A phaseshift analysis of experimental angular distributions of electrons elastically scattered from He, Ne and Ar over the range 0·5 to 20 eV

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Abstract. Absolute differential elastic cross sections have been measured for electron scattering by helium, neon and argon atoms over the incident electron energy range of 0·5 to 20 eV, and over the scattered electron angular range of 15 to 150°. The experimental method uses crossed electron and modulated atom beams, 127° electrostatic energy analysis of incident and scattered electrons, quadrupole mass analysis of the target gas and single-particle counting techniques. It is shown how the use of a chi-squared optimisation analysis leads to better knowledge of apparatus behaviour and of cross section determinations. Absolute cross section values have been established by the methods of (i) the parametrisation of the relative elastic angular distributions in terms of the first three phases at 22 energies and 27 angles within the above ranges, (ii) a phaseshift analysis around the 19·3 eV (^{2}S) resonance in helium and (iii) the measurement of elastic scattering signal ratios in Ne and Ar at any energy and scattering angle (here 19·2 eV and 60°) for known relative source pressures. The errors in the differential cross section value at 19·2 eV and 60° in He determined by these methods are found to be ±4%, ±2% and ±11%, respectively. However, only the first method gives a calibration over the full energy and angular range of this paper. The present cross section values for helium, neon and argon generally agree, within the combined experimental errors, with the data of Andrick and Bitsch but disagree with most other measured values. In the case of helium the p and d phaseshifts calculated from a variational method by Sinfailam and Nesbet give the best agreement with the present values while the calculated polarised-orbital values of Callaway and colleagues also agree closely. For the s-wave phase an error of 1·4% is generally not sufficient to indicate a preference for any one theoretical set of values.

1. Introduction

This paper is the last of a series which studies the angular distributions of electrons elastically scattered from inert-gas atoms with the aim of determining absolute cross section values against which theoretical predictions may be evaluated. Previous papers studied the scattering of 20 to 400 eV electrons from argon (Williams and Willis 1975a) and from neon, krypton and xenon (Williams and Crowe 1975).

The basic calibration method of measuring absolute cross section values (Bederson and Kieffer 1971) is to measure accurately the values of all quantities which determine

the cross section, i.e. the incident and scattered electron beam fluxes, the target atom density and the interaction path length. However, this simple approach becomes complicated and difficult in practice because of non-uniformities in the beam fluxes, the non-ideal behaviour of particle detectors and the temporal behaviour of the apparatus; such factors are discussed at length by Bederson and Kieffer (1971) and Kieffer and Dunn (1966) for example. Moreover with this approach one must always ask what experimental proof shows that the measurements were made validly and accurately. The basic response is that an independent measurement in a different apparatus must be made for verification. While this approach must apply to all measurements, this paper presents some evidence to show that the method, based upon an energy and angular parametrisation of the experimental data in terms of phaseshifts leads to a better understanding of the apparatus functions, a demonstration of internal consistency of the measurements and to more accurate cross section values.

A phaseshift analysis method of deducing absolute elastic cross section values has been clearly demonstrated by Andrick and Bitsch (1975). Similar procedures have been described previously by Westin (1946), Hoeper *et al* (1968), Bransden and McDowell (1969), reviewed by McDowell (1970) and used by Naccache and McDowell (1974) in analysing the experimental data of McConkey and Preston (1975), Andrick and Bitsch (1975) and Gibson and Dolder (1969) for elastic scattering in helium and neon. If measurements are made of relative elastic angular distributions at several energies, then the phaseshift analysis may be made either independently at each energy or simultaneously at all energies by imposing, for example, some constraints on the energy dependence of the phaseshifts (for example, see Bransden and McDowell 1969). This paper follows the latter procedure and then shows how energy and/or angular-dependent calibration factors either for the whole apparatus or its components may be determined.

A special case of the phaseshift analysis method arises for a non-overlapping resonant state lying below the first inelastic threshold. Then because the resonance occurs in only a single partial wave whose phase changes by π at the resonance energy, a simple analysis (Shore 1967, Comer and Read 1972) of the angular dependence of the resonance profile is able to establish phaseshift values. Phaseshift values determined using this method for the ^2S (19·35 eV) resonance in helium and for the $^2P_{3/2,1/2}$ (11·07 and 11·24 eV) resonances in argon are compared with those determined using the first method.

Generally these methods should be used for each target gas. However, they are very time-consuming procedures. A simpler method of transferring the absolute calibration from one gas to another is to measure relative beam densities for each gas (Williams and Willis 1974, 1975a, b, Williams and Crowe 1975, Srivastava *et al* 1975) and then check the relative energy calibration of the apparatus. Finally, cross section values in helium and argon determined using this transfer method are compared with those obtained using the previous two methods.

2. Experimental considerations

2.1. Apparatus

The apparatus, experimental method and measurement procedures are described in detail by Williams and Willis (1975b). Briefly the apparatus is based upon the conventional crossed electron and modulated atom beams technique with good energy

and angular resolutions (0·050 eV and 2°, respectively) of the incident and scattered electrons by 127° cylindrical electrostatic analysers. Mass and angular analyses of the scattered atoms are made by a rotatable mass filter which has an electron impact ioniser. The scattered electrons are detected with channel electron multipliers whose charge-pulse outputs are processed with standard 50 Ω (EGG) electronics. The resulting pulses are stored in a multichannel analyser. Detailed studies of the validity of the experimental procedures and of the sources of error have been made for an atomic hydrogen beam (Williams and Willis 1975b) and for helium and argon beams (Williams and Willis 1975a). Similar but unpublished studies have been made for neon.

2.2. Cross section determination

The required elastic differential cross section, $I(k^2, \theta)$, for an electron energy, k^2 au, and scattering angle, θ, is related to the prime measured quantity, $N(k^2, \theta)$, the number of elastically scattered electrons/s at an angle θ into a solid angle, $d\Omega$, by the relationship

$$I(k^2, \theta) = N(k^2, \theta)\left(\int_\Omega \int_\tau n(x, y, z)J_e(x, y, z, k^2)\zeta(x, y, z, k^2, \theta)\, d\Omega\, d\tau\right)^{-1} \tag{1}$$

where $n(x, y, z)$ is the number density of target atoms, $J_e(x, y, z, k^2)$ is the flux density of incident electrons and $\zeta(x, y, z, k^2, \theta)$ is the apparatus calibration factor representing the non-ideal behaviour of the apparatus.

In initial studies (Williams and Willis 1974) the crossed beams were both of circular cross section, which necessitated the measurement of the beams overlap integral for each value of k^2. However, as was recognised during the course of that work and as has been pointed out by many people subsequently, such complicated procedures are avoided (Dolder 1969) by using a square cross section atomic beam and a rectangular cross section electron beam such that the cross section of the interaction volume viewed along the axis of the atomic beam is square. Then provided the flux density of either beam is constant across the height (that is the distance measured normal to the plane containing both incident beams) of the other, the overlap integral of the beams which occurs in equation (1) is simply equal to unity. In this work the atom beam is most simply arranged to be of constant flux density across its height. While such procedures are well established for crossed electron and ion beams (Dolder 1969), it is believed that the present experiments are the first published report of their use and implications for crossed electron and modulated neutral atom beams. It is stressed that such simplifications to the experiment in no way remove the necessity of scanning both beams to ensure the required conditions are met, especially after any changes are made to the beam-producing elements of either beam.

Since a low-density modulated atomic beam is used, it is not feasible to measure in absolute terms the atomic beam density in the interaction region, whereas all other quantities in equation (1) have been measured absolutely. The advantages of using a modulated atomic beam rather than either a non-modulated beam or a static gas target (see, for example, Williams and Willis 1975b) outweigh this disadvantage.

2.3. Calibration methods

Thus the need arose for an alternative method of absolute calibration of the measured angular distributions to obtain cross section values. Two alternative methods have been

used in this laboratory. The first method is to calculate an absolute cross section value from the phaseshifts determined from an analysis of the resonant profiles (Shore 1967, Comer and Read 1972) at numerous scattering angles of the elastically scattered electrons from a non-overlapping resonant state below the first inelastic threshold. The error of this method is ±8%. The calibration can then be transferred to another target gas by measurement of relative beam densities which introduces a further ±3% error. In this paper this method has been used as follows. An analysis of the $^2S(2s2p)$ 19·35 eV resonance in helium (Williams and Willis 1975a) yields an absolute elastic scattering differential cross section value at 19·2 eV of $0·774\ a_0^2\ sr^{-1}$ ±8% at 60°. From relative beam density measurements, the neon elastic scattering value at 19·2 eV and 60° is then $1·65\ a_0^2\ sr^{-1}$ ±11% and the corresponding value for argon is $2·02\ a_0^2\ sr^{-1}$ ±11%. The self-consistency of the method was checked by an analysis of the 11·07 and 11·24 eV $^2P_{3/2}$ and $^2P_{1/2}(3s^23p^64s)$ resonances in argon (Williams and Willis 1975a) which yielded elastic differential cross section values ±11% at 11·1 eV and 60° of $4·28$ $a_0^2\ sr^{-1}$ in argon, $1·75\ a_0^2\ sr^{-1}$ in neon and $0·957\ a_0^2\ sr^{-1}$ in helium. The measurement of the relative energy behaviour of the apparatus then showed that these separate determinations at 19·2 and 11·1 eV were consistent within the claimed error of ±11%.

However, because the statistical counting error in these values is only ±0·5%, and indeed this error could readily be reduced further, it is clear that a more accurate cross section calibration method should include all the measured elastic scattering signals at all energies and angles. From this approach, the second calibration method was based on the phaseshift analysis of non-resonant elastic angular distributions. The description of this calibration method as used in this laboratory has been prompted by the recent data analysis in helium by Andrick and Bitsch. The basis of the method, as used in a dispersion relation analysis, has been given by Naccache and McDowell (1975) (and earlier references therein) and, as used to analyse experimental relative angular distribution data, has been given by Andrick and Bitsch (1975). The phaseshift analysis method is simply a systematic parameter optimisation exercise. Those parameters, which are formally equated to the phaseshifts $\eta_l(k^2)$, are substituted in the well known formulae (Mott and Massey 1965) to calculate an elastic differential cross section, $I(k^2, \theta)$ and they are then varied so that the calculated cross section most accurately describes the measured cross section values.

2.4. Data analysis

In order to fit the calculated angular distribution to the measured shape it is necessary to choose a quantitative measure of the goodness of fit (Orear 1958) and to devise a systematic method of arriving at the next best trial set of phaseshifts from the comparison of the results of the previous set of phaseshifts with the measured data. The choice of the measure of goodness of fit is to some extent arbitrary, but it should take into account all the available information in a statistically acceptable way. This is achieved using the statistical chi-squared criterion which is defined as

$$\chi^2 = \frac{1}{n-p} \sum_{i=1}^{n} \frac{(N_c^i - N_{ex}^i)^2}{N_c^i} \tag{2}$$

where N_c^i and N_{ex}^i are the calculated and experimental count rates for the ith measurement at a given scattering energy, k^2, and scattering angle, θ; also n is the number of data points and p is the number of parameters to be varied. The factor $n - p$ normalises the optimum value of χ^2 to be unity.

For two reasons, firstly because count rates cannot be calculated without knowledge of the experimental conditions and secondly because the use of N_{ex}^i as the only experimental quantity in the χ^2 test would not make use of other experimentally measured quantities describing the scattering event and appearing in equation (1), it is advantageous to replace scattered electron count rates by cross sections, $I_{ex}(k^2, \theta)$. Then

$$\chi^2 = \frac{1}{n-p} \sum_{i=1}^{n} \frac{(I_c^i(\eta_l) - I_{ex}^i)^2}{(\delta I_{ex}^i)^2} \frac{I_{ex}^i}{I_c^i(\eta_l)}.$$

When the fit is good, $I_{ex} \simeq I_c$ and I_{ex}/I_c is symmetrically distributed about unity then

$$\chi^2 = \frac{1}{n-p} \sum_{i=1}^{n} \frac{(I_c^i(\eta_l) - I_{ex}^i)^2}{(\delta I_{ex}^i)^2}. \tag{3}$$

The χ^2 criterion in this form can be rigorously applied to evaluate the consistency of the data only if the measured observables are uncorrelated and represent a statistical distribution. This is true at any one k^2 and θ of the $N^i(k^2, \theta)$, which have a Poisson distribution with a standard deviation of $N_i^{1/2}$ but it is not true of the $I_{ex}^i(k^2, \theta)$. It is assumed that the theoretical model, i.e. a description of the cross section in terms of phaseshifts is correct but an uncertainty arises as to the number of phaseshifts to include in the analysis and to the size of the systematic errors in the measured cross section.

However, in the present work cross section values are not directly measured. The experiment measures electron count rates as a function of scattered electron energy and angle, which when multiplied by the measured angle and energy-dependent apparatus calibration factors, $\beta^j(k^2, \theta)$, produces relative energy and angular distributions. These distributions are then used in the chi-squared analysis by fitting to them the calculated cross section with the phaseshifts as the parameters to be optimised. Only from these phaseshifts can the experimental cross section values be determined. All of the $\beta^j(k^2, \theta)$, which are discussed in detail by Williams and Williams (1975a, b), have been measured absolutely with the exception of the beam density. The effect of all experimental errors in the total error $\Sigma \Delta \beta^j$ of the function β^j, is taken into account by multiplying each β^j by a normalisation factor λ^j so as to minimise χ^2. All of the λ^j are of the order of unity for correct absolute measurement of each of the β^j with the exception of that applied to the beam density for which only the product $\lambda^j\beta^j$ can be specified. Then, where $I_{ex}^i(k^2, \theta) = \lambda^j\beta^j(k^2, \theta)N^i(k^2, \theta)$ and m is the number of normalisation parameters, the modified χ^2 criterion is

$$\chi^2(\lambda) = \sum_{j=1}^{m} \sum_{i=1}^{n} \left(\frac{I_c^i(\eta_l) - I_{ex}^i(k^2, \theta)}{I_{ex}^i(k^2, \theta)} \right)^2 + \sum_{j=1}^{m} \left(\frac{\lambda^j - 1}{\delta\lambda^j} \right)^2. \tag{4}$$

This aspect of the analysis was the single most important feature for the present measurements which spanned the most difficult energy range from 0·5 to 10 eV over which the parameter β^j for the transmission factors alone varied by a factor of 2·3 and which invoked two modes of operation of the electron optics. An excessive variation in λ is avoided, i.e. data can be excluded, by specifying a permissible range $\delta\lambda^j$ as the maximum acceptable experimental variation about a given value λ_{ex}^j. In this work a variation of 20% was allowed above the statistical variation of usually not more than 2% and frequently 0·3%. In practice this procedure was found to be a suitable means of rejecting errors in the raw data which arose from either paper-tape machine errors or electronic noise bursts, for example.

Two specific sources of errors in the measured quantities have also been included in the χ^2 criterion. Since some angular distributions have been found to vary rapidly over a given angular region, the finite angular resolution, $d\Omega$, of the detector must be allowed for. This has been done by defining an experimental angular resolution function $\xi(\delta\theta, \theta)$; then the calculated value to be compared with the measured value is

$$\langle I_c(\eta_l)\rangle = \frac{\int I_c(\eta_l)\xi(\delta\theta, \theta_i)\,d\theta}{\int \xi(\delta\theta, \theta_i)\,d\theta} \tag{5}$$

where the integrals extend over the whole extent of $\xi(\delta\theta, \theta_i)$. For the argon data this integral has been approximated by assuming a simple function

$$I_{TH}(\eta_l) = \tfrac{1}{3}[I_c(\eta_l) + I_{ex}(k^2, \theta - \delta\theta) - I_{ex}(k^2, \theta + \delta\theta)] \tag{6}$$

where $\delta\theta = d\Omega/2\sqrt{2}$. For all other data, the integral was evaluated by Gaussian quadrature. In this experiment the measured function ξ was best fitted to a Gaussian distribution of width $2°$ with symmetric exponential wings at less than 25% peak amplitude.

The experimental uncertainty in the measured value of the angle, $\delta\theta$, can be approximately allowed for by assuming that the calculated quantities vary linearly with θ and that the cross section and the angle at which it is measured are normally distributed. These assumptions lead to a corrected experimental error $\overline{\delta I_{ex}(k^2, \theta)}$, which may be written as

$$(\overline{\delta I_{ex}(k^2, \theta)})^2 = (\delta I_{ex}(k^2, \theta))^2 + (\delta\theta)^2\left(\frac{d}{d\theta}(I(k^2, \theta))\right)^2 \tag{7}$$

and where $d(I(k^2, \theta))/d\theta$ may be approximated by a difference quotient.

Then the angular errors and uncertainties and the relative calibration error can be included in the χ^2 function as follows:

$$\chi^2 = \sum_{i=1}^{n} \frac{(I_{TH}^i(\eta_l) - I_{ex}^i(k^2, \theta))^2}{(\delta I_{ex}^i(k^2, \theta))^2 + [(dI^i(k^2, \theta)/d\theta^i)(I_{ex}(k^2, \theta)/I_{TH}(\eta_l))\delta\theta]^2} + \sum_{j=1}^{n}\left(\frac{\lambda - \lambda_{ex}^i}{\delta\lambda_{ex}^i}\right)^2. \tag{8}$$

Further, the inverse of this procedure has been carried out to determine, for example, the energy dependence of the transmission of an analyser or the angular variation of the effective solid angle of acceptance of an analyser. The procedure is to calculate the difference $[I_c(k^2, \theta) - I_{ex}(k^2, \theta)]$ for each point of an angular distribution. It may be found that such differences are of predominantly one sign indicating a difference in the absolute calibration of two curves. If the experimental distribution is multiplied by a number λ such that χ^2 is minimised for that particular calculated curve, then

$$\frac{\partial}{\partial\lambda}\sum_{i=1}^{n}\left(\frac{I_c(\eta_l) - \lambda I_{ex}(k^2, \theta)}{\lambda\delta I_{ex}(k^2, \theta)}\right)^2 = 0$$

and

$$\lambda = \sum_{i=1}^{n}\left(\frac{I_c(\eta_l)}{\delta I_{ex}(k^2, \theta)}\right)^2\left(\sum_{i=1}^{n}\frac{I_{ex}(k^2, \theta)I_c(\eta_l)}{(\delta I_{ex}(k^2, \theta))^2}\right)^{-1}. \tag{9}$$

The value of λ found in this way can be determined as a function of k^2, or θ, for example, and can be compared with a previous known accuracy of an absolute calibration of the experimental results. Such an approach also affords the separation of relative and

absolute experimental errors as well as determining the size and effects of systematic errors on the phaseshifts.

Explicit numerical examples of the use of the method of this section are not given because each calibration function is a unique property of any apparatus.

The value obtained for χ^2 reflects partly on the quality of the experimental data and also partly on the parametrisation of the phaseshifts. This parametrisation has been found to cause problems only in the vicinity of resonances when the shape of the electron energy resolution function needs to be known accurately.

After normalisation of the data, the values of $I_c(\eta_l) - \lambda I_{ex}(k^2, \theta)$ usually have random signs, though sometimes it is found that some points make an abnormally large contribution to χ^2. These points must be checked to see if they arise from measurement or recording errors. If the fitting procedure is proceeding satisfactorily, the values of $\delta\chi^2$ vary smoothly over, for example, an angular distribution, reaching zero when the calculated and measured values agree and rising when discrepancies occur. An uneven variation of $\delta\chi^2$ can indicate for example either that the fitting process is nearly complete, when the $\delta\chi^2$ will be much less than unity, or that the data are inaccurate or too widely spaced, either as a function of angle or energy. When deep minima occur it has been found necessary to make many measurements, for example twenty over a deep minimum in the cross section $10°$ wide.

An indication of the systematic errors present in the experimental data can further be obtained by plotting $dN/d(\delta\xi)$, a distribution function which measures the number of data points having $\delta\xi$ between some value $\delta\xi$ and $\delta\xi + d(\delta\xi)$. For statistically random errors one expects to obtain the normal error function distribution symmetric about $\delta\xi = 0$ while deviations from this distribution may be attributed to a systematic error. $\delta\xi$ is defined to be

$$\frac{I_c(k^2, \theta) - I_{ex}(k^2, \theta)}{\delta I_{ex}(k^2, \theta)}.$$

A cosec θ variation of the interaction volume (of equation (1)), and hence of $I(k^2, \theta)$ is clearly seen with this procedure. Systematic effects may include experimental effects such as variation of detector efficiency with beam energy and angle, background variations, discriminator bias and electronics dead times, which are best studied in separate tests designed for that specific purpose. However, in general, such effects and their errors can be studied by a chi-squared minimisation procedure and they can then be folded into the distribution function of the main experiment.

The fitting procedure finally reduces to the problem of minimising χ^2 for several variables. Many methods exist for the minimisation of a function of several variables, such as equation (7) (see Powell 1966 for a review). The following minimisation procedures (Kowalik and Osborne 1968, Arndt and MacGregor 1966) have been used: (i) a generalised Newton–Raphson method, i.e. an iterative method based on a Taylor series expansion about a given initial set of phaseshifts, (ii) the method of steepest descent, (iii) the Gauss method which is particularly suited to the difference of squares (Powell 1965), (iv) a linear programming method (Spang 1962) and (v) Marquardt's least-squares method. The convergence criterion used was for several successive function values to change by less than one part in 10^5. General problems encountered with these methods were (i) the convergence criterion is functional dependent and depends markedly on the size of the errors in the raw data and (ii) the step size between iterations is important and also depends markedly on the errors in the raw data. The success of a method was determined solely by the shortest time required to reach

convergence, irrespective of the number of iterations required or the number of function calls in the program. Methods (iii) and (v) were generally best and required up to 5 s of ICL 1906 S computer time. All the data presented in this paper were obtained using method (iii).

Only the first three phases (four for argon) were varied in the optimisation routine while the next seventeen phases ($l = 3$ to 19) were included in the cross section calculation. The justification for this procedure is similar to that indicated in an earlier analysis for atomic hydrogen data (Williams 1975). This limitation on the number of phaseshifts was also imposed for ease of evaluation of equation (5) in which I_c is both l and θ dependent since

$$I_c = |f(\theta)|^2$$

where

$$f(\theta) = \frac{1}{2ik} \sum_l (2l + 1)[\exp(2i\eta_l) - 1]P_l(\cos \theta)$$

and $|f(\theta)|^2$ was evaluated in the form

$$|f(\theta)|^2 = \frac{1}{k^2} \sum_l \sum_{l'} (2l + 1)(2l' + 1) \sin \eta_l \sin \eta_{l'} \cos(\eta_l - \eta_{l'})P_l(\cos \theta)P_{l'}(\cos \theta). \qquad (10)$$

The average of equation (5) also meant that the infinite sum of higher partial waves given by Thompson (1971) could not be used. The fitted phaseshifts were initially constrained, when making single energy fits, to within the larger of $\pm 10\%$ or $\pm 0 \cdot 1$ rad of the values from the relationships

$$\eta_0(k^2) = \pi\alpha/3a_0^2 - \frac{1}{a_0k} + \frac{2\alpha k}{3a_0} + \ln\left(\frac{\alpha k^2}{16}\right) + \sum_{i=1}^{4} a_i k^i$$

$$\eta_l(k^2) = \pi a_5 \alpha k^2[(2l + 3)(2l + 1)(2l - 1)]^{-1} \qquad (11)$$

where α is the static dipole polarisability of the target atom and the a_i are variable parameters. The physical bases for these relationships are the effective-range expansion for $l = 0$ (O'Malley *et al* 1961a,b) and the first Born expansion for $l > 1$ (Thompson 1966). The reason for these initial constraints was to ensure that the minimisation routines converged within a reasonable time and to force a fit to these frequently quoted forms for the phases. However, these constraints were not used for the multiple energy fits, from which the final phases were obtained, as they gave poor χ^2 values. No rigorous attempt has been made to verify that the obtained minima are global minima but plots of χ^2 against combinations of values of the first three phases, in which each phase was varied by $\pm 50\%$, showed only one minimum. All fits to a given set of measurements for which $\chi^2 \leq 2$ were accepted. The range in each phaseshift for that fit was taken as the error in that phaseshift.

3. Results and discussion

The analysis of the previous section permits the elastic angular distributions to be represented by an optimised set of s-, p- and d-wave (and f-wave for argon) phaseshifts for electron energies in the range $0 \cdot 54$ to 20 eV.

3.1. Helium

Table 1 lists the s-, p- and d-wave phaseshifts and figures 1, 2 and 3 show the present values and other experimental and theoretical values. At all energies the experimental data from the present experiments, from Andrick and Bitsch (1975) and McConkey and Preston (1975) agree within their combined error limits which are, however, considerably different in the three experiments. The statistical errors of the present data are generally 0·3% and the total error limits (i.e. one standard deviation in the s-wave phase) are ±2% at 0·54 eV and decrease approximately linearly to ±1·4% from 10 to 20 eV. The errors in the p-wave phase are about 2% and in the d-wave phase about 8%. The error limits claimed by Andrick and Bitsch are ±20% at 5 eV and decreases to ±5% at 12 eV and above for their cross sections and are presumably similar for their phases. The error limits of the phases determined by the latter group were not stated but the error limits of their cross section values were ±12%. Some indication of their errors are apparent from the large scatter in their phaseshift values. The calibration procedures of McConkey and Preston appear to be valid so that one can only suggest that their limited angular range of 20 to 90° did not present sufficient data points for more accurate phaseshifts to be obtained. The data of Gibson and Dolder (1969), who measured angular distribution but did not determine phaseshifts, have been adequately

Table 1. Phaseshifts in radians for the elastic scattering of electrons from helium atoms.

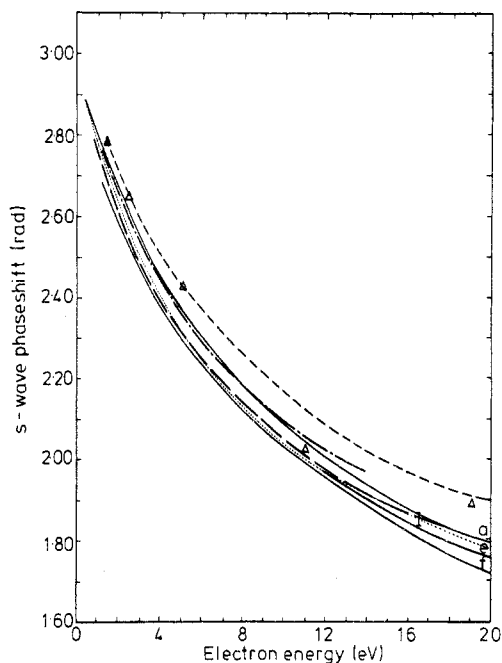| Energy (eV)	s-wave phaseshift $l = 0$	p-wave phaseshift $l = 1$	d-wave phaseshift $l = 2$
0·58 (±0·24)	2·868	0·015	0·0014
1·23	2·745	0·035	0·0031
1·51	2·702	0·043	0·0038
2·176	2·613	0·060	0·0056
2·75	2·534	0·077	0·0068
3·40	2·464	0·093	0·0087
3·90	2·417	0·105	0·0107
4·44	2·370	0·116	0·0118
4·91	2·332	0·127	0·0132
5·02	2·322	0·129	0·0136
5·51	2·283	0·140	0·0152
6·10	2·242	0·152	0·0172
6·66	2·207	0·161	0·0188
7·01	2·181	0·168	0·0198
8·00	2·134	0·186	0·0228
8·71	2·098	0·196	0·0251
10·0	2·036	0·216	0·0302
11·0	2·003	0·229	0·0334
12·0	1·968	0·242	0·0372
13·0	1·936	0·254	0·0406
14·0	1·908	0·267	0·0444
15·0	1·881	0·278	0·0471
16·0	1·857	0·289	0·0501
17·0	1·833	0·298	0·0527
18·0	1·815	0·305	0·0556
19·0	1·800	0·311	0·0580
20·0	1·784	0·315	0·0602
Error (%)	1·4	2·2	8

Figure 1. The s-wave phaseshift for the elastic scattering of electrons from helium atoms. ......, present data with a representative error bar shown at 16·5 eV. — — —, Andrick and Bitsch (1975); △, McConkey and Preston (1975); – – –, Bransden and McDowell (1969); —·—·–, Naccache and McDowell (1974); —ᵃ—, polarised-orbital values; —ᵉ—, Wichmann and Heiss (1974), and —ᶠ—, static exchange values. Data set (b) (not shown) is close to data set (a).
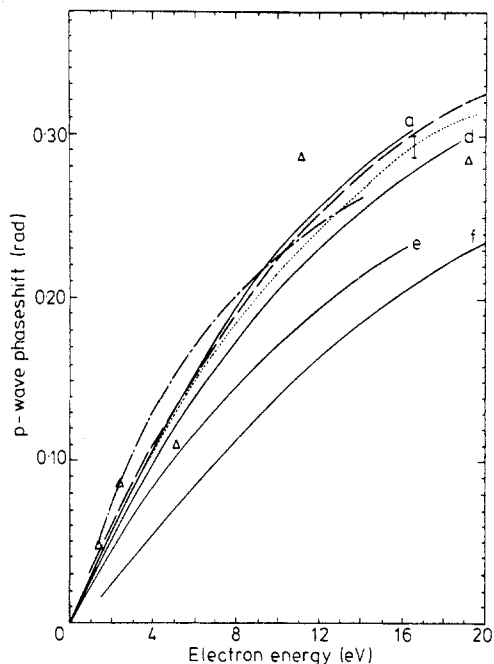
Figure 2. The p-wave phaseshift for the elastic scattering of electrons from helium atoms. Data legend as for figure 1. Data set (b) (now shown) is close to the measured values.

discussed by Andrick and Bitsch. The smallest errors occur in the present data and those of Andrick and Bitsch. Their common experimental technique of a well defined target atomic beam distinguishes those experiments from the static gas target studies. The question must be asked whether this latter technique can yield accurate low-energy (~20 eV) angular distribution data. A critical assessment of the work of these other authors will not be given here.

Two separate consistency checks involving phaseshift analyses of earlier experimental measurements of elastic angular distributions have been made by Bransden and McDowell (1969) and Naccache and McDowell (1974). The former authors obtained s and p phases which were consistent with the dispersion relations and experimental values of the total elastic scattering cross section, the diffusion cross section and the elastic cross section of Gibson and Dolder (1969). Their phases thus represent the earlier work and as shown in figures 1 and 2 are outside the error limits of the present data. The latter authors also made a similar analysis but based on the more recent and extensive elastic scattering data discussed in the previous paragraph. They deduce a set of s-, p- and d-wave phaseshifts which, together with Born approximation values for the higher partial waves, simultaneously fits all the experimental data. These phases are shown in figures 1, 2 and 3. It is seen that all three phaseshifts so determined are of a
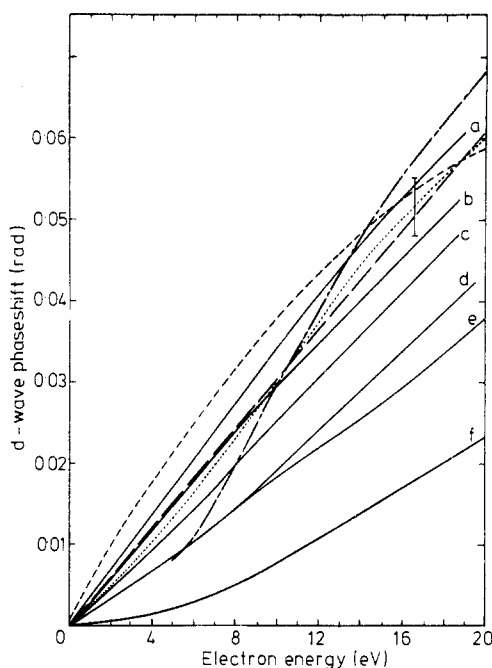
Figure 3. The d-wave phaseshifts for the elastic scattering of electrons from helium atoms. Data legend as for figure 1 and including ——^{b}——, Sinfailam and Nesbet (1972); ——^{c}——, Knowles and McDowell (1973); ——^{d}——, Yarlagadda *et al* (1973).

different energy dependence to all the other experimental and theoretical data. It is apparent that some of the basic experimental data are either incorrect or not accurate enough for the phaseshift analysis method.

It is emphasised that the present phaseshift analysis method has been made for relative angular distributions of scattered electrons for 22 energies and 27 angles and that absolute determinations of all quantities and apparatus calibration functions appearing in equation (1), except the gas beam density, have been made (as discussed in detail by Williams and Willis 1975a). In that way a calibration of the phaseshifts, and a determination of their errors, has been made over the whole energy range. For comparison one can consider two other methods of absolute cross section determination, namely (i) a phaseshift analysis of an isolated resonance below the first inelastic threshold and (ii) the measurement of ratios of elastic scattering signals in two gases for known relative beam source pressures. The latter method then depends upon method (i) for cross section determination in the 'reference' target gas and has been discussed elsewhere (Williams and Willis 1975b).

The resonance analysis is simply a special case of the general phaseshift analysis method for a very small range of energies over the width of the resonance. The resonance phaseshifts then properly serve as constraints to be used in the phaseshift analysis over the wider energy range in which one wishes to determine absolute cross section values.

Williams and Willis (1975a) analysed the $19 \cdot 35$ eV ^{2}S resonance in helium by using Born approximation values of n_l, $l = 3$ to 10, to deduce $\eta_0 = 1 \cdot 852 \pm 1\%$, $\eta_1 = 0 \cdot 309 \pm 2 \cdot 6\%$ and $\eta_2 = 0 \cdot 066 \pm 11\%$. The percentage errors were one standard

deviation or 68% confidence limits. Those measurements were made in the same apparatus as used for the present studies for which the only significant change has been a reduction in the random-noise level. Another analysis of that resonance has been made in the present studies to yield $\eta_0 = 1 \cdot 822 \pm 0 \cdot 5\%$, $\eta_1 = 0 \cdot 310 \pm 1 \cdot 5\%$ and $\eta_2 = 0 \cdot 061 \pm 4\%$ where the percentage errors are again one standard deviation. It is seen that both analyses of this resonance are consistent with one another and with the present multiple-energy phaseshift determination. This agreement confirms the accuracy of the present phaseshift determination in the vicinity of $19 \cdot 3$ eV.

A wide variety of theoretical descriptions of the elastic scattering process is available. Recent reviews have been given by Moiseiwitsch (1977) and Burke and Williams (1978). The results of a number of these approaches are tabulated in the form of phaseshifts in the paper by Naccache and McDowell and are also shown in figures 1, 2 and 3. The approximation methods, such as the polarised orbital and the pseudostate close-coupling methods and the variationally based methods, which were considered on theoretical grounds to describe fully and include the coupling to higher excited and continuum states, have been shown to predict elastic scattering cross section values for atomic hydrogen below the first inelastic threshold which agree within 8% error limits with recent experimental values (Williams 1975). The results of those and similar approximation methods used for inert-gas atoms will now be discussed and compared with the experimental values obtained from the same apparatus as used for the hydrogen studies.

The non-relativistic e–He scattering system differs fundamentally from the atomic hydrogen problem in that the target eigenfunctions are not known exactly. It is then necessary to formulate a model scattering problem to which the approximation methods used to solve the e–He problem can be applied. Early calculations used simple Hartree–Fock waveformulations in an exchange adiabatic model as discussed by Lawson et al (1966). This model generally was a simplified version of Temkin's (1959) polarised-orbital model which includes the effect of distortion (polarisation and exchange) of the atomic wavefunction by the low-energy incident electron. Thompson (1966, 1971) extended their work by including virtual np to d transitions. Callaway and colleagues (Callaway et al 1968, LaBahn et al 1970, Garbaty and LaBahn 1971) have gradually improved upon this approximation until a complete polarised-orbital calculation was achieved. The effects of all outer-shell transitions in which $\Delta l = \pm 1$ and of exchange polarisation were included (Duxler et al 1971). The differences between their phaseshifts would be barely discernible on the scale of figure 1. Their data are labelled as Callaway et al and are generally the highest theoretical values. Their p- and d-wave phases are consistent with the present measured values but their s-wave phases are too high.

More recent work has centred on the many-body Green's function methods which are capable in principle of giving results of high accuracy. The method depends upon the formulation of an optical potential to include the effects of distortion of the target electrons. Knowles and McDowell (1973) used the model of Pu and Chang (1966) in which N electrons interact through two-body potentials and included the effect of exchange in the second-order optical potential. Somewhat similarly, Yarlagadda et al (1973) used the random-phase approximation in solving their response function. Both of these studies produced s- and p-wave phaseshifts slightly below these of Duxler et al and good agreement with the measured data. Their d-wave phases were considered to be less accurate and indeed they fall outside the error limits of the present measurements.

Both the polarised-orbital and many-body theories take distortion of the atomic wavefunction by the slow incident electron into account by formulating an effective Hamiltonian. On the other hand the close-coupling method uses the original e–He Hamiltonian and expands the total wavefunction in a basis function which corresponds essentially to the various atomic-state wavefunctions. Burke *et al* (1969) have applied the close-coupling method with an expansion of the full three-electron wavefunction in terms of the wavefunctions of the five lowest states of the helium atom. They calculated only s-wave phases which, on the scale of figure 1, are indiscernible from the values of Duxler *et al*. The most recent variational calculation is by Wickmann and Heiss (1974) who started from a three-state close-coupling approximation. Their s-wave phaseshifts agree with the measured values within the error limits; however their p- and d-wave phaseshifts are low.

Of all the theoretical approaches, the variational calculation of Sinfailam and Nesbet (1972), which takes into account polarisation and correlation effects by means of continuum Bethe–Goldstone equations, gives best agreement with the present data when the whole energy range is considered. They used a representation of the trial wavefunction involving a linear expansion over a complete set of basis functions of the form

$$\Phi_i = N r^n \exp(-\alpha r) Y_{lm}(r)$$

and have shown that convergent values for the phases were obtained. A similar approach was used by Schwartz in obtaining e + H elastic scattering phases which agreed well with the experimental values (Williams 1975).

The greatest relative spread in the theoretical values occurs for the d-wave phases shown in figure 3. The error limits of the present experimental values enclose only the predictions of Callaway and colleagues and Sinfailam and Nesbet as well as the measured values of Andrick and Bitsch at all energies.

The best set of composite measurements used by Naccache and McDowell deduce a d-wave phase which crosses the present data at about 10 eV but the two data sets diverge with both increasing and decreasing electron energy. One reason may be an inaccuracy in the total cross section values of Golden and Bandel (1965) used in their analysis. Recent evidence in support of this assertion has been provided indirectly from electron-swarm-derived momentum-transfer cross sections (Milloy and Crompton 1977). The analysis of electron swarms, concerned with electron motion under conditions of ratios of electric field strength to gas number density of $100 \text{ V cm}^{-1}/10^{19}$ atoms cm^{-3}, relies upon solving the Boltzmann transport equation to produce momentum-transfer cross sections. Angular differential cross sections are then needed to extract values of the total cross section. The validity of such an indirect method has recently been supported by a Monte-Carlo analysis (Milloy and Watts 1977) over the range of experimental parameters of electric field and gas density required to cover the equivalent electron energy range of 0·5 to 12 eV. Milloy and Crompton advance arguments supporting the claimed accuracy of ±5% in their data from 7 to 12 eV and ±2% from 4 to 7 eV. These arguments show that the data of Golden and Bandel is probably correct in energy dependence but calibrated about 10% too low. This conclusion was also reached by Andrick and Bitsch and is supported by recent total cross section measurements by Kauppila *et al* (1977).

The present phaseshifts have been used to calculate the momentum-transfer cross section values which can be compared with those calculated from indirectly measured electron swarm parameters of Crompton *et al* (1967, 1970). The momentum-transfer

cross section, defined as

$$2\pi \int_0^\pi I(k, \theta)(1 - \cos \theta) \sin \theta \, d\theta$$

is not as sensitive a test of the present measurements as either the differential cross section or the phaseshifts because of the two integrations and the weighting given to 90° scattering. The two data sets agree within their summed error limits of one standard deviation.

3.2. Neon

The present experimentally derived phaseshifts are listed in table 2 and graphed in figure 4. The agreement between the present data and those of Andrick and Bitsch is within their combined error limits of ±2% and ±11% (±3% above 10 eV) respectively. The 'best fit' derived set of phases by Naccache and McDowell, and discussed at length by them, are in reasonable agreement with the present values except for energies above 10 eV when their values are smaller.

Table 2. Phaseshifts in radians for the elastic scattering of electrons from neon atoms.

Energy (eV)	s-wave phaseshift	p-wave phaseshift	d-wave phaseshift
0·58	−0·114	+0·002	0·002
1·22	−0·212	−0·002	0·004
2·18	−0·310	−0·019	0·011
3·00	−0·379	−0·038	0·016
3·40	−0·413	−0·048	0·018
4·00	−0·456	−0·066	0·021
4·90	−0·523	−0·087	0·027
6·00	−0·594	−0·119	0·038
6·66	−0·632	−0·135	0·044
8·00	−0·710	−0·171	0·057
8·70	−0·745	−0·187	0·063
10·00	−0·800	−0·220	0·076
11·00	−0·837	−0·243	0·086
12·0	−0·877	−0·265	0·099
13·00	−0·913	−0·288	0·112
14·00	−0·951	−0·309	0·125
15·00	−0·992	−0·328	0·137
16·00	−1·029	−0·348	0·148
17·00	−1·064	−0·367	0·159
18·00	−1·092	−0·388	0·172
19·00	−1·117	−0·406	0·184
20·00	−1·140	−0·423	0·196
Error (%)	1·6	2·8	8

The theoretical values from a polarised-orbital approximation by Garbaty and LaBahn (1971) are close to, but outside, the error limits of the present values. The values of Thompson (1971) are similar to the Garbaty and LaBahn values.
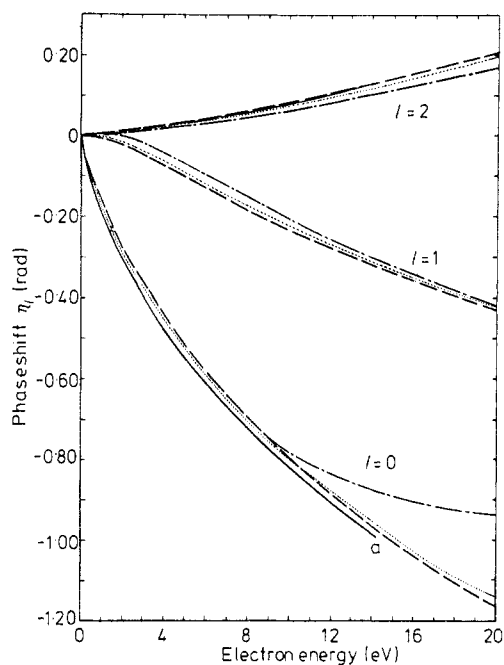
Figure 4. The s-, p- and d-wave phaseshifts for the elastic scattering of electrons from neon atoms.·Data legend as for figure 1.
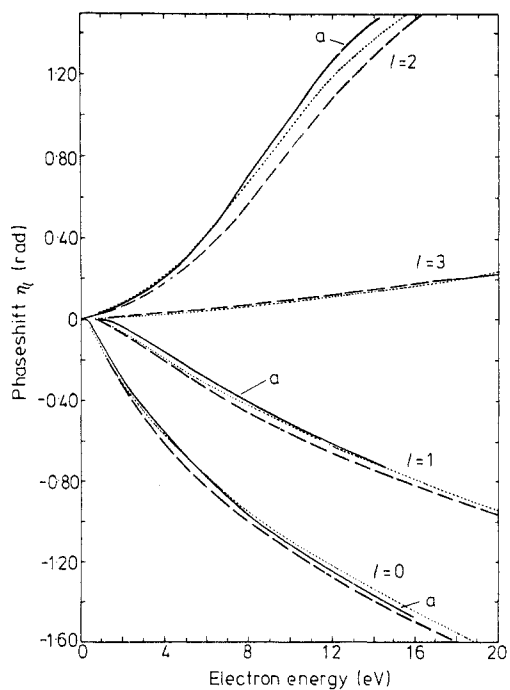

Figure 5. The s-, p-, d- and f-wave phaseshifts for the elastic scattering of electrons from argon atoms. Data legend as for figure 1.

3.3. Argon

The present experimentally derived s-, p-, d- and f-wave phaseshifts are tabulated in table 3 and graphed in figure 5. These phaseshifts also agree within the experimental error limits with the data of Andrick and Bitsch. The polarised-orbital values of Thompson (1971) and Garbaty and LaBahn (1971) and the many-body perturbation values of Pindzola and Kelly (1974) are in fair agreement with one another. The values of Garbaty and LaBahn are plotted in figure 5. A detailed comparison with theoretical values for neon and argon can be made when further theoretical values become available. Generally it can be said that for the heavier inert gases the wavefunctions are less well known and consideration should be given to inner-shell effects, departures from LS coupling, spin–orbit interactions and relativistic effects.

Table 3. Phaseshifts in radians for the elastic scattering of electrons from argon atoms.

Energy (eV)	s-wave phaseshift $l = 0$	p-wave phaseshift $l = 1$	d-wave phaseshift $l = 3$	f-wave phaseshift $l = 3$
0·58	−0·057	−0·006	0·021	0·002
1·22	−0·184	−0·025	0·043	0·004
2·18	−0·346	−0·083	0·092	0·014
3·00	−0·457	−0·134	0·142	0·021
3·40	−0·507	−0·157	0·165	0·023
4·00	−0·575	−0·197	0·210	0·030
4·90	−0·672	−0·252	0·303	0·038
6·02	−0·789	−0·321	0·431	0·052
6·67	−0·850	−0·361	0·516	0·060
8·00	−0·961	−0·432	0·683	0·069
8.70	−1·011	−0·464	0·770	0·075
10·00	−1·098	−0·528	0·936	0·093
11·00	−1·163	−0·578	1·069	0·105
12·00	−1·218	−0·626	1·191	0·118
13·00	−1·282	−0·673	1·285	0·132
14·00	−1·336	−0·712	1·373	0·145
15·00	−1·394	−0·750	1·451	0·154
16·00	−1·445	−0·793	1·539	0·168
17·00	−1·495	−0·834	1·600	0·181
18·00	−1·574	−0·870	1·661	0·193
19·00	−1·602	−0·904	1·709	0·215
20·00	−1·653	−0·935	1·747	0·241
Error (%)	1·8	2·8	8·4	23

4. Conclusions

It has been shown that, by detecting elastically scattered electrons at 27 angles and 22 energies from 0·54 to 20 eV and analysing all those data with a statistical chi-squared test, a consistent and optimised set of phaseshifts may be deduced. The statistical error due to counting fluctuations in the raw data is generally 0·3% and the s-, p- and d-wave phaseshifts have been determined with percentage errors (one standard deviation) of 1·4, 2·2 and 8% respectively. These reduced errors generally arise from small statistical

errors and from the inclusion of a separate chi-squared analysis of energy and angular-dependent apparatus functions.

For all the target atoms, He, Ne and Ar, the present data agree with the data of Andrick and Bitsch within the combined error limits. In helium the p and d phaseshifts calculated from a variational method by Sinfailam and Nesbet give best agreement with the present values while the polarised-orbital calculated values of Callaway and colleagues also agree closely. For the s-wave phase a percentage error of $1 \cdot 4\%$ is generally not sufficient to indicate a preference for any one theoretical set of values.

Acknowledgments

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