Full quantum calculations of astrophysically important atomic collision processes

Description of the project

Atomic and molecular physics lies at the foundation of much of modern astrophysics, since in most cases the only information we can obtain on celestial objects such as stars, supernovae, comets, galaxies etc., is from the light they emit shaped by atomic and molecular processes, through spectroscopy (for a review on stars, see Barklem, 2016). In this project we propose to perform full quantum calculations of atomic collision processes important in understanding the spectra of stars and supernovae ejectae. An example is the charge transfer process \( C + O^+ \rightleftharpoons C^+ + O \), which has been shown by Jerkstrand et al. (2011) to be important in determining the oxygen production in type II supernovae. As such, it influences our understanding of how and where oxygen, the universe’s third most common element and playing an important role in the origin of life, is produced.

Charge transfer processes involving singly ionised atoms with neutrals are unfortunately very difficult to estimate via simple methods (e.g. Stancil, 2001; Sterling and Stancil, 2011). Thus, full quantum calculations using quantum chemistry methods to describe the molecular electronic structure, and quantum scattering to describe the dynamics of the collision, are needed. In this project it is proposed to perform quantum chemistry type calculations of required diatomic molecular systems (the CO\(^+\) molecule in the above example), and apply them in quantum scattering calculations.

Across a four year project, we anticipate that the student will be able to address several collision systems of interest. The project will include at least one benchmark system accessible to experiment with the DESIREE (Double ElectroStatic Ion Ring ExpEriment) national facility in Stockholm. The student will be heavily involved in the application of the results to astrophysical modelling, i.e. modelling spectra of supernovae ejectae, stellar atmospheres, or other objects and interpreting the results.

Who will be involved (Advisor and co-advisors)

The student will be hosted at the Division of Astronomy and Space Physics, within the Department of Physics and Astronomy, with the main advisor being Paul Barklem, professor in the Theoretical Astrophysics programme. Ignacio Fernández Galván, researcher at the Department of Chemistry–BMC, and Jon Grumer, postdoc within the Division of Astronomy and Space Physics, will be co-advisors. Barklem is an expert on atomic and molecular collisions and their application to astrophysical spectroscopy. Fernández Galván is an expert on quantum chemical calculations for molecules, and a developer and maintainer of the OpenMolcas code (Aquilante et al., 2016; Ope). Grumer is an expert on atomic structure calculations, especially with the GRASP code (Fischer et al., 2018; GRA). There are significant similarities in the theoretical and numerical methods used in the molecular and atomic structure problems, that allow us to understand each other, while still individually bringing significant unique expertise.

Why the project is interdisciplinary and the mathematical content of it

The project combines expertise from quantum chemistry, atomic and molecular physics, and astronomy, and thus is clearly interdisciplinary. The project’s mathematical content is two-fold,
namely with significant components in theory and numerical methods. In particular, both the molecular structure and quantum dynamics problems involve solution of different forms of the Schrödinger equation (SE), making extensive use of linear algebra, differential equations and boundary value problems, both analytically and numerically. The main mathematical problem to be solved, is the need for reliable numerical algorithms suited to problems with high-dimensionality. In some cases existing methods can be used, in some existing methods extended, and in others perhaps new methods developed.

The specific problems to be solved are:

1. **Time-dependent, non-relativistic, SE for all nuclei and electrons.**
   \[
   i \frac{d}{dt} \Phi = \hat{H} \Phi
   \]
   This leads to coupled equations expressed in terms of the eigenfunctions of the

2. **Time-independent SE.**
   \[
   \hat{H} \Phi = E \Phi
   \]
   Then the Born–Oppenheimer (BO) approximation is invoked, which allows the nuclear and electronic degrees of freedom to be separated, and thus to solve the

3. **Time-independent, electronic, SE**

These problems need to be solved from the bottom up. Solving 3 is usually expressed as an eigenvalue problem in terms of basis functions. Solving 2 requires introducing the coupling terms that were neglected by the BO approximation. Solving 1 can then in principle be done by propagating the system in time.

Problem 3 can be stated, in atomic units, for \( n \) electrons (charge \(-1\)) and \( m \) nuclei (charge \(+Z_\alpha\)):

\[
\left[ \sum_i \left( -\frac{i}{2} \nabla_i - \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} + \frac{1}{2} \sum_j \frac{1}{r_{ij}} \right) \right] \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n) = E \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n)
\]

where the unknown function \( \Psi \) depends on the coordinates of all electrons, and the nuclei are considered fixed at the coordinates \( r_{\alpha} \). The term representing the electron–electron repulsion \((1/r_{ij})\) prevents finding closed analytical solutions for systems with more than one electron, therefore approximations are used to solve it numerically. The standard approach is expressing the unknown multidimensional function \( \Psi \) as a linear combination of products of simple pre-defined one-electron (i.e., three-dimensional) basis functions. This allows replacing the differential equation with an eigenvalue problem:

\[
HC = EC
\]

where \( H \) is a matrix representing the Hamiltonian operator and the eigenvector \( C \) contains the coefficients representing \( \Psi \). However, by doing this the dimensionality of the problem increases from \( 3n \) to something closer to \( n^N \) (\( N \geq n/2 \) being the number of basis functions).
Practical methods further approximate the solution by keeping only a reduced number of all possible basis function products, and differ in how these are selected, and in the additional corrections applied to the solution to compensate for the approximation. The most appropriate approximate methods in the context of this project are multiconfigurational methods, which are capable of describing simultaneously and with similar accuracy several electronic states, but the complexity scales exponentially with the size of the system. There has been significant recent development in approaches that extend the practical range of application of these methods, such as the density matrix renormalization group (Keller et al., 2015) or the quantum Monte-Carlo (Li Manni et al., 2016) full configuration interaction. These approaches will therefore be explored and improved.

The solution of 2 requires the introduction of matrices that describe how electronic wavefunctions couple to nuclear motion. These coupling matrices are not available in the standard codes such as OpenMolcas (see above). A significant part of the project would be to explore the theory and numerical algorithms for calculation of these matrices in the context of the existing theory and codes. The main mathematical problem to be solved here is the consistent calculation of the phases of the wavefunctions at all internuclear distances, which if not handled correctly leads to unphysical sign changes in the matrix elements, and affects the solution of 1. In the past this problem has been solved by introducing a biorthogonalisation procedure (e.g. Guitou et al., 2010; Wendland, 2017). Though such methods exist in principle, the algorithm will need to be tailored to our particular theoretical method and code.

The equations described by 1, are multi-dimensional partial differential equations which require numerical solutions. Standard methods, such as the log-derivative method (Johnson, 1973; Manolopoulos, 1986), can very likely be used safely for this part of the problem. An important mathematical aspect of the project will be to test the convergence properties of this method for the particular collision problems.

**How the hosting institution will co-finance the student**

The remaining 50% will be financed by Barklem’s VR grant, “Atomic processes in stellar atmospheres: towards high-accuracy stellar abundances for galactic archaeology” (Project id: 2016-03765), which was granted 3.2 MSEK for 2017-2020.

**References**


P. S. Barklem. Accurate abundance analysis of late-type stars: Advances in atomic physics. 


