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A relativistic approach to the elastic scattering of electrons by argon

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Abstract. Phase shifts and total and differential cross sections are calculated for the elastic scattering of unpolarised electrons by argon atoms in the impact energy range of 0.1 to 40 eV. The target atom is represented by a frozen core in a continuum relativistic Hartree-Fock calculation with dipole and quadrupole polarisation corrections. Exchange is calculated exactly and the parameters of the model polarisation potential are fixed by independent calculations. The results are in good agreement with experiment and with some of the non-relativistic coupled Hartree-Fock calculations; they demonstrate the importance of core polarisation effects as well as of relativistic effects at low incident energies.

1. Introduction

The object of this paper is to test a fully relativistic Hartree-Fock method using a frozen core with polarisation corrections in calculations of elastic electron-argon scattering at low energies. This system provides an example of a collision involving a representative of the heavier noble gases, where both electron exchange and relativistic effects may be significant.

The system has been extensively studied in many experiments. Total cross section measurements have been made by Charlton *et al* (1980), Golden and Bandel (1966), Gus'kov *et al* (1978), Kauppila *et al* (1981), Nickel *et al* (1984) and Wagenaar and de Heer (1980). Differential cross sections have been measured by Andrick and Bitsch (1983), DuBois and Rudd (1976), Lewis *et al* (1974), Srivastava *et al* (1981), Williams and Willis (1975) and Zhou Qing *et al* (1982). Phaseshifts have been deduced from experimental elastic cross sections by Andrick and Bitsch (1983), Srivastava *et al* (1981) and Williams (1979).

The system has also been the subject of a number of theoretical treatments. R-matrix calculations which neglect relativistic effects have been performed by Bell *et al* (1984) and Fon *et al* (1983). McEachran and Stauffer (1983b) have examined the effects of polarisation and exchange within a polarised orbital approximation. Garbaty and LaBahn (1971) and Thompson (1971) have employed a simplified polarised orbital calculation. Amusia *et al* (1982) and McCarthy *et al* (1977) have used an optical potential model, whereas most recently Datta *et al* (1985) have made calculations with a model potential method. All these calculations are based on the non-relativistic Schrödinger equation.

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The relativistic calculations for this system have been performed by Walker (1971), who has solved the continuum Hartree–Fock equations with the incident electron and argon atom represented by a single determinant wavefunction. He has treated accurately the exchange between the scattered electron and the electrons of a target atom, but he has not included any polarisation effects. In our approach, we make relativistic calculations in a frozen-core approximation with model dipole and quadrupole polarisation corrections, and investigate the sizes of both relativistic and polarisation effects.

2. Method

To calculate the scattering of an electron by an argon atom including relativistic effects, we substitute the one-electron central-field potential V and the exchange terms X_P and X_Q into the inhomogeneous radial Dirac equation (Desclaux 1975), which in atomic units can be written as

$$\left(\frac{\mathrm{d}}{\mathrm{d}r}+\frac{\kappa}{r}\right)P=[2/\alpha+\alpha(E-V)]Q+X_Q$$
$$\left(\frac{\mathrm{d}}{\mathrm{d}r}-\frac{\kappa}{r}\right)Q=-\alpha(E-V)P-X_P \tag{1}$$

where P and Q are the radial parts of the large and small components of the Dirac wavefunction, $\alpha = 1/137.036$ is the fine-structure constant, E is the energy of the scattering electron and κ is related to the total j and orbital l angular momentum quantum numbers by

$$\kappa = \pm(j+\tfrac{1}{2}) \qquad \text{for} \qquad l = j \pm \tfrac{1}{2}. \tag{2}$$

The potential V comprises two parts, namely the relativistic frozen-core potential V_{FC} and the polarisation model potential V_{P} (both are treated in more detail in §§ 3 and 4). The radial equation (1) is solved by means of a new direct and stable integration algorithm with a small seventh-order error (see appendix 1).

Phaseshifts are obtained by comparing the numerical solution of (1) to the analytical one at large r where $rV \to 0$:

$$P(r)/r = j_l(kr)\cos\delta_l - n_l(kr)\sin\delta_l \tag{3}$$

$$Q(r)/r = \alpha\left(\frac{E}{E\alpha^2+2}\right)^{1/2}(j_{\tilde{l}}(kr)\cos\delta_l - n_{\tilde{l}}(kr)\sin\delta_l). \tag{4}$$

Here, $k = (2E+\alpha^2E^2)^{1/2}$ is the momentum of the incident electron, and the quantum number $\tilde{l} = l \pm 1$ for $j = l \pm \frac{1}{2}$.

We calculate the phaseshifts for the partial waves from $l = 0$ to $l = 7$. In calculating total and differential cross sections, we use the effective-range formula

$$\tan\delta_l = k^2\alpha_{\mathrm{d}}a_l + k^4(\alpha_{\mathrm{d}}b_l + \alpha'_{\mathrm{q}}c_l) \tag{5}$$

of Ali and Fraser (1977) to estimate phaseshifts for l values from 8 to 50. Here, α_{d} and α'_{q} are the dipole and effective quadrupole (see equation (7) below) polarisabilities of the atom, and a_l, b_l and c_l are analytical coefficients given by Ali and Fraser.

3. Direct frozen-core and exchange potentials

The direct frozen-core potential V_{FC} and the exact exchange terms X_P and X_Q are calculated with the relativistic 'MCDF' program of Desclaux (1975) with some modifications. A new integration algorithm (see appendix 1) replaced the five-point predictor-corrector algorithm used by Desclaux. Also, an error in the coefficients for the asymptotic forms of the radial Dirac wavefunctions was corrected and spurious nodes in the long-range tails of the wavefunctions were thereby eliminated. Accurate asymptotic forms of the wavefunctions (see appendix 2) were introduced into the code for a potential which at long range becomes Coulombic. To ensure high accuracy, the step in the logarithmic grid was changed from 0.05 to 0.01. First results with the modified code were published elsewhere (Baylis and Sienkiewicz 1987).

4. Polarisation potential

The polarisation potential which arises as a correlation correction to frozen-core calculations (Baylis 1985), is taken in the form

$$V_P(r) = -\frac{1}{2}\frac{\alpha_d r^2}{(r^3+\langle r^3\rangle)^2} - \frac{1}{2}\frac{\alpha'_q r^4}{(r^5+\langle r^5\rangle)^2} \tag{6}$$

where α_d is the static dipole polarisability, α'_q is the effective quadrupole polarisability and is defined as

$$\alpha'_q = \alpha_q - 6\beta. \tag{7}$$

The above definition contains the static quadrupole polarisability α_q and the dynamical first-order correction -6β to the static dipole polarisabilty. Divergence at $r \doteq 0$ in the polarisation term is avoided by introducing cut-off parameters $\langle r^n\rangle$ which are mean values of r^n for the outermost orbital of the target atom.

The dipole polarisation term in formula (6) is the best simple model potential to fit the numerical dipole potential of McEachran *et al* (1980) in the case of Xe. As shown in figure 1, this model potential reasonably reproduces the shape and depth of the numerical potential when r_0 is chosen to give the correct position of the minimum. The dynamic correction to the static dipole polarisability has the same asymptotic dependence as the quadrupole term but the opposite sign, and in the case of argon, it almost completely cancels the attractive character of the quadrupole term. Hence, only the dipole contribution to the polarisation term plays a significant role. This conclusion was also drawn by McEachran and Stauffer (1983a, b). In our calculation for argon, we take $\alpha_d = 10.77$ and $\alpha_q = 50.12$ from Johnson *et al* (1983) and $\beta = 8.33$ from Dalgarno *et al* (1968). The calculated values of the cut-off parameters $\langle r^3\rangle$ and $\langle r^5\rangle$ are respectively 7.76 and 65.73.

5. Results and discussion

Table 1 lists the phaseshifts we have calculated for incident electrons with orbital angular momenta l from 0 to 5 in the relativistic case and for $l = 0$, 1 and 2 in the non-relativistic one. The tabulation is for the case $j = l + \frac{1}{2}$, but in the case of argon,

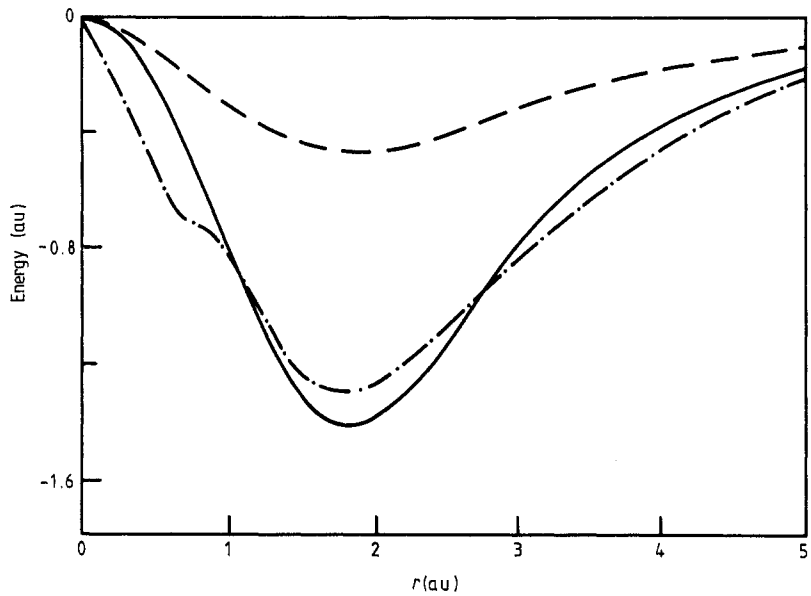

Figure 1. Dipole polarisation potentials of Xe: –·–, numerical (McEachran 1985); ——, $\alpha_d r^2/2\ (r^3+r^3)^2$; – – –, $\alpha_d r^2/2\ (r^2+r^2)^3$. In the last two cases, r_0 is chosen so that the potential minimum occurs at $r = 1.8$ au.

the results are not very different for $j = l - \frac{1}{2}$ (Walker 1971). 'Non-relativistic' phaseshifts are calculated with the *same* numerical code as 'relativistic' ones, but with the fine-structure constant reduced to practically zero. In the non-relativistic case, the cut-off parameters $\langle r^n \rangle$, calculated for the outermost core orbital (see equation (6)), are only about 0.2% larger than in the relativistic case and do not cause a significant change in the polarisation term.

The $l = 0$ relativistic phaseshifts lie above the non-relativistic ones and the discrepancy between them decreases from 11% at an energy of 0.4 eV to about 0.6% at 20 eV. The $l = 1$ and 2 relativistic phaseshifts lie, with the exception of the first seven values for $l = 2$, below the non-relativistic phaseshifts, and the difference between them is smaller than for $l = 0$.

In order to understand the rather surprising magnitude of the relativistic effects, especially for s-wave scattering at low energy, we made additional test calculations which isolate the relativistic effects on the Ar target from those on the wavefunction of the scattered electron.

First we combined the relativistic scattering equation (1) with the non-relativistic version of the Ar target. Relativistic effects cause a slight contraction of the atomic orbitals, so that the nuclear charge is better screened and the target potential is slightly more repulsive. Relativistic effects in the target therefore cause a slight *reduction* in the phaseshifts.

Next we investigated the relativistic effects on the scattering electron with the target (including the polarisation terms) fixed in its relativistic version. The effect of relativity is again to 'pull in' the wavefunction, but this now *increases* the scattering phaseshifts. The effect can be seen in the r^γ dependence of the radial functions at the origin, where $\gamma = (\kappa^2 - Z^2\alpha^2)^{1/2}$. In the non-relativistic limit ($\alpha \to 0$), γ is larger and the radial wavefunctions smaller or less 'pulled in'.

Table 1. Elastic scattering phaseshifts δ_l for argon.

Energy (eV)	Relativistic ($j = l+\frac{1}{2}$) δ_0	δ_1	δ_2	δ_3	δ_4	δ_5	Non-relativistic δ_0	δ_1	δ_2
0.1	2.846^{-2}†	1.094^{-2}	2.516^{-3}	7.504^{-4}	3.701^{-4}	2.638^{-4}	2.518^{-2}	1.096^{-2}	2.508^{-3}
0.2	6.933^{-3}	1.756^{-2}	4.973^{-3}	1.628^{-3}	8.240^{-4}	4.900^{-4}	2.138^{-3}	1.762^{-2}	4.968^{-3}
0.3	-1.780^{-2}	2.133^{-2}	7.414^{-3}	2.445^{-3}	1.225^{-3}	7.334^{-4}	-2.260^{-2}	2.145^{-2}	7.408^{-3}
0.4	-4.284^{-2}	2.308^{-2}	1.001^{-2}	3.241^{-3}	1.637^{-3}	9.713^{-4}	-4.807^{-2}	2.326^{-2}	1.000^{-2}
0.5	-6.743^{-2}	2.326^{-2}	1.265^{-2}	4.057^{-3}	2.048^{-3}	1.214^{-3}	-7.300^{-2}	2.349^{-2}	1.264^{-2}
0.7	-1.146^{-1}	2.000^{-2}	1.821^{-2}	5.619^{-3}	2.862^{-3}	1.697^{-3}	-1.206^{-1}	2.036^{-2}	1.820^{-2}
1.0	-1.799^{-1}	8.873^{-3}	2.731^{-2}	8.022^{-3}	4.080^{-3}	2.439^{-3}	-1.865^{-1}	9.416^{-3}	2.731^{-2}
2.0	-3.631^{-1}	-5.346^{-2}	6.521^{-2}	1.613^{-2}	7.689^{-3}	4.858^{-3}	-3.706^{-1}	-5.239^{-2}	6.525^{-2}
3.0	-5.107^{-1}	-1.280^{-1}	1.179^{-1}	2.434^{-2}	1.152^{-2}	6.462^{-3}	-5.188^{-1}	-1.265^{-1}	1.180^{-1}
5.0	-7.483^{-1}	-2.743^{-1}	2.725^{-1}	4.194^{-2}	1.908^{-2}	1.076^{-2}	-7.569^{-1}	-2.723^{-1}	2.735^{-1}
6.0	-8.478^{-1}	-3.419^{-1}	3.753^{-1}	5.120^{-2}	2.290^{-2}	1.289^{-2}	-8.567^{-1}	-3.398^{-1}	3.772^{-1}
7.5	-9.804^{-1}	-4.345^{-1}	5.611^{-1}	6.625^{-2}	2.869^{-2}	1.596^{-2}	-9.896^{-1}	-4.321^{-1}	5.649^{-1}
8.0	-1.021	-4.637^{-1}	6.266^{-1}	7.156^{-2}	3.067^{-2}	1.703^{-2}	-1.030	-4.613^{-1}	6.311^{-1}
9.0	-1.098	-5.194^{-1}	7.675^{-1}	8.238^{-2}	3.459^{-2}	1.910^{-2}	-1.107	-5.170^{-1}	7.736^{-1}
10.0	-1.169	-5.719^{-1}	9.032^{-1}	9.343^{-2}	3.863^{-2}	2.123^{-2}	-1.178	-5.693^{-1}	9.109^{-1}
12.0	-1.298	-6.680^{-1}	1.149	1.173^{-1}	4.663^{-2}	2.544^{-2}	-1.308	-6.654^{-1}	1.159
14.0	-1.414	-7.542^{-1}	1.343	1.423^{-1}	5.525^{-2}	2.960^{-2}	-1.423	-7.515^{-1}	1.353
15.0	-1.467	-7.941^{-1}	1.419	1.530^{-1}	5.944^{-2}	3.181^{-2}	-1.477	-7.914^{-1}	1.430
18.0	-1.612	-9.033^{-1}	1.582	1.924^{-1}	7.054^{-2}	3.830^{-2}	-1.622	-9.006^{-1}	1.592
20.0	-1.698	-9.685^{-1}	1.658	2.190^{-1}	7.951^{-2}	4.070^{-2}	-1.708	-9.657^{-1}	1.667
25.0	-1.888	-1.111	1.781	2.833^{-1}	1.026^{-1}	5.111^{-2}	-1.898	-1.108	1.790
30.0	-2.048	-1.231	1.850	3.488^{-1}	1.263^{-1}	6.212^{-2}	-2.058	-1.229	1.858
35.0	-2.187	-1.335	1.900	4.074^{-1}	1.474^{-1}	7.331^{-2}	-2.198	-1.332	1.907
40.0	-2.310	-1.426	1.927	4.650^{-1}	1.712^{-1}	8.516^{-2}	-2.320	-1.424	1.934

† The superscript denotes the power of 10 by which the number is to be multiplied.

For $l > 0$, the relativistic effects on the target dominate and consequently the phaseshifts tend to be slightly lower than in the non-relativistic calculation. For $l = 0$ however, the effect on the scattering wavefunction is dominant and the relativistic phaseshift is larger than the non-relativistic one. The magnitude of the relativistic increase in δ_0 grows from about 3.3 mrad at 0.1 eV to 6.6 mrad at 1 eV and to about 9 mrad at 10 eV. Of course, one may argue that relativistic effects on the scattering electron can be significant when the electron is close to the nucleus even if its kinetic energy at large r is quite small. However, to verify that the predicted changes in δ_0 are of reasonable size, we compare the relativistic shift $\Delta\delta_0$ of an electron in a pure Coulomb potential, $-Z/r$. From the analytic expression for δ_0 (Bethe and Salpeter 1957) one can show that to terms of order $\alpha^4 Z^4$ and $\alpha^2 Z^2 (v/Z)^3$, where v is the asymptotic velocity of the electron,

$$\Delta\delta_0 \equiv \delta_0 - \delta_0^{(NR)} = \tfrac{1}{2}\alpha^2 Z^2 (\pi - v/Z) \tag{8}$$

and for $v \ll \pi Z$, $\Delta\delta_0 \simeq 27$ mrad if $Z = 18$ and $\Delta\delta_0 \simeq 3$ mrad if $Z = 6$. Since the Ar nucleus is strongly screened by atomic electrons, it seems reasonable that at low energy the $\Delta\delta_0$ for argon is similar to that for a bare nucleus with $Z \simeq 6$, and it is not surprising that the energy dependence of $\Delta\delta_0$ is different in the two cases.

In figure 2 we show the influence of the polarisation potential on the $l = 0$, 1 and 2 phaseshifts. The phaseshifts calculated without any polarisation potential lie

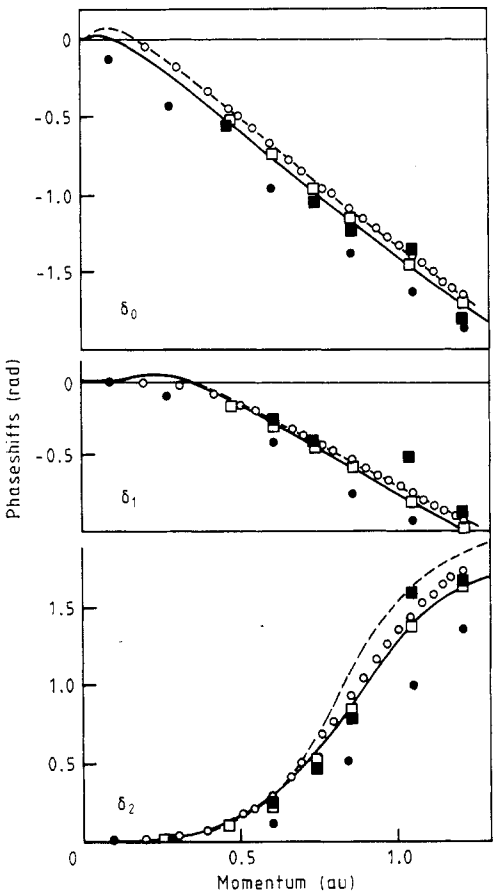

Figure 2. Phaseshifts for elastic scattering of electrons by argon. Theory: ——, present results; ●, present results without the polarisation potential; ---, McEachran and Stauffer (1983b). Experiment: □, Andrick and Bitsch (1983); ■, Srivastava *et al* (1981); ○, Williams (1979).

significantly below those calculated with the polarisation potential (see equation (6)). We also compare our relativistic phaseshifts with values derived from the measurements of differential cross sections by Andrick and Bitsch (1983), Srivastava *et al* (1981) and Williams (1979), and with theoretical values by McEachran and Stauffer (1983b). For $l = 0$, 1, 2 and for the momentum of the scattering electron $k > 0.5$ au, our values agree with values of Andrick and Bitsch (1983). For $l = 1$ and below $k = 0.5$ au, our results are in very good agreement with values calculated by McEachran and Stauffer (1983a, b), but the experimental values of Williams (1979) lie slightly lower. For $l = 2$ in the range from $k = 0$ to $k = 1.2$ au, the present values follow the experimental points but lie somewhat below those of McEachran and Stauffer (1983b) for $k > 0.7$ au.

A comparison with an R-matrix calculation of Fon *et al* (1983) shows that their phaseshifts for $l = 0$ lie some 3% above ours, their results for $l = 1$ to 4 are in good agreement with ours.

Recently Bell *et al* (1984) have also performed R-matrix calculations for this system. Their results for $l = 0$ lie within about 0.03 rad of ours. We have good agreement in

Table 2. Differential cross sections $d\sigma_{el}/d\Omega$ ($a_0^2\,sr^{-2}$) and total elastic cross sections σ_{el} (a_0^2) for argon.

Angle (deg)	Energy (eV)							
	3.0	5.0	7.5	10.0	15.0	20.0	30.0	40.0
0	1.361	6.236	22.294	43.963	58.249	53.450	49.083	50.626
5	0.969	5.105	49.702	40.384	54.953	50.012	43.636	42.860
10	0.665	3.950	16.572	35.610	50.256	45.531	37.546	34.644
15	0.565	3.124	13.712	30.704	44.972	40.771	32.097	27.874
20	0.642	2.630	11.238	25.984	39.243	35.719	27.119	22.275
25	0.853	2.428	9.188	21.333	33.243	30.427	22.456	17.532
30	1.162	2.473	7.580	17.174	27.220	25.058	18.071	13.470
35	1.523	2.705	6.412	13.548	21.435	19.812	14.012	9.994
40	1.894	3.058	5.647	10.537	16.129	14.904	10.324	7.049
45	2.246	3.475	5.231	8.188	11.519	10.537	7.112	4.626
50	2.554	3.899	5.093	6.475	7.751	6.887	4.463	2.727
55	2.798	4.280	5.149	5.356	4.888	4.043	2.431	1.348
60	2.969	4.581	5.313	4.733	2.924	2.041	1.040	0.477
65	3.065	4.774	5.500	4.478	1.769	0.835	0.264	0.073
70	3.079	4.830	5.618	4.435	1.269	0.311	0.022	0.062
75	3.011	4.733	5.589	4.450	1.233	0.312	0.199	0.350
80	2.866	4.480	5.361	4.387	1.460	0.659	0.658	0.820
85	2.647	4.073	4.901	4.141	1.761	1.168	1.252	1.359
90	2.366	3.535	4.217	3.661	1.990	1.681	1.848	1.859
95	2.040	2.907	3.363	2.966	2.055	2.078	2.332	2.232
100	1.691	2.239	2.424	2.126	1.927	2.283	2.625	2.419
105	1.340	1.592	1.511	1.263	1.639	2.276	2.688	2.401
110	1.012	1.029	0.748	0.529	1.273	2.082	2.519	2.182
115	0.728	0.603	0.254	0.083	0.946	1.766	2.154	1.801
120	0.501	0.355	0.123	0.069	0.794	1.426	1.666	1.328
125	0.340	0.311	0.423	0.597	0.944	1.168	1.144	0.839
130	0.249	0.478	1.182	1.730	1.498	1.098	0.674	0.411
135	0.224	0.848	2.392	3.481	2.507	1.280	0.347	0.117
140	0.259	1.398	4.006	5.803	4.509	1.775	0.217	0.002
145	0.346	2.091	5.943	8.590	5.917	2.569	0.303	0.081
150	0.472	2.881	8.091	11.687	8.132	3.614	0.589	0.342
155	0.623	3.715	10.314	14.898	10.496	4.818	1.025	0.737
160	0.783	4.527	12.450	17.986	12.816	6.059	1.538	1.206
165	0.932	5.250	14.334	20.711	14.889	7.205	2.050	1.676
170	1.055	5.823	15.817	22.854	16.530	8.137	2.478	2.069
175	1.136	6.143	16.765	24.224	17.583	8.731	2.761	2.328
180	1.162	6.313	17.079	24.680	17.939	8.939	2.867	2.432
σ_{el}	20.619	36.203	60.895	83.470	86.705	71.763	51.902	41.387
σ_{el}†	21.041	36.641	61.577	84.300	86.918	71.700	51.785	41.301

† Non-relativistic case.

the case of $l = 1$ and 3 but there is a significant discrepancy for $l = 2$ (for instance, their value is only 75% of our result at $k = 0.8$ au).

The present results of the differential and total elastic cross sections for the unpolarised incident beam are summarised in table 2. The contribution to the total cross section of the partial waves from $l = 8$ to 50, estimated with the help of equation (5), never exceeds 0.05%, while in the case of the differential cross sections for some particular energies and angles, it can reach 3–4%. Comparing the relativistic with

non-relativistic total cross sections (see the bottom of table 2), we find the biggest difference of up to 2% occurs at energies between 3 and 7.5 eV, whereas between 15 and 40 eV the relativistic effects are negligible.

Figure 3 shows the present total cross section values and other theoretical and experimental results. The theoretical values from the present work are in good agreement with the experimental data of Andrick and Bitsch (1983), Nickel *et al* (1985) and Wagenaar and de Heer (1980), which lie below the present calculations of McEachran and Stauffer (1983b), but above the theoretical values of Bell *et al* (1984), at least at energies below about 20 eV.

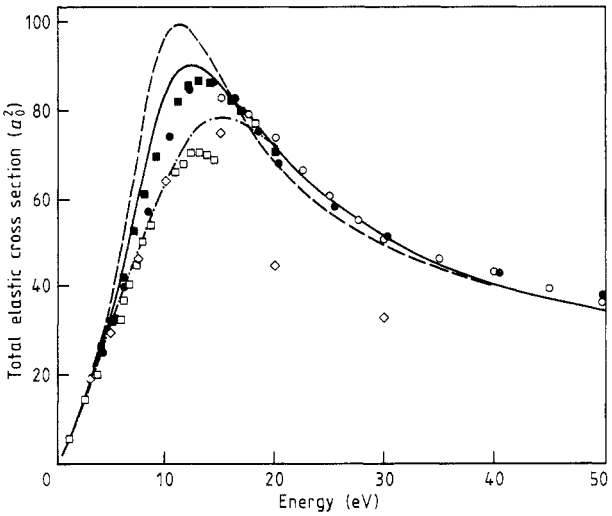

Figure 3. Total elastic scattering cross section. Theory: ——, present results; –·–, Bell *et al* (1984); – – –, McEachran and Stauffer (1983b). Experiment: ■, Andrick and Bitsch (1983); □, Golden and Bandel (1966); ●, Nickel *et al* (1985); ◇, Srivastava *et al* (1981); ○, Wagenaar and de Heer (1980).

Our differential cross sections at 3, 10 and 20 eV from table 2 are plotted in figure 4 together with theoretical (McEachran and Stauffer 1983b) and experimental (Andrick and Bitsch 1983, Srivastava *et al* 1981) differential cross sections.

At 3 eV (figure 4(*a*)), our curve is in good agreement with experiment for $\theta < 120°$. At 10 eV (figure 4(*b*)), our results agree well with the data of Andrick and Bitsch (1983) for $\theta > 50°$. At 20 eV (figure 4(*c*)), we note good agreement with McEachran and Stauffer as well as Andrick and Bitsch for almost all angles. However, we differ from Srivastava *et al* for $\theta < 60°$ and $\theta > 90°$.

6. Conclusions

We have presented a relativistic approach to the elastic scattering of electrons on argon. We note that relativistic effects play a significant role for small energies of the incident electron. With increasing energy, the relative difference between relativistic and non-relativistic results vanishes. We expect that the importance of relativistic effects will increase for heavier noble gases like krypton and xenon.

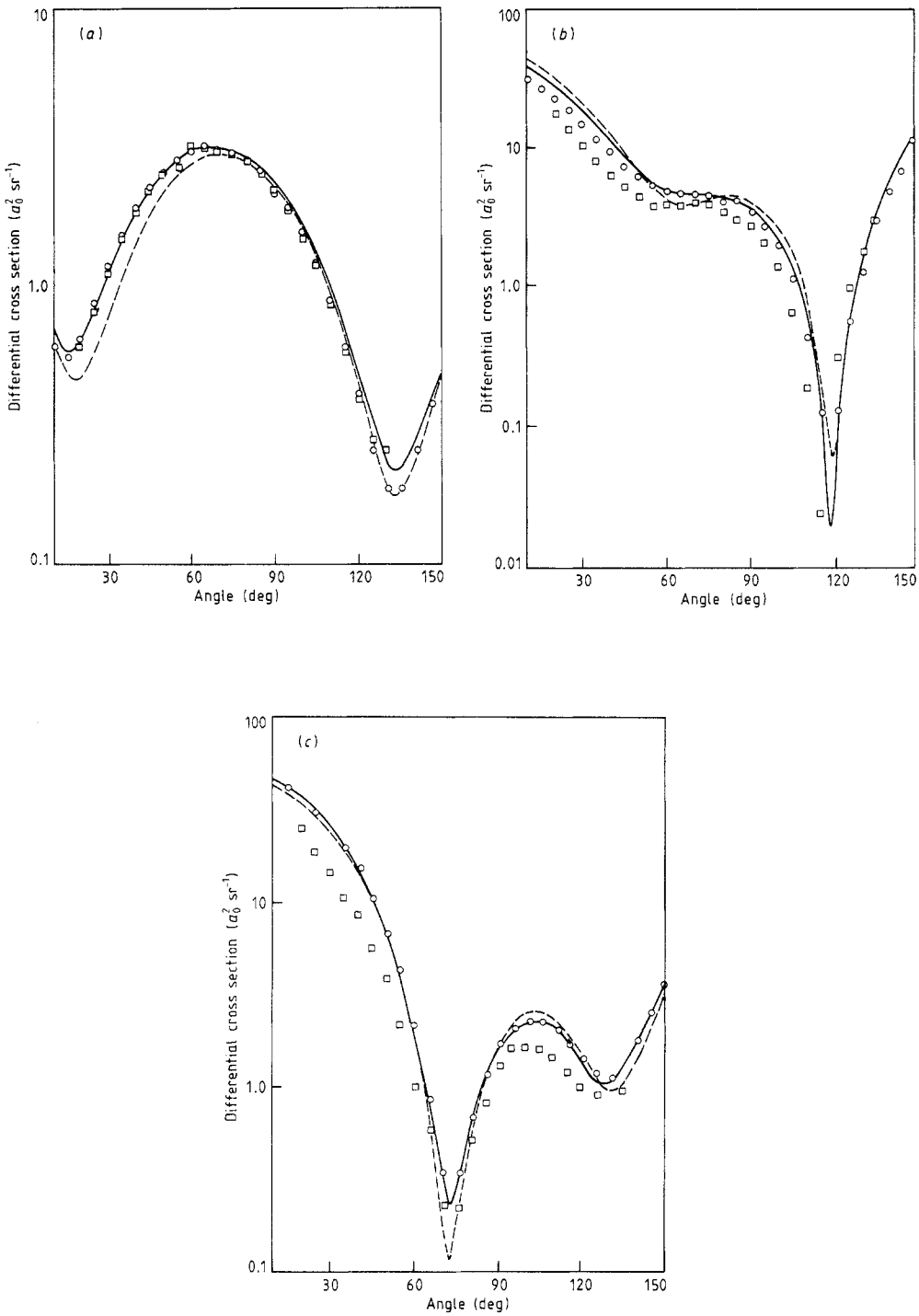

Figure 4. Differential cross sections for elastic scattering by argon: (*a*) 3 eV; (*b*) 10 eV; (*c*) 20 eV. Theory: ——, present results; - - -, McEachran and Stauffer (1983a, b). Experiment: ○, Andrick and Bitsch (1983); □, Srivastava *et al* (1981).

Although a relatively simple model of the target atom has been employed, we have achieved quite good general agreement with available theoretical and experimental data. The influence of the polarisation potential was found to be substantial at all energies considered.

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Appendix 1. Integration algorithm

To solve coupled differential equations like the Dirac equation for a central field

$$y'(x) = K(x)y(x) + X(x) \tag{A1.1}$$

where K is a 2×2 matrix, X is the exchange vector and $x = \ln r$ is the radial variable, we seek an extrapolation routine, possibly requiring iteration, to generate the solution at $x_{n+1} = (n+1)h$, given y and y' at the grid points $x_m = mh$ for $m \leqslant n$.

Let us consider five-point routines of the general form

$$y_1 = \sum_{m=0}^{4} A_m y_{-m} + h \sum_{m=-1}^{4} B_m y'_{-m} + e_1 \tag{A1.2}$$

where $y_m = y(x_m)$ and e_1 is the truncation error. If $B_{-1} \neq 0$, (A1.2) gives an implicit algorithm since the derivative y' is required at the extrapolated position. Since there are eleven coefficients A_m and B_m, it is possible to derive five-point methods with an eleventh-order truncation error, but such algorithms would be made useless by severe instability. One can help control stability by making the four parasitic roots of the difference equation

$$y_1 = \sum_{m=0}^{4} A_m y_{-m} \tag{A1.3}$$

significantly smaller than 1 in magnitude and distinct (Ceschino and Kuntzmann 1966). These constraints severely limit the number of possibilities.

A direct algorithm can be generated from a combination of (A1.1) and (A1.2):

$$y_1 = (1 - hB_{-1}K_1)^{-2}\left(x_{-1} + \sum_{m=0}^{4}(A_m y_{-m} + hB_m y'_{-m})\right) \tag{A1.4}$$

where $K_1 = K(x_1)$ and $X_{-1} = X(x_{-1})$. In Desclaux's program (1975), a fifth-order Adams–Bashforth predictor is combined with a fifth-order Adams–Moulton corrector (Gear 1971), and a final mixture of predictor and corrector solutions is chosen which eliminates the sixth-order truncation error. Such a mixture is identical to the sixth-order Adams–Mouton algorithm, in which the roots of (A1.3) are 1, 0, 0, 0, 0:

$$y_1 = y_0 + (h/1440)(475y'_1 + 1427y'_0 - 798y'_{-1} + 482y'_{-2} - 173y'_{-3} + 27y'_{-4}) - (863/12)h^7 y^{(7)}/7!. \tag{A1.5}$$

The direct method (A1.4) which uses the coefficients of (A1.5) is equivalent to iterating (A1.5) and (A1.1) to convergence, and the resulting solutions are more accurate than those obtained with the methods used by Desclaux.

By playing with the location of the roots of (A1.3), we were able to find a stable algorithm of still somewhat higher accuracy, at least for the problem at hand. Choosing roots $1, 0, -\frac{1}{2}, -\frac{1}{2}(1\pm i)$, we obtained

$$y_1 = -\tfrac{1}{2}y_0 + \tfrac{1}{2}y_{-1} + \tfrac{3}{4}y_{-2} + \tfrac{1}{4}y_{-3} + (h/5760)(1771y'_1 + 9235y'_0 + 5890y'_{-1} + 4610y'_{-2} + 35y'_{-3} + 59y'_{-4}) - \tfrac{113}{16}h^7 y^{(7)}/7!. \tag{A1.6}$$

We replaced the predictor-corrector integration in Desclaux's program with the direct algorithm of (A1.4) based on the coefficients of (A1.6). Tests for a wide variety of wavefunctions confirmed the expected stability and accuracy.

Appendix 2. Asymptotic solutions to the Dirac equation

In order to start the inward integration of the radial wavefunction y in (A1.1), one needs an asymptotic formula from which the outermost five points of y and its first derivation can be derived. In the original Dirac-Fock program (Desclaux 1975), the asymptotic forms were taken to be simple exponentials. Furthermore, a missing factor in the starting values of the derivatives of y caused false tails in the wavefunctions. We have inserted the missing factor and have replaced the exponentials by asymptotic bound Coulomb wavefunctions.

The required functions have been discussed by Rose (1961) but are more easily obtained for our purposes by direct substitution of the asymptotic expansion

$$\begin{pmatrix} P(r) \\ Q(r) \end{pmatrix} \sim \sum_{m \geqslant 0} \begin{pmatrix} e^{-\beta r} p_m r^{g-m} \\ e^{-\beta' r} q_m r^{g'-m} \end{pmatrix} \tag{A2.1}$$

with $p_0 \neq 0$ into the Dirac equation (1) with $v(r) = -z/r$ and $X_Q = X_P = 0$. One easily finds $\beta = \beta'$, $g = g'$, and

$$\begin{pmatrix} P(r) \\ Q(r) \end{pmatrix} \sim e^{-t/2} \sum_{m=0}^{[\nu-\gamma]} C_m \frac{t^{\nu-m}}{m!} \begin{pmatrix} (\kappa - z/\beta + m)\beta \\ (\kappa - z/\beta - m)\alpha E \end{pmatrix} \tag{A2.2}$$

where

$$C_{m+1} = [\gamma^2 - (\nu - m)^2] C_m \tag{A2.3}$$

$$\beta = [-E(2 + \alpha^2 E)]^{1/2} \tag{A2.4}$$

$$\nu = (z/\beta)(1 + \alpha^2 E) \tag{A2.5}$$

$$t = 2\beta r \tag{A2.6}$$

$$\gamma^2 = \kappa^2 - z^2\alpha^2. \tag{A2.7}$$

The expansion coefficient $C_0 \neq 0$ is a normalisation constant. In our use of (A2.2), we truncate the expansion as indicated at the largest integer m smaller than or equal to $\nu - \gamma$. For hydrogenic ions, $\nu - \gamma$ is an integer ($= n - |\kappa|$, where n is the principal quantum number) and (A2.2) is the exact solution.

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