

## Relativistic Intermediate-coupling Calculations for Ions of the Beryllium Isoelectronic Sequence

R. Glass

Department of Physical and Inorganic Chemistry,  
University of Western Australia, Nedlands, W.A. 6009.

### Abstract

Relativistic intermediate-coupling wavefunctions are used to evaluate wavelengths and oscillator strengths for the resonance transition  $2s^2\ ^1S_0 \rightarrow 2s2p\ ^1P_1^0$  and the intercombination transition  $2s^2\ ^1S_0 \rightarrow 2s2p\ ^3P_1^0$  for iron, krypton, molybdenum and tungsten beryllium-like ions. The convergence of the results with respect to the basis set of orbitals is considered. It is shown that the same degree of accuracy can be achieved by using the three configuration basis composed of  $2s^2$ ,  $2s2p$  and  $2p^2$ . The question of at what stage the Breit interactions should be included in the Hamiltonian is discussed. We also compare our calculated  $2s^2\ ^1S_0 \rightarrow 2s2p\ ^3P_1^0$  intercombination oscillator strengths with those deduced from beam-foil experiments for iron and krypton.

### 1. Introduction

The study of relativistic effects in the beryllium isoelectronic sequence has attracted much attention from theoreticians. The aim has been to develop a theory for calculating energy levels, wavelengths, oscillator strengths and transition probabilities accurately. However, discrepancies still exist between the different theories (Lawson and Peacock 1980).

Theoretical calculations are based on several approaches, and one method is to form relativistic intermediate-coupling wavefunctions. The radial functions are calculated in the  $LS$  coupling scheme and the relativistic corrections are treated in the Pauli approximation as first-order perturbations of the nonrelativistic energy (Weiss 1976; Cowan and Griffin 1976; Glass and Hibbert 1978*a*, 1978*b*; Glass 1979*a*, 1979*b*; Nussbaumer and Storey 1979; Glass 1981*a*, 1981*b*). Another approach is the relativistic multi-configurational Hartree-Fock approximation (Kim and Desclaux 1976; Armstrong *et al.* 1976; Cheng and Johnson 1977). The relativistic random-phase approximation method has also been used by Lin and Johnson (1977).

The major unresolved question is that of how the relativistic effects should be included and of what changes they induce in the wavefunctions. Armstrong *et al.* (1976) and Cheng and Johnson (1977) using the relativistic multi-configurational Hartree-Fock method have evaluated oscillator strengths for the resonance transition and the intercombination (spin-orbit electric dipole) transition from boron to uranium in the beryllium sequence. They only included configurations in the wavefunctions which could be formed from the  $n = 2$  complex keeping a  $1s^2$  core. Nussbaumer and Storey (1979) have evaluated transition probabilities for calcium, iron, krypton and molybdenum beryllium-like ions using 57 configuration basis wavefunctions. They did not consider the possibility of using the three-configuration basis composed of  $2s^2$ ,  $2s2p$  and  $2p^2$ .

In this paper we wish to report relativistic intermediate-coupling calculations for ions of the beryllium isoelectronic sequence which can be used in the theoretical and computational study of low-energy collisions of electrons by complex atoms and ions. The  $R$ -matrix method describing the scattering of low-energy electrons by complex atoms and ions has been extended by Scott and Burke (1980) to include terms of the Breit–Pauli Hamiltonian. The  $R$ -matrix code is compatible with the relativistic intermediate-coupling code used here (Glass and Hibbert 1978*b*). The large-scale configuration interaction expansion needed by Nussbaumer and Storey (1979) to obtain very accurate transition probabilities is too extensive to be used in the  $R$ -matrix method for electron–atom scattering. It is therefore of interest to investigate how few configurations are necessary in order to achieve configuration interaction wavefunctions corresponding to reasonably accurate transition energies and probabilities.

In reporting this set of results it is also our aim to consider: (i) agreement between theory and available experimental data; (ii) the validity of the relativistic intermediate-coupling scheme at moderately high  $Z$ .

## 2. Relativistic Intermediate-coupling Wavefunctions

The relativistic intermediate-coupling wavefunctions are represented by the configuration interaction expansion

$$\Psi(JM_J) = \sum_i c_i^J \Phi_i(\alpha_i L_i S_i JM_J), \quad (1)$$

where the  $\{\Phi_i\}$  are single-configuration wavefunctions constructed from the one-electron functions (spin orbitals)

$$u(r, m_s) = r^{-1} P_{nl}(r) Y_l^{m_l}(\theta, \phi) \chi(m_s). \quad (2)$$

The angular momentum functions of the orbitals are combined according to coupling schemes  $\{\alpha_i\}$  to form  $(L_i, S_i)$  and the total angular momentum  $J$  arises from the vector coupling

$$\mathbf{J} = \mathbf{L} + \mathbf{S}. \quad (3)$$

The radial functions are expanded in analytic form as

$$P_{nl}(r) = \sum_{j=1}^k C_{jnl} \phi_{jnl}(r), \quad (4)$$

where  $k \geq n-l$  and where

$$\phi_{jnl}(r) = \{(2\zeta_{jnl})^{2l_{jnl}+1}/(2l_{jnl}!)\}^{\frac{1}{2}} r^{l_{jnl}} \exp(-\zeta_{jnl} r). \quad (5)$$

We also require the radial functions, for a given value of  $l$ , to form an orthonormal set:

$$\int_0^\infty P_{nl}(r) P_{n'l}(r) dr = \delta_{nn'}, \quad l+1 \leq n' \leq n. \quad (6)$$

We have used the configuration interaction code CIV3 (Hibbert 1975; Glass and Hibbert 1978*b*) in the  $LS$  coupling mode to determine the radial functions  $\{P_{nl}\}$ . We chose the 1s, 2s and 2p functions as the Hartree–Fock functions of the  $1s^2 2s 2p^3 P^0$  state.

With this set of radial functions, the relativistic intermediate-coupling wavefunctions in equation (1) were determined by including in the summation for each symmetry ( $J$  and  $\pi$ ) all possible configurations with a common  $1s^2$  core, with the different  $L_i$  and  $S_i$  satisfying (3). The expansion coefficients  $\{c_i^J\}$  were determined by diagonalizing the Hamiltonian matrix with respect to this basis. The Hamiltonian consists of the nonrelativistic electrostatic terms, plus the Darwin, mass-correction, spin-orbit, spin-other-orbit, spin-spin, spin-contact and orbit-orbit contributions.

**Table 1. Wavelengths and oscillator strengths for the  $2s^2 \rightarrow 2s2p$  transitions in the beryllium sequence**

Notation: A, present calculation; B, Armstrong *et al.* (1976); C, Kim and Desclaux (1976); D, Lin and Johnson (1977); E, Cheng and Johnson (1977); F, Nussbaumer and Storey (1979); G, Dietrich *et al.* (1978); H, Dietrich *et al.* (1980). Note that G and H are experimental results

Ion	Calc.	$2s^2 \ ^1S_0 \rightarrow 2s2p \ ^1P_1^0$		$2s^2 \ ^1S_0 \rightarrow 2s2p \ ^3P_1^0$		
		$\lambda$ (Å)	$f$	$\lambda$ (Å)	$f (\times 10^{-2})$	
Fe XXIII	A	131.52	0.157	263.96	0.149	
	B	130.03	0.156		0.150	
	C				0.150	
	D		0.150		0.150	
	E	130.03	0.155		0.150	
	F	133.03	0.157		264.48	0.157
	G	132.83			263.74	$0.24 \pm 0.07$
Kr XXXIII	A	73.72	0.138	170.52	0.534	
	B	71.61	0.137	165.44	0.54	
	C			165.68		
	D		0.137			
	E	71.61	0.137	165.44	0.54	
	F	74.19	0.137	172.52	0.527	
	H			169.9	0.564	
Mo XXXIX	A	51.45	0.140	138.65	0.762	
	B	49.20	0.140	132.95	0.75	
	C	49.20	0.141			
	D		0.140		0.589	
	E	49.20	0.140	132.95	0.75	
	F	51.83	0.138	141.96	0.722	
WLXXI	A	7.81	0.268	59.19	0.985	
	B	7.03	0.265	53.66	0.99	
	C	7.05	0.266			
	E	7.03	0.267	53.66	0.99	

### 3. Results and Discussion

In Table 1 we compare our results for the wavelengths  $\lambda$  and oscillator strengths  $f$  (length form) for the resonance transition  $2s^2 \ ^1S_0 \rightarrow 2s2p \ ^1P_1^0$  and the intercombination transition  $2s^2 \ ^1S_0 \rightarrow 2s2p \ ^3P_1^0$  with the various theoretical and experimental results. For the oscillator strengths, agreement between the different theoretical calculations is very good. Experimentally derived oscillator strengths for the intercombination line in iron and krypton have been given by Dietrich *et al.* (1978) (entry G) and Dietrich *et al.* (1980) (entry H). For iron, agreement between theory and

experiment is poor; there is disagreement by almost a factor of two. For krypton, calculated and experimentally derived oscillator strengths agree to better than 6%. The discrepancy between theory and experiment for iron is, perhaps, due to the difficulties experienced in the beam-foil experiment. It would be highly desirable to measure the lifetime of the intercombination line in iron by another method.

Agreement between our calculated wavelengths and the corresponding theoretical results is good. The discrepancy ranges from 1% for iron to 10% for tungsten. It is interesting that where the relativistic intermediate-coupling scheme and the relativistic multi-configurational Hartree-Fock results differ the former results are in better agreement with the experimental measurements. Dietrich *et al.* (1980) argued that the discrepancy between theory and experiment is due to the omission of the Lamb shift contribution by the theoreticians. If the discrepancy is due to the contribution from the radiative corrections ( $13940 \text{ cm}^{-1}$  for krypton; see Dietrich *et al.* 1980) the effect of configuration mixing upon the radiative corrections should be properly taken into account. However, this is not an easy task.

Inclusion of additional correlation effects in the wavefunctions has been looked at by Lin and Johnson (1977) using the relativistic random-phase approximation method (calculation D) and by Nussbaumer and Storey (1979) using the relativistic intermediate-coupling method (calculation F). In both calculations correlation effects within the  $n = 2$ , between the  $n = 2$  and  $n = 1$  and within the  $n = 1$  shells were included. From the results in Table 1 it is seen that, for the higher members of the sequence, wavefunctions formed from configurations from the  $n = 2$  complex while keeping a  $1s^2$  core are adequate.

In the Introduction we pointed to two matters we wished to consider in this paper. As far as the first, we have seen that the wavelengths calculated using the relativistic multi-configurational Hartree-Fock calculations are not in agreement with the experimental results; instead, the relativistic intermediate-coupling calculations appear to give better agreement with experiment.

Our second aim was to look at the validity of the relativistic intermediate-coupling scheme at moderately high  $Z$ . The question is of how the relativistic effects should be included and of what changes they induce in the wavefunctions. Armstrong *et al.* (1976), Kim and Desclaux (1976) and Cheng and Johnson (1977) in determining the relativistic radial functions used the Dirac operator which includes the nuclear spin-orbit term. As the calculation of the Breit interaction with wavefunctions of the correct symmetry are complicated the relativistic contributions to the energy levels are evaluated as a spherical average over configurations. However, Cheng *et al.* (1978) have shown that the use of  $J^2$  eigenfunctions, instead of a configuration average, in evaluating the Breit interaction leads to a substantial improvement in the fine structure.

Perhaps the resolution of the problem lies in the size of errors introduced in the two schemes. One must remember that the Breit operator is itself an approximate expression for use in a relativistic treatment. Although its use in higher order perturbation theory incorrectly gives higher order corrections both to the energy and wavefunction, these corrections are very small for low  $Z$  (i.e.  $\alpha Z$  is small). We have shown that the error associated with including the spin-orbit, spin-other-orbit, spin-spin, Darwin contact and mass correction terms in the Hamiltonian in order to determine the configuration mixing is not too serious. For high  $Z$ , when a full relativistic treatment is needed, the nuclear spin-orbit term dominates the others.

Hence the use of first-order perturbation theory, with the wavefunction determined as an eigenfunction of a sum of one-electron Dirac operators, gives satisfactory results. From the variation with  $Z$  of the relative importance of the relativistic operators it would seem that a satisfactory dovetailing of the two philosophies can be achieved when the transition from one to the other becomes necessary.

A further modification to the relativistic intermediate-coupling scheme would be the inclusion of the one-electron Darwin and mass-correction terms as well as the usual nonrelativistic terms in the Hamiltonian at the optimization stage of the radial functions. The major relativistic effects would be incorporated into the radial functions while still retaining a  $J$ -independent relativistic formalism.

While the main qualitative features of the beryllium sequence described here are probably correct, it is more difficult to assess the quantitative accuracy, especially for the more highly ionized systems. The results for tungsten should probably be treated with some caution, although it is almost impossible to give a quantitative estimate of the reliability. For highly ionized atoms, quantum electrodynamic effects such as the Lamb shift contribution could be more important than the Breit interaction in attaining accurate transition energies between configurations. Highly ionized atoms thus provide a sensitive test of the theoretical treatment of relativistic and quantum electrodynamic effects.

The purpose of the present work was not only to present accurate theoretical calculations but to investigate how few configurations are necessary in order to achieve configuration interaction wavefunctions corresponding to reasonably accurate wavelengths and oscillator strengths. From the results presented here it is seen that for highly ionized atoms in the beryllium isoelectronic sequence the same degree of accuracy can be achieved by using the three configuration basis composed of  $2s^2$ ,  $2s2p$  and  $2p^2$ . That is, it is not necessary to include additional radial functions ( $n > 2$ ) in the basis set.

## References

- Armstrong, L., Fielder, W. R., and Lin, D. L. (1976). *Phys. Rev. A* **14**, 1114.  
Cheng, K. T., Desclaux, J. P., and Kim, Y.-K. (1978). *J. Phys. B* **11**, L359.  
Cheng, K. T., and Johnson, W. R. (1977). *Phys. Rev. A* **15**, 1326.  
Cowan, R. D., and Griffin, D. C. (1976). *J. Opt. Soc. Am.* **66**, 1010.  
Dietrich, D. D., *et al.* (1978). *Phys. Rev. A* **18**, 208.  
Dietrich, D. D., Leavitt, J. A., Gould, H., and Marrus, R. (1980). *Phys. Rev. A* **22**, 1109.  
Glass, R. (1979a). *J. Phys. B* **12**, 679.  
Glass, R. (1979b). *J. Phys. B* **12**, 689.  
Glass, R. (1981a). *J. Phys. B* **14**, L409.  
Glass, R. (1981b). *Z. Phys. A* **302**, 203.  
Glass, R., and Hibbert, A. (1978a). *J. Phys. B* **11**, 2413.  
Glass, R., and Hibbert, A. (1978b). *Comput. Phys. Commun.* **16**, 19.  
Hibbert, A. (1975). *Comput. Phys. Commun.* **9**, 141.  
Kim, Y.-K., and Desclaux, J. P. (1976). *Phys. Rev. Lett.* **36**, 139.  
Lawson, K. D., and Peacock, N. J. (1980). *J. Phys. B* **13**, 3313.  
Lin, C. D., and Johnson, W. R. (1977). *Phys. Rev. A* **15**, 1046.  
Nussbaumer, H., and Storey, P. J. (1979). *J. Phys. B* **12**, 1647.  
Scott, N. S., and Burke, P. G. (1980). *J. Phys. B* **13**, 4299.  
Weiss, A. W. (1976). 'Beam-Foil Spectroscopy', Vol. 1, p. 51 (Plenum: New York).

