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Effective single-particle potential for photoabsorption of open-shell atoms

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A method to obtain an effective single-particle potential for the photoabsorption of open-shell atoms is discussed and applied to the calculation of the photoionization cross section of neutral chlorine. The potential includes, in an approximate way, the effects of interaction among many final channels. For chlorine, the results are in very good agreement with elaborate many-body calculations except for the failure to describe resonance structure.

I. INTRODUCTION

The photoionization cross section of neutral chlorine has been the subject of numerous theoretical calculations.[1-7] The most recent[7] of these uses the open-shell transition matrix method of Starace and Shahabi[8] and contains a review of previous calculations. All of the recent calculations are in agreement that Hartree-Fock calculations are inadequate because of a failure to include final-state interactions between channels based on the $3p^4(^3P)$, $3p^4(^1D)$, and $3p^4(^1S)$ ionic cores.

Until very recently, the only experimental studies were the striking measurements of resonance structure below the ^1S ionic threshold by Ruščić and Berkowitz[9] and a ratio of partial cross sections at 21.2 eV by Kimura *et al.*[10] The measurements by Ruščić and Berkowitz confirmed the many-body prediction[4] of a single series of broad resonances leading to the $3p^4(^1D)$ edge, but discovered two series of narrow resonances rather than the single narrow series calculated in the *LS*-coupling approximation.[4] The second narrow series has been accounted for by including effects of spin-orbit interaction.[11]

Very interesting recent measurements by Samson and co-workers[12] give an unnormalized total cross section from the $3p^4(^1S)$ edge near 16.3 to 62 eV. The various theoretical calculations which include final-state interactions are in fairly reasonable agreement with the measurements by Samson.[12] However, an absolute measurement would be desirable.

It is interesting to note that for argon $3p^6$, with only one more electron than chlorine, the effects of final state interactions are small as compared with the case of chlorine. This, however, is only true for argon when Hartree-Fock orbitals are used with the final states coupled to $3p^5k\,^1P$, where k refers to a continuum electron with $l=0$ or 2. In this case, the final state interactions are largely accounted for by the Hartree-Fock potential. The two final-state channels are $3p^5kd\,^1P$ and $3p^5ks\,^1P$ and the $3p^5kd\,^1P$ channel dominates. In the case of chlorine, final-state interactions within a given channel are accounted for by the Hartree-Fock potential but there are large contributions due to interaction between the different channels. For example, for the channels with total $L=2$ and $S=\frac{1}{2}$, there are interactions among the following channels: $3p^4(^3P)kd(^2D)$, $3p^4(^1D)kd(^2D)$, $3p^4(^1S)kd(^2D)$, and $3p^4(^1D)ks(^2D)$. Of these, the most important channels are those with *kd*. There are also additional *kd* channels $3p^4(^3P)kd(^2P)$, $3p^4(^1D)kd(^2P)$, and $3p^4(^1D)kd(^2S)$. In chlorine, then, if Hartree-Fock orbitals are used, one must calculate six different sets of *kd* orbitals.

The purpose of this paper is to examine more closely the final-state interactions in open-shell atoms such as chlorine with the hope of finding an appropriate single-particle potential which includes a large part of the final-state interactions just as the Hartree-Fock potential does for closed-shell atoms. Section II contains a discussion of the methods to determine an effective single-particle potential which includes interactions between different channels and Sec. III contains results using this potential to calculate the photoionization cross section of chlorine along with comparison with other theoretical calculations and the experimental results by Samson.[12]

II. CHOICE OF THE SINGLE-PARTICLE POTENTIAL

Before considering open-shell atoms, it is advisable to consider closed-shell atoms and to determine how final-state interactions are included for them. For a given channel such as $3p^5kd\,^1P$ in argon, we determine the potential by requiring that the perturbation H' satisfy

$$\langle \psi_k \mid H' \mid \psi_k \rangle = 0 \,, \tag{1}$$

where

$$H' = \sum_{\substack{i,z=1 \\ i<j}}^{N} v_{ij} - \sum_{i=1}^{N} V(r_i) \,, \tag{2}$$

$\mid \psi_k \rangle = \mid 3p^5kd\,^1P \rangle$, and similarly for *ks*. The Coulomb interaction e^2/r_{ij} is represented by v_{ij}. As pointed out by Amus'ya, Cherepkov, and Chernysheva,[13] this choice of potential causes all the diagrams of Fig. 1 to cancel, where the cross represents interaction with $-V$, and where the summation over single-particle states q is restricted to those in the same subshell as p. This procedure was used by Ishihara and Poe[14] to obtain the $1skp(^1P)$ excited states of He.

Suppose we now wish to consider an open-shell atom such as chlorine $3p^5(^2P)$. We could again try to cancel the diagrams of Fig. 1 by appropriate choice of V. We recall for a closed-shell atom such as argon we could effect this because all $3p$ orbitals (p and q in Fig. 1) have the same single-particle energy E_p, and so in Fig. 1 diagram (d) differs from (b) only by an angular factor. Another way of saying this is to note that the configuration $3p^5$ has the same energy (neglecting spin-orbit effects) regardless of the m_l and m_s quantum numbers of the electron removed from $3p^6$. This is no longer true for chlorine since the configuration $3p^4$ has ^3P, ^1D, and ^1S multiplets. However, if we neglect the multiplet splitting of $3p^4$ in a first approximation and consider $3p^4$ as four degenerate single-particle states, we can then attempt to cancel diagrams (a)—(d) in Fig. 1 by the choice of V.

We start from $3p^5$ with m_l and m_s of each electron prescribed (which also prescribes M_L and M_S). We then choose p in Fig. 1 to correspond to a $3p$ electron with particular m_l and m_s. The summation over q then corresponds to the other $3p$ electrons. The matrix elements of V are then chosen to cancel diagrams (a)—(d) for the particular electron labeled p. We label this potential $V_p(M_L)$ since it is independent of M_S but depends on M_L.

From Fig. 1, we determine $V_p(M_L)$ in terms of its matrix elements.

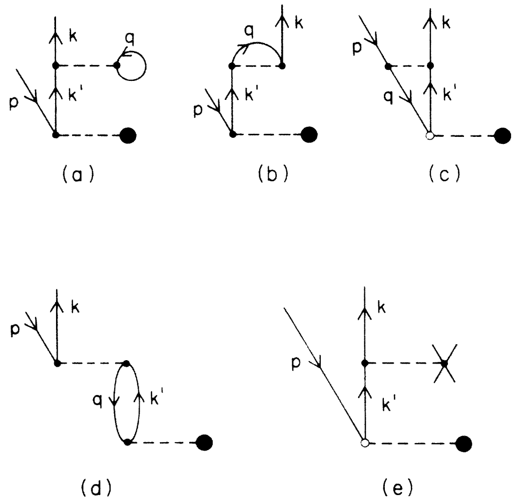

FIG. 1. Diagrams representing first-order final-state interactions contributing to the many-body dipole matrix element $\langle \psi_k | z | \psi_0 \rangle$. Only singly-excited configurations are included. The heavy dot represents the dipole operator z (length form) or d/dz (velocity form). In (e) the cross represents interaction with $-V$, where V is the potential used to generate the single-particle states. For closed-shell atoms, when the Hartree-Fock potential of Eq. (1) is chosen, all the diagrams of Fig. 1 add to zero for the case that q is in the same subshell as p.

$$\langle k | V_p(M_L) | k' \rangle = \sum_q [(\langle kq | v | k'q \rangle - \langle qk | v | k'q \rangle)\langle k' | z | p \rangle + (-\langle qk | v | pk' \rangle + \langle kq | v | pk' \rangle)\langle k' | z | q \rangle] / \langle k' | z | p \rangle , \qquad (3)$$

where the sum over q includes all single-particle states in the same subshell as p. Note that all the denominators in the diagrams of Fig. 1 are assumed identical and so cancel on both sides of Eq. (3). Also the radial parts of the matrix elements $\langle k' | z | p \rangle$ and $\langle k' | z | q \rangle$ are identical and therefore cancel out in Eq. (3). However, the angular factor in $| k' \rangle$ will be different for the cases $\langle k' | z | p \rangle$ and $\langle k' | z | q \rangle$ and is determined in each case by $| p \rangle$ or $| q \rangle$.

This potential is then averaged over all five electrons of $3p^5$ with each potential weighted by the square of the single-particle dipole matrix element to find an effective potential corresponding to the given M_L:

$$V_{\text{eff}}(M_L) = \frac{\sum_p V_p(M_L) | \langle k | z | p \rangle |^2}{\sum_p | \langle k | z | p \rangle |^2} . \qquad (4)$$

In Eq. (4) the radial parts of the matrix elements $\langle k | z | p \rangle$ in the numerator and denominator cancel and only angular factors need be considered. Also note that $V_{\text{eff}}(M_L)$ depends on the orbital quantum number l of the excited electron, and in Eq. (4) the orbital labeled k has the l value associated with $V_{\text{eff}}(M_L)$. The final potential V_{av} is then averaged over M_L.

$$V_{\text{av}} = (2L+1)^{-1} \sum_{M_L} V_{\text{eff}}(M_L) , \qquad (5)$$

with $V_{\text{eff}}(M_L) = V_{\text{eff}}(-M_L)$.

We can also obtain V_{av} using LS coupling and again assuming the same radial orbitals for all electrons of given n and l. By analogy with Eq. (3), we write

$$\langle F | V_F | F \rangle = \sum_I \frac{\langle F | v | I \rangle \langle I | z | G \rangle}{\langle F | z | G \rangle} . \qquad (6)$$

where $| G \rangle$ represents the LS-coupled ground or initial state, $| F \rangle$ represents the final channel of interest, and $| I \rangle$ may be any channel of the same l. Again, consider the case of chlorine with $| G \rangle$ representing $3p^5(^2P)$ and let $| F \rangle$ represent, for example, the final channel $3p^4(^1D)kd(^2D)$. The channels $| I \rangle$ which may give nonzero contributions to the sum in Eq. (6) in this case are $3p^4(^3P)kd(^2D)$, $3p^4(^1D)kd(^2D)$, and $3p^4(^1S)kd(^2D)$. We do not include channels in which the continuum has l different from that in channel $| F \rangle$ such as $3p^4(^1D)ks(^2D)$. In Eq. (6) v represents $\sum_{i<j} v_{ij}$ and z represents $\sum_i z_i$. Using the Wigner-Eckart theorem, the M_L dependence in $\langle I | z | G \rangle$ will cancel that from $\langle F | z | G \rangle$ in Eq. (6). Note that we recover the Hartree-Fock result when $\sum_I$ includes only the state $| F \rangle$. One may also calculate an average potential using LS-coupled states as was done in Eq. (4) for the many-body single particle case. We then have

$$V_{LS\mathrm{av}}(M_L)=\frac{\sum\limits_F V_F\,|\langle F\,|\,z\,|\,G\rangle|^2}{\sum\limits_F |\langle F\,|\,z\,|\,G\rangle|^2}\;. \tag{7}$$

We recognize that the sums in Eq. (7) may be chosen in different ways depending on which type of average potential is desired. For example, in chlorine, if we desire an average potential for the $kd(^2D)$ channel the sum over F will only include $3p^4(^3P)kd(^2D)$, $3p^4(^1D)kd(^2D)$, and $3p^4(^1S)kd(^2D)$. However, a total average could be obtained by letting F represent all channels with a kd electron. As in Eq. (5), we average over M_L to obtain

$$V_{LS\mathrm{av}}=(2L+1)^{-1}\sum_{M_L} V_{LS\mathrm{av}}(M_L)\;. \tag{8}$$

In effect, we are considering the energy levels of the different ionic multiplets as degenerate for purposes of calculating the interactions between different channels. It is anticipated, then, that use of $V_{LS\mathrm{av}}$ of Eq. (8) will, in an approximate way, include the effects of interchannel interaction. Examples of this for the case of chlorine are presented in the next section.

TABLE I. Effective potentials for dipole-excited states of chlorine.[a]

Channel	$J_{3p}^{(2)\mathrm{b}}$	$K_{3p}^{(1)\mathrm{c}}$	$K_{3p}^{(3)\mathrm{d}}$
$(^3P)kd(^2D)$	$-\frac{1}{5}$	$\frac{13}{15}$	$-\frac{3}{35}$
	$(-\frac{1}{5})$	$(\frac{1}{2})$	0
$(^3P)kd(^2P)$	$\frac{1}{5}$	$\frac{9}{15}$	$-\frac{9}{35}$
	$(\frac{1}{5})$	$(\frac{1}{10})$	$(-\frac{9}{35})$
$(^1D)kd(^2D)$	$-\frac{1}{7}$	$\frac{13}{15}$	$-\frac{81}{245}$
	$(\frac{3}{35})$	$(-\frac{1}{6})$	$(-\frac{12}{49})$
$(^1D)kd(^2P)$	$-\frac{1}{5}$	$\frac{9}{15}$	$-\frac{9}{35}$
	$(-\frac{1}{5})$	$(\frac{1}{10})$	$(-\frac{9}{35})$
$(^1D)kd(^2S)$	$-\frac{2}{5}$	$\frac{4}{15}$	$-\frac{9}{35}$
	$(-\frac{2}{5})$	$(\frac{4}{15})$	$(-\frac{9}{35})$
$(^1S)kd(^2D)$	$-\frac{2}{5}$	$\frac{13}{15}$	$-\frac{18}{35}$
	(0)	$-(\frac{4}{15})$	$(-\frac{6}{35})$
$V_{LS\mathrm{av}}(kd)$	−0.161 76	0.746 57	−0.205 46
$V_{LS\mathrm{av}}(ks)$[e]	0	$-\frac{1}{3}$	0

[a] Values in parentheses are Hartree-Fock values for the given channel.

[b] Coefficient of

$$\int\int P_{3p}^2(r_1)r_<^2/r_>^3 P_{k_1}(r_2)P_{k_2}(r_2)dr_1\,dr_2$$

in $\langle k_1\,|\,V_{LS\mathrm{av}}\,|\,k_2\rangle$.

[c] Coefficient of

$$\int\int P_{k_1}(r_1)P_{3p}(r_2)(r_</r_>^2)P_{3p}(r_1)P_{k_2}(r_2)dr_1\,dr_2$$

in $\langle k_1\,|\,V_{LS\mathrm{av}}\,|\,k_2\rangle$.

[d] Coefficient of

$$\int\int P_{k_1}(r_1)P_{3p}(r_2)(r_<^3/r_>^4)P_{3p}(r_1)P_{k_2}(r_2)dr_1\,dr_2$$

in $\langle k_1\,|\,V_{LS\mathrm{av}}\,|\,k_2\rangle$.

[e] Since there is no mixing of channels for ks states, the Hartree-Fock results and $V_{LS\mathrm{av}}$ results coincide.

III. RESULTS FOR CHLORINE

The average, or effective, potential of Eq. (6) is listed in Table I for the case of neutral chlorine for the various possible final-state channels and is compared with the corresponding Hartree-Fock potential. The total average potential $V_{LS\mathrm{av}}$ of Eq. (6) is also tabulated both for ks and kd orbitals. The effective potentials were calculated both in the LS-coupling method of Eq. (8) and in the many-body description leading to Eq. (5), and both methods gave identical results for the effective potential averaged over all channels. The most significant contributions to the potential are from the term $K_{3p}^{(1)}$, and it is generally much more positive for $V_{LS\mathrm{av}}$ than for the Hartree-Fock potential. For argon, the coefficient of $K_{3p}^{(1)}$ is $\frac{14}{15}$. It is interesting to note that when we scale by $\frac{4}{5}$, the ratio of the number of residual ionic electrons in chlorine to that for argon, we obtain 0.7466, in agreement with the coefficient for $K_{3p}^{(1)}$ for chlorine in $V_{LS\mathrm{av}}$.

The $V_{LS\mathrm{av}}$ potentials of Table I were used to calculate the $3p\rightarrow kd$ and $3p\rightarrow ks$ photoionization cross sections for neutral chlorine, and the sum of the ks and kd cross sections are shown in Fig. 2 along with Hartree-Fock results and calculations by Brown *et al.*[4] Experimental removal energies were taken from the tables by Moore.[15] We note that the geometric mean of length and velocity cross sections from $V_{LS\mathrm{av}}$ is in good agreement with the

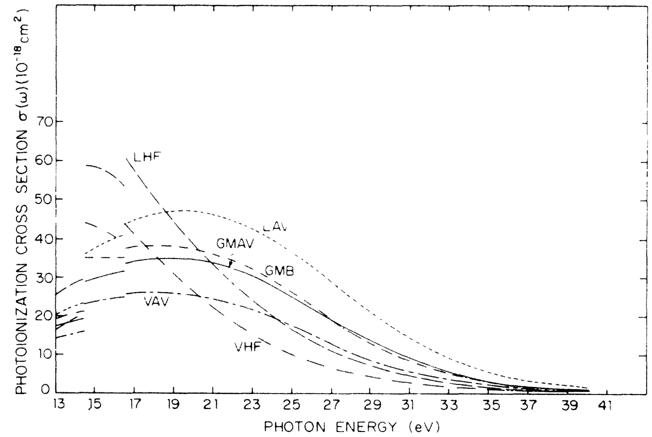

FIG. 2. Sum of the $3p\rightarrow ks$ and $3p\rightarrow kd$ photoionization cross sections for neutral chlorine. — — — —, Hartree-Fock length result (LHF). — · · — · ·, Hartree-Fock velocity result (VHF). - - - -, length calculation using $V_{LS\mathrm{av}}$ of this work (LAV). — — —, velocity calculation using $V_{LS\mathrm{av}}$ of this work (VAV). ——, geometric mean of LAV and VAV curves (GMAV). — · — ·, geometric mean of length and velocity calculations by Brown, Carter, and Kelly, Ref. 4.

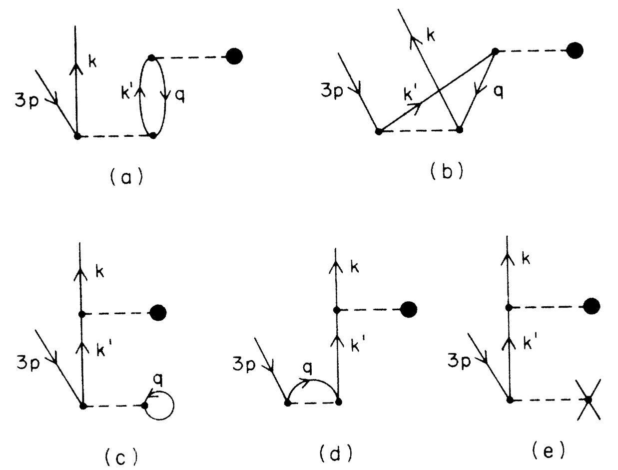

FIG. 3. Diagrams representing ground-state correlations to first order in the Coulomb interaction. The solid dot represents the dipole operator, either z or d/dz. In diagram (e), the cross represents interaction with $-V$.

geometric mean cross section calculated by Brown *et al.*[4] which explicitly included the interchannel coupling, at high computer expense. Also these cross sections differ qualitatively from the Hartree-Fock cross sections which omit effects of interchannel coupling. When interchannel coupling is included, the resulting cross section more closely resembles the cross section for neutral argon. We have also calculated the various final channel cross sections using the different appropriate potentials for each channel listed in Table I. There are some differences from the results calculated with $V_{LS\mathrm{av}}$ but the total cross section calculated this way is very close to the total with $V_{LS\mathrm{av}}$ in Fig. 2.

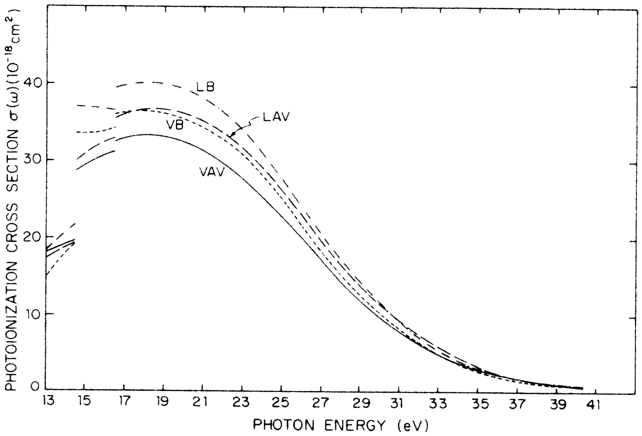

FIG. 4. Calculations of the photoionization cross section for the $3p^5$ subshell of neutral chlorine. Comparison of the length and velocity calculations using $V_{LS\mathrm{av}}$ of this work and including ground-state correlations with the corresponding many-body calculations of Ref. 4. — — — —, length calculations using $V_{LS\mathrm{av}}$. ——, velocity calculations using $V_{LS\mathrm{av}}$. — · — ·, length calculation, Ref. 4. - - - -, velocity calculation, Ref. 4.

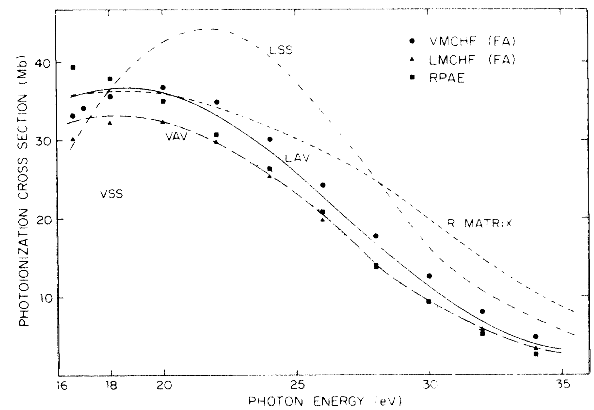

FIG. 5. Comparison of calculations of the $3p$ subshell photoionization cross section of neutral chlorine beyond the ^1S edge of Cl^+. ——, length calculation of this work (LAV). — — — —, velocity calculation of this work (VAV). — · — ·, length calculation, Ref. 7 (LSS). · · · ·, velocity calculation, Ref. 7 (VSS). - - - - R-matrix calculation, Ref. 5. ●●●●, MCHF velocity calculation, Ref. 6. ▲▲▲, MCHF length calculation, Ref. 6. ■, RPAE calculation, Ref. 3.

It is also interesting to check whether the large length-velocity discrepancy in Fig. 2 can be greatly reduced by including the lowest-order ground-state correlation diagrams as in the calculations by Brown *et al.*[4] for chlorine as well as for argon.[16] In Fig. 3 the lowest-order ground-state correlation diagrams are shown. Diagrams (c), (d), and (e) add to zero when V is the Hartree-Fock potential for a closed-shell system. For an open-shell system such as chlorine, there are small contributions due to the sum of diagrams (c), (d), and (e). They were calculated, however, by Brown[17] and found to be small. In Fig. 4 we present the results of the length and velocity calculations using $V_{LS\mathrm{av}}$ including ground-state correlations and com-

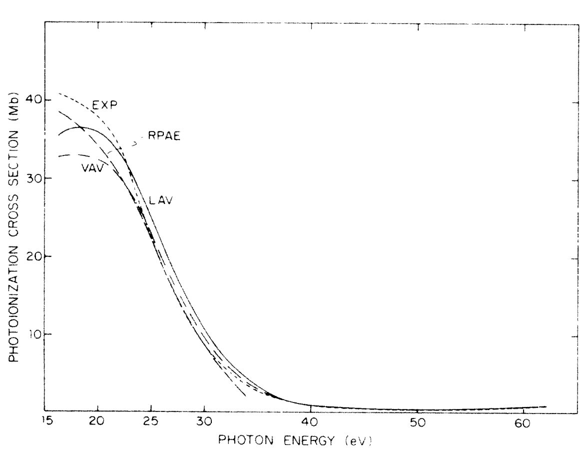

FIG. 6. Photoionization cross section of the $3p$ subshell of chlorine. ——, length calculations of this work (LAV). — · — ·, velocity calculation of this work (VAV). — — — —, RPAE results, Ref. 3. - - - -, experimental results, Ref. 12, normalized to the RPAE results in the range of 25 eV.

TABLE II. Ratios of partial cross sections of chlorine at 21.2 eV photon energy.

Final state[a]	LO[b]	GSC[c]	CEM[d]	OSTM[e]	MCHF[f]	EXPT.[g]
^3P	1.5	1.5	1.5	1.5	1.5	
^1D length	0.93	0.94	0.69	1.01	0.78	0.87
velocity	0.84	0.85	0.71	1.10	0.83	
^1S length	0.21	0.16	0.11	0.20	0.19	0.17
velocity	0.16	0.15	0.12	0.17	0.19	

[a] State of Cl^+ $3s^2 3p^4$.

[b] Lowest-order (LO) calculation, this work.

[c] Lowest-order plus ground state correlations (GSC), this work.

[d] Coupled-equations method (CEM), Ref. 4.

[e] Calculations using open-shell transition-matrix (OSTM) method, Ref. 7.

[f] Multiconfiguration Hartree-Fock (MCHF) results, Ref. 6.

[g] Experimental (EXPT.) results, Ref. 10, as corrected for angular distribution effects by Shahabi *et al.*, Ref. 7.

pare with the corresponding calculations by Brown *et al.*[4] It is seen that inclusion of ground-state correlations brings the length and velocity results into reasonable agreement.

In Fig. 5 at energies beyond the ^1S edge we compare our length (LAV) and velocity (VAV) calculations including ground state correlations with calculations by Fielder and Armstrong using a multiconfiguration Hartree-Fock (MCHF) approach,[6] by Cherepkov and Chernysheva using an open-shell random-phase approximation exchange (RPAE) formalism,[3] by Shahabi, Starace, and Chang[7] using an open-shell transition-matrix method (OSTM),[8] and by Lamoureux and Combet-Farnoux[5] using the *R*-matrix method.[18] When the geometric mean of length and velocity is taken, the MCHF, OSTM, and RPAE results are in reasonable agreement although there are some discrepancies close to the ^1S edge. The MCHF calculations of Fielder and Armstrong did not include the $3p \rightarrow ks$ channel. Their result for the $3p \rightarrow kd$ channel is very close to ours in geometric mean approximation.

In Fig. 6 we compare our calculations using $V_{LS\mathrm{av}}$ with a very recent experiment by Samson and co-workers.[12] The experimental data are relative and were normalized to the calculated curve by Cherepkov and Chernysheva.[3] It is apparent that, although the calculation by Cherepkov and Chernysheva is in a little better agreement with experiment, the calculations using $V_{LS\mathrm{av}}$ are also in reasonable agreement with experiment. This is rather remarkable considering the simplicity of the $V_{LS\mathrm{av}}$ calculation compared with the other calculations on chlorine.

Our results for ratios of partial cross sections leaving Cl^+ in the $3p^4(^3P)$, $3p^4(^1D)$, and $3p^4(^1S)$ multiplets are given in Table II and compared with results of other calculations and with the experimental results by Kimura *et al.*[10] at 21.2 eV. Again, the calculations using our potential are seen to be in reasonable agreement with much more sophisticated calculations and with experiment.

IV. CONCLUDING REMARKS

In the preceding sections we presented a method of defining a single-particle potential for open-shell systems which has the virtue of approximately accounting for final-state interactions between channels which involve the same angular momentum of the continuum electron and excitation of a bound orbital from the same subshell. That is, the only difference is in the *LS* quantum numbers of the core. The use of this potential has been demonstrated for chlorine, where the total calculated cross section is in reasonable agreement with other calculations of much greater sophistication and with experiment. We are presently using this potential scheme in a large number of other cases.

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