

## Scientific Report

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# Positron scattering off polyatomic molecules with the *ab initio* R-matrix method

computer implementation and study of the  
correlation polarization potential

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## Purpose of the visit

The purpose of the visit in the group of Prof. Jonathan Tennyson at the University College London (UCL) was to re-implement positron molecule scattering into the polyatomic part of the UK molecular R-Matrix program package [1]. Furthermore some simple applications have been planned including a study of the correlation polarization potential.

## Discription of the work carried out during the visit

The UK molecular R-Matrix program package has been adopted to treat electronic positronic wavefunctions. The major changes include the two modules CONGEN and SCATCI . The program CONGEN generates the configurations from orbital occupation patterns provided by the user. The program SCATCI builds up the Hamilton matrix and diagonalizes it. Furthermore SCATCI writes out the informations to build up the R-matrix.

In contrast to electron molecule scattering calculations a number of additional integrals are needed to describe the positron nuclei attraction integrals, the positron kinetic energy integrals and the positron electron attraction integrals. These integrals can be build up from the corresponding electronic integrals as processed by the MOLECULE program package[2, 3]. The data flow between the affected modules is scetched in figure 1.

The total wavefunction to describe  $N$  electrons and one positron is given by

$$\Psi = \sum_{Ik} a_{Ik} \Theta_I(\mathbf{x}_1, \dots, \mathbf{x}_N) F_k(\mathbf{x}_p) + \sum_{Jk} b_{Jk} \Lambda_J(\mathbf{x}_1, \dots, \mathbf{x}_N) F_k(\mathbf{x}_p) \quad (1)$$

Here the first sum runs over all direct products of target states  $\Theta_I$  with the positron function. The second sum includes all configurations  $\Lambda_J$  that are necessary to describe the polarization and correlation effects arising from the positron.  $a_{Ik}$  and  $b_{Jk}$  are the corresponding coefficients. The positron wavefunction  $F_k(\mathbf{x}_p)$  is described by the set  $\{\phi_i\}$  of target electronic orbitals and by the set  $\{f_j\}$  of continuum orbitals

$$F_k(\mathbf{x}_p) \in \{\phi_i\} \cup \{f_j\}. \quad (2)$$

The target electronic orbitals are represented by Gaussian Type Orbitals (GTOs). The continuum orbitals are represented by GTOs within the R-matrix sphere and by Bessel-functions outside the sphere.

The accuracy of the calculation mainly depends on the number of terms in the expansion of the wavefunction in equation 1. The SCATCI algorithm employs the structure of the scattering wavefunction in order to allow for a very efficient construction of the matrix elements of the Hamiltonian [4]. The matrix element are given by

$$H_{Ik,I'k'} = \langle I, k | \hat{H} | I'k' \rangle \quad (3)$$

$$= \sum_{\alpha} C_{Ik,I'k'}^{\alpha} X(I_{Ik,I'k'}^{\alpha}) \quad (4)$$

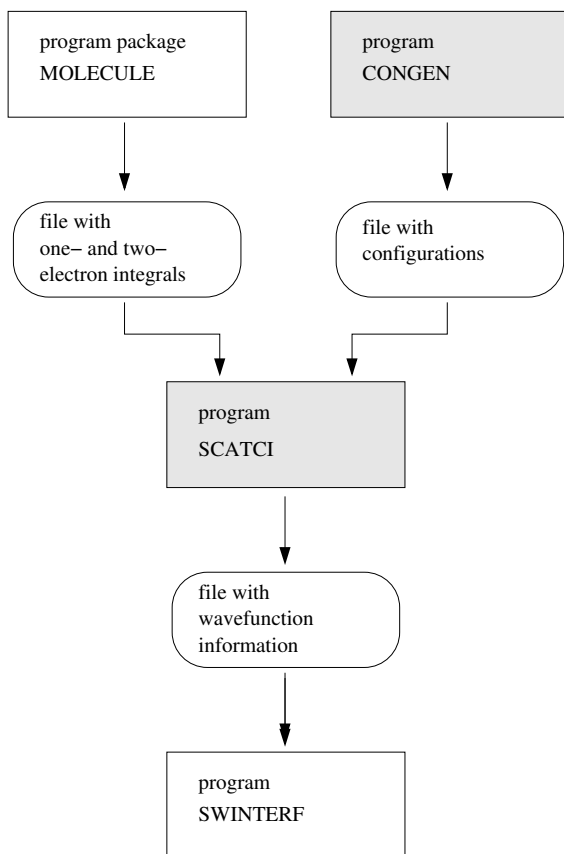


Figure 1: Some parts of the UK molecular R-Matrix program package are shown. The programs CONGEN and SCATCI (shaded boxes) have been modified.

Here  $|Ik\rangle = |I\rangle|k\rangle$  denotes a product of an  $N$  electron wavefunction ( $|I\rangle \in \{\Theta_I\} \cup \{\Lambda_I\}$ ) and one positron wavefunction ( $|k\rangle \in \{F_k\}$ ).  $C_{ij,i'j'}^\alpha$  are coefficients and  $X(I_{ij,i'j'}^\alpha)$  are the integrals of the one and two particle operators of the hamiltonian.  $I_{ij,i'j'}^\alpha$  are indices calculated from the orbital numbers to address the integrals in the integral array. The indexing of integrals that contain only contributions from electronic orbitals is not changed. The integrals for the kinetic energy of the positrons and the positron nuclei repulsion are given by

$$(\bar{a}|\bar{b}) = \int \bar{\phi}_a(\mathbf{x}_1) \left( -\frac{1}{2}\nabla^2 - \sum_A \frac{1}{|\mathbf{R}_{A1}|} \right) \bar{\phi}_b(\mathbf{x}_1) d\mathbf{x}_1 \quad (5)$$

$$= \int \phi_a(\mathbf{x}_1) \left( -\frac{1}{2}\nabla^2 + \sum_A \frac{1}{|\mathbf{R}_{A1}|} \right) \phi_b(\mathbf{x}_1) d\mathbf{x}_1 \quad (6)$$

Here the overbar designates positronic orbitals. The same functions are used for positrons and the electrons. The two contributions to the integrals are calculated

by the routines of the MOLECULE program package and are summed together in the SCATCI program. The integrals are stored and addressed in the same way as the corresponding electronic integrals. The addressing is done by a mapping of the positronic orbital numbers onto the equivalent electronic orbital numbers and calculating the index.

The integrals for the positron electron attraction can be calculated from the electron electron repulsion integrals by changing the sign.

$$(ab|\bar{c}\bar{d}) = \int \phi_a(\mathbf{x}_1)\phi_b(\mathbf{x}_1) \left( +\frac{1}{|\mathbf{r}_{12}|} \right) \bar{\phi}_c(\mathbf{x}_2)\bar{\phi}_d(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (7)$$

$$= - \int \phi_a(\mathbf{x}_1)\phi_b(\mathbf{x}_1) \left( +\frac{1}{|\mathbf{r}_{12}|} \right) \phi_c(\mathbf{x}_2)\phi_d(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (8)$$

$$= -(ab|cd) \quad (9)$$

These integrals are already stored in memory. As for the one-particle integrals the addressing is done by mapping first the positron orbital number onto the electron orbital number and subsequently calculating the index. The change of the sign is taken care of in changing the sign of the corresponding coefficient  $C_{Ik,I'k'}^\alpha$  in equation 4.

In the programs CONGEN and SCATCI several changes have been introduced in order to generalize the input, to perform the mapping of the orbitals and to keep track of the additional informations.

## References

- [1] LA Morgan, J Tennyson, and CJ Gillan. The UK molecular R-matrix codes. *Comput. Phys. Commun.*, 114:120–128, 1998.
- [2] J Almlöf and PR Taylor. In CE Dyskstra, editor, *Advanced Theories and Computational Approaches to the Electronic Structure of Molecules*. Reidel, Dordrecht, 1984.
- [3] J Almlöf and PR Taylor. In E Clementi, editor, *Modern Techniques in Computational Chemistry: MOTTECC-91*. Escom, Leiden, 1991.
- [4] J Tennyson. A new algorithm for Hamiltonian matrix construction in electron-molecule collision calculations. *J. Phys. B: At. Mol. Phys.*, 29:1817–1828, 1996.

## Description of the main results obtained

The implementation has been finished. The program can be used to calculate positron scattering from polyatomic molecules. The scattering process may include polarization and correlation effects. Furthermore the program is capable to

calculate positron bound states of molecules. The modified programs are part of the UK molecular R-Matrix program package and will be made freely available.

### **Future collaboration with host insitution**

I have started to work as Post-Doctoral Research Associate in the group of Prof. J. Tennyson at UCL in October 2005 on positron annihilation in molecules. The project will be funded by the EPSRC for a period of three years.

### **Projected publications/articles resulting or to result from the grant**

A paper on positron scattering off acetylene in the static approximation will be send for publication later this year. It will published together in collaboration with Prof. Gianturco and will deal with a comparison between the results obtained with the R-matrix method and with the single center expansion (sce) method of Prof. Gianturco's group (University of Rome).

We have done all necessary computer implementations into the UK molecular R-matrix program package. The program package is supplied by the EIPAM node at the University College London (UCL). Furthermore the UCL will make the resulting program codes freely available through the UK molecular R-matrix codes web page ([www.tampa.phys.ucl.ac.uk/rmat](http://www.tampa.phys.ucl.ac.uk/rmat)).

### **Other comments**

The original work plan covered a period of six months. We have shortened it to three months. While most of the implementation has been finished, we could not finish the model applications and the studies of the correlation polarization potential.

Parts of the implementation has been done by Prof. K.L. Baluja from the University of Dehli, who has joined the UCL group in the period from May to July 2005. He has implemented the routines to read the modified integrals and has provided a first version of the code.