THEORETICAL STUDIES OF ATOMIC TRANSITIONS

Progress Report

Period: April 1, 1990 - March 31, 1991

Charlotte FROESE FISCHER

Professor of Computer Science, Mathematics, Chemistry, and Physics

Vanderbilt University

Nashville, Tennessee 37235 USA

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

October, 1990

Prepared for the U.S. Department of Energy

under grant number DE-FG05-88ER13867

MASTER

000 1 8 1990

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Research Progress Report

Research during the 1990-91 year has centered on several activities. Each will be discussed separately.

1. Lifetimes of excited states.

The core-excited states of Na I-like ions have been investigated lately, both experimentally and theoretically. The main motivation has been finding candidates for XUV-lasers¹, but they also are of theoretical interest due to their metastability. Competing decay modes make it possible to investigate the accuracy of lifetime calculations, including both autoionisation and optical decays. So far, mainly the lower lying configurations in Na I and Mg II have been identified. Earlier calculations for the quartet levels of these systems have been extended to Al III and, in collaboration experimentalists at the University of Aarhus, Denmark, and Stockholm, Sweden, a level scheme involving quartet levels of the $2p^5 3s 3p$, $2p^5 3p^2$, and $2p^5 3s 3d$ has been established. Autoionization is the dominant decay channel for the levels belonging to the latter two configurations and only for a few levels of these terms is the dominant decay mode an optical transition to a $2p^5 3s 3p$ level. A paper on this work will appear shortly².

In beam-foil spectra of magnesium, there still remain a number of unidentified lines, especially in the region between 2500–4000 Å, which could be attributed to transitions between core-excited states of Mg II³. We have turned our attention to the *second generation* of states, namely $2p^5 \{3s 4f, 3p 3d\}$ as possible candidates for these features. From a study of transitions and autoionization rates, lifetimes have been predicted for many of the levels. Because of the close degeneracy and low populations, the line rich spectra are difficult to analyze. No levels have yet been confirmed and we are awaiting a more detailed analysis of the spectra.

In parallel with this work, calculations were also performed for the high-spin states of Mg I. When this project was started, the quintet system of Mg I was completely unknown. With the support of our theoretical calculations, the experimental group at Aarhus has now identified the $2p^5 3s 3p^2 \ ^5P_3$, $\ ^5D_4$ and $2p^5 3s 3p 4s \ ^5D_4$, $\ ^5P_3$ levels. A paper on this work has been accepted for publication⁴.

2. Core-polarization Studies

The MCHF prediction⁵ of the electron affinity for Ca was in better agreement with experiment⁶ than expected from the theory. Indeed, a more "accurate" calculation⁷ increased the binding of the 4p electron in Ca⁻, resulting in a greater discrepancy between theory and experiment. Omitted from these studies was the effect of correlation with the core, or core-polarization. Studies with quantum chemical codes predict that the binding decreases when core-polarization is included, that the resulting electron affinity so small as to make the prediction of a bound state inconclusive⁸. Large, variational studies of Ca⁻ have been undertaken which include the interaction with the 3p⁶ subshell, but difficult problems were encountered and results are not yet available.

In the meantime, a study in collaboration with M. Godefroid and N. Vaeck at the University of Brussels (facilitated by a NATO grant for travel), has been undertaken in which the effect of core-polarization is included through a modification of the potential of the form

$$V_{CP} = -\frac{1}{2}\alpha \frac{r^2}{(r^2 + r_c^2)^3}.$$

When applied to Ca⁻, the method was found to be unstable. To gain a better understanding of the reliability of this approach a careful comparison was made between *ab initio* core-polarization calculations and the modified potential approach. The latter also requires a modification of the transition operator.

Table 1. compares some oscillator strengths in Ca⁺. The *ab initio* methods MCHF-CV_{1,2} include correlation between the outer electron and the 3p⁶ core and differ only in the way the core orbitals were obtained; MCHF-CV₃ also includes those core-valence correlation configuration states from the 1s²2s²2p⁶3s² core that make a direct contribution to the oscillator strength. On the whole there is not a great deal of difference, though MCHF-CV₃ is expected to be the most accurate. MP₁ is based on the modified potential used as a correction after the orbitals have been obtained, whereas MP₂ includes the modified potential at the variational stage when orbitals are determined; MP₃ is like MP₂ but adjusts the value of r_c . Clearly the latter two are in much better agreement with the *ab initio* calculations. A paper on this work is in preparation⁹. Further studies are needed to assess the reliability of the approach in complex situations.

4. Large relativistic calculations

Relativistic calculations for the lanthanides or actinides, where states have partially filled *f*-shells, lead to large wave function expansions. A case of interest is the mixing of 4f⁷(⁸S)5d²6s

Table 1 : Oscillator strengths of E1 and E2 transitions in Ca^+

	HF(FC)	MCHF-CV ₁	MCHF-CV ₂	MCHF-CV ₃	MP ₁	MP ₂	MP ₃
$4s^2S - 4p^2P^o$							
gf _L	2.38	1.88	1.9826	1.9803	2.1456	2.0378	1.9189
gf _V	1.87	2.07	2.0623	2.1015	—	—	—
$4s^2S - 3d^2D$							
gf _L (10 ⁻⁷)	1.01	0.62	0.6732	0.6723	0.9945	0.7021	0.6849
gf _V (10 ⁻⁷)	2.15	0.49	0.6497	0.6786	—	—	—
$3d^2D - 4p^2P^o$							
gf _L	0.98	0.57	0.6376	0.6377	0.9147	0.6629	0.6625
gf _V	0.004	0.79	0.8260	0.6777	—	—	—

and $4f^7(^8S)5d6s^2 J=5$ levels of Gd. The J-dependent mixing of the levels is predicted to affect the hyperfine structure. Such calculations have never been attempted because of the large interaction matrices that need to be diagonalized. Similarly, configuration interaction of $5d^{10}5f^26s^26p^6$ with $5d^85f^46s^26p^6$ in U^{+4} has not been investigated. The Davidson algorithm for the large, sparse interaction problem, has been installed into the most recent version of the relativistic program, GRASP-2¹⁰, though problems still remain in the final Breit energy analysis. In large calculations, selecting appropriate dimensions is virtually impossible since problems grow in unexpected ways. For this reason, dynamic memory allocation was added to the code so that arrays could be increased at execution time. This implementation is in the process of being tested.

4. MCHF Atomic Structure Package (MCHF ASP)

Over the years, the MCHF atomic structure software for wave functions, energy levels, and transition probabilities has been organized into an atomic structure software package, capable of predicting a variety of atomic properties. The last year has seen a considerable effort in writing up the basic package for publication in *Computer Physics Communication* and its distribution by the *CPC Program Library*.

The package is designed around a library supporting a series of programs, each performing a specific task. Many of the programs have been developed with different collaborators and so the package is described by a series of papers — an overview¹¹, a description of the library and some basic utilities¹², and seven programs¹²⁻⁻¹⁹. These have been submitted for publication,

and hopefully will appear in a single issue of the journal. Not included in the basic package are programs for the specific mass shift, field shift, autoionization rates/line widths, and hyperfine interactions for which codes are in development.

The programs as submitted to CPC are dimensioned for moderately sized problems. By making dimensions larger, they can also be used for larger problems requiring the use of the Cray. However, unlike systems like the VAX, the Cray is not a virtual memory machine. The dimensions are not allowed to exceed the memory capacity of the machine. Of course, it is possible to transfer to a Cray 2 with a larger memory, but response time is greatly affected by memory size. Both Sun and Cray computers now have compilers that support dynamic memory allocation. Thus it is possible to write programs requesting only as much memory as needed. Most of the programs have been converted in this manner, but a few still require further testing. Sparse matrix versions also have been developed.

However, in spite of these improvements which greatly improve the efficiency with which large-scale calculations can be performed, convergence difficulties are encountered when the effect of core-polarization is included in an *ab initio* manner in calculations such as those for Ca^+ where wave function expansions are in the range of 2,000 – 3,000 configuration states. In large calculations, stability and a rapid rate of convergence are extremely important. Preliminary tests have indicated that such improvements are possible if the underlying numerical "technology" of finite differences is replaced by one built on spline approximations, provided also that the self-consistent field (SCF) iterative process is abandoned. Such algorithms have better vector/concurrent performance as well²⁰.

The spline approach has been tested for the study of photoionization of He^{21} . Further work is planned on integrating continuum wave functions into the MCHF package. Once the wave functions have been determined, a number of processes may be investigated.

4. MCHF Codes for the Hypercube

It is generally believed that the supercomputers of the future will not be vector processors like the CRAY which has a few very fast processors, but parallel computers with many, albeit slower, processors. Certainly, computers in the latter category will make it possible for small groups to perform large-scale calculations on computers in a dedicated mode, not shared by many users competing for the same resource as is necessary on Cray computers.

In this connection, a project was undertaken to see how the MCHF atomic structure software

Table 2: Node timing data for angular integrations on the Intel iPSC/2 at Oak Ridge. Execution was timed in different ways as indicated by the symbols:

i - initialize the calculations

r - receive data from the host

c - compute

s - sort the generated data

z - send data to the host

Node timing for $nonhHN$, $M = 410$			
<i>nnodes</i>	<i>ics</i>	<i>rics</i>	<i>ricsz</i>
8	209.170—219.820	209.183—219.833	211.875—725.221
	209.183—219.773	209.196—219.786	216.775—1012.332
16	102.232—115.977	102.245—115.990	102.946—674.741
	102.233—115.959	102.246—115.972	102.961—669.967
32	46.154—65.505	46.167—65.518	46.571—654.615
	46.223—65.498	46.236—65.511	47.005—702.382
	46.161—65.536	46.174—65.549	46.709—659.779

could be adapted to the distributed memory environment of a hypercube²². The angular integrations for interactions were easy to implement and, as Table 2. shows, the decrease in time is close to the theoretical speed-up. The timing data was obtained from an iPSC/2 with 4Mbytes per node and at least 8 nodes were required to satisfy basic memory requirements of this case with $M = 410$ configuration states in the wave function expansion. The ratio of time with 8 nodes compared with 32 nodes is between 3.36 and 4.5 which is excellent. For MCHF, the distribution of the tasks was not as straight forward and was dictated by the distribution of the data into available memory. Not nearly as good performance was achieved – increasing the number of nodes by a factor of 8 only halved the execution time. Clearly the latter is a more challenging problem and further studies would like to be undertaken.

References

* Papers listed with titles are papers submitted for publication or technical reports prepared as part of the current research.

- [1] D.E. Holmgren, D.J. Walker, D.A. King and S.E. Harris, Phys. Rev. A **31** 677 (1985).
- [2] J.O. Gaardsted, T. Brage, C. Froese Fischer, and D. Sonnek, *Experimental and theoretical study of core-excited states of Al III*, (to appear in Physica Scripta) (1990).
- [3] J.O. Gaardsted, T. Andersen, D. Sonnek, S. Mannervik and R.T. Short, Physica Scripta **38** 27 (1988).
- [4] T. Andersen, J.O. Gaardsted, L. Sorenseni, and T. Brage, *Search for an optical transition in the negative magnesium ion*, Phys. Rev. A. (accepted) (1990).
- [5] C. Froese Fischer, J.B. Lagowski, and S.H. Vosko, Phys. Rev. Lett. **59**, 2263 (1987).
- [6] D.J. Pegg, J.S. Thompson, R.N. Compton, and G.D. Alton, Phys. Rev. Lett. **59**, 2267 (1987).
- [7] C. Froese Fischer, Phys. Rev. A **39**, 963 (1989).
- [8] P. Fuentealba, A. Savin, H. Stoll, and H. Preuss, Phys. Rev. A **41**, 1238 (1990).
- [9] C. Froese Fischer, M. Godefroid, and N. Vaeck, *Core-valence correlation in Ca II*, (in preparation).

- [10] F.A. Parpia, I.P. Grant, and C. Froese Fischer (in preparation).
- [11] C. Froese Fischer, *The MCHF Atomic Structure Package*, (submitted to Comp. Phys. Commun.) (1990).
- [12] C. Froese Fischer, *MCHF Atomic Structure Package: Support Libraries and Utilities*, (submitted to Comp. Phys. Commun.) (1990).
- [13] C. Froese Fischer and B. Liu, *A Program to Generate Configuration State Lists*, (submitted to Comp. Phys. Commun.) (1990).
- [14] A. Hibbert and C. Froese Fischer, *A General Program for Computing Angular Integrals of the Non-relativistic Hamiltonian with Non-orthogonal Orbitals*, (submitted to Comp. Phys. Commun.) (1990).
- [15] C. Froese Fischer, *A General Multiconfiguration Hartree-Fock Program*, (submitted to Comp. Phys. Commun.) (1990).
- [16] A. Hibbert, R. Glass, and C. Froese Fischer, *A General Program for Computing Angular Integrals of the Breit-Pauli Hamiltonian*, (submitted to Comp. Phys. Commun.) (1990).
- [17] C. Froese Fischer, *A Configuration Interaction Program*, (submitted to Comp. Phys. Commun.) (1990).
- [18] C. Froese Fischer, M. R. Godefroid, and A. Hibbert, *A Program for Performing Angular Integrations for Transition Operators*, (submitted to Comp. Phys. Commun.) (1990).
- [19] C. Froese Fischer and M. R. Godefroid, *Programs for computing LS and LSJ transitions from MCHF Wave Functions*, (submitted to Comp. Phys. Commun.) (1990).
- [20] C. Froese Fischer, *Vector Concurrent Algorithms for the Helium pair equation*, Int'l J. Supercomputer Appl. (accepted).
- [21] C. Froese Fischer and M. Idrees, *Spline Methods for resonances in photoionization cross-sections*, J. Phys. B: **23**, 679 – 691 (1990).
- [22] M. Bentley and C. Froese Fischer, *Hypercube Conversion of Serial Codes for Atomic Structure Calculations*, Technical Report, DOE/ER/13867-7 (1990)

- END -

DATE FILMED

11 / 05 / 90