PHYSICAL REVIEW A VOLUME 15, NUMBER 2 FEBRUARY 1977

Multiconfiguration Hartree-Fock calculation of photoionization cross sections of the rare gases*

John R. Swanson and Lloyd Armstrong, Jr.
Physics Department, Johns Hopkins University, Baltimore, Maryland 21218
(Received 26 August 1976)

A multiconfiguration Hartree-Fock calculation is used to test the hypothesis that ground-state correlations involving excitation of a single pair of electrons from an outer p shell into d orbitals are the dominant ones in the photoionization cross sections of Ne, Ar, Kr, and Xe. Dramatic improvement in the agreement of dipole length and dipole velocity forms of the cross section is obtaining in going from a Hartree-Fock to a multiconfiguration Hartree-Fock calculation. Results are found to be comparable to recent values obtained using the random-phase approximation with exchange and the R matrix.

I. INTRODUCTION

Photoionization cross sections in the rare gases have been extensively studied, both experimentally[1] and theoretically.[2-7] The first really successful calculation of these cross sections was performed by Amus'ya *et al.*[2] using a form of many-body theory called the random-phase approximation with exchange (RPAE). Kelly and Simons[3] later obtained extremely accurate results for Ar using diagramatic many-body perturbation theory (MBPT). More recently, good results have been obtained for Ne and Ar by Burke and Taylor[4] using R-matrix techniques.

There are many equivalent formulations of the RPAE.[8] These approaches can be classified roughly as either "matrix methods" or "coupled differential equation methods." In either case, the results obtained do not lead directly to a very clear physical picture of the interactions being included in the calculation or to an identification of the dominant excitations for the case being studied. The RPAE also has many benefits, among them being the fact that certain types of both ground- and excited-state correlations are evaluated simultaneously, and that length and velocity forms of the dipole transition operator are equivalent. The traditional description of the RPAE is that it, in general, sums to all orders the contribution from pairs of excited electrons, including simultaneous excitation of several pairs. This interpretation, however, is not universally accepted.[9]

The MBPT calculation of Kelly and Simons[3] and the RPAE calculation of Amus'ya *et al.*[2] utilize a $V^{N-1(^1P)}$ potential in obtaining the continuum wave functions. As explained below, this has the effect of incorporating certain types of excited-state correlation into the zeroth-order calculation.[2] Beyond this, the work of Kelly and Simons[3] indicates that ground-state correlations involving excitation of a single pair of electrons from the filled $3p$ shell into d orbitals are the dominant ones for the $3p \to \epsilon d$ photoionization channel in Ar. Since this type of excitation is also included in the RPAE, these results are consistent with the RPAE results of Amus'ya *et al.*[2] However, these results also indicate that some of the supposed advantages of the RPAE—excitation of multiple pairs and summation to all orders—are not important in the rare gases.

One can, based on the results of Kelly and Simons,[3] make the hypothesis that only excited-state correlations included by use of a $V^{N-1(^1P)}$, and only ground-state correlations involving excitation of a single pair are important in determining the photoionization cross sections for the rare gases. In order to test this hypothesis in the simplest and most direct manner, we have carried out multiconfiguration Hartree-Fock (MCHF) calculations of these cross sections, choosing configurations so as to include only these very restricted classes of excitations.

In Sec. II, we describe the general theory involved in the application of the MCHF to the calculation of photoionization cross sections in rare-gas systems. In Sec. III, we describe the calculations in Ne, Ar, Kr, and Xe. Our calculations take into account the $np \to \epsilon s, \epsilon d$ and $ns \to \epsilon p$ channels. No resonant structure is included. Finally in Sec. IV, we discuss our results and their implications.

II. THEORY

The total photoionization cross section in the dipole approximation is given by

$$\sigma(E) = 4\pi^2 \alpha a_0^2 \sum_{fm} |\langle \psi_f | T | \psi_i \rangle|^2 E_{fi} \quad , \tag{1}$$

where

$$T = T_L = \sum_{j=1}^{n} z_j$$

in the length form,

$$T = T_V = \sum_{j=1}^{n} \frac{\nabla_j^z}{iE_{fi}}$$

in the velocity form. The matrix elements are evaluated in atomic units; E_{fi} is the photon energy; ψ_f and ψ_i denote the final and initial states, respectively, and the sum runs over final configurations and all magnetic quantum numbers. When the initial and final states are exact solutions to the same Hamiltonian equation, the length and velocity forms of the cross section will agree. In the procedure described below this conditions is not met and thus length and velocity forms may not coincide. In this work we evaluate both the length and velocity forms. The degree of agreement between the two forms is a necessary, but not sufficient, test of the validity of the method and of the accuracy of the results.

A. Initial state

One of the simplest approximations we can make for the ground state is to take it to be a pure np^6 state and to use single-configuration Hartree-Fock wave functions. Using this approximation, together with the approximation for the final state specified below in Sec. II B, in Eq. (1) leads to cross sections in the length and velocity forms which in most instances are widely disparate. The two forms of this approximation are hereafter denoted HFL and HFV.

The most significant improvements over the HF approximation have been made using MBPT[3] and the RPAE.[2] The essential interactions in both of these methods which lead to large improvements over the first-order approximation for the cases considered here are the so-called ground-state correlations. In particular, the work of Kelly[3] has demonstrated that the virtual excitation of a pair of outer np electrons to $n'd$ states is the dominant correlation effect.

We can attempt to include excitations of this type by taking the ground state to be given, not by the single configuration np^6, but by the combination

$$|\psi_i\rangle = a|np^6\,{}^1S\rangle + \sum_{\substack{n'n'' \\ LS}} b^{SL}_{n'n''}\,|(np^4)SL, (n'\,dn''\,d)SL;\,{}^1S\rangle \;, \tag{2}$$

where the coefficients a and b and the single-electron wave functions are chosen so as to minimize the energy of the state described by $|\psi_i\rangle$, in other words, by MCHF. As it stands, the wave function of Eq. (2), although it describes the type of excitation of interest, is not too useful, since the double sum over n' and n'' includes not only all bound d states of the atom, but also a double integration over all continuum states $\epsilon'd$ and $\epsilon''d$. However, Froese Fischer[10] has shown that wave functions of the type given by Eq. (2) can be rewritten in a much more tractable form.

Because the coefficients $b^{SL}_{n'n''}$ form a matrix B which is symmetric in the indices n' and n'' there exists an orthogonal matrix $O_{n'n''}$ which diagonalizes B (i.e., $O^\dagger B O = D$, where D is a diagonal matrix). If we operate $O^\dagger$ on a vector whose componets are the kets in (2), we will then form a new expansion for the ground state:

$$\begin{aligned} |\psi_i\rangle &= a|np^6\,{}^1S\rangle + \sum_{S,L,\bar{n}} d^{SL}_{\bar{n}}\,|(np^4)SL, (\bar{n}\bar{d})^2SL;\,{}^1S\rangle \\ &= \sum w_j \psi_i^j \;, \end{aligned} \tag{3}$$

where we now have a single summation over $\bar{n}$ and where the single-particle states $\varphi_{\bar{n}\bar{d}}$ are superpositions of the original φ_{nd} basis, including an admixture of continuum states. Thus, for example, the $3\bar{d}$ is not the usual $3d$ wave function, although the dominant component of the $3\bar{d}$ will probably be the $3d$. These new wave functions $\varphi_{\bar{n}\bar{d}}$ are similar to the natural spin orbitals of Löwdin.[11]

This transformation would be of little practical significance if one had to carry out all the calculations indicated above to obtain the functions $\varphi_{\bar{n}\bar{d}}$. Fortunately, it has been shown[10] that one can obtain a similar basis set by solving the corresponding MCHF. That is to say, if one does a MCHF calculation involving the configurations np^6 and $np^4\bar{n}\bar{d}^2$ (all $\bar{n}$), that is equivalent to doing a MCHF involving the configurations np^6 and $np^4n'\,dn''d$ (all n', n''), the two calculations being related to each other by an orthogonal transformation. In addition, Froese Fischer has shown that the expansion of Eq. (3) usually converges rapidly, meaning that only a few values of $\bar{n}$ need be taken to get a very large percentage of the correlation energy. Accordingly, we have chosen to use our ground-state wave function the expansion (3) where the weights a and d and the wave functions $\varphi_{\bar{n}\bar{d}}$ are solutions of the MCHF. These ground-state wave functions were obtained using the program MCHF 75.[12] The angular coefficients of the Slater integrals were calculated using the program WEIGHTS.[13] We discuss below the number of terms in the expansion over $\bar{n}$ which kept in specific cases.

B. Final state

In the cases considered here, where the initial state is a ${}^1S$, the final state is a superposition of Slater determinants forming a ${}^1P$ state. The bound single-particle states of the determinants are chosen to be those obtained as solutions of the single-configuration (np^6) Hartree-Fock equations for the ground state of the atom. The continuum electron state is solved for in the $V^{N-1}(^1P)$ potential so that

$$\varphi_{\epsilon l m_l m_s} = [P_{\epsilon l}(r)/r] Y_{l m_l}(\theta, \phi) \chi_{m_s}(S) , \tag{4}$$

where

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + 2\epsilon + V(r)\right) P_{\epsilon l}(r) + X(r) = 0 , \tag{5}$$

$$V(r) = \frac{2}{r}\left(Z - \sum_{j n' l'} a_{j n' l'} Y^j(n' l', n' l' ; r)\right) , \tag{6}$$

$$X(r) = \frac{2}{r} \sum_{j n' l'} b_{j n' l'} Y^j(n'l', \epsilon l; r) P_{n' l'}(r) + \sum_{n'} \lambda_{n' l} P_{n' l}(r) . \tag{7}$$

The a and b coefficients appropriate for a $V^{N-1}(^1P)$ potential are given by Kennedy and Manson.[14] The Lagrange multipliers $\lambda_{n' l}$ in Eq. (7) are included to insure orthogonality between bound and continuum states with the same l. We shall discuss the effects of these multipliers below. The normalization of the continuum states is such that as $r \rightarrow \infty$

$$P_{\epsilon l}(r) \rightarrow (2/\pi k)^{1/2} \sin[kr + (q/k)_l n 2kr + \tfrac{1}{2} l\pi + \sigma_l + \delta_l] , \tag{8}$$

where $\sigma_l = \arg[\Gamma(l+1-iq/k)]$ is the Coulomb phase shift; δ_l is the residual phase shift and $q = Z - N$ is the net charge of the ion. The normalization has been carried out using the method of Strömgren as given by Bates and Seaton.[15]

Amus'ya and co-workers have shown that by using this potential, one effectively sums a set of perturbation diagrams which are diagonal in the hole state and involve only a single channel. This means that the perturbation Hamiltonian

$$H_p = \sum \frac{e^2}{r_{ij}} - V^{N-1}(^1P) \tag{9}$$

does not couple the state $np^5 \epsilon d\, ^1P$ to any state of the type $np^5 \epsilon' d\, ^1P$. Thus, this choice of potential enables one to automatically include a large class of final state correlation terms. We have not included any other type of final state correlation in our calculation.

C. Cross section

Given the specifications of the initial and final states and Eq. (1), it is now convenient for the sake of calculation to separate the angular and radial integrals involved in the transition amplitude. For the cases considered here where the transition is always $^1S \rightarrow {^1P}$ Eq. (1) may be rewritten

$$\sigma(E) = \tfrac{4}{3}\pi^2 \alpha a_0^2 \sum_f |\langle \psi_f \| T \| \psi_i \rangle|^2 E_{fi} , \tag{10}$$

where the sum over magnetic quantum numbers has been done.

The reduced matrix elements which are left are of two types. The first type corresponding to a ground-state configuration without virtual excitation ($np^6\, ^1S$) factors into

$$w_1 A_1 (\epsilon l | T^r | nl') , \tag{11}$$

where w_1 is the weight of the configuration $(np)^6\, ^1S$ [Eq. (3)], A_1 is the angular part of the reduced matrix element given by $A_1 = (\psi_f \| C^1 \| \psi_i^1) \equiv (\psi_f \| C^1 \| np^6\, ^1S)$, and

$$(\epsilon l | T_L^r | nl') = \int_0^\infty P_{\epsilon l}(r) r P_{nl'}\, dr \quad \text{(length form);}$$
$$(\epsilon l | T_V^r | nl') = \frac{1}{E_{fi}} \int_0^\infty P_{nl'}(r) \left(\frac{d}{dr} \pm \frac{2l' + 1 \pm 1}{2r}\right) P_{\epsilon l}(r) \quad \text{(velocity form).} \tag{12}$$

In this last equation, the ± is taken as $l = l' \pm 1$. The second type of matrix element, corresponding to a ground configuration with an excited pair, factors into

$$w_j A_j (nl' | T^r | n'l)(n'l | \epsilon l) \quad (j \neq 1) , \tag{13}$$

where $A_j = (\psi_f \| C^1 \| \psi_i^j)$ and $(n'l | \epsilon l)$ is a radial overlap integral between the virtually excited state $P_{n'l}$ and the continuum state $P_{\epsilon l}$. The channels $np \rightarrow \epsilon s$ and $ns \rightarrow \epsilon p$ involve only the first type of reduced matrix element in our calculation. Table I gives the values of the factors which were used to evaluate the cross section for argon at a photon energy of 1 a.u. Note that the overlap integral is of the order of 1. For the cases considered here, we find that the overlap integral peaks at an energy near the peak in the cross section, and tends to zero at higher energies. Here and in all subsequent tables and graphs cross sections are given in units of megabarns (10^{-18} cm^2).

III. RARE GASES

Within the framework of the above method there remains some latitude in the specifics of the calculation. We have investigated several different approaches in order to find the one which gives the best results with a reasonable amount of calculation, since our aim is to apply the technique to a fairly large number of systems. We will describe in this section several variations which were considered, since knowing what is not important in the calculation may be as useful as knowing what is.

For convenience of calculation, we used the same core wave functions in the ground state and in the final state. Two methods were considered for obtaining these core functions. In the first,

TABLE I. Numerical factors used in calculation of $\sigma(3p \rightarrow \epsilon d)$ for argon with $E_{fi} = 1.0$ a.u.

Configuration	Weight	Angular coeff.	T_L^r	T_V^r	Overlap	RME$_L$	RME$_V$
$3p^6[^1S]$	0.9775	2	−2.009	−1.3858	⋯	−3.9276	−2.7092
$3p^4\,{}^1S3d^2\,{}^1S[^1S]$	−0.1139	$2/\sqrt{15}$	−1.6038	1.1412	1.0949	0.1033	−0.0735
$3p^4\,{}^3P3d^2\,{}^3P[^1S]$	−0.1287	$3/\sqrt{5}$	−1.6038	1.1412	1.0949	0.3032	−0.2157
$3p^4\,{}^1D3d^2\,{}^1D[^1S]$	−0.1222	$\sqrt{7}/15$	−1.6038	1.1412	1.0949	0.1416	−0.1043
				Total		−3.3745	−3.1027

$$\sigma_{L(V)}(3p \rightarrow \epsilon d) = \left(\sum \text{RME}_{L(V)}\right)^2 (2.688\ \text{Mb}) E_{fi}; \quad \sigma_L = 30.61\ \text{Mb}, \quad \sigma_V = 25.88\ \text{Mb}$$

they are obtained from a MCHF in which all orbitals were allowed to vary. In the second they are obtained from a single configuration HF calculation using only the configuration np^6; in this case, only the $\overline{nd}$ functions were allowed to vary in the ground-state MCHF, with all other orbitals being frozen. It was found that the latter method resulted in cross sections slightly superior to those obtained from the former method. Since, in addition, the latter method requires slightly less computer time than the former, it was decided to use this method in all calculations.

It is also possible in the MCHF to use different $\overline{nd}$ wave functions for each value of S and L in Eq. (3). This has the effect of absorbing certain other types of higher-order correlation effects. We carried out calculations using a different $\overline{nd}$ function for each of the three possible values of S and L—^1S, ^1D, and ^3P; calculations were also made using only a single $\overline{nd}$ for the three terms. It was found that, in the former case, all three $\overline{nd}$ functions were quite similar, to each other and to the single $\overline{nd}$ function obtained in the latter calculation. In addition, the cross sections in the two calculations were almost identical. Since the latter method is, once again, considerably more efficient in terms of computer time, it was decided to use it exclusively.

In calculations of this type, the Lagrange multipliers of Eq. (8) are often set equal to zero, with the result that continuum states $P_{\epsilon l}(r)$ are not strictly orthogonal to occupied states of the same angular momentum. We found that including these terms has the benefit of reducing somewhat the discrepancy between length and velocity cross sections as well as aiding convergence of the solution of (6) by reducing the effect of exchange terms. It is, of course, the reduction of the importance of the exchange terms which brings the length and velocity forms closer together, since it is the nonlocal exchange potential which destroys the equality between the two forms originally. Obviously, this inclusion of Lagrange multipliers affects only the relatively small $ns \rightarrow \epsilon p$ and $np \rightarrow \epsilon s$ cross sections in Ne and Ar; in Kr and Xe, it also affects the dominant $np \rightarrow \epsilon d$ cross section. We show, in Table II, the photoionization cross section for the $np \rightarrow \epsilon s$ channel in Ar for several values of photon energy calculated both with and without Lagrange multipliers.

As mentioned above, Froese Fischer[10] has found that the series of Eq. (3) is usually very rapidly converging, and that only a few terms need be kept to obtain a good energy. We have found that rapid convergence in the cross section results also. Table III gives the coefficients w_i obtained in a study of Ar. The coefficients of the $4\overline{d}$ are seen to be an order of magnitude smaller than those of the $3\overline{d}$ states. In Table IV, we show the cross sections obtained using these ground-state wave functions, as well as those obtained using ground-state functions containing only $3\overline{d}$ excitations. Similar results were obtained for Ne, Kr, and Xe. Because

TABLE II. Effect of including orthogonality for argon $\sigma(3p \rightarrow \epsilon s)$. A superscript "O" means orthogonality included; "NO" means no orthogonality; $\nabla = [(\sigma_L - \sigma_V)/\sigma_L] \times 100\%$.

Photon energy (a.u.)	σ_L^O	σ_V^O	∇^O (%)	σ_L^{NO}	σ_V^{NO}	∇^{NO} (%)
0.7	3.282	2.929	11	3.643	2.579	29
1.0	1.672	1.493	11	1.924	1.349	30
2.0	0.442	0.407	8	0.531	0.384	28
3.0	0.194	0.185	5	0.235	0.177	25

TABLE III. Weights for the ground state of argon.

Configuration	Weight
$3p^6[^1S]$	0.9773
$3p^4\,{}^1S3d^2\,{}^1S[^1S]$	−0.1132
$3p^4\,{}^3P3d^2\,{}^3P[^1S]$	−0.1287
$3p^4\,{}^1D3d^2\,{}^1D[^1S]$	−0.1219
$3p^4\,{}^1S4d^2\,{}^1S[^1S]$	−0.0148
$3p^4\,{}^3P4d^2\,{}^3P[^1S]$	−0.0142
$3p^4\,{}^1D4d^2\,{}^1D[^1S]$	−0.0156

TABLE IV. Comparison of $\sigma(3p \rightarrow \epsilon d)$ in argon for the 1, 4, and 7 configuration ground state. (HF removal energy is used here.)

Photon energy (a.u.)	σ_L^1	σ_V^1	σ_L^4	σ_V^4	σ_L^7	σ_V^7
0.6	26.01	15.13	21.62	17.66	21.29	17.95
1.0	44.19	20.67	31.35	25.85	30.97	26.06
1.5	7.17	2.06	3.40	3.13	3.53	3.08
2.5	0.41	0.51	0.61	0.43	0.53	0.45

the difference between the cross sections calculated using two $\bar{d}$ functions and those obtained using only the lowest $\bar{d}$ function is so small, we decided to use only the lowest $\bar{d}$ in subsequent calculations.

Kelly,[3] in his Ar calculation, used experimentally determined ionization energies, rather than calculated energies, in the denominators of his perturbation terms. This makes it rather difficult to compare our results to his, since we have no way of making an equivalent use of the experimental energies in our calculations. We can, however, use experimental energies in Eq. (1) rather than HF energies. In Figs. 1, 2, 3, and 4 we have plotted total photoionization cross sections for Ne, Ar, Kr, and Xe, respectively. Included in these figures are the HFL and HFV curves and the length and velocity curves obtained using the correlated ground state (CL and CV, respectively). All curves are obtained using experimental energies. The cross sections were evaluated at intervals of 0.1 a.u. in all cases. Also included are the experimental points of Samson.[16] In Table V, we give the coefficients w_i used in these calculations.

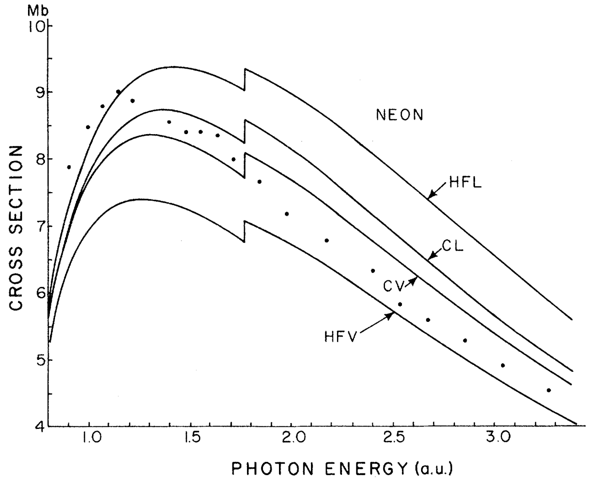

FIG. 1. Photoionization cross section for Ne in Hartree-Fock length (HFL), Hartree-Fock velocity (HFV), correlated-length (CL), and correlated-velocity (CV) approximations.

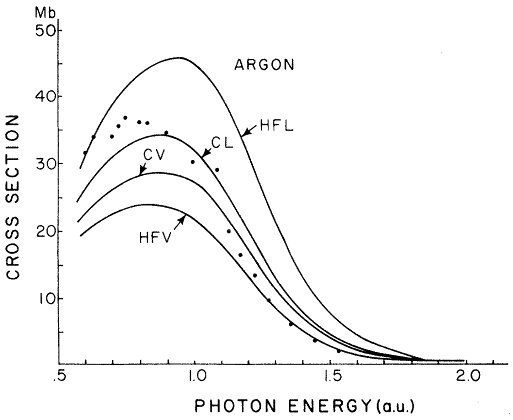

FIG. 2. Photoionization cross section for Ar (same designations as in Fig. 1).

Figures 1–4 clearly show the importance of the ground-state correlation which is included by taking the ground state to be $np^6 + np^4 n'\bar{d}^2$. The two most significant imporvements obtained by adding this ground-state correlation are (1) the difference between length and velocity forms near threshold is significantly reduced; and (2) the Cooper minimum appears at the same energy for both length and velocity forms. A general feature of all the MCHF curves is that agreement with experiment is better for the length form at lower energies, and for the velocity form at higher energies.

It is to be noted in the Ne case that the opening of the $2s \rightarrow \epsilon p$ channel at 1.76 a.u. produces a large bump theoretically which is apparently not present in the experimental data. Amus'ya[17] has shown that there is a significant interchannel interaction in Ne between the $2p \rightarrow \epsilon d$ and $2s \rightarrow \epsilon p$ channels

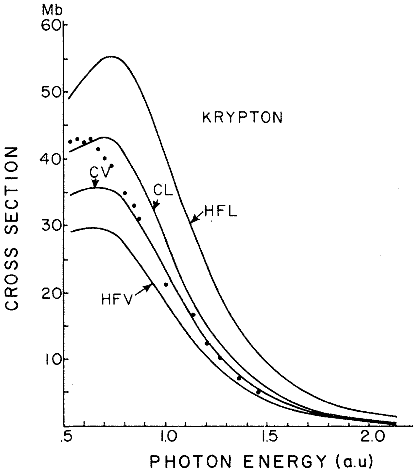

FIG. 3. Photoionization cross section for Kr (same designations as in Fig. 1).

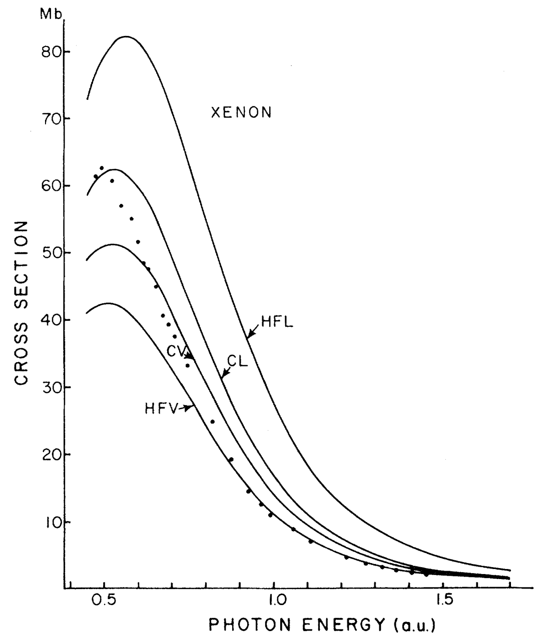

FIG. 4. Photoionization cross sections for Xe (same designations as in Fig. 1).

which reduces the magnitude of this bump. Since the total cross section in this channel is small we have neglected this effect.

One can verify that excitations of the type described by Eq. (3) are indeed the most important ones in the MCHF picture. This can be done in a straightforward manner by adding other configurations to the MCHF calculation. We have carried out calculations in which the configurations $|np^4\,{}^1D,\bar{n}s\bar{n}d\;{}^1D;\,{}^1S)$ and $|np^4\,{}^1S,\,(\bar{n}s)^2\,{}^1S;\,{}^1S)$ were added to the configurations of Eq. (3). These are the only configurations which contribute to a "first-order" MCHF theory for np shell ionization. In such a theory only admixtures into the ground state are included which couple to the "nominal" excited states [in this case $|np^5\epsilon d)$ and $|np^5\epsilon s)$]. The MCHF coefficients of the configurations above were found to be at least an order of magnitude smaller than those of the lowest $|np^4SL,\bar{n}\bar{d}^2SL;\,{}^1S)$ states. The inclusion of these extra configurations had a negligible effect on the calculated cross sections. Thus, the MCHF calculations confirm the results of the RPAE and MBPT that the configurations of Eq. (3) are the only important ones in the rare gases.

TABLE V. Weights for ground states of neutral rare gases.

Configuration	Neon	Argon	Krypton	Xenon
$np^6[{}^1S]$	0.9957	0.9775	0.9799	0.9779
$np^4\,{}^1Sn^1d^2\,{}^1S[{}^1S]$	−0.0466	−0.1139	−0.1074	−0.1138
$np^4\,{}^3pn^1d^2\,{}^3P[{}^1S]$	−0.0627	−0.1287	−0.1222	−0.1262
$np^4\,{}^1Dn^1d^2\,{}^1D[{}^1S]$	−0.0499	−0.1222	−0.1148	−0.1217

IV. CONCLUSIONS

The calculations described in the previous section seem to support the hypothesis made in Sec. I—that is, that the main correlation effects of importance in photoionization cross sections in the rare gases are the excited-state correlations included in the $V^{N-1(^1P)}$ and the ground-state correlations produced by the excitation of a single pair. In particular, we see that this type of correlation effect can be evaluated relatively easily using a MCHF. Because of this, a large fraction of the correlation effects included in the RPAE can, at least in the rare gases, be obtained using a MCHF with no corrections (other than the $V^{N-1(^1P)}$) to the final state.

Chang and Fano[9] have suggested in their derivation of the RPAE that only single pair excitation are actually included in the RPAE. If this is the case our calculation should give a good first-order approximation to the RPAE. In their derivation the function $\phi(r)$ introduces ground-state correlation analogous to the role of $P_{\overline{nd}}(r)$ in our method. When the angular integrals and overlap integrals of Eqs. (11) and (13) are combined with the appropriate wave functions our equation for the cross section is the same as their Eq. (16).

Recent calculations by Burke and Taylor[4] using the R-matrix method incorporated a large number of configurations into both initial (36 configurations) and final states (67 configurations). The inclusion of final state interchannel interactions has allowed them to give a detailed analysis of the $ns \rightarrow np$ resonance region and confirms earlier work by Amus'ya *et al.*[17] concerning the near-threshold behavior of the $ns \rightarrow \epsilon p$ channel. Despite the large number of configurations considered their work gives little better cross sections outside the resonance region than our own. We conclude from this that (i) there are a large number of effects we have neglected which have little influence on the total cross section, and (ii) the method chosen for incorporating ground-state correlations and the precise form of the correlating orbitals used are important in minimizing the number of configurations needed to achieve a given degree of accuracy.

We have pointed out that there are a number of more subtle effects which we have neglected. It is possible to take some of these into account by incorporating other techniques. For example, final-state interaction can be included by using a K-matrix approach[18] or solving the close-coupling equations.[7] Furthermore, Lindgren[19] has shown that a multiconfiguration basis set can be incorporated into a many-body perturbation theory, thereby making the current approach more flexible and potentially exact, but certainly extracting a cost in its complexity.

A number of questions have been raised by this study and will require further investigation. Among these questions are: (i) How well will the method work for closed-shell configurations other than np^6? (ii) When will interchannel interaction have to be taken into account? (iii) What refinements will be necessary to extend the method to open-shell systems?

The third question above is particularly interesting. The usual RPAE is, with a very few exceptions, applicable only to closed-shell systems. Extensions of the RPA to open-shell systems do exist,[20,21] but their application is very complicated and the results obtained thus far for atomic systems are somewhat ambiguous.[22] The MCHF can, of course, be applied to open-shell systems without any particular difficulty. Thus one should be able to use this approach to study ground-state pair excitations in open-shell atoms, thereby doing an RPA-like calculation. For open-shell atoms, however, interchannel interactions may also become important because of the number of allowed parent states. These interchannel interactions could be taken into account by including a close-coupling calculation in the determination of the final state.

---

*Work supported in part by the United States Energy Research and Development Administration.

[1] A compilation of experimental data is given by R. D. Hudson and L. J. Kieffer, At. Data 2, 205 (1971).

[2] M. Ya. Amus'ya, N. A. Cherepkov, and L. V. Chernysheva, Zh. Eskp. Teor. Fiz. 60, 160 (1971) [Sov. Phys.-JETP 33, 90 (1971)].

[3] H. P. Kelly and R. L. Simons, Phys. Rev. Lett. 30, 529 (1973).

[4] P. G. Burke and K. T. Taylor, J. Phys. B 8, 2620 (1975).

[5] C. D. Lin, Phys. Rev. A 9, 181 (1974).

[6] A. F. Starace, Phys. Rev. A 2, 118 (1970).

[7] R. J. W. Henry and L. Lipsky, Phys. Rev. 153, 51 (1967).

[8] D. L. Thouless, *The Quantum Mechanics of Many Body Systems* (Academic, New York, 1972).

[9] T. N. Chang and U. Fano, Phys. Rev. A 13, 263 (1976).

[10] C. Froese Fischer, J. Comput. Phys. 13, 502 (1973).

[11] P. O. Löwdin, Phys. Rev. 97, 1474 (1955).

[12] C. Froese Fischer, Comput. Phys. Commun. 4, 107 (1972) and private communication.

[13] A. Hibbert, Comput. Phys. Commun. 1, 359 (1969).

[14] D. J. Kennedy and S. T. Manson, Phys. Rev. A 5, 227 (1972).

[15] D. R. Bates and M. J. Seaton, Mon. Not. Roy. Astro. Soc. 109, 698 (1949).

[16] J. A. R. Samson, Adv. At. Mol. Phys. 2, 178 (1966).

[17] M. Ya. Amus'ya, V. K. Ivanov, N. A. Cherepkov, and L. V. Chernysheva, Phys. Lett. A 40, 361 (1972).

[18] C. D. Lin, Phys. Rev. A 9, 171 (1974).

[19] I. Lindgren, J. Phys. B 7, 2320 (1974).

[20] L. Armstrong, Jr., J. Phys. B 7, 2320 (1974).

[21] C. Ngo-Trong and D. J. Rowe, Rev. Mod. Phys. 47, 471 (1975).

[22] A. Starace and L. Armstrong, Jr., Phys. Rev. A 13, 1850 (1976).