AIP | Conference Proceedings

Accurate transition probabilities from large-scale multiconfiguration calculations - A tribute to Charlotte Froese Fischer

Per Jönsson, Michel Godefroid, Gediminas Gaigalas, Jacek Bieroń, and Tomas Brage

Citation: [AIP Conf. Proc.](#) **1545**, 266 (2013); doi: 10.1063/1.4815863

View online: <http://dx.doi.org/10.1063/1.4815863>

View Table of Contents: <http://proceedings.aip.org/dbt/dbt.jsp?KEY=APCPCS&Volume=1545&Issue=1>

Published by the [AIP Publishing LLC](#).

Additional information on AIP Conf. Proc.

Journal Homepage: <http://proceedings.aip.org/>

Journal Information: http://proceedings.aip.org/about/about_the_proceedings

Top downloads: http://proceedings.aip.org/dbt/most_downloaded.jsp?KEY=APCPCS

Information for Authors: http://proceedings.aip.org/authors/information_for_authors

ADVERTISEMENT

Submit Now

Explore AIP's new open-access journal

- Article-level metrics now available
- Join the conversation! Rate & comment on articles

Accurate Transition Probabilities from Large-Scale Multiconfiguration Calculations – a Tribute to Charlotte Froese Fischer

Per Jönsson*, Michel Godefroid[†], Gediminas Gaigalas**, Jacek Bieroń[‡]
and Tomas Brage[§]

*Group for Materials Science and Applied Mathematics, School of Technology, Malmö University, Sweden

[†]Chimie Quantique et Photophysique, CP160/09, Université Libre de Bruxelles, Brussels, Belgium

**Vilnius University, Institute of Theoretical Physics and Astronomy,
A. Goštauto 12, LT-01108 Vilnius, Lithuania

[‡]Instytut Fizyki imienia Mariana Smoluchowskiego, Uniwersytet Jagielloński, Reymonta 4,
30-059 Kraków, Poland

[§]Department of Physics, Lund University, Sweden

Abstract. The development of multiconfiguration computer packages for atomic structure calculations is reviewed with special attention to the work of Charlotte Froese Fischer. The underlying theory is described along with methodologies to choose basis expansions of configuration state functions. Calculations of energies and transitions rates are presented and the accuracy of the results is assessed. Limitations of multiconfiguration methods are discussed and it is shown how these limitations can be circumvented by a division of the original large-scale computational problem into a number of smaller problems.

Keywords: atomic structure, transition rates, multiconfiguration Hartree-Fock, multiconfiguration Dirac-Hartree-Fock

PACS: 31.15.A-, 31.15.V-, 32.70.Cs

INTRODUCTION

The quality and resolution of solar, stellar, and other types of plasma observations, have so improved that the accuracy of atomic data is frequently a limiting factor in the interpretation of these new observations. An obvious need is for accurate transition probabilities. Laboratory measurements, e.g. using ion/traps, beam-foil or laser techniques, have been performed for isolated transitions and atoms, but no systematic laboratory study exists or is in progress. Instead the bulk of these atomic data must be calculated. Multiconfiguration methods, either non-relativistic with Breit-Pauli corrections (MCHF+BP) or fully relativistic (MCDHF), are useful to this end. The main advantage of multiconfiguration methods is that they are readily applicable to excited and open-shell systems, including open f -shells, across the whole periodic table, allowing for mass production of atomic data. The accuracy of these calculations depends on the complexity of the atomic shell structure and on the underlying model for describing electron correlation. By systematically increasing the number of basis functions in large-scale calculations, as well as exploring different models for electron correlation, it is often possible to provide both transition energies and transition probabilities with some error estimates.

The success of atomic structure calculations also depends on available computer software. In this paper we describe the development of multiconfiguration computer packages, new numerical methods, and strategies of large-scale calculations with reference to Professor Charlotte Froese Fischer's work. At the end we discuss limitations of current multiconfiguration methods and we point to ways of circumventing these limitations by a division of the original large-scale computational problem into a set of smaller problems according to the Computer Science paradigm "Divide and Conquer".

COMPUTATIONAL ATOMIC STRUCTURE

Influenced by Louis de Broglie's hypothesis of the wave properties of matter, Schrödinger in 1926 formulated an equation for these matter waves and applied it to the hydrogen atom [1]. Schrödinger's equation is valid for any atom or molecule, but the practical difficulties of solving the equation for many-electron systems are, however, significant. Computational atomic structure can be said to have started already in 1928 when D.R. Hartree derived an equation for a many-electron system, where each electron moves in a central field due to the nucleus and to the charge distribution of all other electrons in the system, averaged over the sphere for each radius [2]. The wave functions that came out as solutions to Hartree's equation did not satisfy the Pauli exclusion principle but, as shown by Fock [3], this limitation could be overcome by adding an extra term for electron exchange and the resulting equation is known as the Hartree-Fock (HF) equation. Hartree continued to solve the HF equation for several systems during the next decade. These were hand calculations aided by mechanical machines.

Hartree-Fock is an approximation where the electron interaction is averaged. As the next step in the development many-body effects arising from the direct interaction between the electrons were included, and in 1935 Hartree et al. performed calculations with a superposition of configurations [4]. This was the first multiconfiguration Hartree-Fock (MCHF) calculation. Later the importance of many-body effects, called electron correlation effects in atomic theory, was fully recognized, and much of the research efforts were centered around the question how to best account for these effects.

Atomic structure calculations have from the very start been at the computational forefront. With the advent of electronic computers focus was shifted to programs for the solution of the equations and to new numerical techniques. As a PhD student of D.R. Hartree, Charlotte Froese in 1957 wrote a program for solving the wave equation with exchange [5]. The calculations at that time were not fully automated, but the operator monitored the program and made decisions as the calculation proceeded (see figure 1). With increasing computer power attention shifted to many-body effects and correlation and in 1969 Charlotte Froese Fischer published the first multiconfiguration Hartree-Fock (MCHF) program [6]. The program was dimensioned to allow up to five configuration states functions in the expansion. The program had a very large impact on the field and was designated a *Citation Classic* by *Current Contents*. Many calculations at that time were for states lowest of their symmetry, but practical applications were putting demands on excited states and new numerical methods had to be developed [7]. With the numerical procedures in place the development was quite rapid.

FIGURE 1. Charlotte Froese computing on the Electronic Delay Storage Automatic Calculator (EDSAC) at Cambridge.

In 1991 Charlotte Froese Fischer and co-workers published a series of papers in *Computer Physics Communications* that defined the MCHF atomic structure package [8]. The package allowed a number of properties to be computed, such as energy structure, including Breit-Pauli relativistic effects, transition rates and autoionization rates, hyperfine effects and isotope shifts [9, 10, 11, 12, 13, 14]. The atomic structure package opened new possibilities and triggered intense activity. In the following years important results were published in many areas, often in collaboration with experimentalists [15, 16, 17, 18]. The codes of the MCHF atomic structure package were later modified for large-scale computation on parallel systems using Message Passing Interface (MPI) [19]. In addition the algebra underlying the angular integration was improved, and a combination of second quantization in the coupled tensorial form, angular momentum theory in three spaces (orbital, spin and quasispin), and a generalized graphical technique made it possible, for the first time, to perform calculations for systems with open f -shells [20, 21, 22]. The latest release, the ATSP2K package [23], also implements a fast biorthogonal transformation technique that allows the initial and final states in a transition to be independently optimized [24].

In recent years splines have been recognized as a powerful and flexible computational tool and together with Oleg Zatsarinny, Charlotte Froese Fischer combined MCHF with B-spline R-matrix methods [25]. In parallel with these activities, multiconfiguration methods based on the fully relativistic Dirac formalism were developed, with releases of well-known packages such as GRASP92 [26] and GRASP2K [27, 28].

Much of the research activities in computational atomic structure took place in Charlotte Froese Fischer's research group at Vanderbilt University, where many post-docs and graduate students from around the world were invited. In the atmosphere of hard work and high expectations paired with support and encouragement, research was carried out in different fields, but mainly in computer science and code development. Figure 2 is a picture of Charlotte Froese Fischer's research group in 1992.

FIGURE 2. From Charlotte Froese Fischers research group at Vanderbilt University: Ming Tong, Farid Parpia, Charlotte, and Tomas Brage.

In the remaining sections the theory of MCHF calculations will be reviewed and some systematic studies presented for different properties. At the end we will look at new advancements in multiconfiguration methods.

THEORY OF MULTICONFIGURATION CALCULATIONS

The many-electron wave equation can be written

$$H\Psi = E\Psi, \quad (1)$$

where H is the Hamiltonian operator and E the energy. In the non-relativistic formalism (in atomic units), the Hamiltonian operator is

$$H = -\frac{1}{2} \sum_{i=1}^N \left(\nabla_i^2 + \frac{2Z}{r_i} \right) + \sum_{i<j} \frac{1}{r_{ij}}, \quad (2)$$

where Z is the nuclear charge, r_i the distance of the i^{th} electron from the nucleus, and r_{ij} the distance between electrons i and j . The wave function Ψ of the system is an eigenfunction of the total orbital L^2, L_z and spin S^2, S_z momenta and projection operators. In the MCHF method an approximate wave function, $\Psi(\gamma LS)$, for a state labeled γLS is written as an expansion of configuration state functions (CSFs), $\Phi(\gamma_i LS)$, with the appropriate LS symmetry

$$\Psi(\gamma LS) = \sum_{j=1}^M c_j \Phi(\gamma_j LS). \quad (3)$$

Here γ_i represents the configuration and other quantum numbers needed to specify the state i . The CSFs are vector-coupled and antisymmetrized products of one-electron spin-

orbitals

$$\phi(r, \theta, \varphi, \sigma) = \frac{1}{r} P_{nl}(r) Y_{lm_l}(\theta, \varphi) \chi_{m_s}(\sigma), \quad (4)$$

where the spherical harmonics Y_{lm_l} and spinors χ_{m_s} are known. The radial functions, $P_{nl}(r)$, are unknown and should be determined on a grid. Introducing the multipole expansion for $1/r_{ij}$, the total energy of the atom

$$E = \langle \Psi(\gamma LS) | H | \Psi(\gamma LS) \rangle = \sum_{j,k} c_j c_k \langle \Phi(\gamma_j LS) | H | \Phi(\gamma_k LS) \rangle \quad (5)$$

can be expressed as a weighted sum over radial integrals, where the weights of the integrals are products of expansion coefficients and angular factors. Requiring the energy to be stationary with respect to perturbations in the expansion coefficients leads to a matrix eigenvalue problem

$$(\mathbf{H} - E)\mathbf{c} = \mathbf{0}, \quad \text{where } H_{jk} = \langle \Phi(\gamma_j LS) | H | \Phi(\gamma_k LS) \rangle. \quad (6)$$

The stationary condition with respect to variations in the radial functions, in turn, leads to a system of coupled integro-differential equations of the form

$$\left(\frac{d^2}{dr^2} + \frac{2}{r} [Z - Y_{nl}(r)] - \frac{l(l+1)}{r^2} - \epsilon_{nl,nl} \right) P_{nl}(r) = G_{nl}(r) + \sum_{n' \neq n} \epsilon_{nl,n'l} P_{n'l}(r), \quad (7)$$

subject to boundary conditions at the origin and the infinity. The energy parameters $\epsilon_{nl,n'l}$ are related to Lagrange multipliers assuring orthonormality of the radial functions. The equations are iterated until a self-consistent solution is found [29]. In the Breit- Pauli approximation, $\mathbf{L}$ and $\mathbf{S}$ are coupled to form a resultant angular momentum $\mathbf{J}$. In this approximation, the MCHF atomic structure package assumes that the radial functions are known and adopts the following form

$$\Psi(\gamma LSJ) = \sum_{j=1}^M c_j \Phi(\gamma_j L_j S_j J) \quad (8)$$

for the total wave function. In other words, the wave function is a sum of configuration states for possibly different LS terms. The determination of the expansion coefficients is an eigenvalue problem.

EVALUATION OF ATOMIC PROPERTIES

Once the wave functions have been determined, measurable properties like hyperfine structures and isotope shifts can be expressed as sums of reduced matrix elements of tensor operators between CSFs in the wave function expansion. The reduced matrix elements, in turn, can be obtained as a sum over radial integrals.

The evaluation of radiative transition data (transition probabilities, oscillator strengths) between two states $\gamma' L' S' J'$ and $\gamma L S J$ is more complicated. These data

are all related to the transition moment which is defined as

$$\langle \Psi(\gamma LSJ) \| \mathbf{T} \| \Psi(\gamma' L' S' J') \rangle = \sum_{j,k} c_j c'_k \langle \Phi(\gamma_j L_j S_j J) \| \mathbf{T} \| \Phi(\gamma'_k L'_k S'_k J') \rangle, \quad (9)$$

where $\mathbf{T}$ is the transition operator. For electric dipole (E1) transitions there are two forms of the transition operator, the length and velocity forms, that for exact solutions of the Schrödinger equation give the same value. The calculation of the transition moment breaks down into reduced matrix elements between different CSFs. These can be evaluated using standard techniques assuming that both left and right CSFs are formed from the *same* orthonormal set of spin-orbitals. This constraint is severe, since a high-quality and compact wave function requires one-electron orbitals optimized for a specific electronic state, see for example [30]. It has been shown that for very general configuration expansions, where the initial and final states are described by different orbital sets, it is possible to transform the wave function representations of the two states in such a way that standard techniques can still be used for the evaluation of the matrix elements in the new representation [24]. The procedure for calculating the transition matrix element can be summarized as follows:

1. Perform MCHF calculations for the initial and the final states, where the orbital sets $\{\phi_i\}$ and $\{\phi'_j\}$ of the two wave functions are not assumed to be the same.
2. Change the wave function representation by transforming the two orbital sets

$$\{\phi_i\} \rightarrow \{\tilde{\phi}_i\}, \quad \{\phi'_j\} \rightarrow \{\tilde{\phi}'_j\} \quad (10)$$

to a biorthonormal basis, i.e. satisfying $\langle \tilde{\phi}_i | \tilde{\phi}'_j \rangle = \delta_{i,j}$. The orbital transformation in effect changes the CSFs and we obtain

$$\{\Phi(\gamma_j L_j S_j J)\} \rightarrow \{\tilde{\Phi}(\gamma_j L_j S_j J)\}, \quad \{\Phi(\gamma_k L_k S_k J)\} \rightarrow \{\tilde{\Phi}(\gamma_k L_k S_k J)\}. \quad (11)$$

This transformation is followed by the countertransformation of the expansion coefficients $\{c_j \rightarrow \tilde{c}_j\}$, $\{c'_k \rightarrow \tilde{c}'_k\}$ that leaves the total wave functions invariant.

3. In the transformed representation we have

$$\langle \Psi(\gamma LSJ) \| \mathbf{T} \| \Psi(\gamma' L' S' J') \rangle = \sum_{j,k} \tilde{c}_j \tilde{c}'_k \langle \tilde{\Phi}(\gamma_j L_j S_j J) \| \mathbf{T} \| \tilde{\Phi}(\gamma'_k L'_k S'_k J') \rangle \quad (12)$$

for which the standard techniques can be used to evaluate the matrix elements between the CSFs, thanks to the orbital biorthonormality property.

The biorthogonal transformation by itself is very fast and does not add much to the total computational cost.

LARGE-SCALE MULTICONFIGURATION CALCULATIONS

An MCHF calculation is determined by the CSFs in the wave function expansion. Early calculations included, by necessity, only a few CSFs carefully selected to account for

the largest correlation contributions. As the computational resources increased, expansions became larger and systematic methods were developed for selecting the CSFs. A frequently used method, which can be derived from Z -dependent perturbation theory, is to select a set of closely degenerate CSFs that form a so called multireference (MR). As a second step CSFs are generated by single- and double- (SD) replacements of orbitals in the MR with orbitals in an active set [31, 29]. Higher-order correlation effects can be included by either increasing the multireference, or by allowing also some triple- and quadruple- (TQ) replacements. For small systems the replacements are from orbitals in all shells of the CSFs in the MR. For larger systems, or systems with several open shells, the expansions often become unmanageably large and it is necessary to restrict replacements and allow only the ones from orbitals in the outer shells for properties sensitive to the description of the valence shells. The resulting expansion would then mainly account for valence and core-valence correlation. By systematically increasing the size of the active set, as well as investigating the effect of different rules for orbital replacement, it is often possible to give some estimation of the accuracy of a computed property [32, 33, 34]. Below we illustrate systematic multiconfiguration calculations, both in non-relativistic and relativistic formalisms, in a few cases.

I. The resonance line $1s^2 2s^2 \ ^1S - 1s^2 2s 2p \ ^1P^o$ in B II

As the first example of systematic multiconfiguration calculations we look at $1s^2 2s^2 \ ^1S - 1s^2 2s 2p \ ^1P^o$ in B II [35]. Starting from a single reference CSF and allowing SD replacements from orbitals in the outer shell, the CSF expansions will describe valence correlation. The next step would be to allow SDT replacements, but with the restriction that there is at most one replacement from the $1s$ orbital. The resulting expansions describe valence and core-valence correlation effects. As a final step CSFs are generated by allowing all SDTQ replacements to some subset of orbitals. This expansion is augmented by CSFs generated by SD replacements from orbitals in all shells of the reference CSF to the full orbital set. The total expansion describes valence, core-valence and core-core correlation effects. The results of the calculations are displayed in Table 1. The active set of orbitals is denoted by the highest principal quantum number. For example, $n \leq 3$ denotes the orbital set $\{1s, 2s, 2p, 3s, 3p, 3d\}$. N is the number of CSFs in the expansion. Within each correlation model there is a good convergence as the active set of orbitals is enlarged. We also see that there is a convergence of energies and weighted oscillator strengths in length and velocity forms computed with different correlation models. Based on the convergence trends and the consistency of the length and velocity forms it is possible to obtain a final value of the oscillator strength together with an error estimate. In this case the uncertainties come from the neglected relativistic effects. The final value from the calculation is $gf = 0.999$, with an uncertainty estimate of 0.005. This should be compared with the experimental values $gf = 0.971(79)$ [36] and $gf = 0.965(20)$ [37].

II. Spectrum calculations for B-like ions

For astrophysical and plasma applications massive data are needed. To generate large amounts of data, calculations are performed on a weighted energy average of a number of odd and even parity states. The procedure is often referred to as extended optimal

TABLE 1. Energies and weighted oscillator strengths for $1s^2 2s^2 \ ^1S - 1s^2 2s 2p \ ^1P^o$ in B II as functions of the increasing active set of orbitals for different correlation models.

$n \leq$	E	N	E	N	$g f_l$	$g f_v$	ΔE
	$1s^2 2s^2 \ ^1S$		$1s^2 2s 2p \ ^1P^o$		$1s^2 2s^2 \ ^1S - 1s^2 2s 2p \ ^1P^o$		
Valence correlation							
HF	-24.237575	1	-23.912873	1	1.44934	0.73292	71260
2	-24.296082	2	-23.912873	1	1.06474	0.78927	84100
3	-24.298330	7	-23.956320	6	1.03593	1.06883	75059
4	-24.298647	16	-23.960103	17	1.02566	1.05692	74298
5	-24.298826	30	-23.961101	36	1.02296	1.05715	74105
6	-24.298852	77	-23.961607	106	1.02191	1.05683	74013
Valence and core-valence correlation							
2	-24.296373	3	-23.913062	3	1.06522	0.79143	84132
3	-24.300685	23	-23.958255	36	1.02683	1.08208	75151
4	-24.304799	100	-23.966961	185	1.00565	0.99767	74143
5	-24.305673	318	-23.969633	650	1.00107	0.99919	73749
6	-24.305998	831	-23.970655	1810	1.00059	0.99889	73595
7	-24.306153	1892	-23.971064	4312	1.00028	0.99836	73539
Valence, core-valence and core-core correlation							
2	-24.296413	5	-23.913062	4	1.06522	0.79143	84132
3	-24.334812	63	-23.989668	98	1.02150	0.99381	75966
4	-24.346046	460	-24.001844	713	1.01860	1.02582	74741
5	-24.346046	1066	-24.008886	2300	1.00413	1.00375	73994
6	-24.347410	2306	-24.011624	5211	1.00075	0.99978	73693
7	-24.347943	4200	-24.012990	9772	0.99924	0.99961	75510
8	-24.348296	6865	-24.013636	16298	0.99903	0.99915	73449
Exp .					73397		

level (EOL) calculations. The CSF expansion should be chosen so that correlation is balanced for all the states in the calculation. EOL calculations are extremely useful, but one problem is that convergence with respect to the increasing active set of orbitals is comparatively slow since the orbitals need to describe correlation in a number of states at the same time. As an example of EOL calculations we look at the states of O IV. The lowest states of odd and even parity belong to the $2s^2 2p$ and $2s 2p^2$ configurations, respectively. Among the lower states there are also those that arise from configurations including one $3s, 3p$ or $3d$ orbital. In table 2 energies from multiconfiguration Dirac-Hartree-Fock (MCDHF) calculations are shown for 24 low lying states [38]. Even and odd states were calculated separately. The starting point was one MR with CSFs spanning the even parity states and another MR with CSFs spanning the odd parity states. The wave function expansions were then obtained by allowing SD replacements from all orbitals of the CSFs in the MR to orbitals belonging to the active set. Just as in the previous example the active set of orbitals was systematically increased and the largest active set included orbitals with principal quantum number up to $n = 8$. To account for higher-order correlation effects, SDTQ replacements were allowed to a subset of the active set. The largest expansions contained around 800 000 CSFs for the even states and around 1 000 000 CSFs for the odd states. Quantum electrodynamic corrections

as well as the Breit interaction were accounted for perturbatively. The calculations are well converged with respect to the increasing active set of orbitals, the mean relative change in energies when increasing the orbital set from $n = 7$ to $n = 8$ is only 0.05 %, and the multireferences would need to be enlarged to improve the energy differences further. Calculated transition rates in length and velocity form are in general in very good agreement, and systems of this and similar types can be said to be well understood.

TABLE 2. Energy levels for O IV from large-scale multireference calculations.

Level	Level (cm ⁻¹)			Splitting (cm ⁻¹)		
	Theory	Obs.	Diff.	Theory	Obs.	Diff.
$2s^2 2p^2 \ ^2P^o_{3/2}$	384.97	385.9	-0.9	385.0	385.9	-0.9
$2s 2p^2 \ ^4P^o_{1/2}$	71 309.65	71 439.8	-130.1			
$2s 2p^2 \ ^4P^o_{3/2}$	71 440.48	71 570.1	-129.6	130.8	130.3	0.5
$2s 2p^2 \ ^4P^o_{5/2}$	71 624.16	71 755.5	-131.3	314.5	315.7	-1.2
$2s 2p^2 \ ^2D^o_{5/2}$	127 193.45	126 936.3	257.1			
$2s 2p^2 \ ^2D^o_{3/2}$	127 206.92	126 950.2	256.7	13.5	13.9	-0.4
$2s 2p^2 \ ^2S^o_{1/2}$	164 790.37	164 366.4	424.0			
$2s 2p^2 \ ^2P^o_{1/2}$	180 856.34	180 480.8	375.5			
$2s 2p^2 \ ^2P^o_{3/2}$	181 098.83	180 724.2	374.6	242.5	243.4	-0.9
$2p^3 \ ^4S^o_{3/2}$	231 509.54	231 537.5	-28.0			
$2p^3 \ ^2D^o_{5/2}$	255 376.18	255 155.9	220.3			
$2p^3 \ ^2D^o_{3/2}$	255 405.01	255 184.9	220.1	28.8	29.0	-0.2
$2p^3 \ ^2P^o_{1/2}$	289 457.37	289 015.4	442.0			
$2p^3 \ ^2P^o_{3/2}$	289 466.27	289 023.5	442.8	8.9	8.1	0.8
$2s^2 3s \ ^2S^o_{1/2}$	357 523.45	357 614.3	-90.8			
$2s^2 3p \ ^2P^o_{1/2}$	390 055.90	390 161.2	-105.3			
$2s^2 3p \ ^2P^o_{3/2}$	390 142.83	390 248.0	-105.2	86.9	86.8	0.1
$2s^2 3d \ ^2D^o_{3/2}$	419 559.14	419 533.9	25.2			
$2s^2 3d \ ^2D^o_{5/2}$	419 575.44	419 550.6	24.8	16.3	16.7	-0.4
$2s 2p 3s \ ^4P^o_{1/2}$	438 764.99	438 849.0	-84.0			
$2s 2p 3s \ ^4P^o_{3/2}$	438 900.03	438 983.9	-83.9	135.0	134.9	0.1
$2s 2p 3s \ ^4P^o_{5/2}$	439 146.82	439 230.9	-84.1	381.8	381.9	-0.1
$2s 2p 3s \ ^2P^o_{1/2}$	452 925.95	452 806.6	119.3			
$2s 2p 3s \ ^2P^o_{3/2}$	453 191.76	453 071.5	120.3	265.8	264.9	0.9

III. Database calculations: the MCHF/MCDHF collection

For systems with open s - and p -shells it is possible to design systematic computational schemes in the EOL mode that produce accurate and reliable results for both energy separations and transition rates. This methodology has successfully been pursued by Charlotte Froese Fischer, and in collaboration with Georgio Tachiev and Andrei Irimia the complete lower spectra of the beryllium-like to argon-like isoelectronic sequences have been covered, amounting to the publication of data for over 150 ions [39, 40]. Data from this large effort are collected in the MCHF/MCDHF Database at NIST <http://nlte.nist.gov/MCHF/view.html>. The database contains records for different transitions giving the LS -designation of the levels involved in the multiplet,

Z = 4 Be I : Be-like (4 electrons).									

Multiplet									
Terms	g_i	g_k	Type	E_i	E_k	E(cm-1)	L(vac)	S	A_ki

2s(2) - 2s.2p									
1S 3P*									
	1	3	E1	0.00	21964.54	21964.54	4552.79	1.965e-07	1.311e-08 1.4048e+00
1S 1P*	1	3	E1	0.00	42623.43	42623.43	2346.13	1.070e+01	1.385e+00 5.5884e+08
	1	3	E1	0.00	42623.43	42623.43	2346.13	1.070e+01	1.385e+00 5.5884e+08
2s(2) - 2s.3p									
1S 3P*									
	1	3	E1	0.00	58759.88	58759.88	1701.84	2.529e-08	4.515e-09 3.4617e+00
1S 1P*	1	3	E1	0.00	60069.10	60069.10	1664.75	5.804e-02	1.059e-02 8.4866e+06
	1	3	E1	0.00	60069.10	60069.10	1664.75	5.804e-02	1.059e-02 8.4866e+06

FIGURE 3. An extract from the MCHF/MCDHF database.

values of transition energies, vacuum wave lengths, line strengths, oscillator strengths and transition rates. An extract from the database is shown in figure 3.

CHALLENGES AND LIMITATIONS

Whereas multiconfiguration methods are straightforward to apply to small systems with mainly open s - and p -shells, challenges remain for large systems and systems with nearly half-filled d - and f -shells. The main problem is that the number of CSFs increases very rapidly with the increasing active set of orbitals, exhausting the available computational resources [41]. Another problem is due to the variational principle itself. In variational calculations the shape and location of the radial orbitals are determined by how much they contribute to the total energy. Depending on the expansion the orbitals in the active set may be localized in some part of space that is important for lowering the total energy, but not necessarily for getting accurate results for other properties. A typical example is the hyperfine structure that is highly sensitive to the region of space close to the nucleus. This should be contrasted against transition probabilities that often depend on the outer part of the wave function, at least for transitions involving outer shells. The CSF expansions can be targeted to account for different correlation effects, but it still remains a challenge to handle these difficulties. A way forward is to perform a large number of smaller calculations, probing different regions of space and then assume approximate additivity of different contributions to the computed property. In this way values can be obtained also for very large systems. A typical example is given in [42], where the hyperfine structures of the $5d^9 6s^2 \ ^2D_{3/2}$ and $5d^9 6s^2 \ ^2D_{5/2}$ levels of atomic gold were estimated based on a number of multiconfiguration Dirac-Hartree-Fock calculations. Combined with the measured values of the hyperfine splittings the calculations were used to derive a new value of the nuclear quadrupole moment Q of ^{197}Au , with an error estimate.

PARTITIONED CORRELATION FUNCTION INTERACTION

The rapid increase of the CSFs with respect to the active set of orbitals is an inherent problem of all multiconfiguration methods and it is essential to find ways around this problem. An ordinary MCHF (or MCDHF) calculation often starts with a calculation for the multireference (MR) expansion that constitutes the zero-order approximation. To account for correlation this multireference expansion is augmented by an expansion in additional CSFs. The latter expansion builds a correlation function that we denote Λ and we have

$$\Psi = \sum_{j=1}^{N_{MR}} a_j \Phi^{MR}(\gamma_j LS) + \underbrace{\sum_{j=1}^{N_c} b_j \Phi(\gamma_j LS)}_{\Lambda}. \quad (13)$$

The orbitals in multireference are kept fixed and everything else is varied in the self-consistent field procedure. This determines the expansion coefficients a_j of the multireference, the expansion coefficients b_j of the correlation function, and a number of correlation orbitals that together with the orbitals in the multireference define an orbital set $\{\phi_k\}$. Due to the rapid increase of the number of CSFs in the correlation function this scheme soon gets impracticable. Verdebout et al. [43] proposed to split the originally large problem into several smaller problems (“Divide and Conquer”). This amounts to splitting the correlation function Λ into several smaller functions Λ_i , $i = 1, 2, \dots, n$, where Λ_i is referred to as a partitioned correlation function (PCF). Instead of one large calculation there is now a series of smaller MCHF calculations

$$\Psi^i = \sum_{j=1}^{N_{MR}} a_j^i \Phi^{MR}(\gamma_j LS) + \underbrace{\sum_{j=1}^{N_c^i} b_j^i \Phi^i(\gamma_j LS)}_{\Lambda_i}, \quad i = 1, 2, \dots, n \quad (14)$$

that determine the expansion coefficients a_j^i , b_j^i and the radial orbital sets $\{\phi_k^i\}$. Each of the PCFs accounts for some correlation effect and in the final step we write the total wave function as an expansion in CSFs and n normalized PCFs $\tilde{\Lambda}_i$

$$\Psi = \sum_{j=1}^{N_{MR}} c_j \Phi^{MR}(\gamma_j LS) + \sum_{i=1}^n d_i \tilde{\Lambda}_i. \quad (15)$$

The expansion coefficients c_j and d_i are obtained by constructing and diagonalizing the total Hamiltonian matrix. The calculation of matrix elements between CSFs in the multireference or between a CSF in the multireference and a normalized PCF $\tilde{\Lambda}_i$ is done using standard techniques. To evaluate matrix elements between two PCFs

$$\langle \tilde{\Lambda}_i | H | \tilde{\Lambda}_j \rangle = \sum_{k,l} b_k^i b_l^j \langle \Phi^i(\gamma_k LS) | H | \Phi^j(\gamma_l LS) \rangle \quad (16)$$

built on non-orthonormal orbital sets $\{\phi_k^i\}$ and $\{\phi_k^j\}$, a biorthonormal transformation is performed and the calculation follows the prescription for transition moments (see

above). Instead of having a single expansion in CSFs we now have an expansion into CSFs and PCFs and the new method is referred to as the Partitioned Correlation Function Interaction (PCFI) approach.

To illustrate the effectiveness of the method we look at the ground state of Be [43]. Using a multireference $\{1s^2 2s^2, 1s^2 2p^2, 1s^2 3s^2, 1s^2 3d^2\}$ and three separately optimized PCFs Λ_v, Λ_{cv} and Λ_{cc} describing, respectively, valence, core-valence, and core-core correlation, we obtain rapid energy convergence and lower total energies than for a very large ordinary MCHF calculation (see table 3). The expansion for the PCFI method is based on five CSFs in the MR and three PCFs, and is thus of dimension 8. In the table the energy is denoted $E_{8 \times 8}$. The sizes of the PCFs expansions are quite moderate, around a few thousand CSFs for each of them for the largest orbital set $n \leq 10$. The ordinary MCHF calculation is based on an expansion where all SDTQ substitutions have been allowed (CAS expansion) and this expansion contains around 650 000 CSFs for the largest orbital set. The energies for the ordinary MCHF method are denoted $E_{CAS-MCHF}$.

TABLE 3. Energies for the PCFI method compared with energies from the ordinary MCHF method.

$n \leq$	$E_{8 \times 8}$	$E_{CAS-MCHF}$
4	-14.660 679 48	-14.661 403 17
5	-14.665 553 46	-14.664 839 93
6	-14.666 582 83	-14.666 067 32
7	-14.666 905 87	-14.666 541 14
8	-14.667 047 86	-14.666 857 41
9	-14.667 122 76	-14.667 012 75
10	-14.667 168 08	-14.667 114 20

Due to the splitting of large-scale calculations into a set of small ones, the PCFI method seems to provide new opportunities to treat correlation in systems that were previously inaccessible. The potential of the method is currently explored in a number of different systems [44].

ACKNOWLEDGMENTS

The authors would like to acknowledge the support and encouragement of Professor Charlotte Froese Fischer during many years of exciting and fruitful collaboration. Charlotte, thank you for having been such a wonderful post-doctoral research supervisor, and for friendship you extended to us. PJ, TB, GG, and JB thank the Visby program of the Swedish Institute for a collaborative grant. MG thanks the Communauté française of Belgium (ARC convention) and the Belgian National Fund for Scientific Research (FRFC/IISN convention) for financial support. JB acknowledges support by the Polish Ministry of Science and Higher Education (MNiSW) in the framework of the project No. N N202 014140 awarded for the years 2011-2014, as well as by the European Regional Development Fund in the framework of the Polish Innovation Economy Operational Program (contract no. POIG.02.01.00-12-023/08).

REFERENCES

1. E. Schrödinger, *Phys. Rev.* **28**, 1049 (1926).
2. D.R. Hartree, *Proc. Camb. Phil. Soc.* **24**, 89 (1928); **24**, 111 (1928).
3. V. Fock, *Z. Phys.* **61**, 126 (1930).
4. D.R. Hartree, W. Hartree and B. Swirles, *Phil. Trans. Roy. Soc. A* **238**, 229 (1939).
5. C. Froese, *Proc. Camb. Phil. Soc.* **53**, 206 (1957).
6. C. Froese Fischer, *Comput. Phys. Commun.* **1**, 151 (1969).
7. C. Froese Fischer, *J. Comput. Phys.* **27**, 221 (1978).
8. C. Froese Fischer, *Comput. Phys. Commun.* **64**, 431 (1991).
9. C. Froese Fischer, *Comput. Phys. Commun.* **64**, 473 (1991).
10. C. Froese Fischer and M.R. Godefroid, *Comput. Phys. Commun.* **64**, 501 (1991).
11. C. Froese Fischer, M.R. Godefroid, A. Hibbert, *Comput. Phys. Commun.* **64**, 486 (1991).
12. C. Froese Fischer and T. Brage, *Comput. Phys. Commun.* **74**, 381 (1993).
13. P. Jönsson, C.G. Wahlström, C. Froese Fischer, *Comput. Phys. Commun.* **74**, 399 (1993).
14. C. Froese Fischer, L. Smentek-Mielczarek, N. Vaeck, G. Miecnik, *Comput. Phys. Commun.* **74**, 415 (1993).
15. T. Brage, C. Froese Fischer, and P. Jönsson, *Phys. Rev. A* **49**, 2181 (1994).
16. N. Vaeck M. Godefroid, and C. Froese Fischer, *Phys. Rev. A* **46**, 3704 (1992).
17. T. Brage, C. Froese Fischer, N. Vaeck, M. Godefroid and A. Hibbert, *Phys. Scr.* **48**, 533 (1993).
18. P. Jönsson, S.G. Johansson and C. Froese Fischer, *ApJ.* **L45**, 429 (1994).
19. C. Froese Fischer, M. Tong, M. Bentley, Z. Shen, C. Ravimohan, *The Journal of Supercomputing* **8**, 117 (1994).
20. G. Gaigalas, Z. Rudzikas and C. Froese Fischer, *J. Phys. B* **30**, 3747 (1997).
21. G. Gaigalas, Z. Rudzikas and C. Froese Fischer, *At. Data Nucl. Data Tables* **70**, 1 (1998).
22. G. Gaigalas, S. Fritzsche and Z. Rudzikas, *At. Data Nucl. Data Tables* **76**, 235 (2000).
23. C. Froese Fischer, G. Tachiev, G. Gaigalas, M.R. Godefroid, *Comput. Phys. Commun.* **176**, 559 (2007).
24. J. Olsen, M. Godefroid, P. Jönsson, P.Å. Malmqvist and C. Froese Fischer, *Phys. Rev. E* **52**, 4499 (1995).
25. O. Zatsarinny and C. Froese Fischer, *Comput. Phys. Commun.* **180**, 2041 (2009).
26. F.A. Parpia, C. Froese Fischer, and I.P. Grant, *Comput. Phys. Commun.* **94**, 249 (1996).
27. P. Jönsson, X. He, C. Froese Fischer, and I.P. Grant, *Comput. Phys. Commun.* **177**, 597 (2007).
28. P. Jönsson, G. Gaigalas, J. Bieroń, C. Froese Fischer, and I.P. Grant, *Comput. Phys. Commun.* submitted (2012).
29. C. Froese Fischer, T. Brage, and P. Jönsson, "Computational Atomic Structure - an MCHF approach", *IoP*, (1997).
30. S. Fritzsche and I.P. Grant, *Phys. Lett A* **186**, 152 (1994).
31. D. Layzer, *Ann. Phys.* **8**, 271 (1959).
32. T. Brage and C. Froese Fischer, *Phys. Scr.* **T47**, 18 (1993).
33. C. Froese Fischer, *Phys. Scr.* **T134**, 014019 (2009).
34. J. Bieroń, P. Jönsson, and C. Froese Fischer, *Phys. Rev. A* **60**, 3547-3557 (1999).
35. M. Godefroid, J. Olsen, P. Jönsson and C. Froese Fischer, *ApJ.* **450**, 473 (1995).
36. S. Bashkin et al., *Nucl. Instr. Meth. B* **9**, 593 (1985).
37. N. Reistad and I. Martinson, *Phys. Rev. A* **34**, 2632 (1986).
38. P. Jönsson, J. Li, G. Gaigalas, and C. Dong, *At. Data Nucl. Data Tables* **96** 271 (2010).
39. C. Froese Fischer, G. Tachiev, *At. Data Nucl. Data Tables* **87**, 1 (2004).
40. C. Froese Fischer, G. Tachiev, and A. Irimia, *At. Data Nucl. Data Tables* **92**, 607 (2006).
41. S. Fritzsche, *Phys. Scr.* **T100**, 37 (2002).
42. J. Bieroń, C. Froese Fischer, P. Indelicato, P. Jönsson, and P. Pykkö, *Phys. Rev. A* **79**, 052502 (2009).
43. S. Verdebout, P. Jönsson, G. Gaigalas, M. Godefroid, and C. Froese Fischer, *J. Phys. B* **43**, 074017 (2010).
44. S. Verdebout, P. Rynkun, P. Jönsson, G. Gaigalas, C. Froese Fischer, M. Godefroid, *J. Phys. B*, manuscript in preparation (2012).