

Born cross sections for the excitation of the resonance lines of magnesium and calcium

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Abstract. Optical oscillator strengths, generalized oscillator strengths, first Born total cross sections and the polarization of impact radiation are calculated for the excitation of the resonance ($^1S-^1P$) lines of atomic magnesium and calcium. Large multi-configuration wavefunctions are used to represent the initial and final states, and excellent agreement is obtained with recent experimental results.

1. Introduction

In a previous paper (Burke *et al* 1972) the method of superposition of configurations, was used to obtain configuration interaction (CI) type wavefunctions for the calculation of optical oscillator strengths for the resonance transition in the beryllium isoelectronic sequence. Recently Hibbert (1973) has extended these calculations to other higher beryllium transitions. Having established that CI can be used to determine dipole oscillator strengths of high accuracy, the author (Robb 1973) has investigated the effect of CI on the calculation of other atomic properties such as polarizabilities and Van der Waals coefficients. It has further been shown by Hibbert (1970) and Glass and Hibbert (1973) that CI wavefunctions can produce accurate values for the hyperfine splitting in the ground states of lithium and boron. In the present calculation the computer program that calculated the optical oscillator strengths has been extended to calculate generalized oscillator strengths and Born cross sections between various M_L states of atoms. The results obtained compare well with previous calculations and show good agreement, in the calcium transition, with the recent experimental results of Ehlers and Gallagher (1973).

2. Theory

The generalized oscillator strength can be written, in atomic units, as:

$$f_{0n}(K) = \frac{(E_n - E_0)}{K^2} \left| \left\langle \Psi_n \left| \sum_{j=1}^N e^{i\mathbf{K} \cdot \mathbf{r}_j} \right| \Psi_0 \right\rangle \right|^2$$

where the N -electron atom is initially in the state Ψ_0 with energy E_0 and the incident electron has a wavevector \mathbf{k}_0 . After the collision the atom is in the state Ψ_n with energy E_n , and the scattered electron has a wavevector \mathbf{k}_n .

The wavefunctions Ψ_0 and Ψ_n are expanded in terms of a predetermined set of configurations ϕ_i , as:

$$\Psi = \sum_i c_i \phi_i. \quad (2)$$

Further details about the configurations ϕ_i can be obtained from Burke *et al* (1972), but it should be noted that in the present calculations, the sign of the coefficients c_i depends on the fact that the phase convention of Fano and Racah (1958) for the spherical harmonic functions is used.

The momentum transfer \mathbf{K} is defined as:

$$\mathbf{K} = \mathbf{k}_0 - \mathbf{k}_n. \quad (3)$$

Equation (1) is evaluated by making the substitution

$$e^{i\mathbf{K} \cdot \mathbf{r}_j} = \sum_{l=0}^{\infty} (2l+1) i^l j_l(Kr_j) C^{*l}(\hat{\mathbf{K}}) \cdot C^l(\hat{\mathbf{r}}_j) \quad (4)$$

and in the case of transitions between terms, where one averages over initial states and sums over final states, we have that

$$f_{0n}(K) = \frac{(E_n - E_0)}{K^2} \sum_{l=0}^{\infty} \frac{(2l+1)}{(2L_0+1)(2L_n+1)} \left| \left\langle \Psi_n \left\| \sum_{j=1}^N j_l(Kr_j) C^l(\hat{\mathbf{r}}_j) \right\| \Psi_0 \right\rangle \right|^2. \quad (5)$$

The evaluation of the reduced matrix element in equation (5) has been discussed by the author (Robb 1973b). In the case of an optically allowed $^1S-^1P$ transition only the $l=1$ term remains in equation (5) and, in the limit of $K \rightarrow 0$, $f_{0n}(K)$ becomes the optical oscillator strength.

The total cross section for the transition is given (in units of πa_0^2) by

$$\sigma_{0n} = Q = \frac{8}{k_0^2(E_n - E_0)} \int_{K_{\min}}^{K_{\max}} f_{0n}(K) d(\ln K) \quad (6)$$

where both k_0^2 and $(E_n - E_0)$ are in rydbergs. In the case of a $^1S-^1P$ transition it can be shown that the cross section for the excitation of the $M_L = 0$ state of the 1P term is given by

$$(\sigma_{0n})_{M_L=0} \equiv Q_0 = \frac{8}{k_0^2(E_n - E_0)} \int_{K_{\min}}^{K_{\max}} \left(\frac{K^2 + E_n - E_c}{2Kk_0} \right)^2 f_{0n}(K) d(\ln K). \quad (7)$$

The cross sections for the excitation of the $M_L = \pm 1$ states are then given by

$$Q_{\pm 1} = \frac{1}{2}(Q - Q_0) \quad (8)$$

and thus, according to Percival and Seaton (1958), we have that the percentage polarization of the radiation emitted in the subsequent spontaneous decay of the 1P state, is given by

$$P = 100 \frac{Q_0 - Q_{\pm 1}}{Q_0 + Q_{\pm 1}}. \quad (9)$$

3. Magnesium calculations

Three calculations were performed using different numbers of configurations in the initial and final states. In all cases however, the radial orbital functions were those determined by Weiss (1967). The configurations are listed in table 1, and the total state energies and configuration weightings of the wavefunctions used in the cross section calculation, are listed in table 2. In all of the present calculations the experimental energy difference is used in evaluating the oscillator strength.

It is apparent from table 3 that the convergence of the length value of the oscillator strength, with increasing configuration interaction in both states, is extremely good. However, the introduction of core polarization configurations $1s^2 2s^2 2p^5 3s^2 nd\ ^1P$ significantly affects the velocity value, even though their mixing coefficients are extremely small. It was observed that the

$$\int_0^\infty R_{2p}(r) \left(\frac{d}{dr} + \frac{3}{r} \right) R_{nd}(r) r^2 dr$$

radial integrals, which are involved in the calculation of the velocity value, are extremely large and negative for the orbitals used here. It would seem that better agreement between length and velocity values can only be obtained if the d-orbital exponents are optimized

Table 1. Configurations used in the magnesium calculations

¹ S	¹ P
1 $1s^2 2s^2 2p^6 3s^2$	1 $1s^2 2s^2 2p^6 3s 3p$
2 $1s^2 2s^2 2p^6 3s 4s$	2 $1s^2 2s^2 2p^6 3s 4p$
3 $1s^2 2s^2 2p^6 4s^2$	3 $1s^2 2s^2 2p^6 3s 5p$
4 $1s^2 2s^2 2p^6 3s 5s$	4 $1s^2 2s^2 2p^6 3s 6p$
5 $1s^2 2s^2 2p^6 5s^2$	5 $1s^2 2s^2 2p^5 3s^2 3d$
6 $1s^2 2s^2 2p^6 3p^2$	6 $1s^2 2s^2 2p^5 3s^2 4d$
7 $1s^2 2s^2 2p^6 4p^2$	7 $1s^2 2s^2 2p^5 3s^2 5d$
8 $1s^2 2s^2 2p^6 5p^2$	8 $1s^2 2s^2 2p^6 4s 4p$
9 $1s^2 2s^2 2p^6 3d^2$	9 $1s^2 2s^2 2p^6 4s 5p$
10 $1s^2 2s^2 2p^6 4d^2$	10 $1s^2 2s^2 2p^6 3p 4d$
11 $1s^2 2s^2 2p^6 4f^2$	11 $1s^2 2s^2 2p^6 3d 4p$
12 $1s^2 2s^2 2p^6 3s 6s$	12 $1s^2 2s^2 2p^6 3d 5p$
13 $1s^2 2s^2 2p^5 3s^2 3p$	13 $1s^2 2s^2 2p^6 3d 6p$
14 $1s^2 2s^2 2p^5 3s^2 4p$	14 $1s^2 2s^2 2p^6 4p 4d$
15 $1s^2 2s^2 2p^5 3s^2 5p$	15 $1s^2 2s^2 2p^6 3p 3d$
16 $1s^2 2s^2 2p^6 4s 5s$	16 $1s^2 2s^2 2p^6 3p 5d$
17 $1s^2 2s^2 2p^6 3p 4p$	17 $1s^2 2s^2 2p^6 3d 4f$
18 $1s^2 2s^2 2p^6 3p 5p$	18 $1s^2 2s^2 2p^6 3p 4s$
19 $1s^2 2s^2 2p^6 4p 5p$	19 $1s^2 2s^2 2p^6 3p 5s$
20 $1s^2 2s^2 2p^6 3d 4d$	20 $1s^2 2s^2 2p^6 3p 6s$
21 —	21 $1s^2 2s^2 2p^5 3s^2 4s$
22 —	22 $1s^2 2s^2 2p^5 3s^2 5s$
23 —	23 $1s^2 2s^2 2p^5 3s^2 6s$

Calculation No. 1... used configurations 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 ¹S

1, 2, 3, 4, 8, 9, 10, 14, 15, 16, 17 ¹P

Calculation No. 2... used configurations 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 ¹S

1, 2, 3, 5, 8, 9, 10, 14, 15, 16, 17 ¹P

Calculation No. 3... used all of the configurations.

Table 2. Calculated energies and configuration weightings † for the wavefunctions used in the magnesium Born calculation

¹ S $E = -199.64825$ au		¹ P $E = -199.47088$ au	
Configuration No.	Weighting	Configuration No.	Weighting
1	0.9644287	1	-0.9288377
2	0.0270172	2	0.234053
3	-0.0404918	3	0.0256362
4	-0.0197748	4	-0.0024094
5	-0.0036053	5	0.0082886
6	-0.2568975	6	-0.0121385
7	-0.0106292	7	-0.0139558
8	-0.0013221	8	0.0592954
9	-0.0288990	9	0.0039228
10	-0.0048798	10	0.0555289
11	-0.008694	11	-0.0094420
12	0.0022445	12	-0.0015028
13	0.0060082	13	-0.0000611
14	-0.0016646	14	-0.0118507
15	0.0037368	15	0.2637965
16	-0.0003340	16	-0.0040909
17	0.0000081	17	0.0275233
18	0.0001576	18	-0.0641209
19	0.0003377	19	0.0067128
20	-0.0000093	20	-0.0000794
		21	0.0056932
		22	0.0034509
		23	0.0015211

† The sign of these weightings is dependent upon the fact that we use the Fano and Racah (3) convention for the spherical harmonic functions.

Table 3. Oscillator strengths for the resonance line of magnesium

	f_i	f_v
Present Work Calculation No. 1	1.823	1.958
Present Work Calculation No. 2	1.816	1.894
Present Work Calculation No. 3	1.814	1.421
Treffitz (1950)	1.68	
Weiss (1967)	1.77	
Zare (1967)	1.72	
Wiese <i>et al</i> (1969)	1.81†	
Hameed (1972)	1.99	
Kim and Bagus (1973)	1.71	
Norcross (1973)	1.835‡	

† This number represents a weighted average of the available experimental results.

‡ This number was calculated using the Thomas-Fermi CI code of Eissner and Nussbaumer (1969), with six configurations in the ground state and four configurations in the excited state.

on a multi-configurational excited state wavefunction. This is because the d-orbitals, in their role as correlation orbitals, would be much more sensitively determined in this calculation through the strongly interacting configurations $1s^2 2s^2 2p^6 3pnd\ ^1P$, rather than the weakly interacting $1s^2 2s^2 2p^6 nd^2\ ^1S$ configurations.

We have plotted the generalized oscillator strength in figure 1, which exhibits almost exactly the same behaviour as the curve of Kim and Bagus (1973). Kim and Bagus used multi-configurational Hartree-Fock wavefunctions, and they discuss in detail the

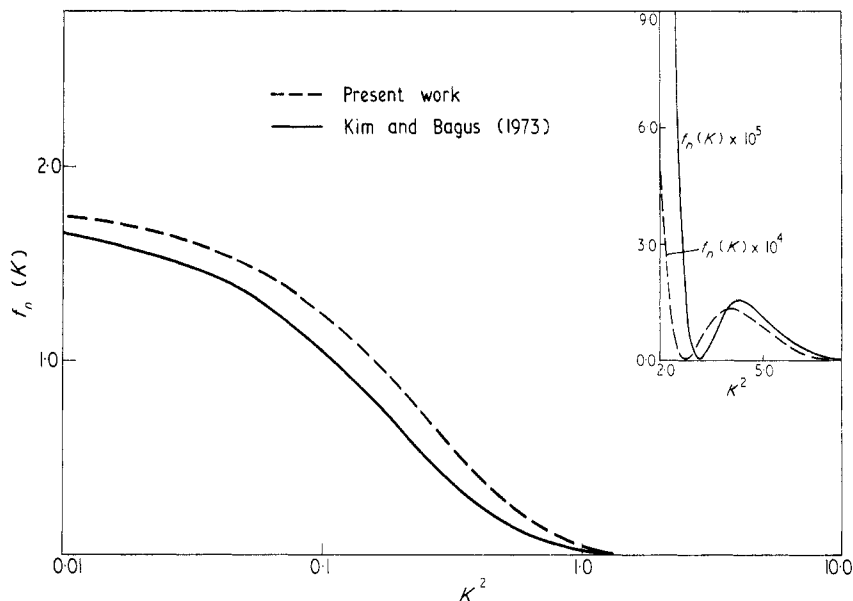


Figure 1. Magnesium $1S-1P$ generalized oscillator strength.

significance of the minimum obtained in the generalized oscillator strength. Although in the present calculation the minimum is much sharper than that of Kim and Bagus, their interpretation and discussion applies equally well. In figure 2 we have plotted the total Born cross section against energy, together with some points computed from the data of Kim and Bagus. The numerical values of the cross section are given in table 4. Unfortunately there does not seem to be any other data, either experimental or theoretical, to compare with in this energy range. It is apparent however, from the results of Van Blerkom (1970), that the Born cross section at 10 eV is too large by a factor of five or six. In figure 3 the high energy linear behaviour of QE versus $\ln E$ is illustrated. The percentage polarization of the radiation emitted in the spontaneous decay of the $1P$ state is plotted against the incident electron energy in figure 4. This shows the correct asymptotic behaviour in the limits of high and low energies, where it tends to -100% and $+100\%$ respectively.

4. Calcium calculations

Two calculations were performed. In the first the ground state wavefunction contained nine configurations, while the excited state had seven configurations. In both these sets

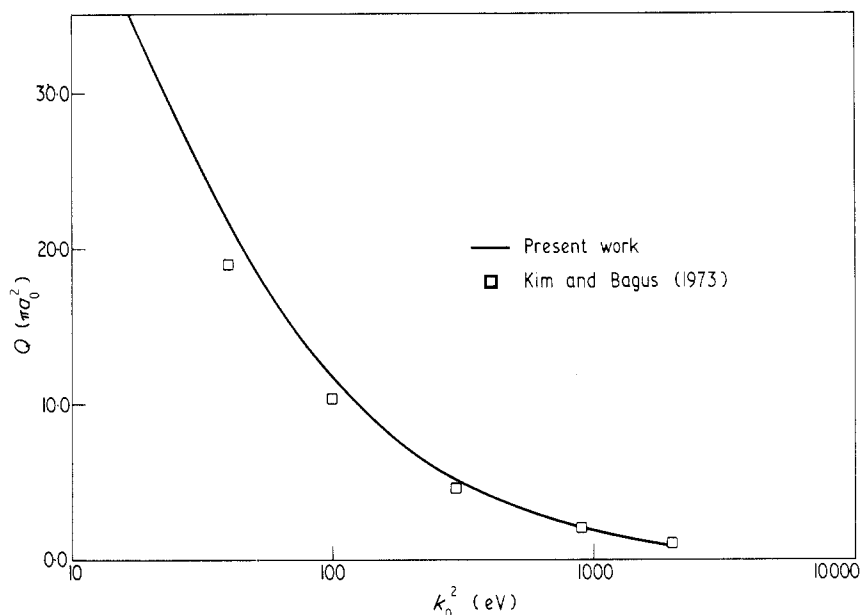


Figure 2. $e^- + \text{Mg}(^1\text{S}-^1\text{P})$ total cross section versus incident electron energy.

only excitation of the valence electrons was allowed, and the configurations are listed in table 5. In both this and the second calculation, the radial orbital functions of Weiss (1967) were used. Using the exact energy splitting of the states, the length and velocity values of the optical oscillator strength were computed. As can be seen from table 6, these are in reasonable agreement with each other and with previously obtained values. In the second calculation, eleven configurations were used for both states, however, the core 3p electrons were now allowed to excite in the ^1P state (see table 5). It is apparent from table 6 that the inclusion of core polarization configurations of the form $1s^2 2s^2 2p^6 3s^2 3p^5 4s^2 nd\ ^1\text{P}$ has a dramatic effect on both the length and velocity values of the oscillator strength. As in the magnesium calculation, the velocity value was adversely affected when the core polarization configurations were introduced, due to the incorrect shape of the ^1S optimized d-correlation orbitals. Various other configurations were added to both states in an attempt to improve the calculation further, but they were found to have a negligible effect on the oscillator strength. It is felt that this second calculation is the best possible with the present set of radial functions, and we have listed the total state energies and mixing coefficients in table 7. These latter wavefunctions, together with the exact term splitting, were used in the ensuing generalized oscillator strength and Born cross sections.

We have plotted the generalized oscillator strength in figure 5 together with the values obtained by Kim and Bagus (1973). We obtain the same general curve shape as they do, and again the reader is referred to their paper for a discussion of the observed minimum. The calculated total cross section is plotted against the incident electron energy in figure 6. The numerical values are given in table 4. Also plotted in figure 6 are some values calculated by Simsic and Williamson (1972), who used a crude one-electron model. Some of the Kim and Bagus (1973) values, and the experimentally determined values of Ehlers and Gallagher (1973) are also plotted. Ehlers and Gallagher have normalized

Table 4. Numerical values of the calculated quantities

Incident electron energy (eV)	Mg		
	Total cross section $Q(\pi a_0^2)$	Partial cross section $Q_0(\pi a_0^2)$	Percentage polarization
10	41.97	25.99	+ 52.99
30	—	—	—
40	21.81	7.69	+ 4.27
100	11.60	3.11	— 15.43
300	5.00	1.04	— 31.43
500	—	—	—
700	2.519	0.443	— 40.20
900	2.045	0.344	— 42.39
1400	1.412	0.221	— 45.86
2000	1.044	0.155	— 48.37

Incident electron energy (eV)	Ca		
	Total cross section $Q(\pi a_0^2)$	Partial cross section $Q_0(\pi a_0^2)$	Percentage polarization
10	76.41	39.56	+ 36.44
30	41.91	14.33	+ 1.92
40	—	—	—
100	17.83	4.34	— 21.66
300	7.53	1.44	— 35.60
500	4.960	0.866	— 40.54
700	3.750	0.618	— 43.40
900	3.037	0.481	— 45.35
1400	2.089	0.309	— 48.48
2000	—	—	—

their results to the Bethe form of the cross section at high energies, using the value of 1.75 for the optical oscillator strength. In their paper they state that there is an uncertainty of several per cent in their normalization procedure. In view of the close agreement between the present work and that of Kim and Bagus, Ehlers and Gallagher (private communication) have recommended that their results be renormalized by 4% to the present calculations.† Consequently the Ehlers and Gallagher values represented in figures 6 and 7 are renormalized values, and are not as in their paper.

In figure 7 the linear dependence of QE on $\ln E$ is demonstrated and this plot more usefully shows the differences between the various calculated and experimental results. The percentage polarization of the radiation emitted in the spontaneous decay of the 1P state is plotted in figure 8. As can be seen, the agreement with the experimentally observed polarization is excellent even down to quite low energies. Such excellent agreement indicates that, whereas the Born approximation is significantly in error at low energies in its estimation of the total cross section, it is extremely accurate in its prediction of the ratio of the cross section for excitation of the various M_L sub-states.

† An erratum is being submitted to this effect.

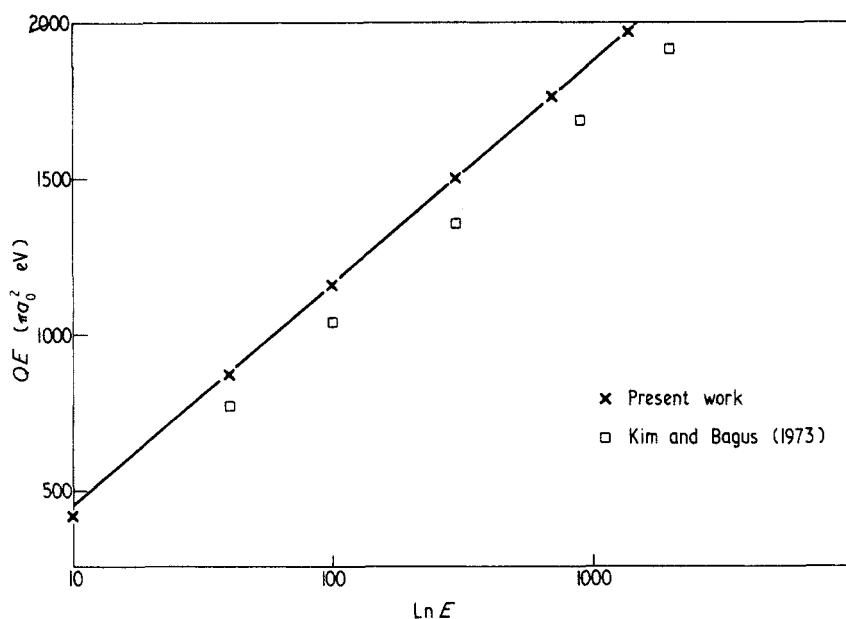


Figure 3. $e^- + \text{Mg } 1\text{S}-1\text{P}$ scattering cross sections QE versus $\ln E$.

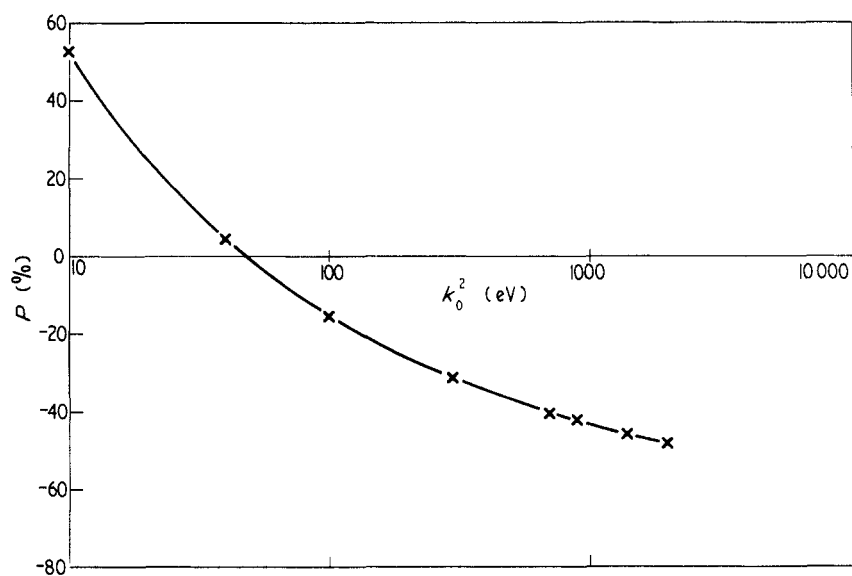


Figure 4. $e^- + \text{Mg } 1\text{S}-1\text{P}$ percentage polarization of radiation. P versus E .

5. Conclusions

The calculations show the importance of using good correlated atomic state wave-functions for the determination of Born cross sections at all energies. It was particularly noted that the observed minima and maxima in the generalized oscillator strength, at

Table 5. Configurations used in the calcium calculations

¹ S	¹ P
1 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ²	1 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s4p
2 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s5s	2 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d4p
3 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 5s ²	3 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4p4d
4 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s6s	4 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 5s5p
5 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4p ²	5 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d4f
6 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 5p ²	6 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s5p
7 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ²	7 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4p5s
8 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4d ²	8 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d5p
9 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4f ²	9 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 5s2d
10 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4p5p	10 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 5s2d
11 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4p6p	11 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 5s2d
	12 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s6p

Calculation No. 1 used the configurations 1, 2, 3, 4, 5, 6, 7, 8, 9 ¹S and 1, 2, 5, 6, 7, 8, 12 ¹P
 Calculation No. 2 used all of the ¹S configurations and the first eleven ¹P configurations.

Table 6. Oscillator strengths for the resonance line of calcium

	f_l	f_v
Present Work Calculation No. 1	1.833	1.764
Present Work Calculation No. 2	1.710	0.842
Wiese <i>et al</i> (1969)	1.75†	—
Friedrich and Trefitz (1969)	1.75‡	—
Hameed (1972)	2.36	—
Kim and Bagus (1973)	1.83	—

† This number represents a weighted average of the available experimental results.

‡ A semiempirical calculation.

Table 7. Calculated energies and configuration weightings† for the wavefunctions used in the calcium Born calculation

¹ S $E = -676.7853679$ au		¹ P $E = -676.67148717$ au	
Configuration No.	Weighting	Configuration No.	Weighting
1	0.95832131	1	0.88715849
2	-0.0220565	2	-0.43364653
3	-0.03902836	3	0.02572416
4	-0.0097872	4	-0.03929983
5	-0.27681577	5	-0.01922964
6	-0.00901456	6	0.12310804
7	-0.05215363	7	-0.04866243
8	0.00131490	8	-0.04285180
9	-0.00930025	9	-0.03625120
10	0.00032601	10	0.03964600
11	-0.00004548	11	0.00996864

† The sign of these weightings is dependent upon the fact that we use the Fano and Racah (3) convention for the spherical harmonic functions.

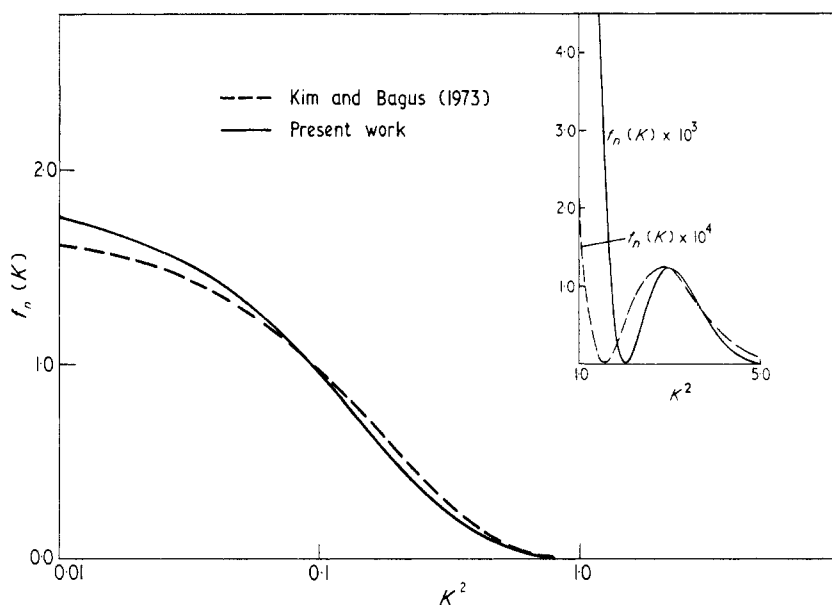


Figure 5. Calcium $1S-1P$ generalized oscillator strength.

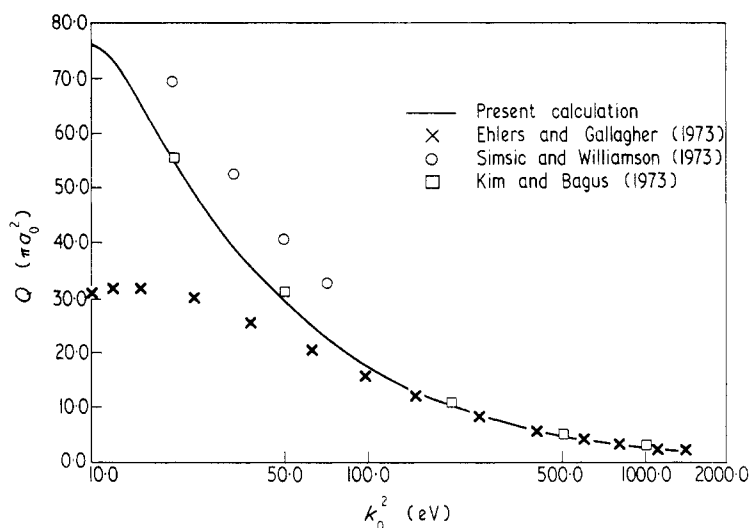


Figure 6. $e^- + \text{Ca } (1S-1P) Q(\pi a_0^2)$ versus E .

larger momentum transfers, are critically dependent on the wavefunctions used. This is because they arise from delicate cancellations in the radial integrals between bound orbitals (which remain fixed throughout the calculation), and the function $j_1(Kr)$, which becomes more oscillatory over the integration range as the momentum transfer K is increased. Thus the quality of the atomic state wavefunctions is stringently tested, at all radial distances, by these large K calculations. It is felt that the present calculations are the best to date in this region, and that the envelope of the maxima should be much

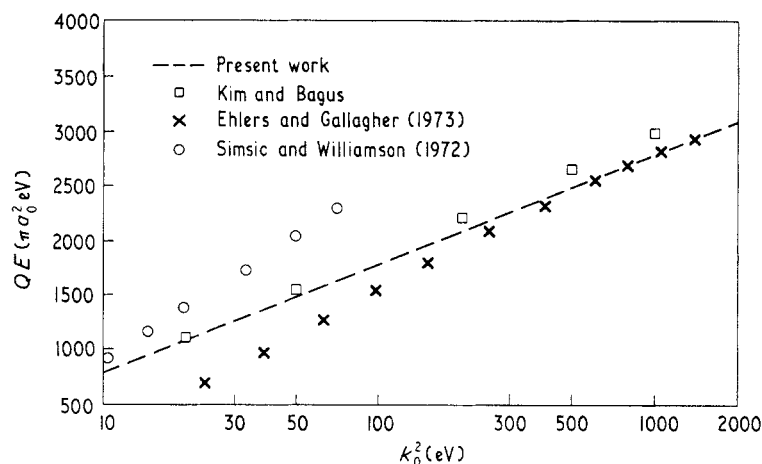


Figure 7. $e^- + \text{Ca } ({}^1\text{S}-{}^1\text{P})$ QE versus $\ln E$.

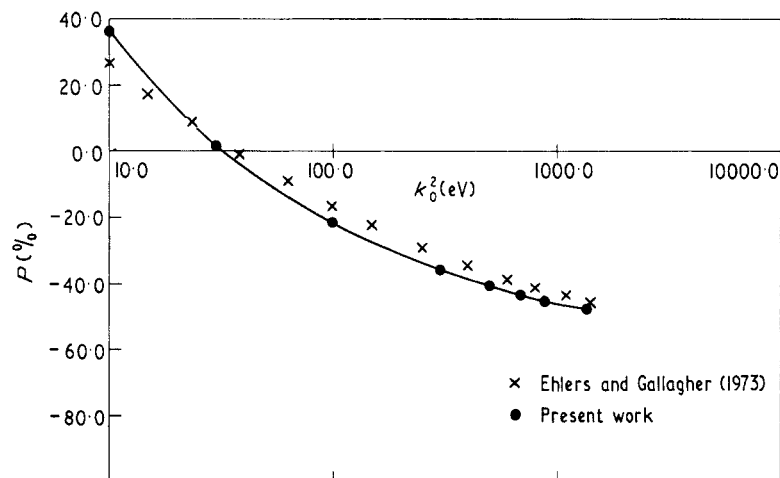


Figure 8. $e^- + \text{Ca } ({}^1\text{S}-{}^1\text{P})$ percentage polarization of emitted radiation versus incident electron energy.

closer to the experimentally observed generalized oscillator strength than that of previous calculations.

We have also shown that the Born approximation can accurately predict the percentage polarization of the impact radiation, even at quite low energies. However further checks of this on more sensitive transitions are necessary.

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