

Allowed and Forbidden $n = 2-2$ Transitions of the Elements Kr and Mo

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Abstract

Relativistic intermediate-coupling wavefunctions are used to evaluate transition energies, line strengths and transition probabilities for all allowed and forbidden $n = 2-2$ transitions for krypton and molybdenum beryllium-like ions. Our results are in very good agreement with those calculated using the relativistic multi-configuration Hartree-Fock approximation. These calculations were carried out under the same physical assumption that the dominant correlation effect is the $n = 2$ intra-shell correlation. We also discuss the importance of relativistic effects on the radial functions, the relativistic intermediate-coupling scheme in the variational process, the importance of radiative corrections for transition energies between states with different occupation of the 2s shell, and the relative importance of intra- versus inter-shell correlation effects.

1. Introduction

Excitation energies and oscillator strengths for transitions in highly stripped ions are needed for estimating the energy loss through impurity ions in plasmas and for plasma diagnostics. Accurate absorption oscillator strengths are also required for determining the density and temperature of the solar corona. Precision spectroscopy both in astrophysical and in beam-foil measurements also demands accurate theoretical calculations.

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 excitation energies, oscillator strengths and transition probabilities accurately. However, discrepancies still exist between the different theories.

Theoretical calculations are based on several approaches; 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; Glass and Hibbert 1978*a*, 1978*b*; Glass 1979*a*, 1979*b*, 1981*a*, 1981*b*, 1982; Nussbaumer and Storey 1979). Another approach is the relativistic multi-configuration Hartree-Fock approximation (Kim and Desclaux 1976; Armstrong *et al.* 1976; Cheng and Johnson 1977; Cheng *et al.* 1978, 1979). The relativistic random-phase approximation has been used (Lin and Johnson 1977; Johnson and Lin 1979), while Johnson and Huang (1982) have also used the multi-configuration relativistic random-phase approximation.

In a nonrelativistic treatment, a transition involving a change in spin is strictly forbidden in LS coupling. However, in a full relativistic treatment this transition is allowed, and it is also allowed in the Breit–Pauli approximation. Armstrong *et al.* (1976), Cheng and Johnson (1977), Lin and Johnson (1977) and Johnson and Huang (1982) have evaluated oscillator strengths for the resonance transition and the inter-combination (spin–orbit electric dipole) transition for ions in the beryllium isoelectronic 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 beryllium-like ions which span the range of nuclear charges $Z = 20$ –42. These authors included the configurations $1s^2 2s^2$, $1s^2 2s 2p$, $1s^2 2p^2$, $1s^2 n l n l'$, $1s^2 n l n' l'$ and $1s 2l^{\alpha} 2l'^{\beta}$, where $n, n' = 2, 3, 4, 5$, l, l' take all allowed values and $\alpha + \beta = 3$. They did not consider the possibility of using the three-configuration basis composed of $2s^2$, $2s 2p$ and $2p^2$. Glass (1982), using relativistic intermediate-coupling wavefunctions, evaluated oscillator strengths for the resonance transition and the spin–orbit electric dipole transition $2s 2p \ ^3P_1^0 \rightarrow 2s^2 \ ^1S_0$ for iron, krypton, molybdenum and tungsten beryllium-like ions. This showed that the same degree of accuracy could be achieved by using the three-configuration basis composed of $2s^2$, $2s 2p$ and $2p^2$; i.e., it is not necessary to include additional radial functions ($n > 2$) in the basis set. For the oscillator strengths, agreement between the different theoretical calculations was very good.

The results reported by Glass (1982) indicate that, for highly ionized atoms in the beryllium isoelectronic sequence, only configurations which can be formed from the $n = 2$ complex, while keeping the $1s^2$ core, are necessary in order to achieve relativistic intermediate-coupling wavefunctions with reasonably accurate transition energies and probabilities for the resonance transition and the inter-combination line $2s 2p \ ^3P_1^0 \rightarrow 2s^2 \ ^1S_0$. However, the same approximations may not be valid for other electric dipole and spin–orbit electric dipole transitions between other $n = 2$ –2 transitions.

Cheng *et al.* (1979) used the relativistic multi-configuration Hartree–Fock approximation and reported results for all electric dipole and spin–orbit electric dipole transitions between the $n = 2$ –2 levels. These calculations were done under the physical assumption that the dominant correlation effect is the $n = 2$ intra-shell correlation.

The present investigation extends these studies by evaluating all electric dipole, spin–orbit electric dipole, magnetic dipole, magnetic quadrupole and electric quadrupole transitions between the $n = 2$ levels for krypton and molybdenum beryllium-like ions, using relativistic intermediate-coupling wavefunctions formed from the three-configuration basis composed of $2s^2$, $2s 2p$ and $2p^2$. 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 theoretical and computational study of low-energy collisions of electrons by complex atoms and ions. It is therefore of interest to investigate how few configurations are necessary in order to achieve wavefunctions corresponding to reasonably accurate excitation energies and transition probabilities.

In reporting this set of results it is thus possible to establish:

- (i) the importance of relativistic effects on the radial functions;
- (ii) the relativistic intermediate-coupling scheme in the variational process;

- (iii) the importance of radiative corrections for transition energies between states with different occupation of the 2s shells;
- (iv) the relative importance of intra- versus inter-shell correlation effects.

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 Φ_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 α_i to form L_i and 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

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

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 choose the 1s, 2s and 2p functions as the Hartree-Fock functions of the $1s^2 2s^2 2p^3 P^0$ 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 π) 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-spin, spin-spin, spin-contact and orbit-orbit contributions.

3. Transition Probabilities

The probability that an N -electron atom or ion in a state $|j\rangle$ will make a transition to a lower state $|i\rangle$ with the emission of dipole radiation is given by

$$A(j \rightarrow i) = \frac{64\pi^4}{3h\lambda_{ji}^3 g_j} \sum_{M_j, M_i, \mu} |\langle J_j M_j | Q_\mu | J_i M_i \rangle|^2, \quad (7)$$

where

$$\text{electric: } \quad \mathbf{Q} = e \sum_{k=1}^N r_k \mathbf{C}^{(1)}(k), \quad (8a)$$

$$\text{magnetic: } \quad \mathbf{Q} = -\frac{e}{mc} \sum_{k=1}^N \{\mathbf{l}(k) + g_s \mathbf{s}(k)\}, \quad (8b)$$

where $g_s = 2.00232$ is the gyromagnetic spin ratio. For spin-allowed transitions we have

$$\text{electric: } \quad \Delta S = 0; \Delta L = 0, \pm 1; 0 \neq 0; \Delta J = 0, \pm 1; 0 \neq 0; \quad (9a)$$

$$\text{magnetic: } \quad \Delta S = 0; \Delta L = 0; \Delta J = 0, \pm 1; 0 \neq 0 \quad (9b)$$

(where $0 \neq 0$ means $J_i = 0, j \rightarrow i, J_j = 0$ is not allowed) and for spin-forbidden transitions

$$\text{electric: } \quad \Delta S = \pm 1; \Delta L = 0, \pm 1, \pm 2; 0 \neq 0; \Delta J = 0, \pm 1; 0 \neq 0; \quad (10a)$$

$$\text{magnetic: } \quad \Delta S = \pm 1; \Delta L = 0, \pm 1, \pm 2; \Delta J = 0, \pm 1; 0 \neq 0. \quad (10b)$$

Similarly for quadrupole radiation we have

$$A(j \rightarrow i) = \frac{64\pi^6}{15h\lambda_{ji}^5 g_j} \sum_{M_j, M_i, \mu} |\langle J_j M_j | Q_\mu | J_i M_i \rangle|^2, \quad (11)$$

where

$$\text{electric: } \quad \mathbf{Q} = e \sum_{k=1}^N r_k^2 \mathbf{C}^{(2)}(k), \quad (12a)$$

$$\text{magnetic: } \quad \mathbf{Q} = \frac{e}{mc\sqrt{6}} \sum_{k=1}^N r_k [\mathbf{C}^{(1)}(k) \times \{2\mathbf{l}(k) + 3g_s \mathbf{s}(k)\}]^{(2)}. \quad (12b)$$

For spin-allowed transitions we have for both electric and magnetic

$$\Delta S = 0; \Delta L = 0, \pm 1, \pm 2; 0 \neq 0, 0 \neq 1;$$

$$\Delta J = 0, \pm 1, \pm 2; 0 \neq 0, 0 \neq 1, \frac{1}{2} \neq \frac{1}{2}; \quad (13)$$

and for spin-forbidden transitions

$$\text{electric: } \quad \Delta S = \pm 1; \Delta L = 0, \pm 1, \pm 2; 0 \neq 0, 0 \neq 1;$$

$$\Delta J = 0, \pm 1, \pm 2; 0 \neq 0, 0 \neq 1, \frac{1}{2} \neq \frac{1}{2}; \quad (14a)$$

$$\text{magnetic: } \quad \Delta S = \pm 1; \Delta L = 0, \pm 1; 0 \neq 0;$$

$$\Delta J = 0, \pm 1, \pm 2; 0 \neq 0, 0 \neq 1, \frac{1}{2} \neq \frac{1}{2}. \quad (14b)$$

Table 1. Radiative transitions from $2s2p\ ^3P_1^0$

Ion	Transition	Type	Calculation	λ (Å)	S^I	A (s ⁻¹)
KrXXXIII	$2s2p\ ^3P_1^0 \rightarrow 2s^2\ ^1S_0$	E1	A	170.52	0.300(-2)	4.089(8)
			B	172.52	0.299(-2)	3.935(8)
			C	169.80	0.293(-2)	4.040(8)
	$\rightarrow 2s2p\ ^3P_0^0$	M1	A	1202.00		9.356(3)
MoXXXIX	$2s2p\ ^3P_1^0 \rightarrow 2s^2\ ^1S_0$	E1	A	138.65	0.331(-2)	8.380(8)
			B	141.96	0.337(-2)	7.966(8)
			C	137.90	0.329(-2)	8.481(8)
		$\rightarrow 2s2p\ ^3P_0^0$	M1	A	849.03	

Table 2. Radiative transitions from $2s2p\ ^3P_2^0$

Ion	Transition	Type	Calculation	λ (Å)	A (s ⁻¹)	
KrXXXIII	$2s2p\ ^3P_2^0 \rightarrow 2s2p\ ^3P_1^0$	M1	A	247.77	8.014(5)	
			B	247.30	8.016(5)	
	$\rightarrow 2s^2\ ^1S_0$	M2	A	101.01	1.503(2)	
			B	101.63	1.462(2)	
	MoXXXIX	$2s2p\ ^3P_2^0 \rightarrow 2s2p\ ^3P_1^0$	E2	A	247.77	1.317(2)
				A	205.43	1.661(2)
$\rightarrow 2s2p\ ^3P_0^0$		E2	B	205.20	1.727(2)	
			A	122.69	6.196(6)	
MoXXXIX	$2s2p\ ^3P_2^0 \rightarrow 2s2p\ ^3P_1^0$	M1	B	122.60	6.182(6)	
			A	65.09	9.248(2)	
	$\rightarrow 2s^2\ ^1S_0$	M2	B	65.79	9.027(2)	
			A	122.69	2.165(3)	
	$\rightarrow 2s2p\ ^3P_0^0$	E2	A	107.12	2.241(3)	
			B	107.00	2.316(3)	

Table 3. Radiative transitions from $2s2p\ ^1P_1^0$

Ion	Transition	Type	Calculation	λ (Å)	S^I	A (s ⁻¹)
KrXXXIII	$2s2p\ ^1P_1^0 \rightarrow 2s^2\ ^1S_0$	E1	A	73.72	0.336(-1)	5.660(10)
			B	74.19	0.334(-1)	5.526(10)
			C	72.27	0.325(-1)	5.809(10)
	$\rightarrow 2s2p\ ^3P_2^0$	M1	A	272.96		1.114(5)
			A	129.88		5.583(5)
			A	117.22		1.126(6)
			A	272.96		1.509(1)
			A	129.88		1.856(2)
MoXXXIX	$2s2p\ ^1P_1^0 \rightarrow 2s^2\ ^1S_0$	E1	A	51.45	0.238(-1)	1.178(11)
			B	51.83	0.235(-1)	1.139(11)
			C	49.74	0.228(-1)	1.249(11)
	$\rightarrow 2p^2\ ^3P_0$	E1	A	432.18	0.917(-3)	7.669(6)
			B	428.10	0.907(-3)	7.806(6)
			C	386.00	0.863(-3)	1.013(7)
			A	245.58		2.371(5)
	$\rightarrow 2s2p\ ^3P_1^0$	M1	A	81.82		3.248(6)
			A	74.61		6.763(6)
			A	245.58		2.068(1)
			A	81.82		1.418(3)
A			81.82		1.418(3)	

Table 4. Radiative transitions from $2p^2\ ^3P_0$

Ion	Transition	Type	Calculation	λ (Å)	S^I	A (s ⁻¹)	
KrXXXIII	$2p^2\ ^3P_0 \rightarrow 2s2p\ ^3P_1^0$	E1	A	119.13	0.173(-1)	2.065(10)	
			B	120.80	0.172(-1)	1.980(10)	
			C	117.20	0.165(-1)	2.082(10)	
	$\rightarrow 2s2p\ ^1P_1^0$	E1	A	1439	0.128(-2)	8.912(5)	
			B	1454	0.126(-2)	8.303(5)	
			C	1701	0.126(-1)	5.192(5)	
	$\rightarrow 2s2p\ ^3P_2^0$	M2	A	229.44		7.267	
MoXXXIX	$2p^2\ ^3P_0 \rightarrow 2s2p\ ^3P_1^0$	E1	A	100.92	0.130(-1)	2.573(10)	
			B	100.85	0.129(-1)	2.539(10)	
			C	97.44	0.122(-1)	2.674(10)	
		$\rightarrow 2s2p\ ^3P_2^0$	M2	A	568.75		4.292(-3)

Table 5. Radiative transitions from $2p^2\ ^3P_1$

Ion	Transition	Type	Calculation	λ (Å)	S^I	A (s ⁻¹)	
KrXXXIII	$2p^2\ ^3P_1 \rightarrow 2s2p\ ^3P_2^0$	E1	A	123.59	0.195(-1)	6.979(9)	
			B	124.35	0.193(-1)	7.765(9)	
			C	122.40	0.185(-1)	6.815(9)	
	$\rightarrow 2s2p\ ^3P_1^0$	E1	A	82.46	0.104(-1)	1.268(10)	
			B	82.74	0.104(-1)	1.239(10)	
			C	80.67	0.102(-1)	1.313(10)	
	$\rightarrow 2s2p\ ^3P_0^0$	E1	A	77.17	0.156(-1)	2.294(10)	
			B	77.42	0.154(-1)	2.243(10)	
			C	75.50	0.153(-1)	2.400(10)	
	$\rightarrow 2s2p\ ^1P_1^0$	E1	A	225.84	0.117(-2)	6.791(7)	
			B	227.13	0.117(-2)	6.736(7)	
			C	224.80	0.116(-2)	6.881(7)	
		$\rightarrow 2p^2\ ^3P_0$	M1	A	270.21		7.334(5)
		$\rightarrow 2s^2\ ^1S_0$	M1	A	55.58		2.493(5)
		$\rightarrow 2s2p\ ^3P_2^0$	M2	A	123.59		0
	$\rightarrow 2s2p\ ^3P_1^0$	M2	A	82.46		4.205(2)	
	$\rightarrow 2s2p\ ^1P_1^0$	M2	A	225.84		2.486(-1)	
MoXXXIX	$2p^2\ ^3P_1 \rightarrow 2s2p\ ^3P_2^0$	E1	A	104.09	0.140(-1)	8.484(9)	
			B	104.40	0.139(-1)	8.253(9)	
			C	101.40	0.131(-1)	8.465(9)	
	$\rightarrow 2s2p\ ^3P_1^0$	E1	A	56.36	0.711(-2)	2.690(10)	
			B	56.39	0.705(-2)	2.656(10)	
			C	53.95	0.684(-2)	2.943(10)	
	$\rightarrow 2s2p\ ^3P_0^0$	E1	A	52.80	0.112(-1)	5.262(10)	
			B	52.85	0.111(-1)	5.091(10)	
			C	50.65	0.110(-1)	5.688(10)	
	$\rightarrow 2s2p\ ^1P_1^0$	E1	A	181.11	0.130(-2)	1.494(8)	
			B	182.37	0.129(-2)	1.440(8)	
			C	176.00	0.125(-2)	1.552(8)	
		$\rightarrow 2p^2\ ^3P_0$	M1	A	127.69		6.608(6)
		$\rightarrow 2s^2\ ^1S_0$	M1	A	40.06		1.095(6)
		$\rightarrow 2s2p\ ^3P_2^0$	M2	A	103.09		0
	$\rightarrow 2s2p\ ^3P_1^0$	M2	A	56.36		2.281(3)	
	$\rightarrow 2s2p\ ^1P_1^0$	M2	A	181.11		3.156(-1)	

For the electric dipole and magnetic quadrupole transitions the parity of the states must change, while for the magnetic dipole and electric quadrupole transitions the parity of the states must not change. The components of the tensor C^α satisfy the equation

$$C_\mu^{(\alpha)} = \left(\frac{4\pi}{2\alpha+1} \right)^{\frac{1}{2}} Y_\alpha^\mu. \tag{15}$$

In general, the electric dipole transitions are the strongest lines. However, even though a transition may be forbidden by the electric dipole selection rules (for example, the depopulation of the $2s2p \ ^3P_2^0$ level), it may not be forbidden if one includes the interaction between the atom and the magnetic vector of the radiation field or the variation of the field in the vicinity of the atom. The magnetic dipole, magnetic quadrupole and electric quadrupole transition probabilities are generally smaller than electric dipole transition probabilities by about a factor of 10^{-8} .

Table 6. Radiative transitions from $2p^2 \ ^3P_2$

Ion	Transition	Type	Calculation	λ (Å)	S^I	A (s ⁻¹)	
KrXXXIII	$2p^2 \ ^3P_2 \rightarrow 2s2p \ ^3P_2^0$	E1	A	112.12	0.281(-1)	7.858(9)	
			B	112.84	0.282(-1)	7.965(9)	
			C	110.80	0.270(-1)	8.036(9)	
	$\rightarrow 2s2p \ ^3P_1^0$	E1	A	77.03	0.242(-1)	2.160(10)	
			B	77.49	0.239(-1)	2.081(10)	
			C	75.47	0.244(-1)	2.302(10)	
	$\rightarrow 2s2p \ ^1P_1^0$	E1	A	190.29	0.246(-1)	1.468(9)	
			B	191.47	0.243(-1)	1.400(9)	
			C	188.60	0.240(-1)	1.449(9)	
	$\rightarrow 2p^2 \ ^3P_1$	M1	A	1209		3.785(3)	
			$\rightarrow 2s2p \ ^3P_2^0$	M2	A	112.12	3.804
				M2	A	77.03	3.108(2)
			$\rightarrow 2s2p \ ^3P_1^0$	M2	A	72.39	3.423(2)
				M2	A	190.29	8.507(-1)
			$\rightarrow 2p^2 \ ^3P_1$	E2	A	1209	2.630(-2)
				$\rightarrow 2p^2 \ ^3P_0$	E2	A	219.29
E2			A		53.14	1.135(4)	
MoXXXIX	$2p^2 \ ^3P_2 \rightarrow 2s2p \ ^3P_2^0$	E1	A	93.98	0.180(-1)	9.907(9)	
			B	94.55	0.178(-1)	8.550(9)	
			C	91.85	0.166(-1)	8.698(9)	
	$\rightarrow 2s2p \ ^3P_1^0$	E1	A	53.22	0.201(-1)	5.439(10)	
			B	53.38	0.198(-1)	5.267(10)	
			C	51.11	0.201(-1)	6.095(10)	
	$\rightarrow 2s2p \ ^1P_1^0$	E1	A	152.23	0.177(-1)	2.008(9)	
			B	154.30	0.175(-1)	1.936(9)	
			C	149.00	0.169(-1)	2.071(9)	
	$\rightarrow 2p^2 \ ^3P_1$	M1	A	955.41		6.818(3)	
			$\rightarrow 2s2p \ ^3P_2^0$	M2	A	93.98	2.470
				M2	A	53.22	1.659(3)
			$\rightarrow 2s2p \ ^3P_1^0$	M2	A	50.07	1.635(3)
				M2	A	152.23	8.711(-1)
			$\rightarrow 2p^2 \ ^3P_1$	E2	A	955.41	3.865(-2)
				$\rightarrow 2p^2 \ ^3P_0$	E2	A	112.58
E2			A		38.46	2.891(4)	

Table 7. Radiative transitions from $2p^2 \ ^1D_2$

Ion	Transition	Type	Calculation	λ (Å)	S^I	A (s^{-1})
KrXXXIII	$2p^2 \ ^1D_2 \rightarrow 2s2p \ ^1P_1^0$	E1	A	100.81	0.476(-1)	1.882(10)
			B	101.38	0.458(-1)	1.781(10)
			C	98.70	0.459(-1)	1.933(10)
	$\rightarrow 2s2p \ ^3P_2^0$	E1	A	73.62	0.294(-1)	2.990(10)
			B	74.06	0.296(-1)	2.949(10)
			C	72.19	0.297(-1)	3.205(10)
	$\rightarrow 2s2p \ ^3P_1^0$	E1	A	56.76	0.999(-3)	2.214(9)
			B	56.99	0.109(-2)	2.375(9)
			C	55.31	0.989(-3)	2.369(9)
	$\rightarrow 2p^2 \ ^3P_2$	M1	A	214.67		1.013(6)
	$\rightarrow 2p^2 \ ^3P_1$	M1	A	182.09		1.129(6)
	$\rightarrow 2s2p \ ^3P_2^0$	M2	A	73.62		1.101(3)
	$\rightarrow 2s2p \ ^3P_2^0$	M2	A	56.76		3.510(2)
	$\rightarrow 2s2p \ ^3P_1^0$	M2	A	54.20		4.119(1)
	$\rightarrow 2s2p \ ^1P_1^0$	M2	A	100.81		8.094(1)
	$\rightarrow 2s^2 \ ^1S_0$	E2	A	42.58		1.912(4)
	$\rightarrow 2p^2 \ ^3P_2$	E2	A	214.67		5.129(2)
	$\rightarrow 2p^2 \ ^3P_1$	E2	A	182.09		3.438(2)
	$\rightarrow 2p^2 \ ^3P_0$	E2	A	108.40		2.035(1)
	MoXXXIX	$2p^2 \ ^1D_2 \rightarrow 2s2p \ ^1P_1^0$	E1	A	63.94	0.319(-1)
B				64.70	0.309(-1)	4.627(10)
C				61.68	0.305(-1)	5.275(10)
$\rightarrow 2s2p \ ^3P_2^0$		E1	A	50.73	0.240(-1)	7.456(10)
			B	51.15	0.239(-1)	7.235(10)
			C	49.05	0.238(-1)	8.177(10)
$\rightarrow 2s2p \ ^3P_1^0$		E1	A	35.89	0.430(-3)	3.769(9)
			B	36.09	0.474(-3)	4.088(9)
			C	34.41	0.414(-3)	4.122(9)
$\rightarrow 2p^2 \ ^3P_2$		M1	A	110.21		7.169(6)
$\rightarrow 2p^2 \ ^3P_1$		M1	A	100.05		7.689(6)
$\rightarrow 2s2p \ ^3P_2^0$		M2	A	50.73		5.211(3)
$\rightarrow 2s2p \ ^3P_1^0$		M2	A	35.89		1.196(3)
$\rightarrow 2s2p \ ^3P_0^0$		M2	A	34.43		1.070(2)
$\rightarrow 2s2p \ ^1P_1^0$		M2	A	63.91		6.429(2)
$\rightarrow 2s^2 \ ^1S_0$		E2	A	28.51		4.124(4)
$\rightarrow 2p^2 \ ^3P_2$		E2	A	110.22		7.523(3)
$\rightarrow 2p^2 \ ^3P_1$		E2	A	100.05		4.041(3)
$\rightarrow 2p^2 \ ^3P_0$		E2	A	55.69		1.597(2)

4. Results and Discussion

Wavelengths λ and probabilities A for transitions between the $n = 2$ levels of beryllium-like krypton and molybdenum ions are shown in Tables 1–8; calculation A is the present calculation while calculations B and C are those of Nussbaumer and Storey (1979) and Cheng *et al.* (1979) respectively. The notation $\alpha(\beta)$ implies $\alpha \times 10^\beta$. For the spin-allowed electric dipole transitions, the line strengths S^I are also listed in Tables 1–8, given by

$$S^I = \sum_{M_{J_i}, M_{J_f}} \left| \langle \Psi^{(f)}(J, M_{J_f}) | \sum_{k=1}^N r_k | \Psi^{(i)}(J, M_{J_i}) \rangle \right|^2, \quad (16)$$

where

$$\langle \Psi^{(j)}(J, M_{J_j}) | \sum_{k=1}^N r_k | \Psi^{(i)}(J, M_{J_i}) \rangle = \sum_j c_j^{(j)} \sum_i c_i^{(i)} \langle \Phi_j(\alpha_j L_j S_j J M_{J_j}) | \sum_{k=1}^N r_k | \Phi_i(\alpha_i L_i S_i J M_{J_i}) \rangle. \quad (17)$$

That is, the line strength is proportional to the transition radial integrals

$$\int_0^\infty P_{nl}(r) r P_{n'l'}(r) dr \quad (n' \geq n; l' \geq l), \quad (18)$$

and the expansion coefficients $c_i^{(j)}$ of the relativistic intermediate-coupling expansion (1). The inclusion of configuration interactions in the calculation of line strengths introduces cumulative or cancellation contributions.

Table 8. Radiative transitions from $2p^2 \ ^1S_0$

Ion	Transition	Type	Calculation	λ (Å)	S^1	A (s ⁻¹)
KrXXXIII	$2p^2 \ ^1S_0 \rightarrow 2s2p \ ^1P_1^0$	E1	A	78.75	0.228(-1)	9.475(10)
			B	79.26	0.221(-1)	8.975(10)
			C	77.11	0.224(-1)	9.911(10)
	$\rightarrow 2s2p \ ^3P_1^0$	E1	A	49.03	0.223(-4)	3.829(8)
			B	49.26	0.287(-4)	4.873(8)
			C	47.81	0.230(-4)	4.264(8)
	$\rightarrow 2p^2 \ ^3P_1$	M1	A	120.92		5.835(6)
	$\rightarrow 2s2p \ ^3P_2^0$	M2	A	61.12		2.498(3)
	$\rightarrow 2p^2 \ ^1D_2$	E2	A	359.95		1.228(2)
$\rightarrow 2p^2 \ ^3P_2$	E2	A	134.86		6.513(3)	
MoXXXIX	$2p^2 \ ^1S_0 \rightarrow 2s2p \ ^1P_1^0$	E1	A	53.42	0.146(-1)	1.936(11)
			B	54.01	0.147(-1)	1.895(11)
			C	51.58	0.147(-1)	2.174(11)
	$\rightarrow 2s2p \ ^3P_1^0$	E1	A	32.32	0.805(-5)	4.837(8)
			B	32.50	0.815(-5)	4.813(8)
			C	31.02	0.524(-5)	3.558(8)
	$\rightarrow 2p^2 \ ^3P_1$	M1	A	76.49		2.675(7)
	$\rightarrow 2s2p \ ^3P_2^0$	M2	A	43.88		1.087(4)
	$\rightarrow 2p^2 \ ^1D_2$	E2	A	324.85		9.931(1)
$\rightarrow 2p^2 \ ^3P_2$	E2	A	83.08		4.020(4)	

Our calculated line strengths (A) for the electric dipole transitions are in excellent agreement with those of Nussbaumer and Storey (1979) (B). This implies that:

- (i) the contribution to the line strength from the additional transition radial integrals (18) due to the additional radial functions is very small;
- (ii) and/or the expansion coefficients $c_j^{(j)}$ of the configurations $1s^2nlnl'$, $1s^2nln'l'$ and $1s2l^{\alpha}2l'^{\beta}$, where $n, n' = 2, 3, 4, 5$, l, l' take all allowed values and $\alpha + \beta = 3$, are very small;
- (iii) or the contribution to the line strength from (i) and (ii) is not small but there are, instead, large cancellation effects.

Point (iii) appears to be rather doubtful in view of the good agreement between both sets of results for *all* electric dipole transitions.

The line strength operator is a one-electron operator. The important correlation corrections to the line strengths for transitions of the type

$$2s2p \rightarrow 2s^2 \quad (19)$$

would be configurations of the type

$$2s2p \rightarrow 2snp, \quad 2s^2 \rightarrow 2sns \quad (20)$$

in the relativistic intermediate-coupling wavefunction (1), and for transitions of the type

$$2p^2 \rightarrow 2s2p \quad (21)$$

the important corrections would be configurations of the type

$$2p^2 \rightarrow 2pnp, \quad 2s2p \rightarrow ns2p. \quad (22)$$

Since our results for *all* electric dipole transitions are, in general, in excellent agreement (with discrepancies generally less than 1%) with those of Nussbaumer and Storey (1979), inclusion of additional *np* functions as corrections to the *2p* function for the $^1P^0$ or $2p^2$ states, or *ns* functions as corrections to the *2s* function for the $^1P^0$ or $2s^2$ states, is not necessary.

In Tables 1–8 we have also included the line strengths for the electric dipole transitions from the relativistic multi-configuration Hartree–Fock approximation (calculation C). Agreement between our relativistic intermediate-coupling calculations and the relativistic multi-configuration Hartree–Fock calculations is very good. The discrepancies range from less than 1% to approximately 5% with the exception of the transitions $2p^2 \ ^3P_2 \rightarrow 2s2p \ ^3P_2^0$ and $2p^2 \ ^1S_0 \rightarrow 2s2p \ ^3P_1^0$ where our results are 10% and 54%, respectively, greater than those of Cheng *et al.* (1979).

Agreement between our calculated wavelengths and the corresponding relativistic multi-configuration Hartree–Fock results is good, with discrepancies ranging from 1% to approximately 5%. However, there is one exception, in the region of crossing of the $2p^2 \ ^3P_0$ and $2s2p \ ^1P_1^0$ levels, where agreement between our results and those of Cheng *et al.* is disappointing. Just before the crossing, the calculated transition energies (for the transition $2s2p \ ^1P_1^0 \rightarrow 2p^2 \ ^3P_0$) differ by approximately 12%. For the energy separation of the $2p^2 \ ^3P_0$ and $2s2p \ ^1P_1^0$ levels we obtained a value of $69\,493 \text{ cm}^{-1}$; Cheng *et al.* obtained values of $70\,124 \text{ cm}^{-1}$ excluding the Lamb shift correction and $58\,790 \text{ cm}^{-1}$ including the correction. For molybdenum we obtained a separation of $231\,385 \text{ cm}^{-1}$, while Cheng *et al.* obtained values of $239\,391 \text{ cm}^{-1}$ excluding the Lamb shift correction and $259\,055 \text{ cm}^{-1}$ including the correction. In general, our calculated transition energies are in better agreement with those of Cheng *et al.* when the Lamb shift corrections are included. However, within the region of level crossing the transition energies evaluated using the relativistic intermediate-coupling method differ quite substantially from those evaluated using the relativistic multi-configuration Hartree–Fock method with the Lamb shift corrections included.

In the Introduction we pointed to four matters we wished to consider in this paper. Our first aim was to look at the importance of relativistic effects on the radial

functions. In the relativistic intermediate-coupling approach, the radial functions are determined in an LS coupled representation; i.e., the radial functions are calculated in the nonrelativistic approximation. The relativistic corrections are included in the Hamiltonian in order to determine the configuration mixing in (1). In the relativistic multi-configuration Hartree-Fock approximation, the Dirac operator which includes the nuclear spin-orbit term is used in determining the relativistic radial functions. The coefficients of the configuration mixing are also determined using the same level of approximation. The Breit operator and the Lamb shift corrections are excluded from the relativistic Hamiltonian with which the variational calculation is carried out. The line strength is proportional to the transition radial integrals in (18) and the expansion coefficients in (1). Good agreement between the line strengths calculated in the relativistic intermediate-coupling approach and those by the relativistic multi-configuration Hartree-Fock approximation implies that the omission of the relativistic terms at the optimization (determination) stage of the radial functions is not serious.

Our second aim was to look at the relativistic intermediate-coupling scheme in the variational process. We have shown that the relativistic intermediate-coupling scheme can be used to obtain accurate results for line strength calculations. The transition energies calculated in the relativistic intermediate-coupling scheme are also in good agreement with those calculated by the relativistic multi-configuration Hartree-Fock approximation. Thus, the error associated with the inclusion of the spin-orbit, spin-other-orbit, spin-spin, Darwin, spin-contact, mass-correction and orbit-orbit terms in the Hamiltonian, in order to determine the configuration mixing, is small. Again, this implies that the omission of the relativistic terms at the optimization of the radial functions is not serious.

Our third aim was to look at the importance of radiative corrections for transition energies between states with different occupation of the $2s$ shell. For beryllium-like ions the Lamb shift corrections are only important for electric dipole and magnetic quadrupole transitions. With the exception of the transition energies within the region of level crossing, agreement between our results and those of Cheng *et al.* is very good. Thus the importance of radiative corrections for transition energies between states with different occupation of the $2s$ shell is not too serious. The Lamb shift corrections included in the relativistic multi-configuration Hartree-Fock calculations of Cheng *et al.* are order-of-magnitude estimates only. As the Lamb shift scales as Z^4 , errors associated with the estimated values can be substantial for high- Z ions.

Our fourth aim was to look at the relative importance of intra- versus inter-shell correlation effects. A comparison of our results with those of Nussbaumer and Storey (1979) shows 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 $2p^2$. Thus, it is not necessary to use the large scale configuration interaction expansion, which Nussbaumer and Storey used to obtain reasonably accurate excitation energies and transition probabilities for highly ionized atoms, because the intra-shell correlation effects are much more important than the inter-shell.

We have also calculated magnetic dipole, magnetic quadrupole and electric quadrupole transition probabilities, and of these, the magnetic dipole transition probabilities are the largest. In some cases they are the same order of magnitude as the electric spin-orbit transition probabilities. Comparison of all three types of higher transition

probabilities with the work of Nussbaumer and Storey (1979) was possible in certain cases, and the agreement is good.

The $2s2p\ ^3P_2^0$ level can decay by the following processes:

- (i) magnetic dipole radiation to $2s2p\ ^3P_1^0$;
- (ii) magnetic quadrupole radiation to $2s^2\ ^1S_0$;
- (iii) electric quadrupole radiation to $2s2p\ ^3P_{0,1}^0$.

From Table 2 it is seen that the $2s2p\ ^3P_2^0$ level will depopulate with the emission of magnetic dipole radiation. That is, for highly ionized ions in the beryllium isoelectronic sequence, the magnetic quadrupole transition plays no part in depopulating the $2s2p\ ^3P_2^0$ level, in contrast to the result implied by Lin and Johnson (1977).

Nussbaumer and Storey (1979) labelled the even parity $J = 2$ levels according to their respective dominant SL parent configurations. However, the energy separation of the levels increases with increasing Z , and therefore in Tables 6 and 7 we have reversed the Nussbaumer and Storey designation.

5. Conclusions

We have shown in the present paper that, by means of the relativistic intermediate-coupling approach for moderately high Z , the calculated transition energies (wavelengths), line strengths and transition probabilities are in very good agreement with those calculated using the relativistic multi-configuration Hartree-Fock approximation. These calculations were carried out under the same physical assumption that the dominant correlation effect is the $n = 2$ intra-shell correlation. We have also discussed the importance of relativistic effects on the radial functions, and the relativistic intermediate-coupling scheme in the variational process. We conclude that the omission of the relativistic corrections from the Hamiltonian with which the variational calculation is carried out is not too serious. Furthermore, we have discussed the importance of radiative corrections to transition energies between states with different occupation of the $2s$ shell. With the exception of the transition energies within the region of level crossing, agreement between our results and those of Cheng *et al.* (1979) is enhanced when radiative corrections are included in their calculations. However, it is important to note that the Lamb shift corrections used by Cheng *et al.* are only estimates and, because the Lamb shift scales as Z^4 , the associated errors could be substantial for high- Z ions. It should also be mentioned that mass polarization effects lead to correction terms that are linear in Z . However, these are much smaller than the Lamb shift corrections, especially for high- Z ions. We have also discussed the question of the relative importance of intra- versus inter-shell correlation effects. Since our results are in very good agreement with those of Nussbaumer and Storey (1979), who included both intra- and inter-shell correlation effects in their study of highly ionized beryllium-like ions, we conclude that the omission of inter-shell correlation effects is not serious.

The good overall agreement between our results and those of Nussbaumer and Storey (1979) has an important physical application 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 large-scale configuration interaction expansion required 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.

Thus, in principle, for highly ionized ions of the beryllium isoelectronic sequence it is possible to introduce relativistic corrections and intermediate coupling through perturbation theory and the Pauli approximation with nonrelativistic wavefunctions. The relativistic multi-configuration Hartree-Fock method, however, accounts for correlation and relativistic effects in the same theoretical framework. One of the major uncertainties at high Z is the contribution of quantum electrodynamic effects such as the Lamb shift correction, which could be more important than the Breit interaction in obtaining accurate transition energies between states. Further refinement of the theory is desirable as it will provide a sensitive test of the theoretical treatment of relativistic and quantum electrodynamic effects. However, while progress is being made at the theoretical level, there is a lack of relevant experimental data. Experimentally determined transition energies and transition probabilities for highly ionized atomic systems would be highly desirable to enable comparisons to be made.

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.
Cheng, K. T., Kim, Y.-K., and Desclaux, J. P. (1979). *At. Data Nucl. Data Tables* **24**, 111.
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. (1982). *Aust. J. Phys.* **35**, 693.
Glass, R., and Hibbert, A. (1978a). *J. Phys. B* **11**, 2413.
Glass, R., and Hibbert, A. (1978b). *Comput. Phys. Commun.* **16**, 19.
Johnson, W. R., and Huang, K.-N. (1982). *Phys. Rev. Lett.* **48**, 315.
Johnson, W. R., and Lin, C. D. (1979). *Phys. Rev. A* **20**, 964.
Kim, Y.-K., and Desclaux, J. P. (1976). *Phys. Rev. Lett.* **36**, 139.
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).

