

The challenge of theoretical predictions of oscillator strengths and lifetimes

ABSTRACT

The prediction of the lifetime of *one* excited state may require the calculation of *many* transition probabilities and possibly also autoionization rates. Some of the important concepts for performing multiconfiguration Hartree-Fock calculations for a portion of a spectrum and for highly accurate results for few electron systems are reviewed. Transitions in C I are used as an example as well as the $1s2s2p^2\ ^5P - 1s2p^3\ ^5S$ transition in Li^- .

INTRODUCTION

There are many challenges to the theoretical prediction of oscillator strengths and lifetimes.

As interest shifts from resonance transitions to transition probabilities for excited states, the amount of needed information increases rapidly. The challenge, in effect, is to perform a calculation for a portion of the spectrum, predicting many transition probabilities along with lifetimes in a single calculation. Such calculations are not "fine tuned" calculations for transitions between a specific pair of levels, but they can provide large amounts of reasonably accurate information. Among the *ab initio* methods, the Energy_Average_Level (EAL) calculations of the General Relativistic Atomic Structure Package (GRASP) (Dyall et al., 1989) can be used to provide such information, but the restriction of a single orthonormal basis for the initial and final state, in effect, limit the code to a study of ionized systems. In this paper, the multiconfiguration Hartree-Fock method with Breit-Pauli corrections for the relativistic effects will be applied to the study of excited state transitions in Carbon.

Another challenge is the prediction of lifetimes for the levels of a Rydberg series. In an unperturbed Rydberg series, the lifetimes increase smoothly as $(n^*)^3$, where n^* is the effective quantum number, but the presence of a perturber may cause an irregular behaviour (Brage et al., 1987). In some instances, the mixing with the perturber causes cancellation in the transition matrix element, resulting in a minimum in the lifetime trend. The correct prediction of the minimum is sensitive to both correlation and relativistic shift effects. Intuitively, one would not think of relativistic effects as being important in Ry-

dberg series, but they may shift the perturber relative to the Rydberg series, thereby affecting the mixing of the perturber with the series and hence the transition probabilities that define the lifetime.

With the availability of supercomputers, it is also a challenge to improve on the accuracy of f-value predictions. Johnson *et al.* (1988) have applied many-body perturbation theory (MBPT) to third order to the study of transitions in alkali atoms: five hours of Cray X-MP/24 time were required for the calculations they describe.

Many other difficult problems remain. In core excited states, a level may decay by a variety of mechanisms, including autoionization to the continuum, as was the case for the core excited $2p^5 3s 3d\ ^4L$ states of Na I (Froese Fischer, 1986). An accurate prediction of the lifetime requires not only accurate radiative transition probabilities, but also reliable autoionization rates. Transition probability calculations are rarely performed for the transition metals where the open *d*-shells greatly magnify the correlation problem. Even correlation studies have not yet been performed in all atomic systems. For example, the ground configuration of U^{+4} is $5f^2$. A relativistic MCDF (EAL) calculation produces results for which a number of levels are inverted. As in Pr^{+3} (Morrison and Rajnak, 1971), important correlation contributions are expected to arise from the interaction of $5d^{10} 5f^2$ with $5d^8 5f^4$. With only those two non-relativistic configurations in the wave function expansion, the total number of *j-j* coupled configuration states is 123, 297, 482, 555, 611, 561, and 505 for $J=0$ to $J=6$, respectively, or 3134 configuration states for an EOL calculation. For many *ab initio* approaches, atomic structure codes need to be revised to deal with wave function expansions 10 - 100 times larger than those presently employed.

Let me now describe how the MCHF Atomic Structure Program has been used to meet some of these challenges.

SPECTRUM CALCULATIONS

Consider the problem of predicting transition data for $3s \rightarrow 3p$, $4p$, $3p \rightarrow 3d$, $4s$, and $4d$, and $3d \rightarrow 4p$ transitions in C I, transitions of interest in astrophysics. In this case, the remaining electrons are in the configuration $1s^2 2s^2 2p$; in the description of the calculation we will omit reference to the $1s^2$ shell and treat the problem as a four electron problem. Our calculation will be one in which a basis of radial functions is obtained from a series of MCHF calculations, and the total energies and wave function expansions will be obtained from a Breit-Pauli interaction matrix. Thus our calculation is essentially non-relativistic but with relativistic corrections that include spin-orbit interaction and non fine-structure effects such as the mass correction, one- and two-body Darwin terms, and spin-spin contact.

For an *ab initio* calculation, several principles need to be kept in mind.

The Complex

The set of configuration states of the same parity, the same LS term, and for which the orbitals all have the same set of principal quantum numbers, form a *complex*. In non-relativistic theory, these are the configura-

ration states which may exhibit substantial configuration mixing in the expansion of a wave function. In a calculation like the one for C I, where all terms are of interest, one may simply classify the configuration states into odd and even configuration states. For example, for the $2s^2 2p 3l$ states, the odd and even configurations are the following:

$$\begin{array}{l} \text{Odd} \quad 2s^2 2p 3s, 2p^3 3s, 2s^2 2p 3d, 2p^3 3d, 2s 2p^2 3p \\ \text{Even} \quad 2s^2 2p 3p, 2p^3 3p, 2s 2p^2 3s, 2s 2p^2 3d \end{array}$$

A similar set defines the $2s^2 2p 4l$ complex. For the Carbon problem under consideration, the two sets should be combined.

The Upper Bound Principle

Experience with many calculations has shown that results are more reliable when the lower lying complex is also included in a wave function expansion. Then, by the Hylleraas-Undheim-MacDonald (1930, 1933) theorem, the n^{th} eigenvalue of the interaction matrix for a given LS term is an upper bound to n^{th} exact energy for that term. For Carbon, this required the inclusion of the following configuration states:

$$\begin{array}{l} \text{Odd} \quad 2s 2p^3 \\ \text{Even} \quad 2s^2 2p^2, 2p^4 \end{array}$$

In neutral atoms, not all of the levels of the lower complex lie below those of the excited complex. In Carbon, the $2s 2p^3$ LS levels lie above those of the $2s^2 2p 3s$ levels, except for $2s 2p^3 \ ^5S$, and play an important role in the interactions.

Term Dependence

The radial functions of orbitals in a given configuration may exhibit considerable LS term dependence, as was shown by Hansen (1973). Such term dependence can readily be checked by performing a series of Hartree-Fock calculations for each term. Table 1. shows the mean radii of $3l$ orbitals for different terms of the same configuration. Note that term dependence is negligible for $3s$ and $3d$ (though not all terms were checked), but considerable for $3p$. The term dependence here, to a large extent,

Table 1: Term Dependence of $3l$ orbitals for the configurations $2s^2 2p 3l$ in Carbon.

$3l$	Term	$\langle r_{3l} \rangle$	$3l$	Term	$\langle r_{3l} \rangle$
3s	3P	5.941	3d	3P	10.597
	1P	6.213		1P	10.770
3p	3D	7.338	3p	1D	9.041
	1P	7.135		3P	8.500
	3S	7.651		1S	9.581

can be classified according to whether the corresponding $2s^2 2p^2$ configuration state is allowed. When the state is not allowed, the mean radius of $3p$ is more contracted than when it is allowed.

Optimization of Orbitals

If no term dependence were present, radial functions could be determined from an MCHF calculation for any term, but when term dependence is present, the LS terms need to be chosen carefully. Term dependence can be incorporated into a calculation like the one being described, by including additional configurations in the expansion to represent this dependence and by carefully selecting the LS term (or calculation) that determines a particular radial function, $P_{nl}(LS; r)$. For example, we could define

$$P_{3p}(^1S) = aP_{3p}(^1P) + bP_{np}(^1S), \quad \langle 3p|np \rangle = 0.$$

Clearly the radial basis could be defined in a number of ways. Generally, the radial basis should include the most contracted orbital as well as a more diffuse orbital so that the term dependence can be represented by a linear combination of these orbitals. In the present case, since the calculations include the $2s^2 2p 4p$ configuration states, we will allow the $4p$ orbital to play the role of the diffuse orbital. This keeps the size of the interaction matrix to a minimum, but may not provide the best possible results. In particular, since there is no radial basis for the representation of the diffuse $4p$, the configuration states for the latter will not be represented well. This will be shown to be the case later.

A limitation in the prediction of transition probabilities and lifetimes by the MCHF Atomic Structure Package (MCHF_ASP) that needs to be kept in mind, is the fact that the codes for performing the angular integrations for the transition operator can deal only with a limited amount of non-orthogonality between the initial and final state. Most angular momentum theories for operators assume a common, orthonormal basis for the initial and final state. The MCHF multipole program (Godefroid et al. 1989) allows for some non-orthogonality but restricts the non-orthogonality in such a way that the number of overlap integrals arising from non-orthogonality be at most two. In the present calculation, it is desirable to have the $\{1s, 2s, 2p\}$ set of orbitals be the same in the initial and final state. Because of the strong interaction between $2s^2 2p \ ^2P$ and $2p^3 \ ^2P$, these orbitals were obtained from a 2×2 MCHF calculation for C^+ with a wave expansion over these two configuration states.

Separate calculations were performed for the odd and even configurations states.

For the odd configuration states, the $3s$, $4s$, $3d$ and $4d$ orbitals were obtained from MCHF calculations for

$$\{2s^2 2p 3l, 2p^3 3l\} \ ^3P.$$

The $3p$ correlation orbital was obtained from an MCHF calculation for the $2p 3s \ ^3P$ state with an expansion over the $n = 3$ odd complex plus the $2s 2p^3$ and $2s 2p^2 3p$ configuration state. In this calculation, only the $3p$ orbital was varied. A similar calculation was performed for the $4p$ correlation orbital, replacing the $n = 3$ complex by the $n = 4$ complex.

For the even configuration states, the $3p$, $3s$, and $3d$ orbitals were obtained from an MCHF calculation for the $2p 3p \ ^1P$ state with a wave function expansion over

$$\{2s^2 2p 3p, 2s 2p^2 3s, 2s 2p^2 3d\} \ ^1P.$$

Table 2: Theoretical total energies (in au) and energies relative to $2s^2 2p^2 \ ^3P$ (in cm^{-1}) along with lifetimes for levels from part of the spectrum of Carbon.

nl LS J	Energy (a. u.)	Energy (cm^{-1})	Tau (ns)
3s 3P 0	-37.48573433	48373.1	3.08e+00
1	-37.48564648	48392.3	3.07e+00
2	-37.48546322	48432.6	3.07e+00
1P 1	-37.47725779	50233.4	3.01e+00
3p 1P 1	-37.44554150	57194.0	1.11e+02
3D 1	-37.44182530	58009.5	4.92e+01
2	-37.44173242	58029.9	4.92e+01
3	-37.44158809	58061.6	4.92e+01
3S 1	-37.43676923	59119.2	3.78e+01
3p 3P 0	-37.42830544	60976.7	2.38e+01
1	-37.42825069	60988.7	2.38e+01
2	-37.42815282	61010.2	2.38e+01
1D 2	-37.41684581	63491.6	2.40e+01
1S 0	-37.41074219	64831.2	2.78e+01
3d 1D 2	-37.40530094	66025.3	1.38e+01
4s 3P 0	-37.40521870	66043.4	6.84e+00
1	-37.40514206	66060.2	6.75e+00
2	-37.40496105	66099.9	6.57e+00
1P 1	-37.40361248	66395.9	7.58e+00
3d 3F 2	-37.40355209	66409.1	7.44e+00
3	-37.40350664	66419.1	5.90e+00
4	-37.40328547	66467.7	3.73e+01
3D 1	-37.40347043	66427.1	3.41e+00
2	-37.40339878	66442.8	4.69e+00
3	-37.40332174	66459.7	5.56e+00

The $n = 4$ orbitals were obtained from a similar calculation for the $2p4p \ ^1P$ state, but now both the $n = 4$ and $n = 3$ complexes were included in the wave function expansion, though only the $n = 4$ orbitals were varied. The $3p$ and $4p$ orbitals had mean radii of 6.843 and 15.231, respectively. If better accuracy is desired, more p orbitals should be introduced and optimized on the 1S state.

Once the radial functions have been determined, a configuration interaction, Breit-Pauli calculation can be performed for each of the odd and even configuration states, for a series of J values, and E1 transition probabilities computed for all possible transitions. Table 2. summarizes some of the energy levels and lifetime data from this calculation.

Table 2. immediately shows that there is not a great

Table 3: Comparison of LSJ-averaged, MCHF+BP term energies with similarly averaged observed values, relative to the $2p3s \ ^3P$ energy, in cm^{-1} .

nl LS	Energy theory	Energy Obs.	Diff
3s 3P	0	0	0
1P	1820	1609	211
3p 1P	8782	8485	297
3D	9628	9349	279
3S	10707	10371	336
3P	12587	11002	1585
1D	15079	12238	2841
1S	16418	13603	2816
3d 1D	17614	17307	307
4s 3P	17668	17760	-91
1P	17986	17965	21
3d 3D	18022	17937	85
3F	18035	17853	182
1F	18279	18158	121
1P	18462	18355	107
3P	18721	18942	-221
4p 1P	20223	20190	33
3D	20489	19829	661
3S	20880	20732	148
3P	21993	20961	1032
4d 1D	23285	23127	158
3F	23443	23388	55
3D	23451	23467	-16
1F	23573	23576	-3
1P	23606	23689	-83
3P	23667	23733	-66
4p 1D	25915	21397	4518
1S	31987	21879	10108

deal of J-dependence in the lifetimes, the only exception being the levels of the $2pnd \ ^3F$ states and to a lesser extent also the 3D state. For the 3F states there is considerable mixing with the 3D states, and in the 3D_1 case, also with $2s^2 2p4s \ ^1P_1$. Thus for most of this spectrum, a non relativistic calculation is expected to be adequate.

Table 3. compares the theoretical term energies relative to the $2p3s \ ^3P$ term with similar observed values, where the observed terms energies are obtained from statistically weighted LSJ levels. With the exception of the of the $2p3p$ and $2p4p \ ^1D, \ ^3P, \ ^1S$ LS terms the predicted and observed levels are in reasonably good agreement.

But such broad brush calculations, unless considerably refined, can only present the general picture. To confirm the accuracy of some of the transition probabilities,

Table 4: Comparison of theoretical Breit-Pauli (LSJ) and MCHF (LS) wavelengths (in air) and line strengths with critically evaluated data.

	λ (Å)	S_l	S_v
$3s^3P \rightarrow 3p^3D$			
LSJ	10383	168.0	
LS	10873	170.0	173.9
NBS ¹⁾	10695	160.0	
$3p^3D \rightarrow 4s^3P$			
LSJ	12434	107.0	
LS	12059	67.4	67.1
NBS	11886	85.	

non-relativistic MCHF calculations using non-orthogonal orbitals were performed for three states over all couplings of the configurations as indicated below:

$$\begin{aligned}
 3s^3P & \{2s^22p_13s_1, 2p_1^23s_1, 2s^22p_33d_3, 2p_1^23d_2, \\
 & 2s^23d_14f_1, 2p_1^23d_14f_1, 2s2p_1^3, 2s2p_13p_1\} \\
 3p^3D & \{2s^22p_13p_1, 2p_1^23p_1, 2s2p_1^23d_1, \\
 & 2s2p_1^23s_1, 2s^23d_24d_2, 2p_1^23d_24d_2, \} \\
 4s^3P & \{2s^22p_14s_1, 2p_1^24s_1, 2s^22p_33d_3, 2p_1^23d_2, \\
 & 2s^23d_14f_1, 2p_1^23d_14f_1, 2s2p_1^3, 2s2p_13p_1\}
 \end{aligned}$$

Thus, in the calculation for $4s^3P$, for example, the $3d$ orbitals are correlation orbitals. Table 4. compares the LSJ averaged data for two multiplets, the LS values from the non-orthogonal, non-relativistic calculation, and the compiled data included in the NBS publication, derived from both theory and experiment. In order to separate the energy prediction from the prediction of the transition matrix element, the line strength, S , is compared rather than the oscillator strength. Clearly evident is the fact that the non-relativistic MCHF calculations, which have included more correlation effects, yield the better wavelengths: indeed, relativistic shift effects would improve agreement with observation. In the non-relativistic scheme, the length and velocity values of the line strength are also compared. In the case of the $3s^3P \rightarrow 3p^3D$ transition, the line strength is essentially unchanged, yet for the $3p^3D \rightarrow 4s^3P$ transition it has reduced substantially, with length and velocity values coming into good agreement. In this case there is extensive mixing of $2s^22p_4s$ and $2s^22p_3d$, mixing which is more accurately represented in the variational MCHF calculation.

ACCURATE FEW-ELECTRON CALCULATIONS

Unlike MBPT, where open shell cases may pose difficult problems, the MCHF method can be used in such cases and, with sufficient CPU time and memory, some accurate results can be obtained for few-electron systems. This was demonstrated by Brage and Froese Fischer (1988) who predicted the wavelengths of the $1s2s2p^2^5P \rightarrow 1s2p^3^5S$ transition in Be I-like ions to spectroscopic accuracy. In such calculations, systematically larger and

larger expansions are used until "convergence" is obtained. Several concepts are used in generating the expansions.

1. *reference set*
Configurations for which a configuration state forms a major component in the wave function expansion define the reference set.
2. *active set*
In a combinatorial approach in which all configuration states are generated that can be constructed from orbitals for a given set of electrons, the latter is called the "active set".
3. *single and double replacements*
Configurations will interact with some members of the reference set only if they differ by no more than two electrons from some member. The single and/or double replacement procedure systematically replaces one and/or two electrons in each configuration of the reference set.
4. *virtual set*
The electrons that are used in the single and double replacement of electrons are electrons from a virtual set.

In the Be I-like calculations, the initial active set consisted of $1s, 2s, 2p, 3s, 3p, 3d$ and $4f$ electrons. Orbitals for the first three were obtained from a Hartree-Fock calculation, and the others from a variational calculation for an expansion over the configuration states generated by the active set. Then $4s, 4p$ and $4d$ orbitals were obtained by adding to the expansion those configuration states that were obtained by single and double replacements from the previous set. Finally, all electrons were placed in the active set and a CI calculation performed with and without relativistic shift effects.

Since these calculations have been performed, it has been found that better accuracy can be obtained by varying all (or almost all) orbitals rather than only the new orbitals. This was done in the study of the binding energies of negative alkaline earths. However, with an active set, a rotation of the radial basis is a transformation that does not change the total energy and so, for uniqueness and stability, it is desirable to delete certain configurations. The best candidates are those for which Brillouin's theorem should hold. Table 5. reports the results from a study of the $1s2s2p^2^5P \rightarrow 1s2p^3^5S$ transition of Li^- , a case not included in the earlier study. The first part of the table shows the convergence of the total energies for the two states, the wavelength (in air) for the transition, and the length and velocity values of the line strength (the observed transition energy was used for the computation of the latter) for a calculation that ignores correlation with the $1s$ electron. Note that the converged wavelength deviates from the observed by 42 Å. The next set of calculations, is for a fully correlated wave function. It was found that the s -orbitals play a much more important role in the 5P state, that the contribution of the $5s$ was considerably larger than the contribution from the highest nl for other l -values, and so a $6s$ was added to the active set for the 5P state. The resulting wavelength

Table 5: Convergence of total energy (in a.u.), wavelength, length and velocity forms of the line strength for the $1s2s2p^2\ ^5P \rightarrow 1s2p^3\ ^5S$ transition in Li^- as the active set is increased. The latter consists of all electrons with $n \leq N$. The symbols s and p are used to indicate an additional s or p electron, respectively.

N	$E(^5P)$	$E(^5S)$	$\lambda(\text{\AA})$	S_l, S_v
<i>Outer Correlation Only</i>				
3	-5.381345	-5.248208	3421.6	39.2, 40.0
4	-5.383501	-5.251369	3447.6	37.2, 38.9
5	-5.383820	-5.251675	3447.2	36.7, 39.1
<i>Full correlation</i>				
3,p	-5.382850	-5.251602	3470.8	
4,p	-5.385691	-5.255043	3486.8	
5,p	-5.386225	-5.255744	3491.2	
5,sp	-5.386251		3491.5	
<i>With relativistic shift effects</i>			3489.4	
Bunge (1980)				
Non-relativistic			3491.1	
With empirical corrections			3489.8 \pm 0.9	
Exp. (Bromander et al. 1973)			3489.7 \pm 0.2	

from the final energies, when corrected for a relativistic shift effect is 3489.4 Å, which deviates from the observed value by about 0.3 Å. The results are also compared with those reported by Bunge (1980).

It should be mentioned that, at each stage, new orbitals for outer correlation were determined and those configuration states retained with a mixing coefficient larger than 0.00005 in magnitude. A subset with mixing coefficients greater than 0.0005 was used as a zero-order set for a first-order perturbation like calculation for the many remaining configuration states. Again, the new orbitals were varied and the new configuration states with mixing coefficients larger than 0.00005 added to the earlier set. Finally, a variational calculation was performed. In this way, very large calculations could be avoided. In the case of the first-order MCHF calculation, where only a few percent of the matrix elements are non-zero, a sparse version of MCHF was used. The expansion lengths of the final wave functions were 604 and 345 configuration states, respectively, for 5P and 5S reflecting the greater difficulty of the calculation for the 5P state.

CONCLUSION

For few electron systems, MCHF calculations for some transition energies can be performed that are close to experimental accuracy. But many challenges remain. One problem that is of particular concern in the MCHF approach is the evaluation of matrix elements between different states. In the MCHF method, orbitals are optimized for a given state and though they may be orthonormal within a state, they are not orthonormal between states. Thus the evaluation of the transition operator

becomes more difficult and no general solution to this problem has been developed.

ACKNOWLEDGEMENTS

This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences.

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