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Multiconfiguration Hartree-Fock calculation of photoionization cross sections of the rare gases. II. Final-state correlation*

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Cross sections and angular distributions for the photoionization of the rare gases have been calculated using a modified Hartree-Fock equation for the continuum orbital and a multiconfiguration Hartree-Fock description of the ground state. The modification of the Hartree-Fock equation for the continuum orbital is produced by virtual pair excitations of the ionic core analogous to those incorporated in the ground state. The modification reduces to the addition of two terms to the standard $V^{N-1(LS)}$ potential when small terms are neglected. The addition of this final-state correlation effect gives improved agreement with experimental cross sections as compared to a previous calculation which included only ground-state correlation effects.

I. INTRODUCTION

In a recent article,[1] we used the multiconfiguration Hartree-Fock (MCHF) method as a means of including ground-state correlation effects in the calculation of photoionization cross sections of rare gases. The continuum wave functions used in those calculations were solutions of the Hartree-Fock equation with a $V^{N-1(^1P)}$ potential.[2] The results of these calculations showed a significant improvement over the single-configuration Hartree-Fock results, but did not reproduce experiment as well as the random phase approximation[3,4] (RPA) or the more detailed many-body perturbation theory (MBPT).[5] In this paper we describe a modification to the $V^{N-1(LS)}$ potential which takes into account the dominant correlation effects in the ion core. Use of this modified $V^{N-1(LS)}$ to determine the final-state wave function, along with the previous improvements in the ground state, brings our calculated values of photoionization cross sections of the rare gases into good agreement with experiment.

The usual $V^{N-1(LS)}$ calculation assumes that the continuum electron moves in the field of the ion which is described by a single configuration of N-1 Hartree-Fock atomic orbitals. If the field which the exiting electron sees is not well described by this single-configuration approximation, there will be significant final-state correlation effects involving virtual excitation of the ion itself. In order to improve upon the usual $V^{N-1(LS)}$, one can define a multiconfiguration $V^{N-1(LS)}$ (MCV) potential in which a more accurate description of the ionic field is given in terms of a superposition of configurations. By letting this multiconfiguration ionic state determine the potential of the ϵl electron, one obtains an MCHF-type equation which can then be simplified by neglecting small terms.

The principal ground-state correlation effects which contribute to the $np \rightarrow \epsilon d$ transition in the rare gases are the virtual excitations $np^6 \rightarrow np^4 n'd^2$. In the present work, we consider analogous excitations in the ground state of the ion; i.e., $np^5 \rightarrow np^3 n'd^2$, and take into account their effect on the ejected (ϵd) electron . After simplification, the modification to the usual $V^{N-1(^1P)}$ potential produced by these ionic excitations is just two terms which result from the nonorthogonality of the radial wave functions for the continuum and correlating orbitals.

In Sec. II we briefly review the material covered in SA and then derive the modified Hartree-Fock equation for the continuum wave function. Details of the calculation and results are given in Sec. III. We suggest possible refinements and extensions, and present our conclusions in Sec. IV.

II. THEORY

As in SA we describe the ground state of a rare-gas atom by the expansion

$$|\psi_g\rangle = a\,|np^{6}\,{}^1S\rangle + \sum_j b_j\,|np^4 S_j L_j, \bar{n}d^2 S_j L_j;\ {}^1S\rangle , \qquad (1)$$

where the weights (a, b_j) and the radial wave functions $P_{1s}(r) \cdots P_{\bar{n}d}(r)$ are solutions of the MCHF equations. The $\bar{n}d$ notation indicates that the wave function so designated is a pseudo-orbital. It can be decomposed into a sum over bound (and integral over continuum) wave functions $P_{nd}(r)$ $(P_{\epsilon d}(r))$ calculated in a $V^{N-1(LS)}$ potential. Consequently, continuum ϵd orbitals are not orthogonal to the correlating $\bar{n}d$ orbitals. The ground-state calculations reported in SA showed that the b_j's are typically of the order of 0.1 for the rare gases.

A similar expansion can be made for the final-state ion core:

$$|\psi_c\rangle = \alpha\,|np^5\,{}^2P\rangle + \sum_{ij} \beta_{ij}\,|np^3 S_i L_i, \bar{n}d^2 S_j L_j;\ {}^2P\rangle . \qquad (2)$$

To avoid overlap complications which arise if different basis sets are used in initial and final states we make the approximation that all single-particle wave functions in the expansion of ψ_c are the same as in the ground state of the atom ψ_g. That is to say, ψ_c is not a solution of the appropriate MCHF equations but rather a superposition of configurations with fixed single-particle wave functions. The description of the ion core is then fixed by determination of the weights (α, β_{ij}).

Two methods have been used to determine the weights (α, β_{ij}). If we view the problem as a standard superposition of configurations problem, the weights are the components of the eigenvector corresponding to the lowest eigenvalue of the energy matrix. A second simpler, albeit more approximate, scheme is to obtain the correlated ionic ground state by annihilating a p electron in the correlated atomic ground state. In this case we find

$$\alpha = a$$

$$\beta_{ij} = (p^4 S_j L_j \{| p^3 S_i L_i, p)(-1)^{L_i+S_i+L_j+S_j-3/2} b_j , \quad (3)$$

where the term in parenthesis is a coefficient of fractional parentage. Since the atomic weights b_j are small and the cfp's are ≤ 1 in magnitude, the ionic weights β_{ij} are also small. We discuss the two methods further in Sec. III and for the time being consider the weights as known.

To complete our description of the final state we need now consider the ejected electron. The excited state wave function is the product of the ion and the continuum electron wave functions:

$$\begin{aligned} |\psi_{\mathrm{ex}}\rangle &= [\,|\psi_c\rangle \times |\psi_{\epsilon d}\rangle]^1 P \\ &= \alpha\, | np^5\, {}^2P, \epsilon d;\, {}^1P\rangle \\ &\quad + \sum_{ij} \beta_{ij} | np^3 S_i L_i, \bar{n}d^2 S_j L_j;\, {}^2P, \epsilon d;\, {}^1P\rangle . \end{aligned} \quad (4)$$

A Hartree-Fock equation for $P_{\epsilon d}(r)$ may be found by the usual variational method, i.e., by setting the variation of $\langle \psi_{\mathrm{ex}} | H-E | \psi_{\mathrm{ex}}\rangle$ with respect to $P_{\epsilon d}(r)$ equal to zero. The wave function $P_{\epsilon d}(r)$ is constrained to be orthogonal to inner shells with $l = 2$. It is not, however, forced to be orthogonal to the pseudo-orbital $P_{\bar{n}d}(r)$ since this wave function is supposed to be a superposition of the "real" $P_{n(\epsilon)d}(r)$ wave functions. This lack of orthogonality means that ψ_{ex} as given in Eq. (4) is not totally antisymmetric; however, the extent to which the exclusion principle is violated is small. Schematically the Hartree-Fock equation is

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + V(r) + V'(r) + 2E\right) P_{\epsilon l}(r) = X(r) + X'(r) + \delta_{l,2} W(r) , \quad (5)$$

where

$$V(r) = \frac{2}{r}\left(Z - \sum_{mk} A_{mk} Y^k(m, m; r)\right);$$

$$X(r) = \frac{2}{r} \sum_{mk} B_{mk} Y^k(m, \epsilon l; r) P_m(r) + \sum_{m(\neq \bar{n}d)} \delta_{l, l_m} \lambda_m P_m(r);$$

$$W(r) = 2\alpha \sum_{ijk} \beta_{ij} C_{ij}^k \left(P_{\bar{n}d}(r) R^k(np, np; \bar{n}d, \epsilon d) + \frac{1}{r} (\bar{n}d | \epsilon d) Y^k(np, \bar{n}d) P_{np}(r)\right);$$

$$(\bar{n}d | \epsilon d) = \int_0^\infty P_{\bar{n}d}(r) P_{\epsilon d}(r)\, dr;$$

$$Y^k(i, j; r) = r^{-k} \int_0^r P_i(r') P_j(r') r'^k\, dr' + r^{k+1} \int_r^\infty P_i(r') P_j(r') r'^{(-k-1)}\, dr' ;$$

$$R^k(i, j; l, m) = \int_0^\infty Y^k(i, l; r) P_j(r) P_m(r) r^{-1}\, dr .$$

The remaining two terms, $V'(r)$ and $X'(r)$, are quite complicated; however, they are quadratic in the small mixing weights β_{ij} and are consequently small. We can, therefore, drop these two terms in a first approximation. The coefficients A_{mk} and B_{mk} are the usual $V^{N-1(LS)}$ direct and exchange coefficients which are given by Kennedy and Manson.[6] The λ_m's are Lagrange parameters which are adjusted to make the $P_{\epsilon l}(r)$ orthogonal to inner-shell wave functions of the same l (excluding $\bar{n}d$, of course). The coefficients C_{ij}^k result from the angular integrations of the Coulomb matrix elements and in this case are given by

$$\begin{aligned} C_{ij}^k &= 6\sqrt{10}(2 \| C^k \| 1)^2 \\ &\quad \times \sum_{S_0 L_0} (-1)^{L_i+S_0+1} [S_j, L_j, S_0, L_0]^{1/2} \\ &\quad \times (p^5\, {}^2P \{| p^3 S_i L_i, p^2 S_0 L_0) \begin{Bmatrix} 2 & 2 & L_0 \\ 1 & 1 & k \end{Bmatrix} \\ &\quad \times \begin{Bmatrix} S_j & S_i & \frac{1}{2} \\ S_0 & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} 2 & 2 & L_0 \\ 1 & 2 & 1 \\ 1 & L_j & L_i \end{Bmatrix} . \end{aligned} \quad (6)$$

where $[a] = 2a+1$, and $(p^5\, {}^2P \{| p^3 S_i L_i, p^2 S_0 L_0)$ is a two-body cfp.[7]

Equation (5) is the usual Hartree-Fock or $V^{N-1(LS)}$ equation with the addition of three terms. Two of these terms, $V'(r)$ and $X'(r)$, will, as indicated above, be ignored. The third term $W(r)$ results from the lack of orthogonality between the $P_{\epsilon d}(r)$ and $P_{\bar{n}d}(r)$. Its structure can be clarified by defining

$$D^k = 2\alpha \sum_{ij} \beta_{ij} C^k_{ij} \tag{7}$$

and

$$W'(r) = \sum_k D^k Y^k(np, \bar{n}d; r) P_{np}(r)/r\,,$$

where $W'(r)$ has no dependence on $P_{\epsilon d}(r)$. Then

$$W(r) = (\bar{n}d \,|\, \epsilon d) W'(r) + P_{\bar{n}d}(r) \int_0^\infty W'(r') P_{\epsilon d}(r')\, dr'\,. \tag{8}$$

Given the correlating functions $P_{\bar{n}d}(r)$ and the coefficients D^k it is then a simple matter to incorporate these two additional terms into an existing $V^{N-1(LS)}$ program. The principal advantage of the usual $V^{N-1(LS)}$ potential is that the forward going perturbation diagrams diagonal in the hole states are diagonal in the energy of the continuum electron. That is,

$$\langle np^5\,{}^2P, \epsilon d;\ {}^1P \,|\, e^2/r_{ij} - V^{N-1(LS)} \,|\, np^5\,{}^2P, \epsilon' d;\ {}^2P) = 0\,, \quad \text{for } \epsilon \neq \epsilon'$$

The MCV potential has an analogous property. If we include all the terms in Eq. (5), the corresponding matrix element is diagonal in the energy of the continuum electron. Discarding the small terms $V'(r)$ and $X'(r)$ introduces small off-diagonal terms.

We have chosen to normalize the wave functions in the energy scale (a.u.) so that asymptotically

$$P_{\epsilon l}(r) = (2/\pi k)^{1/2} \sin[kr + (q/k)\ln(2kr) + \tfrac{1}{2}l\pi + \sigma_l + \delta_l]\,, \tag{9}$$

where $k = (2\epsilon)^{1/2}$, $q = Z - N$ is the net charge of the ion, $\sigma_l = \arg(\Gamma(l + 1 + iq/k))$ is the Coulomb phase shift, and σ_l is the residual phase shift.

Having specified the ground and excited states, we can now calculate the photoionization cross sections and the angular distribution of photoelectrons. The total photoionization cross section is given in the dipole approximation by

$$\sigma = (4/3)\pi\alpha a_0^2 \sum |\langle \psi_{\text{ex}} \| T \| \psi_g \rangle|^2 \omega\,, \tag{10}$$

where

$$T = T_l = \sum_j z_j \quad \text{in the length form,}$$

$$T = T_v = \sum_j \nabla_j^z / i\omega \quad \text{in the velocity form,}$$

the sum is over excited states, and $\omega = E_{\text{ex}} - E_g$ is the photon energy. Substituting the expansions from Eqs. (1) and (4) for ψ_g and ψ_{ex} into Eq. (10) yields three types of nonvanishing terms

$$\alpha a \langle np^5\,{}^2P, \epsilon d;\ {}^1P \| T \| np^6\,{}^1S \rangle\,,$$

$$\alpha b_j \langle np^5\,{}^2P, \epsilon d;\ {}^1P \| T \| np^4 S_j L_j, \bar{n}d\,{}^2S_j L_j;\ {}^1S \rangle\,,$$

$$\beta_{ij} b_j \langle np^3 S_i L_i, \bar{n}d\,{}^2S_j L_j;\ {}^2P, \epsilon d\,{}^1P \| T \| np^4 S_j L_j, \bar{n}d\,{}^2S_j L_j;\ {}^1S \rangle\,.$$

To be consistent with our previous approximations we ignore the last of these which is quadratic in the small mixing coefficients and renormalize the excited state correspondingly, i.e., set $\alpha = 1$. The angular and radial integrals are separated to give

$$\langle np^5\,{}^2P, \epsilon d;\ {}^1P \| rC^1 \| np^6\,{}^1S \rangle = 2R_{np,\epsilon d} \equiv A_1 R_{np,\epsilon d}\,,$$

$$\langle np^5\,{}^2P, \epsilon d;\ {}^1P \| rC^1 \| np^4 S_j L_j, \bar{n}d\,{}^2S_j L_j;\ {}^1S \rangle = (-1)^{L_j} 2[L_j, S_j]^{1/2} \begin{Bmatrix} 2 & 2 & L_j \\ 1 & 1 & 1 \end{Bmatrix} (\epsilon d \,|\, \bar{n}d) R_{\bar{n}d,np} \equiv A_j (\epsilon d \,|\, \bar{n}d) R_{\bar{n}d,np}\,,$$

where

$$R^L_{nl,n'l'} = \int_0^\infty P_{nl}(r) P_{n'l'}(r)\, r\, dr$$

in the length form and

$$R^V_{nl,n'l'} = \frac{1}{\omega} \int_0^\infty P_{n'l'}(r) \times \left(\frac{d}{dr} + \frac{l'(l'+1) - l(l+1)}{2r} \right) P_{nl}(r)\, dr$$

in the velocity form. Then for the ϵd channel

$$\langle \psi_{\text{ex}} \| T \| \psi_g \rangle = a A_1 R_{np,\epsilon d} + \sum_j b_j A_j (\epsilon d \,|\, \bar{n}d) R_{\bar{n}d,np} \equiv A_1 T_{\epsilon d}\,.$$

For the ϵs channel where no correlation is taken into account we have $\langle \psi_{\text{ex}} \| T \| \psi_g \rangle = \sqrt{2} R_{np,\epsilon s} \equiv \sqrt{2} T_{\epsilon s}$.

In the dipole approximations photoelectrons ionized from a particular subshell by light polarized in a direction $\hat{q}$ will have an angular distribution[8]

$$\frac{d\sigma}{d\Omega} \propto 1 + \beta(\epsilon) P_2(\hat{q} \cdot \hat{k})\,,$$

where $\hat{k}$ is the direction of the emitted electron and $\beta(\epsilon)$ is the asymmetry parameter. For the case of rare gases where there is only one final-state angular momentum the Cooper-Zare[9] model is valid. This reduces for our case where $np \to \epsilon s, \epsilon d$ to

TABLE I. Weights for the ionic ground states. α and $\beta({}^{2S_i+1}L_i, {}^{2S_j+1}L_j)$ correspond to α and β_{ij} of Eq. (4). I and II refer to the scheme by which the weights were determined. The coefficients D^1 and D^3 are defined by Eq. (7).

	Neon		Argon		Krypton		Xenon	
	I	II	I	II	I	II	I	II
α	0.9970	0.9957	0.9824	0.9775	0.9846	0.9799	0.9831	0.9779
$\beta({}^4S,{}^3P)$	0.0299	0.0362	0.0644	0.0743	0.0606	0.0706	0.0626	0.0729
$\beta({}^2P,{}^1S)$	−0.0385	−0.0466	−0.0993	−0.1139	−0.0925	−0.1074	−0.0982	−0.1138
$\beta({}^2P,{}^3P)$	0.0267	0.0314	0.0612	0.0643	0.0571	0.0611	0.0593	0.0631
$\beta({}^2P,{}^1D)$	0.0202	0.0250	0.0504	0.0611	0.0469	0.0574	0.0495	0.0608
$\beta({}^2D,{}^3P)$	0.0341	0.0405	0.0765	0.0831	0.0716	0.0788	0.0742	0.0815
$\beta({}^2D,{}^1D)$	−0.0361	−0.0432	−0.0940	−0.1058	−0.0871	−0.0994	−0.0925	−0.1054
D^1	−0.1259	−0.1503	−0.2940	−0.3269	−0.2751	−0.3098	−0.2875	−0.3230
D^3	0.0312	0.0376	0.0766	0.0870	0.0716	0.0822	0.0755	0.0865

$$\beta(\epsilon)=\frac{6T_{\epsilon d}^2-12T_{\epsilon s}T_{\epsilon d}\cos[\xi_d(\epsilon)-\xi_s(\epsilon)]}{3(T_{\epsilon s}^2+2T_{\epsilon d}^2)},$$

with $\xi_l(\epsilon)=\sigma_l(\epsilon)+\delta_l(\epsilon)$.

III. RESULTS

The weights (α, β_{ij}) of the ionic configurations are given in Table I. The weights listed under scheme I are the components of the eigenvector of the energy matrix with the lowest eigenvalue. The scheme II weights are obtained from Eqs. (3) and the ground-state weights given in SA. Observe that the weights obtained by scheme I are 10% to 20% smaller than those from scheme II. Since terms which are quadratic in the small weights are ignored, the only place these weights enter the calculation is through the coefficients D^k. In Table II the coefficients C_{ij}^k are given. Combining these results with the weights from Table I using Eq. (7) gives the D^k's listed in Table I. Again the coefficients D^k determined by scheme I are about 10% smaller (except for the case of neon) than those from scheme II. Cross sections have been calculated using both schemes. We found that a 10% change in the D^k's changes the cross section by at most 2%. That is, to the degree of accuracy which is consistent with the approximations made above, the schemes may be considered to be equivalent. All the results presented here were calculated using the scheme I weights.

TABLE II. The coefficients C_{ij}^k [as defined by Eq. (6)].

		k	
${}^{2S_i+1}L_i$	${}^{2S_j+1}L_j$	1	3
${}^4S$	${}^3P$	$-3\sqrt{10}/25$	$9\sqrt{10}/175$
${}^2P$	${}^1S$	$13\sqrt{10}/150$	$-9\sqrt{10}/175$
${}^2P$	${}^3P$	$-7\sqrt{30}/100$	$-9\sqrt{30}/700$
${}^2P$	${}^1D$	$-\sqrt{70}/60$	$-9\sqrt{70}/980$
${}^2D$	${}^3P$	$-33\sqrt{2}/100$	$9\sqrt{2}/700$
${}^2D$	${}^1D$	$7\sqrt{210}/300$	$-69\sqrt{210}/4900$

The ground-state wave functions used here are exactly as calculated in SA. Specifically, the wave functions for the single configuration np^6 are calculated first; then the $P_{\bar{n}d}$ wave function and the weights $\{a, b_j\}$ are determined with the other wave functions frozen. These calculations, as well as the determination of the weights in scheme I, were carried out using the program MCHF 75.[10] The numerous angular coefficients required by this procedure were computed by the program WEIGHTS.[11]

Figures 1–4 display our results for the photoionization of neon, argon, krypton, and xenon. The channels included are $np\rightarrow\epsilon d$, $np\rightarrow\epsilon s$, and $ns\rightarrow\epsilon p$, where the latter two have relatively small cross sections and are computed using the $V^{N-1(LS)}$ potential without modification. For neon, argon, and krypton the experimental cross sections are given by Marr and West[12] while those for xenon are from Samson.[13]

A comparison with the results of SA where only ground-state correlation (GSC) was included shows that the effects of the MCV are (i) to bring length and velocity forms into better agreement, (ii) to increase the cross section in the vicinity of the maximum and move the maximum closer to threshold, and (iii) to give a sharper drop off

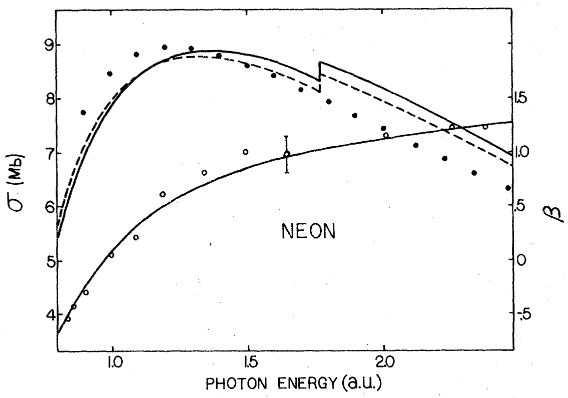

FIG. 1. Photoionization cross section and asymmetry parameter for Ne. The upper solid line gives the length form of the cross section; the dashed line gives the velocity form. In this case the length and velocity forms of the β parameter coincide and are given by the lower solid line. The solid dots are the experimental cross sections (Ref. 12), the open circles are experimental values of the β parameter (Ref. 15). The error bar indicated is representative of those for the other points.

from the maximum. For the cases argon, krypton, and xenon the modifications seem to overcorrect somewhat. At low energies where the GSC cross sections were too small, the MCV results are larger than experiment. At slightly higher energies in argon, and to a lesser extent in krypton, the MCV results dip below experiment before coming back into agreement near the Cooper minimum. The cross sections calculated by the RPA[3,4] show similar behavior although the RPA is in somewhat better agreement with experiment overall.

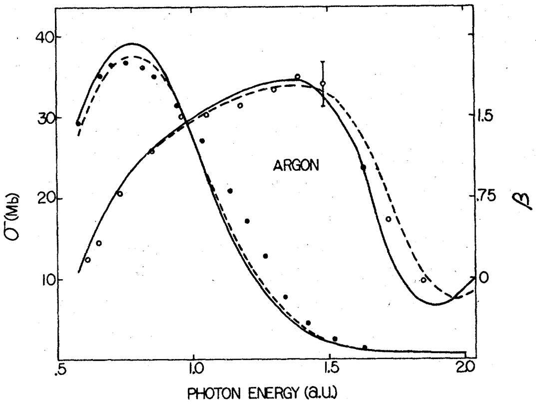

FIG. 2. Photoionization cross section and asymmetry parameter for Ar. Notation is the same as Fig. 1, except the velocity form of the β parameter no longer coincides with the length form and is indicated by a dashed line. The experimental cross sections are from Ref. 12 while the experimental β parameters are from Ref. 16.

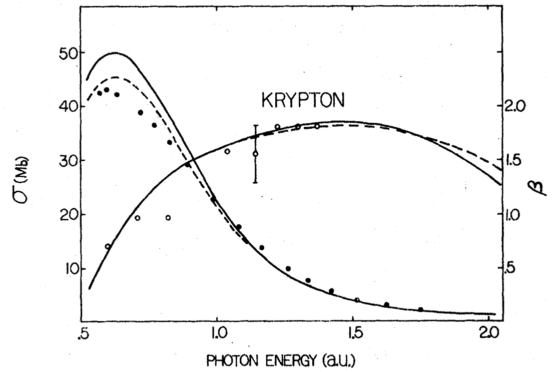

FIG. 3. Photoionization cross section and asymmetry parameter for Kr. Same notations as in Fig. 2. The experimental cross sections are from Ref. 12 and the experimental β parameters are from Ref. 14.

The asymmetry parameters β are also displayed in Figs. 1–4 in both length and velocity forms. The final-state correlation affects the β parameters in two ways: both the transition matrix elements and the phase shifts are modified. The effect of correlations on the β parameters is not as pronounced as their effect on cross sections. Moreover, the experimental values of the β parameters as given in Refs. 14–16 are not as well determined as the cross sections. Experimental evidence for the most part, therefore, does not support the MCV over the HF approximations. Near the Cooper minimum, however, the difference between the

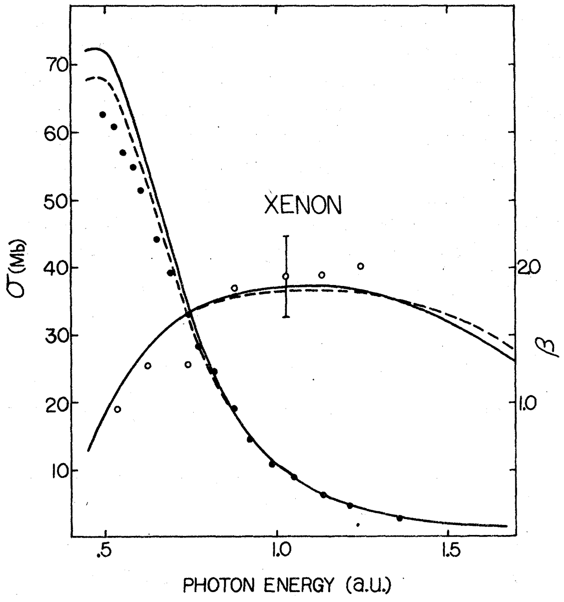

FIG. 4. Photoionization cross sections and asymmetry parameter for Xe. Same notations as in Fig. 2. The experimental cross sections are from Ref. 13 and the experimental β parameters are from Ref. 14.

HF and MCV theories is considerable. This is evident in argon where the MCV gives much better agreement with experiment than the HF calculation.[6]

IV. DISCUSSION AND CONCLUSIONS

The effects we have considered here have been included in previous studies of the rare gases using different methods. The R-matrix calculation of Burke and Taylor[17] for neon and argon photoionization explicitly includes ionic configurations with virtual $np^2 \rightarrow \bar{n}d^2$ excitations. Their calculation also includes interchannel effects, ignored here, which give a good account of the resonances preceding the ϵp threshold. Aside from the method used, the chief differences in the treatment of intrachannel effects are the choice of pseudo-orbitals and their use of a relaxed ionic core basis set. The effect of core relaxation is to lower the maximum and make the descent from maximum less abrupt. Such a change in our results would bring the two calculations into better agreement. Amusya[18] has pointed out, however, that because the rearrangement energy for outer shells is small the rearrangement time is long and therefore core relaxation is essentially a post-collision phenomenon. That is to say, except at energies very near threshold, the field which the ejected electron sees is unrelaxed. While core relaxation effects may, in principle, be taken into account in the R-matrix calculation using an ionic core basis set, fewer pseudo-orbitals may be needed if an atomic basis set is used for outer-shell photoionization calculations.

Though the RPA as derived by Chang and Fano[19] does not explicitly introduce the MCV effects, a comparison of their Eq. (21) with our Eq. (5) reveals some parallels. In particular, their $\phi(r)$ plays a role analogous to $(\bar{n}d|\epsilon d)P_{\bar{n}d}(r)$ while $\psi(r)$ is analogous to $P_{\epsilon d}(r)$. The modification of the HF $V^{N-1(LS)}$ potential in the RPA is proportional to $Y^k(\phi, np; r)P_{np}(r)/r$ which corresponds to the first half of $W(r)$ [Eq. (8)]. Calculations using the coupled differential equation form of the RPA have been performed by Chang for neon and argon using atomic wave functions in the core and neglecting all but the intrachannel effects.[4] Although the RPA is in somewhat better agreement with experiment for argon, the neon results are very similar to the MCV cross sections of Fig. 1.

There are a number of possible refinements and extensions of the treatment given here. We have ignored terms in the potential and in the transition matrix elements which are quadratic in the small weights. While each of these terms is on the order of 1% or less their cumulative effect may be larger. Unfortunately much of the simplicity of this approach is lost when higher-order terms are included. Another effect investigated in SA is the truncation of the ground-state expansion to include only the first $\bar{n}d^2$ terms. In SA we found that the weights of the next terms in the series $(\bar{n}+1)d$ were an order of magnitude smaller, that is, of the same order as the terms which have been neglected here. Modifications to the $V^{N-1(LS)}$ can be derived for other types of correlation but the form may not be as simple as the term $W(r)$. In particular where single-particle virtual excitations are possible a large number of nonignorable terms will arise. Open-shell atoms pose no particular problem in the MCV approach, but other types of correlation and interchannel effects are of greater importance in open-shell atoms and will require in most cases a more sophisticated approach. However, in the case where only one ionic term contributes to a particular final state we expect that most of the final-state correlation will be intrachannel and should be well accounted for by the MCV.

Our conclusions are threefold. First, the photoionization cross sections and asymmetry parameters of the rare gases can be well accounted for quantitatively by the inclusion of a simple correction to the HF approximation. Secondly, while final-state correlations are not as important as ground-state correlations in rare-gas photoabsorption their effect is significant. Lastly, certain terms in the RPA can be interpreted as corresponding to virtual pair excitations in the ion.

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