

# Combining UNICHEM and Electron Momentum Spectroscopy to Study Valence Electronic Structure of Molecules

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## ABSTRACT:

We report on utilization of UniChem computational chemistry codes to help elucidate the valence electronic structure of molecules. The experimental ( $e,2e$ ) coincidence spectroscopy, known as electron momentum spectroscopy (EMS), provides detailed binding energy spectra and orbital momentum distributions. The Flinders-developed AMOLD program computes the angle-averaged molecular structure factor for each orbital. The necessary theoretical input for AMOLD is extracted from the UniChem ab-initio code DGauss.

Our effort to incorporate AMOLD into the UniChem interface is summarized. With the modelling and computation machinery available through UniChem and AMOLD we use standard UniChem features to build the molecule, to minimize the total energy, and to provide input (coordinates and molecular orbitals) to AMOLD computations of the scattering intensity for a range of momenta  $q$ .

The method is illustrated by the results for [1.1.1] propellane.

## I. INTRODUCTION

Electron Momentum Spectroscopy is a coincidence technique involving the complete kinematic determination of high-energy electron impact ionization processes at large momentum transfer under binary encounter conditions [1-4]. We anticipate that EMS will provide specific electron-density information on the reactive portions of the total charge distribution. Combined with the Density Functional Theory method of computation of the electronic density it will provide a very accurate testing method for the quality of the basis sets as well as the state-of-the-art method of determination of the geometry, electronic structure, energy eigenvalues and related molecular properties.

## II. ELECTRON MOMENTUM SPECTROSCOPY

At high enough energy and momentum transfer an ionization reaction cleanly removes an electron from a molecule. The momentum of the knocked-out electron at the instant of ionization is  $q$ :  $q = k_A + k_B - k_0$ . The separation energy of the electron is  $E$ :  $E = E_0 - E_A - E_B$  (see the diagram below).

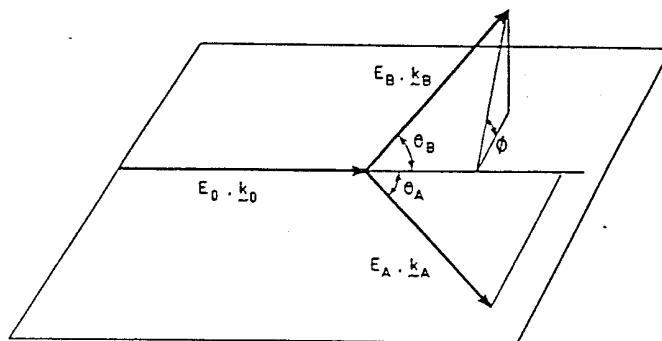


FIG. 1. Definition of the kinematic variables in the ionization reaction.

The experiment measures the momentum distribution of electrons for each separation energy:  $P_E(q)$ .

In the independent particle model each electron is represented by a molecular orbital  $\Psi_i(\mathbf{r})$ . The momentum distribution is given by the square of the molecular orbital in momentum space. Since molecules are randomly oriented the momentum distribution is an angular average

$$P_E(q) = (4\pi)^{-1} \int d\hat{q} |\Psi_i(\mathbf{q})|^2 \quad (2.1)$$

where

$$\Psi_i(\mathbf{q}) = (2\pi)^{-3/2} \int d\mathbf{r} \exp\{-i\mathbf{q} \cdot \mathbf{r}\} |\Psi_i(\mathbf{r})|^2 \quad (2.2)$$

Verification for the hydrogen atom is presented in Fig. 2.

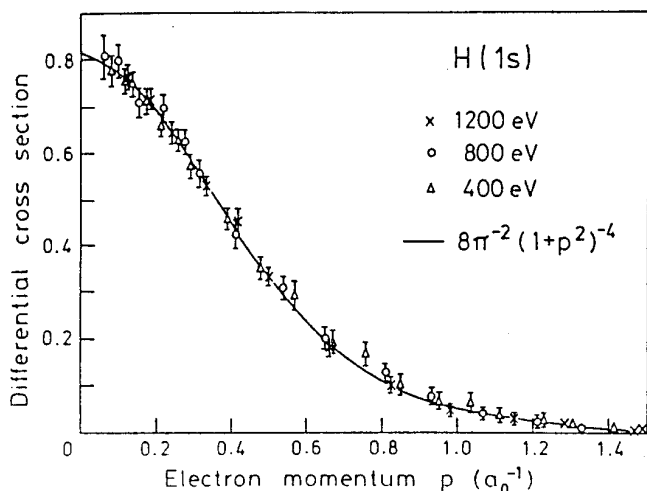


FIG. 2. Momentum distributions for atomic hydrogen measured at different incident energies, compared with the analytic solution.

The schematic of the Electron Momentum Spectroscopy experimental set-up is shown in Fig. 3.

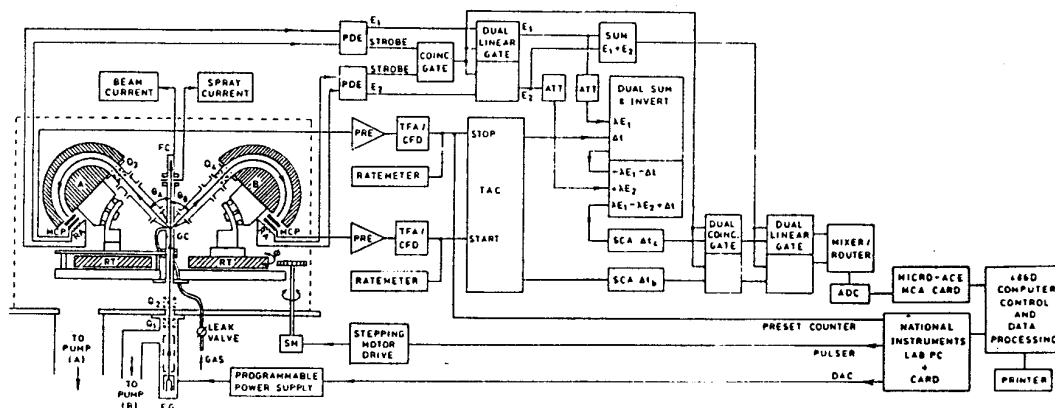


FIG. 3. Experimental set-up for the Electron Momentum Spectroscopy of molecules at The Flinders University of South Australia.

### III. DENSITY FUNCTIONAL THEORY AND UNICHEM

Density Functional Theory (DFT) was developed in the context of solid state physics in the mid-sixties [5,6]. The two main statements of the theory are formulated as the two Hohenberg-Kohn theorems. One states that the

total energy of the electronic system can be expressed as a unique functional of the electronic density (3-D quantity, instead of  $N$  wave functions for all the electrons); the other theorem states that the energy functional is minimized by the true electronic density corresponding to the ground state of the system. In practice the energy functional is minimized by the self-consistent procedure with the help of so-called Kohn-Sham equations [6]. The main points to note here are: i) the DFT is finding wider acceptance in the studies of atoms and molecules [7,8], ii) the total energy expression includes electronic exchange and correlation terms, iii) the method is applicable to covalent, ionic and metallic systems, iv) the computational complexity (scaling) is  $N^3$ , which is much better than the traditional SCF Hartree-Fock method and will allow *ab initio* studies of larger molecules. More on the DFT can be found in the original papers as well as in Refs. [7-11].

*UniChem* is a suite of computational quantum chemistry programs from Cray Research, Inc. [12,13]. It includes the semi-empirical MNDO93 program, SCF Hartree-Fock program CADPAC and the DFT program, developed in Cray Research by Jan Andzelm and co-workers, DGauss. In our studies we use the DFT method and DGauss program. The zeroth order electronic dens-

ity in a molecule is constructed in DGauss from the linear combination of atomic Gaussian orbitals. Upon completion of the run the DGauss gives the minimized energy of a system, the molecular orbital parameters and the many molecular properties derived from it. The coordinate space molecular orbital at the energy minimum is then treated as an input to the Flinders-written AMOLD program which computes the momentum-space spherically-averaged molecular structure factor. This quantity is in turn directly comparable to the scattering cross section in the ( $e, 2e$ ) experiment.

#### IV. TEST STUDIES AND CONCLUSIONS

As part of our programme to extend the technique of Electron Momentum Spectroscopy to larger molecules of chemical and biological interest we have performed a prototypical study on the [1.1.1] propellane ( $C_5H_6$ ) system. The EMS experimental side of this work has been completed (Fig. 4).

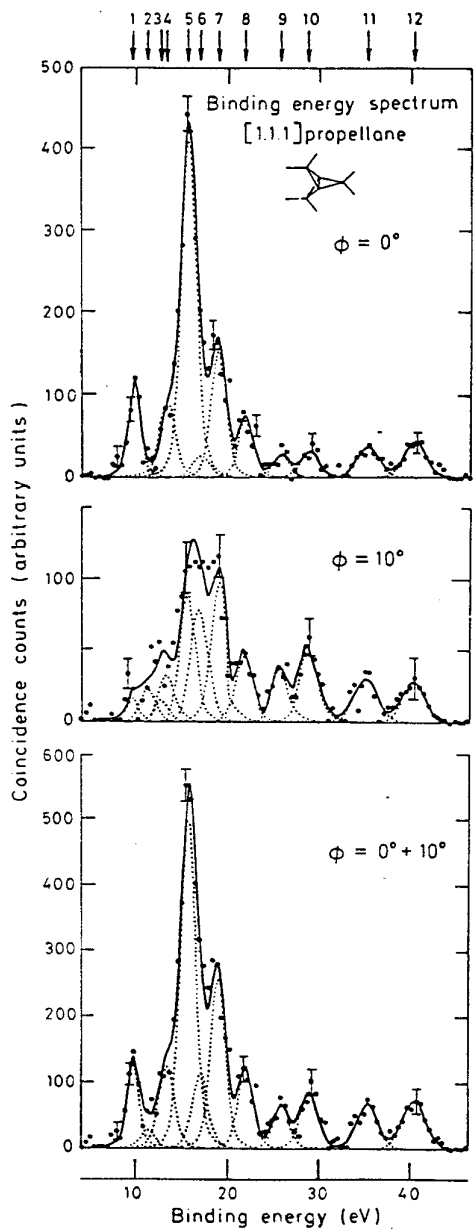


FIG. 4. The 1000eV noncoplanar symmetric EMS separation energy spectra of [1.1.1] propellane at  $\phi = 0^\circ$ ,  $\phi = 10^\circ$  and  $\phi = 0^\circ + 10^\circ$ . The curves show the fitted spectra using the known energy resolution function.

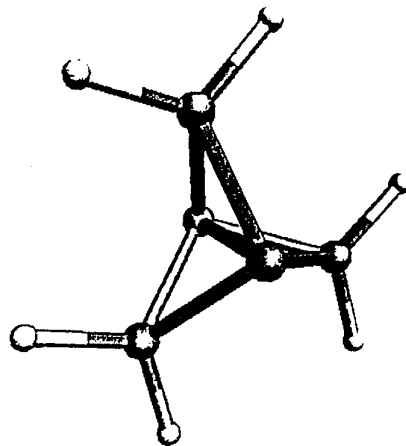


FIG. 5. Energy minimized ball and stick model of [1.1.1] propellane  $C_5H_6$  obtained using *UniChem* DGauss and the DZVP2 basis set.



FIG. 6. 3-D representation of the total electron density obtained using *UniChem* DGauss and the DZVP2 basis set. The bridge bond has low electron density.

Figures 5 and 6 represent the [1.1.1] propellane molecule at the minimum energy computed using the DZVP2 basis set. Now we are fine tuning the optimum theoretical wavefunction with our AMOLD/*UniChem* package on the CSIRO CRAY supercomputer (Figs. 7, 8 and 9.) [14,15].

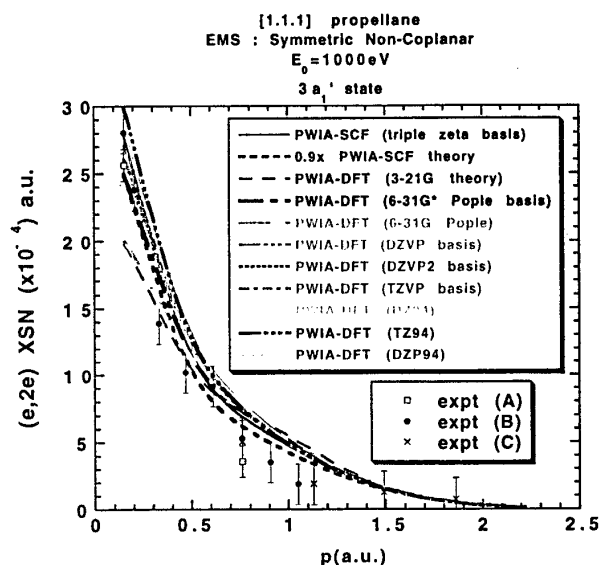


FIG. 7. The 1000eV noncoplanar symmetric momentum profile for  $3a_1'$  state of [1.1.1] propellane.

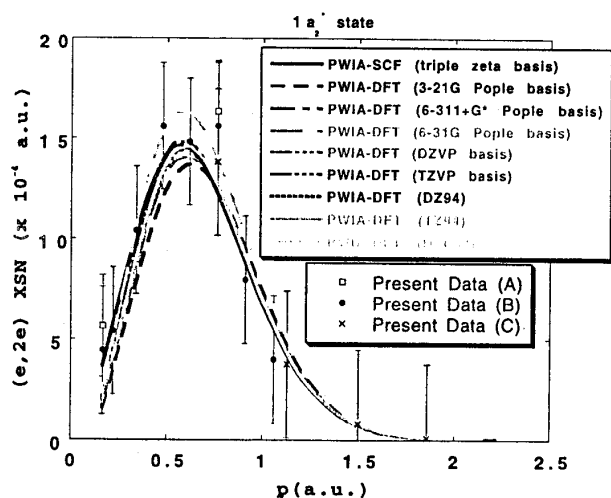


FIG. 8. The 1000eV noncoplanar symmetric momentum profile for  $1a_2''$  state of [1.1.1] propellane.

This work will be further extended by the substitution of *Cl*, *F* and *Br* radicals on the main carbon superstructure. Hence we will be able to experimentally and theoretically study the whole series of organic compounds  $C_5H_6$ ,  $C_5H_5Cl$ ,  $C_5H_5Br$ ,..... The beauty of these experiments is that using standard organic synthesis techniques (in collaboration with Dr W.Adcock) and analysis tools for confirmation (e.g. NMR) our organic colleagues can produce a range of compounds where the radical substitution is *site-specific*. Consequently, we will not only be able to investigate the quality of the molecular wavefunctions we "build" but we will also be able to test for the sensitivity of the EMS technique to site-selectivity in

radical substitution. The importance of having such a predictive tool at the microscopic level for e.g. the drug industry, is transparent.

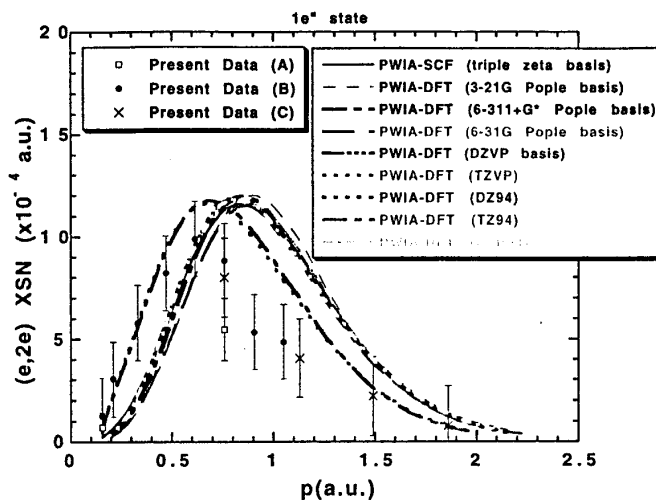


FIG. 9. The 1000eV noncoplanar symmetric momentum profile for  $1e''$  state of [1.1.1] propellane.

#### ACKNOWLEDGMENTS

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