Ab initio calculation for low-energy elastic scattering of electrons from chlorine atoms

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We have performed *ab initio* calculations of scattering length, differential, total, and momentum-transfer cross sections for elastic scattering of electrons from open-shell atoms; in particular, the chlorine atom. The polarization of chlorine atoms due to the scattered electrons and the electron correlation effects that are very important in the calculation are taken into account through the configuration-interaction procedure using the multiconfiguration Hartree-Fock method for continuum wave functions. Phase shifts for various partial waves calculated in this approximation have been used to calculate elastic differential, total elastic, and momentum-transfer cross sections for low energies ranging from 0–27.2 eV. The scattering length is calculated with wave functions computed exactly at zero energy. The results are compared with other available theoretical data.

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I. INTRODUCTION

Accurate calculations of elastic scattering of electrons from closed-shell atoms have been known for a long time. On the other hand, open-shell atoms always present a challenge to the theorist. In particular, elastic scattering of electrons from open-shell atoms is very difficult to calculate because of strong correlations within the target states of the atom, as well as large polarization and electron correlation of the target by the continuum electron at very low energies. Today, there is a significant interest in calculations of electron scattering from such a system because of their applications to plasma processing of semiconductors and also to low-temperature astrophysical plasmas.

In this paper we present the results of our calculations on elastic scattering of electrons from chlorine atoms. Unfortunately there have been no measurements on this process for this atom. There are only two calculations [1,2] available on elastic scattering of electrons from chlorine atoms; one is at electron energies below 1.0 eV and the other, published very recently, is at energies up to 16 eV. The first calculation of elastic scattering of electrons from chlorine was performed by Fabricant [1] by the method of extrapolation of potential parameter along isoelectronic series and among corresponding neutral atoms. He considered energies below 0.6 eV. Griffin *et al.* [2] very recently carried out calculations on elastic and inelastic scattering of electrons from neutral chlorine using the *R*-matrix method [3,4]. The dipole polarization of the chlorine atom by the scattered electron was included by the use of polarized psuedostates. They reported results for elastic total and momentum-transfer cross sections for energies up to 16 eV.

One of the important features of this calculation is the presence of Ramsauer-Townsend minima in the total and momentum-transfer cross sections similar to that found in the case of argon [5–7]. In the present paper we show results of our calculation on elastic scattering of electrons from chlorine atoms using the multiconfiguration Hartree-Fock method for continuum wave functions. We performed this accurate *ab initio* calculation to compare with the available theoretical results and at the same time to encourage experimentalists to measure the cross sections. As the effects of polarization and electron correlations are very important in this calculation in order to obtain accurate cross sections at very low collision energies, their proper inclusion can strongly affect the results of the calculation. Recently, we successfully applied the multiconfiguration Hartree-Fock (MCHF) method to calculate accurately the scattering length, phase shifts, total and momentum-transfer, and differential cross sections for scattering of electrons from noble-gas atoms [8,9] at very low energies. In these calculations, electron correlation and polarization, which are very important, were taken into account by optimizing both excited bound and continuum orbitals at each kinetic energy of the scattered electron through the configuration-interaction procedure. This *ab initio* calculation more accurately takes these effects into account than any other method. These calculations were found to be in excellent agreement with accurate experimental [10] and other accurate theoretical [11] results.

The main purpose of the present investigation is to see how accurately the present MCHF method obtains scattering length and cross sections in the case of electron-chlorine scattering. As the calculation at very low energies is extremely difficult and, in addition, since a great quantity of information is contained in the scattering length and differential cross sections, in this study we used the MCHF method to calculate accurately and completely, *ab initio* the scattering length, differential, integral, and momentum-transfer cross sections through an energy range from 0 to 27.2 eV, an extremely difficult region for *ab initio* calculations. At zero and very low energies, the polarization of the target by the scattering electron and the electron correlation effects are very large and must be taken into account very carefully. As mentioned earlier, the MCHF method takes account of the polarization and the electron-correlation effects more accurately and realistically in the *ab initio* method through the configuration-interaction procedure. In this MCHF approach, the polarization effect, which is different for each different kinetic energy of the projectile, is considered through the bound configurations, which represent the multiple polarization by varying the excited bound and the continuum orbitals simultaneously at each kinetic energy of the projectile. The scattering length and the phase shifts for partial waves computed in the MCHF method have been

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used to calculate the differential, total elastic, and momentum-transfer cross sections [12,13].

In our calculation we shall assume that the spin-orbit interaction and other relativistic effects are not significant in the elastic scattering of electrons on neutral chlorine and that an *LS* coupling calculation may be performed. Moreover, the available theoretical results with which we compared our results are also nonrelativistic.

II. THEORY

In brief, the MCHF method optimizes both the bound and the continuum wave functions simultaneously at each incident energy. The optimized bound orbitals take into account, *ab initio*, the polarization and correlation effects very accurately, resulting in an accurate phase shift. To obtain the scattering length, we solved the coupled integro-differential equations for both bound and continuum wave functions for zero incident energy and zero angular momentum. In the present calculation, the MCHF method for scattering wave functions is used to calculate the scattering length for zero energy and phase shifts δ_l for various partial waves for very low energies. The method of constructing the scattering length and the phase shifts for various partial waves involves the solution of coupled integro-differential equations for the radial functions of the form

$$\left[\frac{d^2}{dr^2}+\frac{2Z}{r}-\frac{l_i(l_i+1)}{r^2}\right]P_i(r)=\frac{2}{r}\left[Y_i(r)P_i(r)+X_i(r)\right.$$

$$\left.+I_i(r)\right]+\sum_{i'}\epsilon_{ii'}P_{i'}(r),$$

$$(1)$$

where $(2/r)\,Y_i(r)$ 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. The off-diagonal energy parameters ϵ_{ii} are related to Lagrange multipliers that ensure orthogonality of the wave functions. These equations are solved by an iterative method with the boundary conditions for the bound radial functions

$$P_i(r)\underset{r\to0}{\to}r^{l+1}\quad\text{and}\quad P_i(r)\underset{r\to\infty}{\to}0\qquad(2)$$

and those for scattering wave functions

$$P_i(r)\underset{r\to0}{\to}r^{l+1}\qquad(3)$$

and

$$P_i(r)\underset{r\to\infty}{\to}C\,\sin\!\left(kr-\frac{l\pi}{2}+\delta_l\right),\qquad(4)$$

where δ_l is the phase shift and $\epsilon_{ii}=-k^2$, k^2 being the kinetic energy of the scattered electron.

For $k^2=0$ and at large r, the scattering wave function for the *s*-partial wave satisfies the condition

$$P_i(r)=A(r-a),\qquad(5)$$

where a is the scattering length and A is the amplitude. The use of explicit zero-energy wave function allows a to be calculated directly.

In the MCHF method the bound and the scattering radial functions are determined by solving the above set of coupled second-order integro-differential equations under the proper boundary conditions. The scattering radial function is normalized by fitting the computed values at two adjacent points to the regular and irregular Bessel functions as soon as the region where the direct and exchange potentials vanish is reached, which may be at considerably smaller values of r than the asymptotic form given by the boundary condition of Eq. (4).

III. COMPUTATIONAL PROCEDURE

The MCHF method employed here to calculate the scattering of electrons from chlorine atoms is basically the same as the one previously used for low-energy elastic scattering of electrons from argon atoms [5,6].

At first, an accurate wave function for the ground state of the chlorine atom was calculated in the multiconfiguration Hartree-Fock approximation [14]. The correlated wave function of the target chlorine atom is calculated by the MCHF wave-function expansion constructed from the single and double replacement of $3s$ and $3p$ orbitals of the chlorine atom by the excited orbitals, coupled to form a ^2P term. The excited orbitals considered are $3d$, $4s$, $4p$, $4d$, $4f$, $5s$, $5p$, $5d$, $5f$, and $5g$. The wave functions obtained from this calculation are used as an input in the calculation of the scattering wave functions and the phase shifts for various partial waves and various final *LS* states.

As already mentioned, polarization and electron correlation of the $3s^2\,3p^5$ target atom by the scattering electrons are very important at zero and at very low-energy $e^-+\text{Cl}$ scattering. These polarizations and electron correlations are considered in the expansion of the scattering wave function. The configurations that represent the multipole polarization are generated by single replacement of the outer two orbitals of the target with excited orbitals representing the dipole, quadrupole, and multipole polarization effects. The dipole polarization effects have been taken into account by the bound configurations generated by the replacement $3s\to np$, $n\leq5$; $3p\to nd$, $n\leq4$; and $3p\to ns$, $n\leq5$. The quadrupole and higher multipole polarization effects are taken into account through the replacements $3s\to n'd,n'f$, $n'\leq4$, and $3p\to n'f,n''g$, $n'=4$ and $n''=5$. All the configurations generated in this way are retained in the expansion of the scattering wave function. These excited bound orbitals, which are responsible for the polarization of the target atom, are determined by optimizing both the excited bound and the scattering electron orbitals kl simultaneously at each kinetic energy of the scattered electron. More than 100 configurations have been used to calculate scattering wave functions for the various partial waves over the range of impact energies considered. For each partial wave and each final state, the same set of configurations, which represents the electron correlation and polarization effects, have been used to calculate the scattering wave functions over the range of the energies considered. As the polarization of the target is energy dependent, both the excited bound and the scattering electron

TABLE I. Comparison of scattering length (in a_0) with Fabricant's [1] result.

Present		HF	1.9433 (singlet)	1.5429 (triplet)
		MCHF	-1.4778 (singlet)	-2.7072 (triplet)
Fabricant		Cl ($^2P_{3/2}$)$\rightarrow[3/2]_1$	-1.97	
		$\rightarrow[3/2]_2$	-2.46	

orbitals are varied simultaneously at each kinetic energy of the scattering electron. It is found that quadrupole polarization is also important in addition to dipole polarization in this case. In the present calculation, partial waves $l=0$ to 6 are calculated directly by the MCHF method. The necessary contributions for higher partial waves are obtained from expression [15],

$$\tan \delta_l = k^2 \alpha a_l + k^4(\alpha^2 b_l + \beta c_l), \qquad (6)$$

where

$$a_l = \frac{\pi}{(2l+3)(2l+1)(2l-1)},$$

$$b_l = \pi \frac{15(2l+1)^4 - 140(2l+1)^2 + 128}{[(2l+3)(2l+1)(2l-1)]^3(2l+5)(2l-3)},$$

$$c_l = \frac{3\pi}{(2l+5)(2l+3)(2l+1)(2l-1)(2l-3)}.$$

The experimental value [16] for the dipole polarizability $\alpha = 14.7 \ a_0^3$ and the extrapolated value [17] for the quadrupole polarizability $\beta = 67.41 \ a_0^5$ are used in the present calculation. Expression [6] provides reasonably accurate higher partial-wave phase shifts, since the contributions to the cross sections in the energy range considered are, in general, quite small.

IV. RESULTS AND DISCUSSION

Detailed and extensive calculations were performed on the low-energy elastic scattering of electrons from chlorine atoms to account for polarization and electron correlation. In the present paper, the scattering length, phase shifts, elastic differential, elastic integral, and momentum-transfer cross sections are calculated for impact energies ranging from 0 to 27.2 eV.

A. Scattering length

In Table I, the scattering length obtained by the MCHF method is compared with theoretical results obtained by Fabricant [1]. As mentioned earlier, Fabricant performed the calculation on elastic scattering of electrons from chlorine by the method of extrapolation of potential parameters along the isoelectronic series of positive ions and corresponding neutral atom. He calculated the scattering length from the initial target state $^2P_{3/2}$ and obtained for the final $[3/2]_1$ state -1.97 a_0 and for the final $[3/2]_2$ state $-2.46 \ a_0$ whereas we obtained results with LS coupling taken into account. We calculated singlet and triplet scattering lengths in both the

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 multipole polarization.

LS	Polarized orbitals	Number of configurations	Scattering length
	$3d,4s,4p$	18	-1.8781
	$+4d,5s,5p$	68	-2.4012
Triplet	$+5d,6p$	131	-2.7015
	$+6s$	143	-2.7072
	$+6d$	167	-2.7072
	$3d,4s,4p$	14	-0.8925
	$+4d,5s,5p$	51	-1.2700
Singlet	$+5d,6p$	103	-1.4710
	$+6s$	112	-1.4778
	$+6d$	130	-1.4778

Hartree-Fock (HF) and MCHF approximations. Notice that the sign of scattering lengths in the HF approximation is reversed in the MCHF approximation. This is due to the effects of polarization and electron correlation. It should be mentioned that the present scattering length is calculated with the wave function computed exactly at zero energy. To show that the present results are converging consistently, the rate of convergence of the scattering lengths for both triplet and singlet with respect to the number of orbitals representing the multipole polarization is shown in Table II. The dipole polarizability of chlorine atom is also calculated with the polarized orbitals computed at zero energy and zero angular momentum. We obtained the dipole polarizability to be $\alpha = 14.58 \ a_0^3$ which compares very well with the experimental result in [16], 14.7 a_0^3. This suggests that the wave functions used to obtain the results reported here are very accurate.

B. Ramsauer minimum

In Table III, we compare the present position and magnitude of the Ramsauer-Townsend minimum with other theoretical data. It is found that the present minimum occurs at slightly higher energy than that obtained by Griffin *et al.* [2] using the R-matrix method, but the position of minimum obtained by Fabricant [1] is much lower. The magnitude of the present minimum is also found to be higher than the result computed by the R-matrix method but is lower than that obtained by Fabricant. It should be mentioned that in the present calculation, both dipole and quadrupole polarization were included completely in an *ab initio* way through the configuration-interaction procedure, whereas in the R-matrix calculation, only dipole polarization was included through the polarized pseudostates. It is found that the position and magnitude of the minimum is very sensitive to the quality of

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

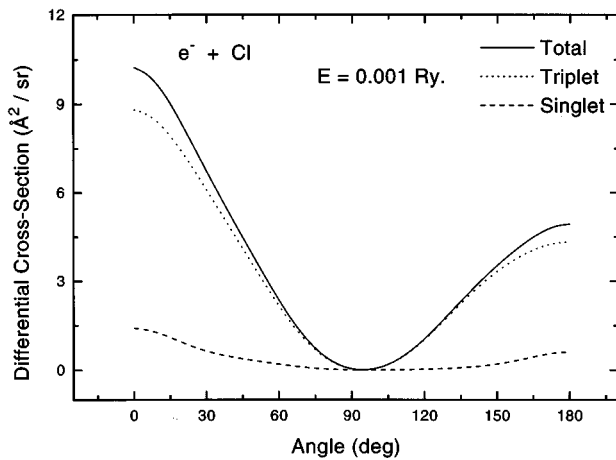| Source	Energy position (eV)	Magnitude (Å^2)
Present work	0.9524	2.4483
Griffin *et al.* [2]	0.7450	2.0895
Fabricant [1]	~ 0.4	~ 3.0

FIG. 1. Differential cross sections for elastic scattering of electrons from chlorine at energy $E=0.001$ Ry as a function of scattering angle.

the wave function. The differences between the present and the R-matrix results may be partly attributed to the differences in the way the polarization is considered in the calculations.

C. Differential cross section

The elastic differential cross sections for incident electron energies 0.001, 0.01, 0.1, and 1.0 Ry are shown in Figs. 1–4. In each figure both singlet and triplet contributions, along with the total, are plotted as a function of scattering angles in degrees. From Fig. 1, it is seen that for energy 0.001 Ry, all the three cross sections initially decrease with increasing angle of scattering, pass through a minimum, and then increase. Triplet cross sections are much larger than those for the singlet. At this energy the triplet has a minimum around 95°, whereas the singlet has a minimum around 100°, hence the sum of the two, i.e., the total, has a minimum around 95°. For energy 0.01 Ry (Fig. 2), the differential cross sections for the triplet and the total have the same features, each having a single minimum around 95°, however, the singlet cross sections in this case, although small, have two minima around 95° and 140°. For energy 0.1 Ry, both triplet and total cross
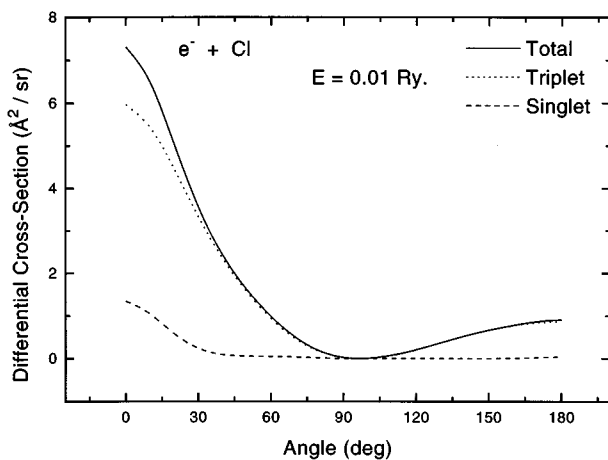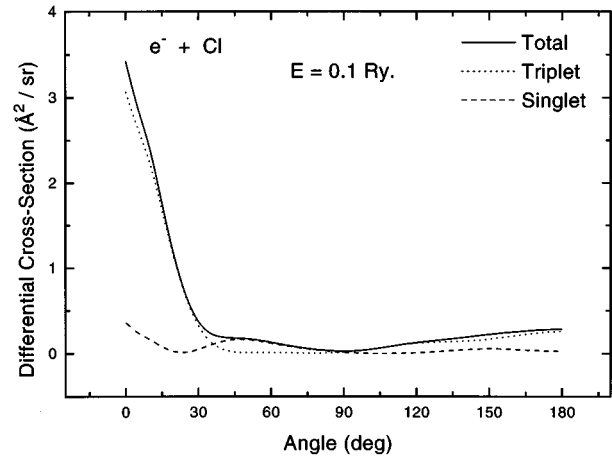

FIG. 3. Same as Fig. 1 for $E=0.1$ Ry.

sections show similar behavior and each has a minimum around 80° and 90°, respectively, whereas the singlet has two minima around 25° and 105°. Each of the cross sections at energy 1.0 Ry has two minima. The triplet has the minima around 65° and 120° and the singlet has around 60° and 140°, whereas the total has the minima around 65° and 120°.

D. Total cross sections

Figure 5 shows the total cross sections obtained by our method of calculation along with corresponding singlet and triplet contributions as a function of incident electron energy from 0.0 to 2.0 Ry. Each exhibits the same gross features. It is seen from the figure that the Ramsauer-Townsend minima occur at 0.09 and 0.04 Ry for triplet and singlet, respectively. The combination of the two has the minimum at 0.07 Ry. The magnitude for minima for the triplet and singlet are, respectively, 1.8663 and 0.2856 Å^2, whereas that for the total is 2.4483 Å^2. It should be mentioned that in order to check the accuracy of expression (6) for the higher ($l>6$) partial waves, we compared in Table IV the phase shifts at $l=6$ obtained with both the MCHF method and the effective range formula (6) for few energies. The phase shifts are found to agree very well, which justifies the use of Eq. (6) for higher partial waves.
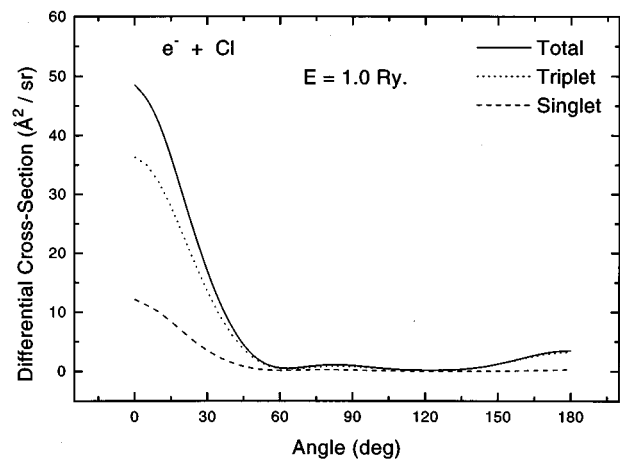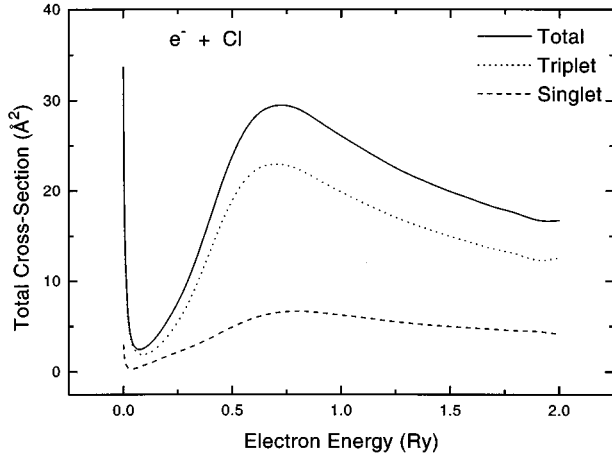

FIG. 2. Same as Fig. 1 for $E=0.01$ Ry.

FIG. 4. Same as Fig. 1 for $E=1.0$ Ry.

FIG. 5. Total cross sections for elastic scattering of electrons from chlorine as a function of kinetic energy.

E. Momentum-transfer cross sections

In Fig. 6, the present momentum-transfer cross sections, along with their singlet and triplet contributions, are shown as a function of incident electron energy ranging from 0.0 to 2.0 Ry. The magnitude of the Ramsauer-Townsend minima for the triplet, singlet, and total are, respectively, 1.1735, 0.3811, and 1.8760 Å^2, and they occur at 0.08, 0.03, and 0.07 Ry, respectively.

Figure 7 compares the present total and momentum-transfer cross sections with those obtained by Griffin *et al.* [2] using the *R*-matrix method as a function of incident energy ranging from 0 to 1.2 Ry. Comparison shows that both total and momentum-transfer cross sections are in qualitative agreement with those obtained by Griffin *et al.* The values of the total and momentum-transfer cross sections reported here, which are very close to zero energy, are slightly higher than those obtained by Griffin *et al.* As stated already, the position and magnitude of the minimum are also higher than their corresponding results obtained using the *R*-matrix method. The *R*-matrix cross sections are slightly smaller than the present results throughout the range of energies shown in the figure except for the energies from the minimum to about
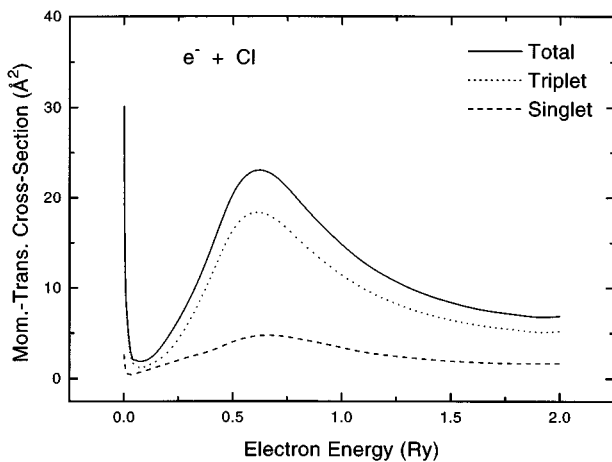

FIG. 6. Momentum-transfer cross sections for elastic scattering of electrons from chlorine as a function of kinetic energy.
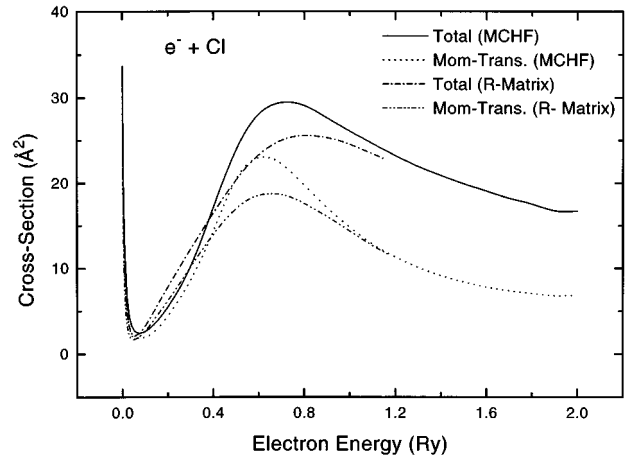

FIG. 7. Comparison of total and momentum-transfer cross sections as a function of kinetic energy with results obtained by Griffin *et al.* [2].

0.4 Ry, whereas the cross sections of Griffin *et al.* are higher and steeper. At the highest energy ($\sim$1.17 Ry) the *R*-matrix cross sections are very close to the present values. The differences between the present and the *R*-matrix results, as mentioned earlier, may be partly due to inclusion of only dipole polarization in the form of pseudostates in the *R*-matrix calculation, whereas in the MCHF method both dipole and quadrupole polarizations were included through the configuration-interaction procedure.

V. CONCLUSION

Very extensive and accurate calculations have been made on the low-energy elastic scattering of electrons from chlorine atoms using the multiconfiguration Hartree-Fock method for continuum wave functions. The polarization and electron correlation effects, which are particularly important in this calculation, have been taken into account in the *ab initio* way through the configuration-interaction procedure. The scattering length in this case is calculated *ab initio* with wave functions computed exactly at zero energy. The phase shifts, elastic differential, total, and momentum-transfer cross sections are found to be in qualitative agreement with those obtained by Griffin *et al.* [2] in the *R*-matrix approach. The advantage of the present method lies in the fact that both the excited bound and the scattering electron wave functions are optimized simultaneously for each kinetic energy of the scattered electron to obtain accurate energy-dependent polar-

TABLE IV. Comparison of phase shifts for $l=6$.

Energy k^2	Phase shifts	
	MCHF	Eq. (6)
0.1	0.00219	0.00217
0.5	0.01168	0.01129
1.0	0.02436	0.02364
1.5	0.03839	0.03704
2.0	0.05394	0.05149

ization. It is found that not only the dipole but also the quadrupole and multipole polarizations are important in this case. Since the present MCHF method for continuum wave functions has been proven to be very accurate in the case of elastic scattering of electrons from noble-gas atoms, we conclude that the present results for open-shell atoms like chlorine are accurate and reliable. As there are no experimental data available for e^-+Cl scattering, we believe that the calculations reported here will stimulate interest for experimental investigation.

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