PHYSICAL REVIEW A VOLUME 47, NUMBER 1 JANUARY 1993

Ab initio calculation of scattering length and cross section at very low energies for electron-argon scattering

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(Received 29 July 1992; revised manuscript received 24 August 1992)

The scattering length for electron-argon scattering is calculated very accurately by an *ab initio* method with wave functions computed exactly at zero energy. The multiconfiguration Hartree-Fock method, which takes into account the effects of target polarization and electron correlation through the configuration-interaction procedure, is used for the calculation. The differential, total, and momentum-transfer cross sections are also calculated for very low energies ranging from 0–1 eV. The present result for the scattering length is found to be in excellent agreement with the experimental results of Buckman and Lohmann [J. Phys. B **19**, 2547 (1986)] and Haddad and O'Malley [Aust. J. Phys. **35**, 35 (1982)].

PACS number(s): 34.80.Bm

At thermal energies, the total, differential, and momentum-transfer cross sections for electron-atom collisions are determined in magnitude and shape primarily by the scattering length. At extremely low energy, extrapolation of the experimental data is difficult and cannot be regarded as reliable. As a result, extremely accurate theoretical calculations are needed to obtain correct cross sections at thermal energies. However, the calculations are made more difficult by the large electron correlations and dynamical polarizations at zero and very low energies. In general, the scattering length is determined by computing phase shifts at lower energies with reasonable accuracy and then extrapolating ($\tan\delta_0/k$) to zero energy. But this does not always guarantee the accuracy of the result.

There have been a number of experimental measurements [1–6] and a few theoretical calculations [7–10] on the scattering length and cross sections with argon. The most accurate determination of the scattering length from experimental measurements is due to Buckman and Lohmann [1] and Haddad and O'Malley [2]. There is considerable disagreement existing between different sets of experimental results, between different theoretical calculations, and between theory and experiment. Moreover, there is no accurate *ab initio* calculation of the scattering length and phase shifts at very low energies for the $e^- + \mathrm{Ar}$ case. Since an *ab initio* calculation of the wave function exactly at zero energy is very difficult, no reliable data for the scattering length have so far been obtained in this way to verify the experimental results. There is therefore an urgent need to perform an accurate *ab initio* calculation.

Very recently we calculated [11] the scattering length and phase shifts at very low energies for electron-neon scattering using the multiconfiguration Hartree-Fock (MCHF) method [12]. The results were in excellent agreement with the measurements. In the present article we intend to apply the same *ab initio* method to calculate the scattering length and total and momentum-transfer cross sections for the first time in the *ab initio* way at very low energies from 0.0 to 1 eV, the extremely difficult region for *ab initio* calculations.

It is well known that at zero and very low energies, the polarization and electron-correlation effects are very strong and hence must be taken into account very carefully. As described earlier, the MCHF method [12] considers the energy-dependent polarization and electron-correlation effects more accurately and realistically in the *ab initio* manner through the configuration-interaction procedure. The polarization, which is different for different kinetic energies of the projectile, is considered through the bound configurations representing the multipole polarization and then optimizing both bound and continuum orbitals simultaneously at each kinetic energy of the scattered electron. The phase shifts for partial waves calculated in the MCHF method have been used to calculate the elastic differential, total, and momentum-transfer cross sections.

Following Saha [13] an MCHF wave function for a scattering state with label γ, energy E, and the term LS may be expressed in a series of the form

TABLE I. Comparison of scattering length (in a_0) with experiments and other theories.

Source	Scattering length (units of a_0)
Theory	
Present work	−1.486
MeEachran and Stauffer [7]	−1.506
Bell, Scott, and Lennon [9]	−1.68
Experiment	
Haddad and O'Malley [2]	−1.492
Buckman and Lohmann [1]	−1.492
Ferch *et al.* [3]	−1.449
Guskov *et al.* [6]	−1.63
Golden and Bandel [5]	−1.65
Golovanivsky and Kabilan [16]	−1.53

TABLE II. The rate of convergence of the scattering length (in units of a_0) with respect to the configurations generated by the orbitals representing the dipole polarization.

Polarized orbitals	Number of configurations	Scattering length
$3d,4s,4p$	6	-1.121
$+4d,5s,5p$	21	-1.481
$+5d,6s,6p$	46	-1.486
$+6d$	52	-1.486

$$\Psi(\gamma LS;N+1)=\sum_j^{m_t} a_j\Phi(\gamma_j L_t S_t;N)\phi_{kl} + \sum_i^{m_b} c_i\Phi(\gamma_i LS;N+1) \ . \tag{1}$$

where $\Phi(\gamma_j L_t S_t;N)$ is the N-electron bound configuration state of the target with configuration γ_j and mixing coefficient a_j and $\Phi(\gamma_i LS;N+1)$ is the $(N+1)$-electron bound configuration state with configuration γ_i and mixing coefficient c_i. m_t and m_b are, respectively, the number of target and $(N+1)$-electron bound configuration states. The above wave function is defined in terms of a set of radial functions, say, $P_i(r)$, $i=1,\dots,m$. First of all, the MCHF method [14] for bound states is used to determine the radial functions $P_i(r)$, $i=1,\dots,N_t$ for the target. In the continuum calculation all the radial functions describing the target are kept fixed, along with the mixing coefficients a_j. Other bound-state radial functions, $P_i(r)$, $i=N_t+1,\dots,m-1$ which account for polarization of the target are determined variationally along with the radial function P_m for the continuum electron. The method of constructing the phase shifts for various partial waves involves the solution of coupled integro-differential equations for the radial functions of the form

$$\left[\frac{d^2}{dr^2}+\frac{2Z}{r}-\frac{l(l+1)}{r^2}\right]P_i(r) = \frac{2}{r}[Y_i(r)P_i(r)+X_i(r)+I_i(r)]+\sum_{i'}\varepsilon_{ii'}P_{i'}(r) \tag{2}$$

by an iterative method [14]. Here $(2/r)Y_i(r)$ is the screening function, $(2/r)X_i(r)$ is the exchange function, and $(2/r)I_i(r)$ represents terms arising from interactions between configuration states. $\varepsilon_{ii'}$ are the off-diagonal energy parameters related to Lagrange multipliers that ensure orthogonality assumptions. The boundary conditions satisfied by the bound radial functions are

$$P_i(r)\xrightarrow[r\to 0]{} r^{l+1} \text{ and } P_i(r)\xrightarrow[r\to\infty]{} 0 \ . \tag{3}$$

The radial functions for the scattering orbital satisfy the conditions

$$P_i(r)\xrightarrow[r\to 0]{} r^{l+1}, \quad P_i(r)\xrightarrow[r\to\infty]{} A\sin\left[kr-\frac{l\pi}{2}+\delta_l\right] \tag{4}$$

where δ_l is the phase shift and $\varepsilon_{ii}=-k^2$, k^2 being the kinetic energy of the scattered electron. At large r, for $k=0$, the s-wave radial function satisfies the condition

$$P_i(r)\rightarrow A'(r-a) \ ,$$

where a is the scattering length and A' is the amplitude. The scattering length a can be calculated directly using explicit zero-energy wave function.

The multiconfiguration self-consistent-field procedures [14] used traditionally in the bound-state calculations can be applied to these system of equations as well, except that the continuum function is obtained by outward integration only, there being no exponentially decaying "tail" region. The same numerical procedures were used as for bound radial functions, except that at larger values of r, outward integration proceeded at half the usual step length with functions $Y_i(r)$, $X_i(r)$, and $I_i(r)$ interpolated at the midpoint. These functions are essentially "bound" in nature and vary smoothly as $r\rightarrow\infty$. In this way, some additional accuracy was acquired for the outward integration. The continuum radial function was normalized at two adjacent points to the regular and irregular Bessel functions as soon as the region where the direct and the exchange potentials are found to be negligible is reached, which may result in considerably smaller values of r than the asymptotic form given by the boundary condition of Eq. (4). In the present approximation, the coefficients c_i need to be determined, and they are solu-

TABLE III. Comparison of position and magnitude of the Ramsauer-Townsend minimum with experiments and other theories.

Source	Energy position (eV)	Magnitude (a_0^2)
	Theory	
Present work	0.30	1.405
Bell, Scott, and Lennon [9]	0.3	1.20
Plenkiewicz *et al.* [10]	0.306	1.07
	Experiment	
Haddard and O'Malley [2]	0.311	0.965
Buckman and Lohmann [1]	0.342±0.005	1.108
Ferch *et al.* [3]	0.345±0.005	1.111
Golden and Bandel [5]	0.285	0.447
Guskov *et al.* [6]	0.33±0.01	0.536±0.214

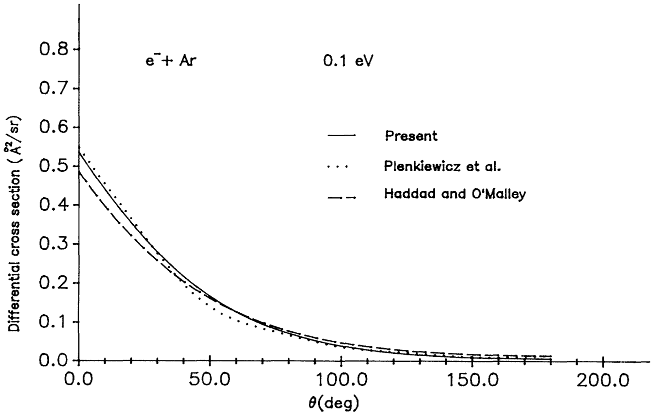

FIG. 1. Comparison of differential cross section at 0.1 eV.

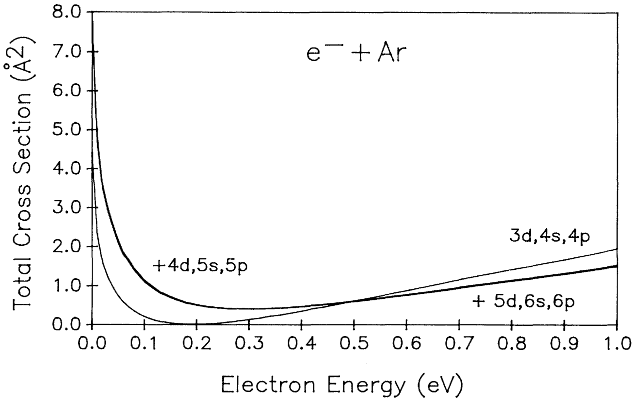

FIG. 3. Rate of convergence of total cross sections with respect to the number of orbitals representing the dipole polarization.

tions of the system of equations [13] derived from the condition that $\langle \psi | H - E | \psi \rangle$ be stationary with respect to variations in the coefficients, where H is the Hamiltonian for the $(N+1)$-electron system and $E = E_c + k^2/2$ (in atomic units).

As we consider here zero and extremely low energies of the scattering electron, where polarization of the target is extremely important, we shall assume that the relativistic effects are not significant in the elastic scattering of electrons on neutral argon and that an *LS* coupling calculation may be performed. Moreover, most accurate methods with which we compared our results are also nonrelativistic. First of all, the ground-state wave function for the argon atom is calculated in the Hartree-Fock approximation. The MCHF wave functions were calculated with configurations constructed from the single and double replacements of the two outermost orbitals $3s$ and $3p$ of the argon atom by the excited orbitals $3d$, $4s$, $4p$, $4d$, $5s$, $5p$, $5d$. These bound-state wave functions are then used as an input to calculate the phase shifts for the various partial waves. As the polarization and electron correlation of the $3s^2 3p^6$ target atom by the scattering electron are extremely important at zero and at very low energies considered in the present paper, all the configurations which account for polarization and correlation are considered in the expansion of the scattering wave function. For the $3s^2 3p^6$ target, the dipole polarization effect can be taken into account very well by including configurations involving the single replacement of the target orbitals according to $3s \rightarrow np$ and $3p \rightarrow n'd$ and $n''s$. These bound orbitals that are responsible for the dipole polarization of the target atom are determined by optimizing both bound and scattering electron orbitals

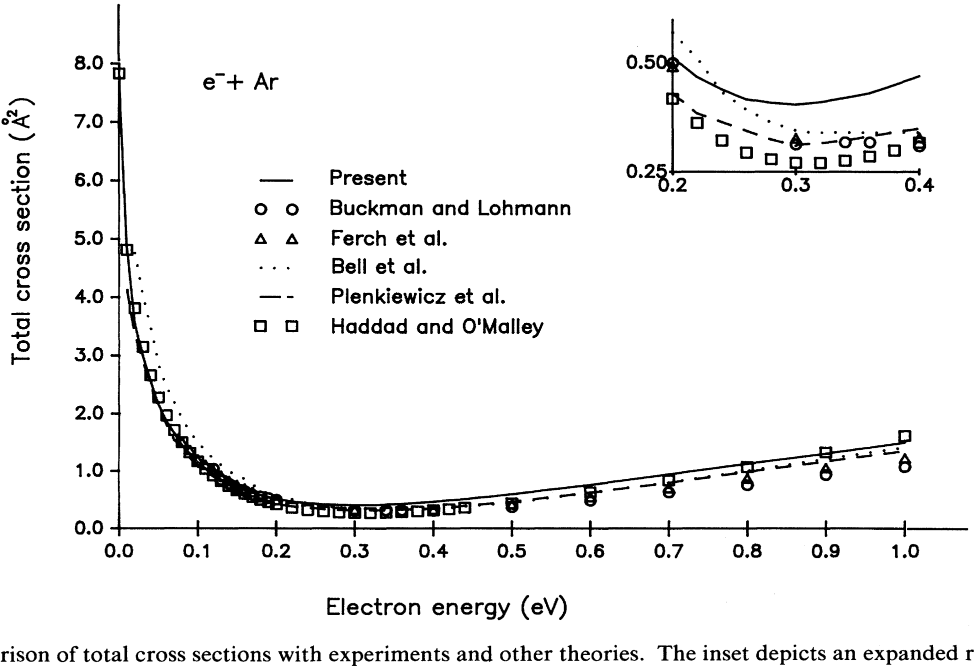

FIG. 2. Comparison of total cross sections with experiments and other theories. The inset depicts an expanded region of the graph between 0.2 and 0.4 eV.

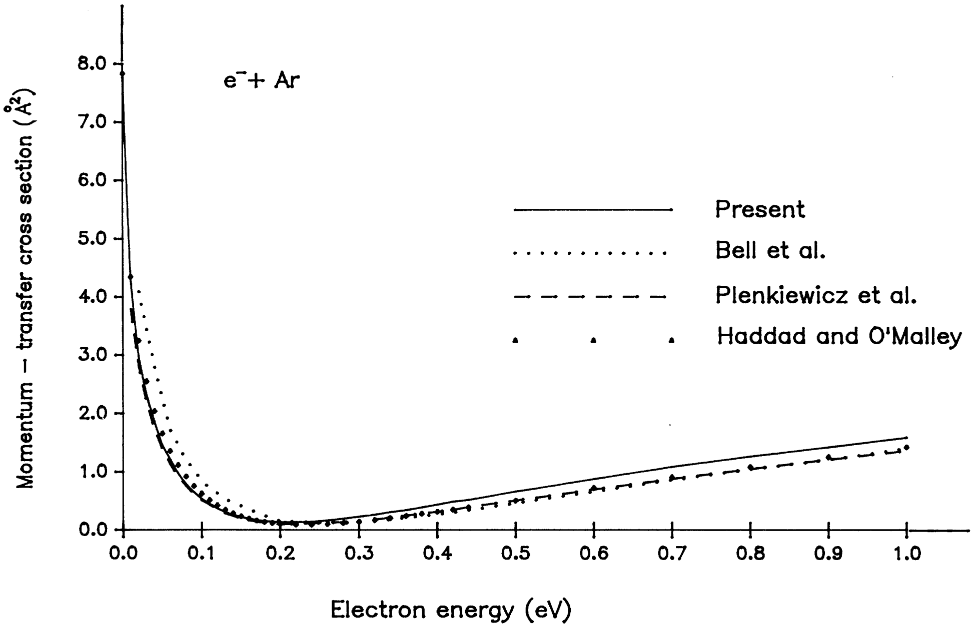

FIG. 4. Comparison of momentum-transfer cross sections with other theories.

simultaneously at each kinetic energy of the scattered electrons. The MCHF program [12] for continuum wave functions was then used to calculate phase shifts for each incident electron orbital angular momentum $l=0$–6. The contributions from higher partial waves were determined from the effective range formula [13] with $\alpha=11.06a_0^3$ as the static dipole polarizability [15].

The present scattering length is compared with results derived from experiments and with other theoretical data in Table I. The present result is in excellent agreement with the most accurate results derived from experiment by Haddad and O'Malley [2] and Buckman and Lohmann [1]. It is also in excellent agreement with the theoretical results obtained by McEachran and Stauffer [7]. The rate of convergence of the scattering length with respect to the number of orbitals representing the dipole polarization is shown in Table II. It was found that quadrupole and multipole polarization do not change the results. It was also tested that double replacements of the outermost orbitals $3s$ and $3p$ do not change the results. Table III compares the present position and magnitude of the Ramsauer-Townsend minimum with results obtained from experiments and with other theoretical data. The present energy position of the Ramsauer-Townsend minimum is in excellent agreement with the experimental minimum obtained by Haddad and O'Malley [2] and the theoretical minima obtained by Bell, Scott, and Lennon [9] and Plenkiewicz, Plenkiewicz, and Jay-Gerin [10]. The magnitude of the present minimum agrees well with the experimental minima measured by Buckman and Lohmann [1] and Ferch *et al.* [3] and the theoretical minima calculated by Bell, Scott, and Lennon [9] and Plenkiewicz, Plenkiewicz, and Jay-Gerin [10], although it is higher than the other results.

The elastic differential cross section at $k^2=0.1$ eV are shown in Fig. 1. They are compared with the results of Plenkiewicz, Plenkiewicz, and Jay-Gerin [10] and Haddad and O'Malley [2]. It is found that the present results are in excellent agreement with the results obtained by Plenkiewicz, Pelnkiewicz, and Jay-Gerin except at angles from 30°–80° where their results are lower. The present results are also in excellent agreement with those obtained by Haddad and O'Malley [2] except at very low angles, where their results are lower. Figure 2 shows the present total cross section as a function of incident electron energy from 0.0 to 1.0 eV. The experimental results of Buckman and Lohmann [1], Ferch *et al.* [3], and Haddad and O'Malley [2] and the theoretical results of Bell, Scott, and Lennon [9] and Plenkiewicz, Plenkiewicz, and Jay-Gerin [10] are included for comparison. The present results are in excellent agreement with the experimental

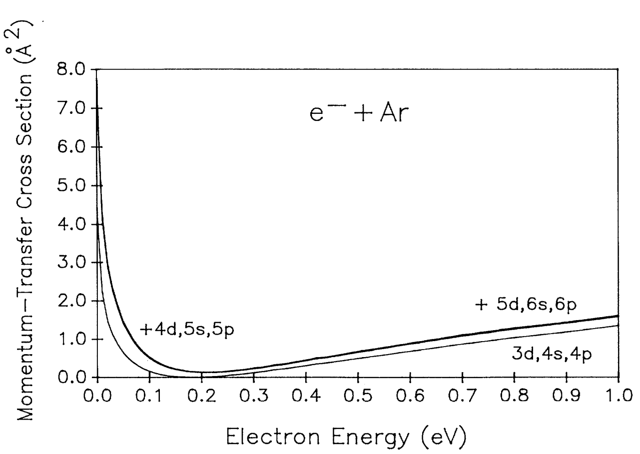

FIG. 5. Rate of convergence of the momentum-transfer cross sections with respect to the number of orbitals representing the dipole polarization.

TABLE IV. The rate of convergence of the cross sections (in units of Å^2) with respect to configurations generated by the orbitals representing the dipole polarization.

	0.01 eV		0.2 eV		1.0 eV	
Polarized orbitals	Total	Momentum transfer	Total	Momentum transfer	Total	Momentum transfer
$3d,4s,4p$	2.3305	2.2361	0.0123	0.0064	1.9549	1.3532
$+4d,5s,5p$	4.7247	4.1959	0.4994	0.1330	1.5361	1.6176
$5d,6s,6p$	4.8574	4.3214	0.5119	0.1340	1.5057	1.5836
$+6d$	4.8580	4.3219	0.5120	0.1341	1.5056	1.5835

results of Haddad and O'Malley [2], Ferch *et al.* [3], and Buckman and Lohmann [1] except for the higher energies, where the results of Ferch *et al.* and Buckman and Lohmann are a little lower. In Fig. 3 the convergence of the total cross sections with respect to the number of orbitals which represent the dipole polarization is shown as a function of electron energy.

In Fig. 4 the present momentum-transfer cross sections are shown as a function of incident electron energy ranging from 0.0 to 1.0 eV. The theoretical results of Bell, Scott, and Lennon [9] and Plenkiewicz, Plenkiewicz, and Jan-Gerin [10] and the experimental results of Haddad and O'Malley are presented for comparison. The present results are seen to be in excellent agreement with the results obtained by Haddad and O'Malley [2] and Plenkiewicz, Plenkiewicz, and Jay-Gerin [10], except at higher energies, where their results are a little lower. The rate of convergence of the momentum-transfer cross sections with respect to the number of configurations generated with the number of orbitals representing the dipole polarization is presented in Fig. 5 as a function of electron energy. In Table IV we have shown the rate of convergence of the total and momentum-transfer cross sections at three electron energies. The quadrupole and multipole polarization effects are found to be negligible in the energy region considered. It was also found that the results are not changed if we increase the number of configurations generated by the double replacements of the outermost orbitals $3s$ and $3p$.

Finally, we would like to mention that the scattering length for electron-argon scattering is calculated in the *ab initio* manner with wave functions computed exactly at zero energy. As the present MCHF method takes into account polarization and the electron-correlation effects in the *ab initio* way more accurately than any other methods, we conclude that the present results are more reliable.

This work was supported by the National Science Foundation and in part by the Petroleum Research Fund, administered by the American Chemical Society. This research was also supported by the Florida State University through time granted on its CRAY-YMP supercomputer.

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[1] S. J. Buckman and B. Lohmann, J. Phys. B **19**, 2547 (1986).

[2] G. N. Haddad and T. F. O'Malley, Aust. J. Phys. **35**, 35 (1982).

[3] J. Ferch, B. Grantza, C. Masche, and W. Raith, J. Phys. B **18**, 967 (1985).

[4] K. Jost, P. G. F. Bisling, F. Eschen, M. Felsmann, and L. Walther, *Proceedings of the Thirteenth International Conference on the Physics of Electronic and Atomic Collisions, Berlin, 1983,* edited by J. Eichler *et al.* (Amsterdam, North-Holland), p. 91.

[5] D. E. Golden and H. W. Bandel, Phys. Rev. **149**, 58 (1966).

[6] Yu K. Guskov, R. V. Savvov, and V. A. Slobodyanyuk, Zh. Tekh. Fiz. **48**, 277 (1978) [Sov. Phys. Tech. Phys. **23**, 167 (1978)].

[7] P. McEachran and A. D. Stauffer, J. Phys. B **16**, 4023 (1983).

[8] A. Dasgupta and A. K. Bhatia, Phys. Rev. A **32**, 3335 (1985).

[9] K. L. Bell, N. S. Scott, and M. A. Lennon, J. Phys. B **17**, 4757 (1984).

[10] B. Plenkiewicz, P. Plenkiewicz, and J.-P. Jay-Gerin, Phys. Rev. A **38**, 4460 (1988).

[11] H. P. Saha, Phys. Rev. Lett. **65**, 2003 (1990).

[12] H. P. Saha (unpublished).

[13] H. P. Saha, Phys. Rev. A **43**, 4712 (1991).

[14] C. Froesce Fischer, Comput. Phys. Commun. **14**, 145 (1978).

[15] T. M. Miller and B. Bederson, Adv. At. Mol. Phys. **13**, 1 (1977).

[16] K. S. Golovanivsky and A. P. Kabilan, Phys. Lett. A **80**, 249 (1980).