Atomic structure calculations: encapsulating knowledge in computer codes

Variational methods are the method of choice for the calculation of properties of bound states for complex atomic systems. With single- and double- (SD) substitutions from a multi-reference set, results of excellent accuracy have been obtained for some systems. ATSP and GRASP are two open source codes that encapsulate the knowledge acquired over nearly half a century and are still evolving.

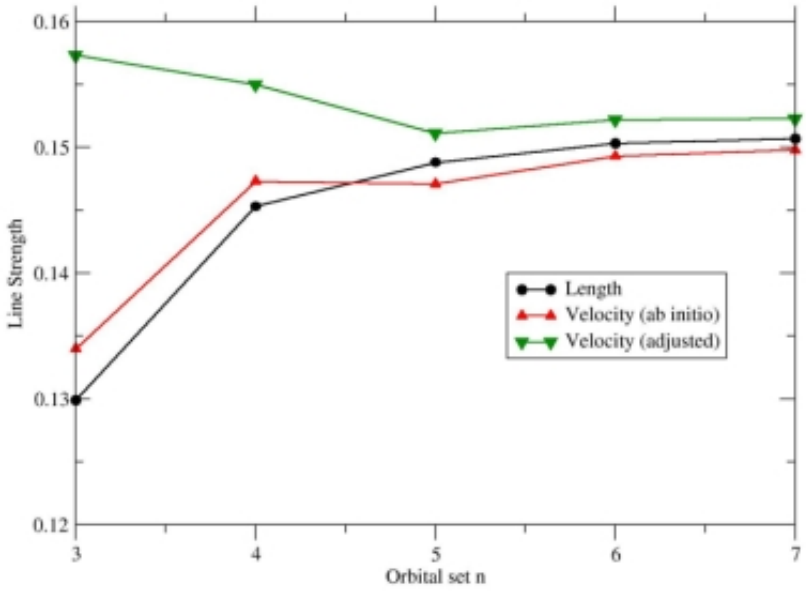

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Figure 1. Convergence for the $3p^2\ ^3P_2 - {}^1D_2$ E2 transition in Fe XIII.

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For electric multipole transition probability calculations, a test of accuracy is the agreement in the length and velocity forms of the line strength, particularly when the velocity form is computed using the exact transition energy. By performing systematic calculations, for larger and larger orbital sets, the convergence of the computational model may be monitored. Figure 1 shows the convergence of the length and velocity form for the $3p^2\ ^3P_2 - {}^1D_2$ E2 transition in Fe XIII as a function of the maximum principal quantum number of the orbital set (published in 2010 *J. Phys. B: At. Mol. Opt. Phys.* **43** 074020 (http://iopscience.iop.org/0953-4075/43/7/074020)). For this fairly highly ionized system convergence is rapid. This convergence along with the accuracy of the transition energy serve as 'indicators of accuracy'.

In the late 1990s, as a check on the capability of their knowledge, researchers used the ATSP code with relativistic effects in the Breit-Pauli approximation in systematic, large-scale calculations to compute all levels up to a given level of a spectrum and all E1 transitions between these levels for light atoms.

Some E2 and M1 transitions were computed as well. Results were collected in a database. Version 2 (http://nlte.nist.gov/MCHF/) also includes current codes that may be downloaded.

Variational methods describe the effect of correlation in the motion of electrons in terms of orbitals that minimize the total energy of the wave function for a multiconfiguration expansion. Figure 2 shows some

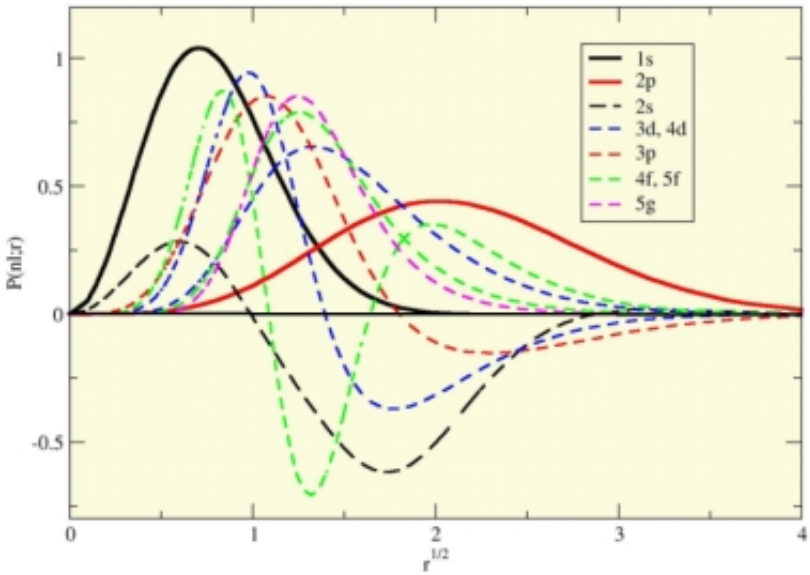

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Figure 2. Correlation orbitals for the 1s2p ^{1}P term of helium.
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correlation orbitals for the 1s2p ^{1}P term of helium. Note how they cluster around the region where 1s and 2p radial functions overlap.

Progress towards heavy elements

Currently there is great interest in heavy elements. For example, tungsten (W) at all stages of ionization is important for the development of future tokamaks and cerium is being used as an additive in a number of high-intensity discharge lamps to dramatically improve luminous efficacy. A large number of lines are needed which effectively precludes experimental determination.

As a first step towards extending the capability of codes to heavier complex atoms, calculations were performed for Mo^{+5} using both the ATSP and GRASP code (published in 2011 *J. Phys. B: At. Mol. Opt. Phys.* **44** 125001 (http://iopscience.iop.org/0953-4075/44/12/125001)). Although the former was able to deal with the more highly excited states, GRASP results were more accurate for the many levels of the $4p^54d^2$ configuration that interact strongly with $4p^65f$. This study showed the importance of fast and reliable code for transforming wavefunction expansion from jj-coupling to LSJ-coupling and the ability to evaluate matrix elements between configuration states with many open shells that may include multiply occupied f-shells. For complex atoms where there are many important overlap regions, the use of non-orthogonal orbitals can greatly simplify the inclusion of correlation.

More details (http://iopscience.iop.org/0953-4075/44/12/125001) of the author's recent work are published in *Journal of Physics B: Atomic, Molecular and Optical Physics*.

About the author

Charlotte Froese Fischer (http://www.vuse.vanderbilt.edu/~cff/cff.html) , Professor Emerita in Computer Science at Vanderbilt University and Guest Researcher at the National Institute of Standards, started the development of the ATSP package in the late 1960s. The code has evolved over the years with the help of many collaborators, primarily Alan Hibbert (http://www.am.qub.ac.uk/amtpt/pers/hibbert/hibbert.html) , Michel

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Michel Godefroid, Per Jönsson and Gediminas Gaigalas
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Charlotte Froese Fischer (http://images.iop.org/objects/jio/labtalk/2/8/26/Fischer.jpg)

(http://www.ulb.ac.be/cpm/people/scientists/mgodefroid/main.html) , and Gediminas Gaigalas (http://www.itpa.lt/~gaigalas/) . In the early 1990s, as relativistic effects gained importance, the GRASP code developed by Ian Grant (http://people.maths.ox.ac.uk/ipg/) and his collaborators was revised to a similar structure for large-scale calculations with the help of Farid Parpia and Per Jönsson (http://homeweb.mah.se/~tspejo/index.htm) . Modules for hyperfine structure and specific mass calculations were added. Biorthonormal transformations were implemented for transition probability calculations. Further developments are in progress for both ATSP and GRASP.