are actually developed in Fortran), partly to the availability of a large set of procedures related to mathematical operations which are quite fast in performance and thus make Fortran more suitable for computationally demanding problems. Whether to use the higher-level and system-independent languages or the lower-level, compiler-dependent languages is arguable and sometimes depends on the problem at hand. But as a matter of fact, especially among computational chemists, Fortran is still the most widely adopted programming language for intensive computing.

Despite the fact that Fortran is widely used in the scientific community and that the OOP concept is quite old, the use of the OOP paradigm with Fortran is quite rare in the scientific community. While many of the OOP features are included in Fortran 90/95 [3–5] thus making of it a so-called 'object-based'[1] language [7] with powerful capabilities (such as array syntax and built-in libraries) oriented to intensive computing, the procedural way of programming is still the prevailing one and Fortran software conceived in a OOP paradigm is very rare (see for instance Refs. [8–10] for some exceptions in the domain of computational chemistry and physics). Hence documenting on object-based implementations of Fortran computational-chemistry programs shall be beneficial for the computational-chemistry community.

In this article, we report on the development of an object-based Fortran program, StarRate, for the calculation of reaction kinetics coupled to anharmonic vibrational perturbative treatments. While doing so, we will discuss the software design and the related data structure in Sect. 2. In Sect. 3 an application is shown on the isomerization reaction of C-cyanomethanimine and the relevant computational details are given. Finally, conclusions and future work are outlined in Sect. 4.

2 Code Design and Data Structure

StarRate is an object-based Fortran program for the modeling of kinetics of multistep reactions such as those outlined, for the unimolecular case, in Fig. 1. It is written in the F language [11,12], a carefully crafted subset of Fortran 95, and is conceived in an OOP paradigm in terms of discrete objects incorporating data and behaviour through the use of Fortran derived datatypes and modules. Accordingly, StarRate is built around three core modules: `molecules`,

[1] Cardelli and Wegner identify using user-defined types for identity and classification without inheritance as object-based programming [6].

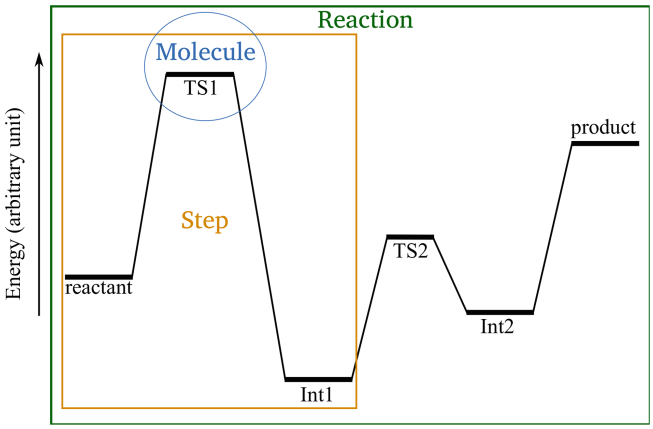


Fig. 1. Reaction scheme of a multistep unimolecular reaction involving two intermediates (Int1 and Int2) and two transition sates (TS1 and TS2).

`steps`, and `reactions`, naturally relating to the three components of the reaction scheme reported in Fig. 1: molecular species, reaction steps, and the whole reaction scheme. Three further modules, `kinds`, `constants`, and `in_out`, allow for handling the machine precision, the physical constants and the input/output operations, respectively.

A Unified Modeling Language (UML) diagram showing the code structure of StarRate focusing on the three core modules is shown in Fig. 2. The first module `molecules` contains the definition of a `molecule` datatype (including the relevant information for kinetics such as densities of states and sums of states, for which see Sect. 3) and the procedures to operate on a variable of the `molecule` type; the second module `steps` is in charge of handling single reaction steps (including the calculations of microcanonical and canonical rate coefficients); the third module `reactions`, which is currently under development, is in charge of combining the elementary reaction steps through a master-equation approach.

Input data are accessed by an interface, which is built on the XML format. At the beginning, the user will have to run a Python script which extracts data from the output files generated by quantum-chemistry calculations. Currently, StarRate supports output files from the Gaussian package (.log extension), though support for other popular electronic-structure programs is currently being pursued (see also Refs. [13,14] for the definition of a common data format for quantum chemistry). The interface is written in a simple script `G2R.py` with Python's `xml.etree.ElementTree` library. Python is chosen for data extraction from the .log files because of its versatility in file processing.

The structure of the XML interface to StarRate is built so as to be fully compatible with the Draw module of the Virtual Multifrequency Spectrometer (VMS-Draw) [15] developed in our laboratory. Accordingly, the whole XML document builds under a root element named `escdata` (electronic-structure

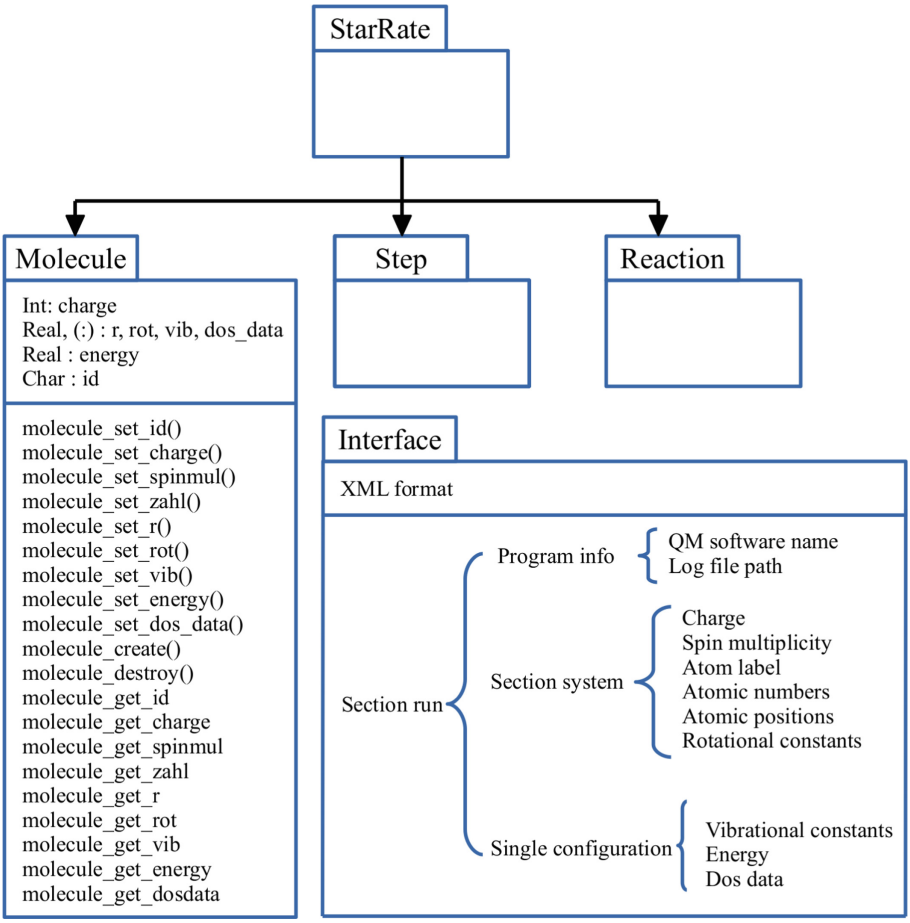


Fig. 2. A UML diagram representing the main module hierarchy of StarRate. Some details on the `molecules` module showing part of the related datatype and procedures are given for illustrative purposes.

calculation data). The `escdata` has one child element for each molecule named `section_run`. Then, `program_info`, `section_system`, and `system_single_configuration_calculation` are the siblings that fall under the `section_run` element. All the information regarding a molecule is handled by these three sibling nodes. The `program_info` node contains two subnodes which keep track of quantum chemical software name and .log file location. The `section_system` node contains basic information which does not require quantum chemical information (*viz.*, molecular charge, spin multiplicity, atom label, atomic numbers, rotational constants). The last sibling, `system_single_configuration_calculation` contains information which requires quantum chemical calculations (*viz.*, vibrational constants, SCF energy, density of state data).

Once the XML for a given reaction has been generated containing the information of all the involved molecular species, these data are read by StarRate through the FoX_DOM [16] library for XML parsing in Fortran.

3 Isomerization of C-Cyanomethanimine

C-cyanomethanimine is a complex organic molecule found in the interstellar medium (ISM) [17,18]. C-cyanomethanimine is essentially a dimer of HCN and a very important molecule in the context of prebiotic chemistry [19]. In fact, the oligomerization of HCN leads to the formation of nucleobases [20,21] via C-cyanomethanimine. Because of the importance of the molecule and availability of a number of works on its isomerization [22,23], we choose the simple yet important Z $\rightleftharpoons$ E isomerization reaction of C-cyanomethanimine as a test case for a calculation with StarRate. The structures of the involved molecular species for this reaction together with the relevant data are summarized in Fig. 3.

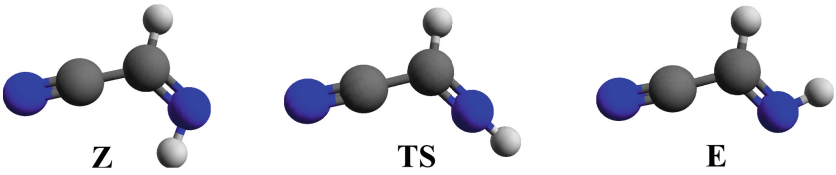


Fig. 3. Molecular species involved in the Z $\rightleftharpoons$ E isomerization reaction. The computed anharmonic zero-point energies relative to the anharmonic zero-point energy of Z are 25.49 Kcal/mol for TS and 0.57 Kcal/mol for E.

A proper treatment of the time evolution of a chemical reaction should rely on the quantum modeling of the underlying nuclear dynamics. However, exact quantum-dynamics calculations are only feasible for systems with up to 3 or 4 atoms [24–27], and approximate quantum-dynamical methods are able to extend this limit only modestly. For the remaining systems, one has in practice to resort either to a (quasi-)classical treatment [28–30] or to more drastic approximations such as transition-state theory (TST) in one of its flavours, simply accounting for the energetic structure of a limited set of important points of the potential energy surface. Within the popular Rice-Ramsperger-Kassel-Marcus (RRKM) theory [31–33], the microcanonical rate coefficient for a unimolecular reaction, such as the above-mentioned one, is given by the equation [34]

$$k(E) = \frac{N^{\ddagger}(E)}{h\rho(E)} \tag{1}$$

where h is Planck's constants, $N^{\ddagger}(E)$ is the sum of states of the TS (or a tunneling-corrected version of it) and $\rho(E)$ is the density of states (DOS) of the reactant molecule. A central quantity in this framework is thus the

molecular rovibrational density of states $\rho(E) = \Delta N(E)/\Delta E$, i.e. the number $\Delta N(E)$ of rovibrational states per energy interval ΔE within the interval $[E, E + \Delta E]$, of the involved molecular species. The cumulative sum of states (SOS) up to energy E, $N(E)$, for a given species is in fact easily worked out from the related DOS:[2]

$$N(E) = \int_0^E \rho(E')\, \mathrm{d}E'. \tag{3}$$

The rotational motion and the vibrational motion of the molecule are usually assumed to be approximately separable from one another (in other words, the energy of the molecule, E, is approximately the sum of the rotational energy, E_r, and the vibrational energy, $E - E_\mathrm{r}$). As a result, the rovibrational density of states can be written as a convolution of its rotational and vibrational counterparts [35]:

$$\rho(E) = \int_0^E \rho_r(E_r)\rho_v(E - E_r)dE_r.$$

While a classical expression can be used for the rotational DOS

$$\rho(E) = \frac{1}{\sigma}\sqrt{\frac{4E}{ABC}}, \tag{4}$$

with σ being the rotation symmetry number and A, B, and C the three rotational constants, a quantum anharmonic treatment is recommended for the vibrational motions. Within second-order anharmonic perturbative approaches [36,37], the vibrational energy E (expressed in cm^{-1}) in terms of the n quantum numbers $\{\nu_i\} \equiv (\nu_1, \ldots, \nu_n)$ is given by

$$E = E_0 + \sum_{i=1}^{n} \nu_i \omega_i + \sum_{i,j=1}^{n} \chi_{ij} \left[\nu_i \nu_j + \frac{1}{2} (\nu_i + \nu_j) \right]. \tag{5}$$

In Eq. 5, E_0 is the zero-point vibrational energy, ω_i are the harmonic frequencies, and χ_{ij} are the elements of the anharmonic matrix (explicit function of cubic and semidiagonal quartic force constants, as well as Coriolis couplings).

While the density and sum of states of a molecule can be in principle computed by an exact state counting using the above expression (see for instance the Stein-Rabinovitch [38] adaptation of the Beyer-Swinehart [39] algorithm for uncoupled anharmonic oscillators), this becomes rapidly unaffordable from a computational point of view with increasing system size. A viable alternative is represented by the Wang-Landau sampling method [40,41] as extended to

[2] The partition function $Q(T)$ can as well be computed from the density of states $\rho(E)$ by a Laplace transform:

$$Q(T) = \int_0^\infty \rho(E) e^{-\frac{E}{k_\mathrm{B}T}}\, \mathrm{d}E \tag{2}$$

with k_B being the Boltzmann constant and T being the absolute temperature.

the quantum anharmonic vibrational problem by Basire et al. [42]. and further refined by Nguyen and Barker [43]. Within such scheme (the reader is referred to the original papers for more details) the DOS $\rho(E_j)$ is obtained iteratively for each j-th bin of an equally spaced energy grid in a given energy range by performing a random walk in the space of quantum numbers $\{\nu_i\}$.

The thermal rate coefficient can be easily computed from the microcanonical rate coefficients using the following equation:

$$k(T) = \frac{1}{Q(T)} \int_0^\infty k(E)\rho(E)e^{-E/k_B T} \mathrm{d}E, \tag{6}$$

with $Q(T)$ being the partition function of the reactant species.

Calculations were performed with a locally modified version of the development version of Gaussian [44] using density-functional theory (DFT) at the B3LYP-D3BJ/SNSD level of theory (B3LYP exchange-correlation functional [45,46], semiempirical dispersion contributions by inclusion of the Grimme's D3BJ model [47], SNSD basis set [48]). Anharmonic calculations were performed with the GVPT2 model [36,49]. Cubic and semi-diagonal quartic force constant

Table 1. Cartesian coordinates in $\mathring{A}$ of the optimized structures for the Z, TS, and E species.

Z			
C	0.695181	0.486229	0.000000
H	0.894724	1.559531	0.000000
H	1.345237	−1.302417	0.000000
N	1.672019	−0.331592	0.000000
C	−0.702977	0.109125	0.000000
N	−1.821969	−0.199372	0.000000
TS			
C	−0.698654	0.482677	−0.000155
H	−0.831811	1.579112	−0.000380
H	−2.384044	−0.978647	0.000108
N	−1.627409	−0.333444	−0.000005
C	0.719560	0.085097	−0.000040
N	1.845003	−0.198736	0.000056
E			
C	0.687014	0.470848	0.000000
H	0.847507	1.554826	0.000000
H	2.525991	0.044966	0.000000
N	1.608625	−0.407966	0.000000
C	−0.703284	0.072983	0.000000
N	−1.836746	−0.173430	0.000000

were computed by numerical differentiation (with displacements of 0.01 $\sqrt{\text{amu}}$ Å) of the analytical Hessian along each active normal coordinate. Optimized geometries for the Z, TS, and E species are reported in Table 1. The anharmonic vibrational densities of states for the three species were calculated by means of the Wang-Landau sampling method as refined in Ref. [43], which was directly implemented in a modified version of Gaussian. The DOS were computed on an energy grid from 10 to 50000 cm^{-1} with spacing 10 cm^{-1} using 1000 trials per

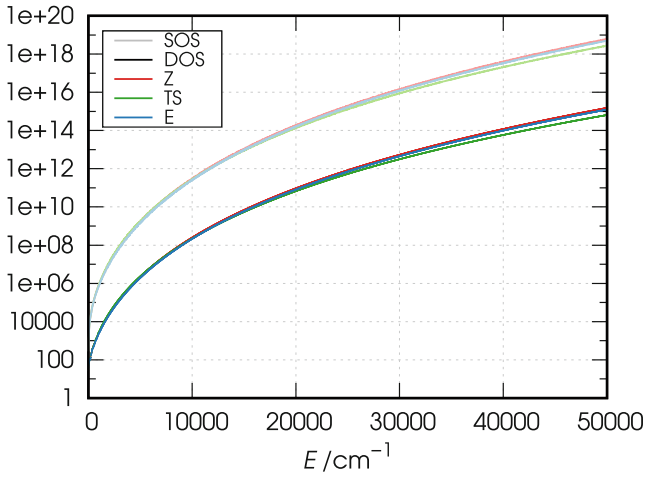


Fig. 4. Rovibrational DOS (full color) and SOS (light color) for the Z (red), TS (green), and E (blue) species. (Color figure online)

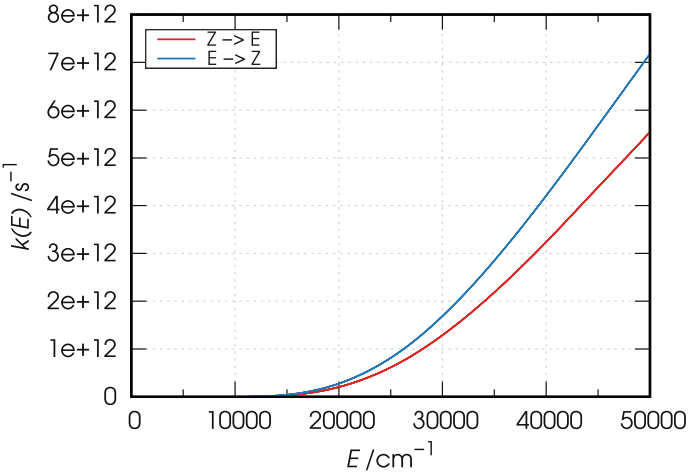


Fig. 5. Microcanonical rate constants for the Z → E (red line) and the E → Z (blue line) reactions. (Color figure online)

energy bin and a number of 21 iterations (the interested reader is referred to Ref. [43] for further details on these parameters). For the transition state, the density of states was computed by excluding the normal mode with an imaginary frequency.

The DOS and SOS of the three species Z, TS, and E are plotted in Fig. 4 as a function of the energy E on an energy scale having as zero the respective zero-point energy. Full-color curves represent the DOS (red for Z, green for TS, and blue for E), while light-color curves represent the DOS. Microcanonical rate coefficients for the Z $\rightarrow$ E (red line) and E $\rightarrow$ Z (blue line) isomerization reaction are reported in Fig. 5 as a function of the energy E on an energy scale having as zero the Z-isomer zero-point energy.

4 Conclusions

In this paper we describe the design and implementation of an object-based program written in the F subset of Fortran 95 for the modeling of chemical kinetics on top of anharmonic vibrational perturbative treatments. The program builds around three main modules relating to the entities that make up a reaction scheme: molecular species, elementary steps, and the whole reaction scheme. As an example, rate constants for the isomerization of C-cyanomethanimine computed within a density-functional theory framework and an anharmonic perturbative treatment are reported. Although test calculations are shown for the case of a unimolecular reaction, the program is being extended to the treatment of bimolecular reactions as well.

Specific care during the code design has been devoted to grant full interoperability with the Virtual Multifrequency Spectrometer (VMS) developed in our group, in order to provide our program with the powerful capabilities of the VMS graphical user interface, and with popular quantum-chemistry packages. This has been achieved through a specific XML interface between the program and the output files of quantum-chemical calculations fostered by dedicated libraries.

Current work is ongoing in our laboratory on the development of StarRate. On one hand the module handling elementary reaction steps is being enriched with a number of methods of different accuracy to compute the density of states, while the module handling the whole reaction scheme is being provided by a master-equation solver. On the other hand, we are developing a module of VMS providing a user-friendly graphical interface for calculating chemical kinetics using the StarRate program. While details on these aspects will be given in a forthcoming publication, the possibility of coupling chemical-kinetics calculations to three-dimensional representation and exploration of the potential-energy surface [50] by state-of-the-art immersive-virtual-reality technology [51] and to the analysis of detailed chemical-bonding features [52–54] is also being explored.

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