

Use of local exchange potentials in the calculation of photoionization and electron-ion scattering

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Several local approximations to exchange are investigated. These are compared against exact static-exchange results for e, Li^+ scattering and for the photoionization of the $2S$ and $2P$ state of Li . All except one are found to be fairly accurate for these cases. Calculations are also performed for photoionization of the $5D$ state of Cs , which exhibits an f -wave resonance. All exchange models studied for this case (including the Slater $X\alpha$) are found to give widely differing results on the position and width of this resonance. Calculations are also performed for the photoionization of the $Cs 6P$ state and compared against experimental results.

I. INTRODUCTION

Riley and Truhlar¹ have studied the use of local-exchange approximations for the elastic scattering of electrons from closed-shell atoms. These approximations were then studied in electron molecule scattering² and atomic photoionization.³ In the present paper, further work is reported on the use of local-exchange models in atomic photoionization.

Local-exchange potentials, in particular the Slater⁴ $X\alpha$, have been used extensively in the calculation of atomic⁵ and molecular⁶⁻⁸ photoelectric cross sections. In the case of the photoionization of the $5D$ state of Cs , an f -wave resonance, which produces a very deep, narrow minimum in the cross section, has been reported⁵ based on results of the $X\alpha$ model. Since the prediction of this "new minimum" has generated some experimental interest,⁹ it would appear worthwhile to study the

behavior of the resonance as a function of various local atomic fields which can be shown to produce reliably accurate nonresonant photoelectric cross sections in such atoms as Li and Cs .

Molecular photoelectric cross sections⁶⁻⁸ have shown a profusion of resonances based on the use of the multiple-scattering $X\alpha$ ($MSX\alpha$ model.¹⁰) Here the atomic fields used in the "muffin-tin" approximation are based on the Slater model. The study of the details of the molecular field which are responsible for shape resonances is a complicated task, beyond the scope of the present studies. It is certain^{6, 11} that in the photoionization of N_2 , for example, the Slater $X\alpha$ model atomic N fields produce no f -wave resonance. However, the model dependence of the atomic cross sections should be known by workers performing molecular calculations based on the use of superposed atomic fields; thus the calculations reported here are expected to be of interest in the field of molecular photoionization.

II. THEORY

First, we tested several local-exchange approximations against exact static-exchange results for Li . The radial equations for electron-atom scattering in the static-exchange approximation are well known, but for completeness we give them here. For e, Li^+ they are (in atomic units)

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - 2V(r) + k^2 \right) \psi_l(r; k) = -ru_{1s}(r) \left(\frac{2}{(2l+1)} \int_0^\infty dr' r' u_{1s}(r') \frac{r_l^i}{r_l^o} \psi_l(r'; k) - \delta_{10}(k^2 - \epsilon_{1s}) \int_0^\infty dr' r' u_{1s}(r') \psi_l(r'; k) \right), \tag{1a}$$

$$V(r) = -\frac{3}{r} + 2 \int_0^\infty dr' r'^2 r_{>}^{-1} u_{1s}^2(r'), \tag{1b}$$

where $u_{1s}(r)$ and ϵ_{1s} are the Li^+ 1s orbital and orbital energy in Ry. The phase shifts for modified Coulomb scattering are determined from the well-known relation

$$\lim_{r \rightarrow \infty} \psi_l(r; k) = \cos \eta_l F_l(kr) + \sin \eta_l G_l(kr), \quad (2)$$

where F_l and G_l are the regular and irregular Coulomb waves, respectively. In the calculation of the radiative-dipole matrix element for photoionization of a given initial orbital, the partial waves $\psi_l(r; k)$ are multiplied by the factor $i^l(2l+1)e^{-i(\sigma_l + \eta_l)}$ (normalization for incoming boundary conditions), where σ_l [Eq. (6c) below] is the Coulomb phase shift. The specific photoelectric cross sections for $\text{Li}(2s)$ and $\text{Li}(2p)$ are

$$\sigma(2s) = \frac{4\pi}{3} \alpha a_0^2 (k_0^2 - \epsilon_{2s}) k d_{01}^2, \quad (3a)$$

$$d_{01} = k^{-1} \int_0^\infty dr r \psi_1(r; k) r u_{2s}(r), \quad (3b)$$

$$\sigma(2p) = \frac{4\pi}{9} \alpha a_0^2 (k^2 - \epsilon_{2p}) k (d_{10}^2 + 2d_{12}^2), \quad (3c)$$

$$d_{11} = k^{-1} \int_0^\infty dr r \psi_1(r; k) r u_{2p}(r), \quad (3d)$$

where $l=0$ or 2 and u_{2s} , u_{2p} and ϵ_{2s} , ϵ_{2p} are the Li 2s and 2p orbitals and orbital energies in Ry, respectively. We take u_{1s} and u_{2s} from the analytic Hartree-Fock (HF) calculation of Roothaan *et al.*¹² and u_{2p} from the numerical HF code of

Froese.¹³ In Eq. (3c) we replace $-\epsilon_{2p}$ by the experimental ionization potential.¹⁴ This replacement is often used in order to improve the agreement with experiment. In this paper we use the replacement to compare with the results of Gezalov and Ivanova,¹⁵ who use the same replacement. Equations (1) are defined by use of the ionic orbital u_{1s} ; thus Eqs. (3b) and (3d) should be multiplied by the overlap factor

$$s = \int dr r^2 u_{1s}(r) u_{1sN}(r), \quad (4)$$

where u_{1sN} is the 1s orbital for Li. We have calculated these and find that their deviation from unity has a negligible effect on the cross sections [Eqs. (3a) and (3c)]. The asymmetry parameter $\beta(2P)$ of the photoelectron angular distribution for $\text{Li}(2P)$,

$$I_p(\theta) = \frac{\sigma(2p)}{4\pi} [1 + \beta(2P) P_2(\cos\theta)], \quad (5)$$

is given by the Cooper-Zare formula¹⁶

$$\beta(2P) = \frac{2(d_{12}^2 - 2d_{10}d_{12}\cos\Delta\eta)}{(d_{10}^2 + 2d_{12}^2)}, \quad (6a)$$

$$\Delta\eta = \sigma_0 + \eta_0 - \sigma_2 - \eta_2, \quad (6b)$$

$$\sigma_l = \arg\Gamma(l+1 - i/k). \quad (6c)$$

Finally, the angular distribution for e , Li^+ elastic scattering is given by¹⁷

$$I_{sc}(\theta) = \left(4k^4 \sin^4 \frac{\theta}{2}\right)^{-1} + \left(k^3 \sin^2 \frac{\theta}{2}\right)^{-1} \sum_l (2l+1) \cos \left[k^{-1} \ln \left(\sin^2 \frac{\theta}{2} \right) + 2(\sigma_0 - \sigma_l) - \eta_l \right] \sin \eta_l P_l(\cos\theta) + \left| k^{-1} \sum_l (2l+1) e^{2i\sigma_l + i\eta_l} \sin \eta_l P_l(\cos\theta) \right|^2. \quad (7)$$

The photoelectron cross sections have been studied only in the length form of the dipole amplitude [Eqs. (3b) and (3d)]. The agreement of the length and velocity forms of the amplitudes is a test of the accuracy of the initial and final quantum states, and this point has been studied by others¹⁸⁻²⁰ for the noble gas atoms. In the present calculation we are concerned with the effect of different exchange potentials on the dipole amplitudes and phase shifts, that is, with choices of approximations in the final state, while a single choice, the HF, is made throughout for the initial state. Length-velocity forms should be compared in studies in which the accuracy of *both* states^{19, 20} is probed. Another motivation for the use of the length form is the prescription²¹ that polarized-orbital calculations (easily calculable corrections

to the final-state motion due to core polarization by the photoelectron), required for the quantitative comparison with experiment,²² should be performed using the length form of the amplitude.

According to Riley and Truhlar¹ the right-hand side (rhs) of Eq. (1a) can be replaced by a local approximation to exchange. One such approximation is the semiclassical exchange (SCE) potential

$$V_{\text{SCE}} = \frac{1}{2} \{ [k^2 - V(r)] - [k^2/2 - V(r)]^2 + \alpha_d^2 \}^{1/2}, \quad (8a)$$

$$\alpha_d^2 = 2u_{1s}(r)^2, \quad (8b)$$

where V , the static potential, is defined by Eq. (1b). The second term on the rhs of Eq. (1a)

arises from the nonorthogonality of the s wave with the Li^+ $1s$ orbital. It cannot be removed in any local-exchange approximation; however, it is assumed to be small for an electron scattering from a closed-shell target and is dropped in Ref. 1. In our static-exchange calculations, the integral

$$c^{-1} \int_0^\infty dr r u_{1s}(r) \psi_0(r; k) \quad (9)$$

is $0.0415a_0^{1/2}$ at $k = 0.1a_0^{-1}$ and $0.289a_0^{1/2}$ at $k = 1.1a_0^{-1}$, where c is the normalization constant determined from the statement given by Eq. (2). Thus it appears to be non-negligible; nevertheless, the use of Eq. (8a) on the rhs of Eq. (1a) (Tables I-III) gives results which are in good agreement with the exact results, obtained by solving Eq. (1a) iteratively.

Riley and Truhlar study another local-exchange potential, the free-electron-gas-exchange (FEGE), proposed by Hara.²³ It is,

$$V_H(\vec{r}) = -\frac{2}{\pi} K_F F(\eta), \quad (10a)$$

$$F(\eta) = \frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln\left(\frac{1+\eta}{1-\eta}\right), \quad (10b)$$

$$\eta = K/K_F, \quad (10c)$$

$$K_F(\vec{r}) = [3\pi^2\rho(\vec{r})]^{1/3}, \quad (10d)$$

$$K(\vec{r}) = [k^2 + I + K_F^2(\vec{r})]^{1/2}, \quad (10e)$$

TABLE I. The $l=0$ phase shifts (in rad) for e, Li^+ modified Coulomb scattering.

$k(a_0^{-1})$	Static	Static-exchange	SCE	NCS
0.1	0.9635	1.2334	1.2134	1.4874
0.2	0.9616	1.2307	1.2105	1.4829
0.3	0.9585	1.2263	1.2057	1.4757
0.4	0.9543	1.2202	1.1991	1.4661
0.5	0.9488	1.2122	1.1907	1.4543
0.6	0.9421	1.2026	1.1805	1.4406
0.7	0.9343	1.1912	1.1687	1.4254
0.8	0.9253	1.1781	1.1552	1.4087
0.9	0.9154	1.1635	1.1403	1.3908
1.0	0.9047	1.1476	1.1241	1.3720
1.1	0.8932	1.1304	1.1068	1.3523
1.2	0.8813	1.1123	1.0887	1.3319
1.3	0.8690	1.0935	1.0700	1.3112
1.4	0.8566	1.0742	1.0509	1.2902
1.5	0.8440	1.0545	1.0306	1.2691
1.6	0.8315	1.0348	1.0122	1.2481
1.7	0.8191	1.0151	0.9930	1.2272
1.8	0.8068	0.9955	0.9739	1.2066
1.9	0.7948	0.9762	0.9552	1.1863

TABLE II. The $l=1$ phase shifts (in rad) for e, Li^+ modified Coulomb scattering.

$k(a_0^{-1})$	Static	Static-exchange	SCE	NCS
0.1	0.0346	0.1108	0.1413	0.5578
0.2	0.0354	0.1130	0.1429	0.5555
0.3	0.0369	0.1164	0.1455	0.5520
0.4	0.0388	0.1210	0.1489	0.5478
0.5	0.0412	0.1266	0.1529	0.5430
0.6	0.0441	0.1329	0.1574	0.5380
0.7	0.0474	0.1399	0.1621	0.5330
0.8	0.0510	0.1470	0.1668	0.5281
0.9	0.0550	0.1543	0.1716	0.5232
1.0	0.0591	0.1615	0.1761	0.5184
1.1	0.0636	0.1685	0.1805	0.5138
1.2	0.0682	0.1752	0.1847	0.5093
1.3	0.0728	0.1815	0.1885	0.5049
1.4	0.0777	0.1874	0.1921	0.5007
1.5	0.0824	0.1928	0.1953	0.4966
1.6	0.0874	0.1977	0.1984	0.4927
1.7	0.0911	0.2021	0.2010	0.4888
1.8	0.0970	0.2061	0.2036	0.4852
1.9	0.1017	0.2096	0.2058	0.4815

where I is the ionization potential in Ry and $\rho(\vec{r})$ is the total electronic density of the target. Two special cases of this potential occur when $F(\eta)$ is replaced by $\eta^{3/4}$ or by $\eta^{24/5}$. These are expressed in a general form, the X_α potential,

$$V_s = -\frac{3}{2\pi} \alpha_x [3\pi^2\rho(\vec{r})]^{1/3}, \quad (11)$$

TABLE III. The $l=2$ phase shifts (in rad) for e, Li^+ modified Coulomb scattering.

$k(a_0^{-1})$	Static	Static-exchange	SCE	NCS
0.1	0.00041	0.0011	0.0022	0.0552
0.2	0.00045	0.0012	0.0024	0.0602
0.3	0.00053	0.0015	0.0029	0.0681
0.4	0.00066	0.0018	0.0035	0.0782
0.5	0.00083	0.0023	0.0042	0.0901
0.6	0.0011	0.0029	0.0052	0.1028
0.7	0.0014	0.0037	0.0063	0.1159
0.8	0.0017	0.0046	0.0076	0.1287
0.9	0.0022	0.0058	0.0090	0.1409
1.0	0.0027	0.0071	0.0106	0.1524
1.1	0.0033	0.0086	0.0123	0.1628
1.2	0.0041	0.0101	0.0141	0.1724
1.3	0.0049	0.0120	0.0160	0.1809
1.4	0.0059	0.0139	0.0181	0.1886
1.5	0.0068	0.0160	0.0201	0.1954
1.6	0.0081	0.0181	0.0224	0.2015
1.7	0.0092	0.0204	0.0245	0.2067
1.8	0.0107	0.0227	0.0268	0.2115
1.9	0.0120	0.0251	0.0290	0.2155

where α_x is 1 or $\frac{2}{3}$, respectively. When I of Eq. (10e) is replaced by zero, such that $K \rightarrow k^2$ at large r , then we have the asymptotically adjusted FEGE (AAFEGE) potential. We note that at zero energy ($k^2=0$), $F(\eta)=\frac{1}{2}$ at all r for the AAFEGE potential, in agreement with the $\alpha_x=\frac{2}{3}$ form of Eq. (11). When a Coulomb tail is present, then I should be replaced by $-2/r$ in the AAFEGE approximation. In this case V_H is distinct from V_s at all energies. The e , Li^+ s -wave phase shift (see Fig. 1) and Li ($2S$) photoelectric cross section show slight differences for the FEGE or AAFEGE approximations. However, the e , Li^+ p -wave phase shift does reflect a significant difference (Fig. 2) at small energies. In the Cs calculations we have used the AAFEGE throughout.

Additional remarks should be made about the definitions of V [Hartree potential of Eq. (1b)] and $\rho(\vec{r})$ of Eq. (11) in the $X\alpha$ model. It turns out that Hartree-Slater (HS) calculations for atomic structures²⁵ in this model replace the second term on the rhs of Eq. (1b), which is the average interaction of the ejected (scattering) electron with the ionic core electrons, with the average interaction of the ejected (scattering) electron with the electrons of the neutral atom, when the latter is calculated using bound HS orbitals which are made self-consistent for a given energy. Likewise, Eq. (11) is calculated using $\rho(\vec{r})$ belonging to the self-consistent field neutral atom. Equation (1b), so modified, decays exponentially. The potential $V+V_s$ is forced to be asymptotically correct by the "Latter tail" procedure,²⁶ which is just the replacement of the modified $V+V_s$ with $-1/r$ at a radius r_0 at which the former becomes less attractive than the latter. This procedure is also used in the self-consistent-field determination of the orbitals used to calculate V and V_s .

There are examples in the literature, however,

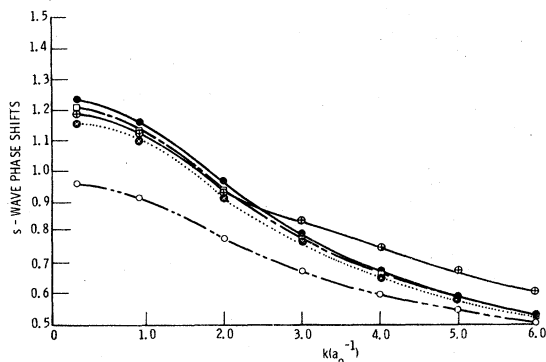


FIG. 1. e , Li^+ s -wave phase shifts for modified Coulomb scattering. \circ : Static (S); \times : Free-electron gas exchange (FEGE); \oplus : Modified Slater (MS); \square : Semiclassical exchange (SCE); \bullet : Static exchange (SE).

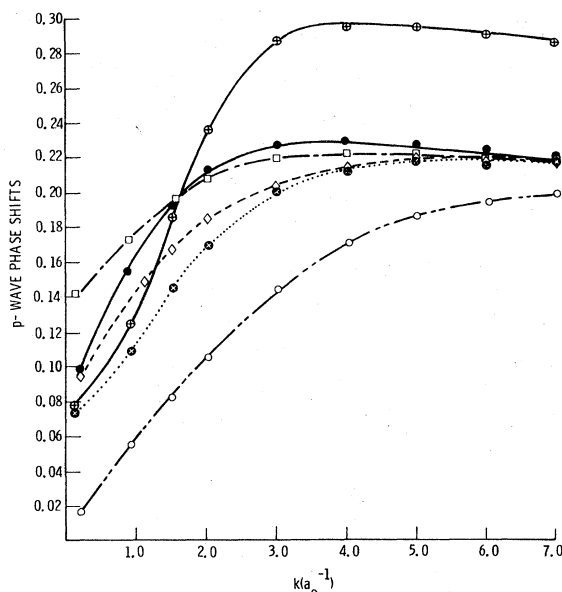


FIG. 2. e , Li^+ p -wave phase shifts for modified Coulomb scattering. Symbols same as in Fig. 1.

for use of the Slater X_α exchange potential (called NCS for no cutoff Slater) in e -atom scattering²⁷ and photoionization²⁸ in which, for the latter process, Eq. (1b) is used unmodified and $\rho(\vec{r})$ of Eq. (11) is calculated using the target atom or ion orbitals. We have included these results for Li (Figs. 3-6 and Tables I-III) and find that the results are quite bad owing to the spuriously long range of $\rho(\vec{r})^{1/3}$ in V_s . Riley and Truhlar¹ have noted a factor-of-2 error in the exchange correction for the e , Ar phase shifts of Ref. 27, presum-

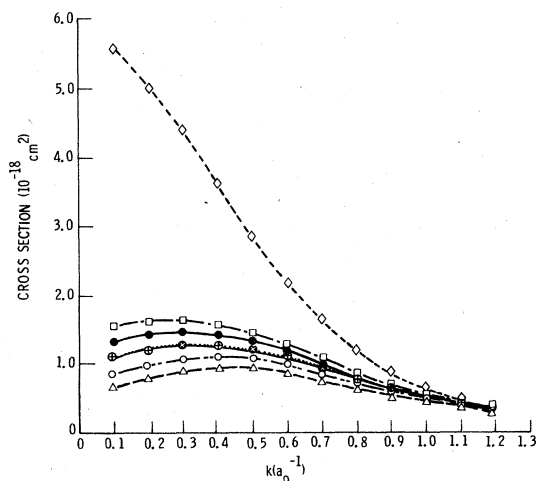


FIG. 3. $\text{Li}(2s)$ photoelectric cross section. \diamond : No cutoff Slater (NCS); \triangle : Coulomb (C); other symbols same as in Fig. 1.

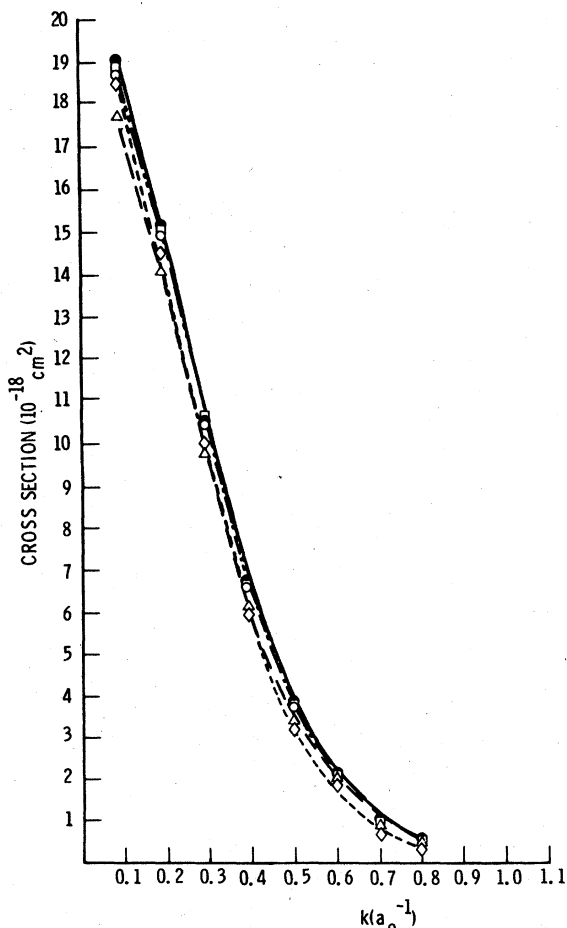


FIG. 4. Li(2p) photoelectric cross section. Symbols same as in Figs. 1 and 3.

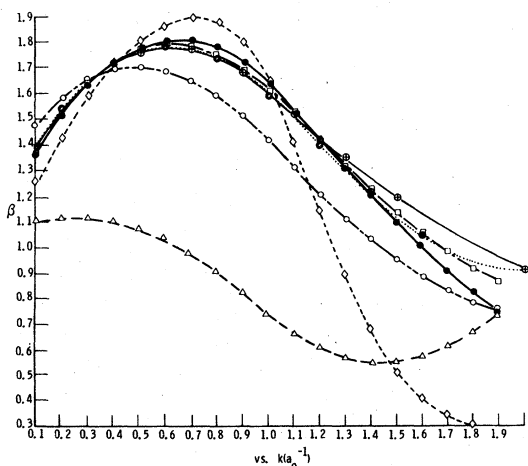


FIG. 5. Li(2p) asymmetry parameter. Symbols same as in Figs. 1 and 3.

ably caused by the spuriously long-range attraction. When the latter procedure [i.e., Eq. (1b) replaced by the Hartree potential for Li targets, calculation of V_s using $\rho(\vec{r})$ for Li, and matching the modified $V+V_s$ to $-1/r$ at r_0] is used, then the results become quite reasonable. We call this set MS (for a modified Slater); however, we remark that this procedure is different from the standard Slater scheme in that we have used HF (Ref. 12) rather than HS (Ref. 25) orbitals for Li. We expect this difference to be slight. MS calculations for Li were made for $\alpha_x = \frac{2}{3}$ in Eq. (11) (Figs. 1-5), and standard Slater $X\alpha$ calculations for Cs were made for $\alpha_x = 1$ in Eq. (11) (Figs. 7-9). The latter choice was made in order to reproduce the results of Ref. 5 for the Cs (5D) photoelectric cross section.

The theory is the same for Cs when the rhs of Eq. (1a) is replaced by one of the local-exchange potentials and when the electronic density is that for Cs^+ or Cs, as appropriate. Specifically, in Eq. (1b) the number 3 is replaced by 55 and $2u_{1s}^2$,

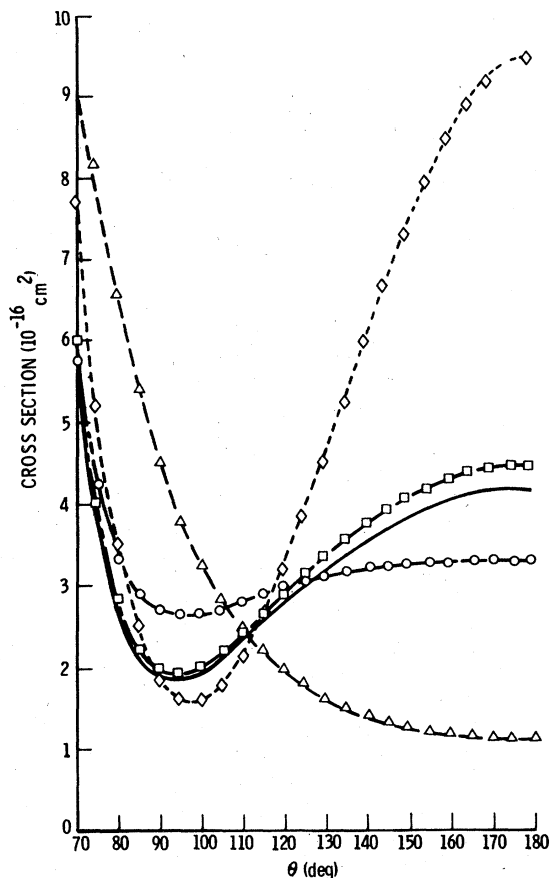


FIG. 6. e, Li^+ angular distribution at $k = 0.5a_0^{-1}$. Solid curve: SE; other symbols same as in Figs. 1 and 3.

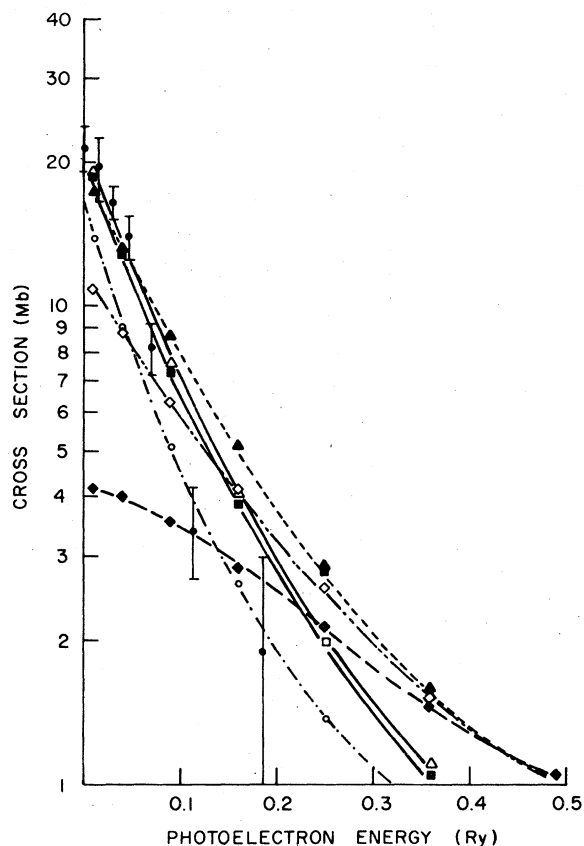


FIG. 7. Cs(6*p*) photoelectric cross section. \blacklozenge : S, no polarization; \diamond : S, with polarization; \circ : X α ; \blacktriangle : SCE, no polarization; \blacksquare : asymptotically adjusted free-electron gas (AAFEGE), with polarization; \square : SCE, with polarization; \blacklozenge : data of Ref. 30.

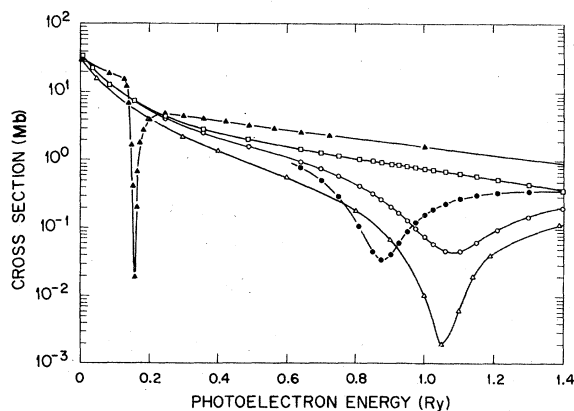


FIG. 8. Cs(5*D*) photoelectric cross section. \blacktriangle : X α ; \triangle : Dirac-Hartree-Fock (DHF) results of Ref. 32; \square : S; \circ : SCE; \bullet : AAFEGE.

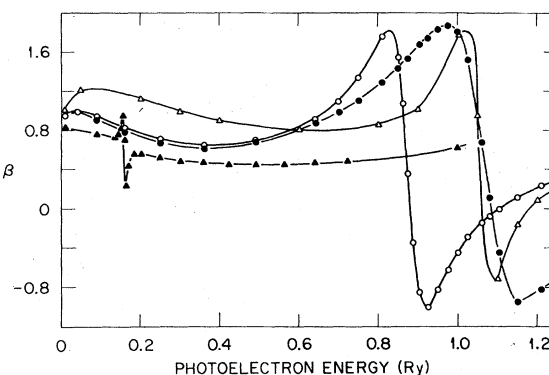


FIG. 9. Cs(5*D*) asymmetry parameter. \blacktriangle : X α ; \circ : AAFEGE; \bullet : SCE; \triangle : DHF.

is replaced by [see Eq. (8b)]

$$\alpha_d^2 = 2 \left(\sum_{n=1}^5 u_{ns}^2 + 3 \sum_{n=2}^5 u_{np}^2 + 5 \sum_{n=3}^4 u_{nd}^2 \right), \quad (12)$$

where the u_{nl} 's are numerical HF orbitals,¹³ or, in the case of the X α model, the u_{nl} 's are generated from a HS calculation²⁵ for the initial-state orbitals, and the spherically averaged contribution of the orbital photoionized, namely $u_{nl}^2/(2l+1)$, is added to the rhs of Eq. (12).

III. RESULTS FOR Li

Our results for $\sigma(2s)$, $\sigma(2p)$, $\sigma(2d)$ and $I_{sc}(\theta)$ in the various approximations are displayed in Figs. 1–4, respectively. For $\sigma(2p)$ it has been necessary to Schmidt orthogonalize the s wave to the $1s$ core of Li, producing a small but non-negligible effect on $\sigma(2p)$. The phase shifts for the s , p , and d partial waves in the various approximations are given in Tables I–III, respectively, and in Figs. 1 and 2. In the static-exchange approximation, these were obtained by solving Eq. (1a) iteratively until the phase shifts were unchanged in the fourth decimal place. We compare our p -wave shifts (Table II) against those of Matese and Labahn¹⁸ and note that we obtain agreement to three places. We obtain two-place agreement with the s -wave phase shifts of Bhatia *et al.*²¹, however, we note that the latter authors use different choices for u_{1s} and u_{2s} . We also note the excellent agreement of our static-exchange $\sigma(2s)$ with that of Matese and Labahn¹⁸ in the same approximation.

In Table II we note the very large error in the NCS approximation p -wave phase shifts. The large p -wave error is also reflected in $\sigma(2s)$, which is about a factor of 4 too large near threshold. In contrast, the s -wave phase shifts (Table I) show a smaller error. However, the d -wave phase shifts (Table III) shows a very large NCS approxi-

mation error. This d -wave error seriously affects the accuracy of $\sigma(2p)$ and $\beta(2p)$ above 1 Ry.

We believe that the relatively small s -wave error derives from the unimportance of the exchange relative to the static potential for *this partial wave*. For example, the static s -wave phase shift is only 22% too small, while the NCS approximation s -wave phase shift is 17% too large at $k=0.1a_0^{-1}$ (Table I). The importance of the static potential is a result of the s -wave probe of the small- r part of the potential where it tends to be dominated by its static component. On the other hand, the static phase shifts are much too small for p and d waves, which probe the region of the potential farther from the nucleus. At the same time the accurate $l > 0$ phase shifts are not very large; however, too much large- r attraction in the NCS potential results in $l > 0$ phase shifts which are much too large. It appears that this overestimate derives from the spuriously long range of the Slater potential. The nonlocal nature of the exact exchange potential makes its large- r behavior difficult to analyze. However, the large- r behavior of the SCE potential is easily deduced.¹ When α_d^2 is small relative to $k^2/s - V(r)$, then the leading term of the SCE potential is

$$V_{\text{SCE}} \approx -\frac{1}{4} [k^2/2 - V(r)]^{-1} \alpha_d^2. \quad (13)$$

Thus it falls off as α_d^2 or as $u_{1s}(r)^2$, while the NCS potential falls off more slowly as $u_{1s}(r)^{2/3}$. We can easily check this point numerically. At $k = 0.5a_0^{-1}$ and $r = 1.35, 2.02, \text{ and } 3.03a_0$ the deviation of the SCE potential from the Coulomb tail is about 5.5, 0.4, and 0.004%, respectively, while the deviation of the NCS potential is about 23, 13, and 4%, respectively.

The dominance of the $2p \rightarrow kd$ dipole amplitude and the small deviation of the d wave from a Coulomb wave at $k = 0.1a_0^{-1}$ are responsible for the good agreement of *all* of the results near threshold for $\sigma(2p)$ (Fig. 4). In fact, the $2p \rightarrow kd$ amplitude is nearly a factor of 3 larger than the $2p \rightarrow ks$ amplitude at $k = 0.1a_0^{-1}$ by all methods of calculation except the pure Coulomb wave calculation, where it is a factor of 20 larger. Thus from Eq. (3c), $2d_{12}^2$ is nearly a factor of 18 larger than d_{10}^2 and a factor of 800 larger for modified Coulomb and Coulomb waves, respectively. Thus we note (Fig. 4) that the Coulomb approximation $\sigma(2p)$, which is an almost pure d -wave contribution, is somewhat smaller than the $\sigma(2p)$'s of the other approximations, owing to a small but non-negligible s -wave contribution in the latter. However, the huge $2p \rightarrow ks$ error in the Coulomb approximation shows up in $\beta(2p)$ (Fig. 5), which we note has nearly the d -wave limit of $\beta(2p) = 1$ [Eq.

(6a)]. By $k = 1.0a_0^{-1}$ the exact static-exchange and SCE $2p \rightarrow ks$ and $2p \rightarrow kd$ amplitudes are about equal in magnitude, but the NC Slater approximation d wave is seriously in error, showing too large a departure from a Coulomb wave (Table III), causing $\sigma(2p)$ to be too small by a factor of 2. This large $2p \rightarrow kd$ amplitude error is also reflected in $\beta(2p)$ above 1 Ry (Fig. 5). Perhaps surprisingly this incorrect behavior is due almost wholly to the error in the $2p \rightarrow kd$ dipole amplitude, owing to the accidental cancellation of individual errors in the s - and d -wave phase shifts when their difference is found [Eq. (6b)].

Finally we note that near threshold our $\sigma(2p)$ in the static-exchange approximation is about 20% larger than that of Gezalov and Ivanova.¹⁵ There are some differences, however, between the two calculations. The latter authors have used an approximate normalization based on fitting their radial waves to the WKB radial waves at large r , where the latter are calculated using only the static potential. Our normalization, on the other hand, is based on Eq. (2) and requires an independent determination of the phase shifts.

Figure 6 shows the e, Li^+ angular distribution at $k = 0.5a_0^{-1}$ using Eq. (7) and the phase shifts of Tables I-III. The large NCS approximation error for back scattering is due primarily to the large p -wave error at this energy. This error causes the s - and p -wave constructive interference to be exaggerated relative to that of the exact static-exchange and SCE results.

IV. RESULTS FOR Cs

We display our results for the Cs $6p$ -state photoelectric cross section in Fig. 7 and for the Cs $5d$ -state photoelectric cross section and asymmetry parameter in Figs. 8 and 9. For CS ($6p$), formulas analogous to Eqs. (3c) and (3d) are used, where $-\epsilon_{op}$ is replaced by the experimental ionization potential.¹⁴ For Cs ($5d$),

$$\sigma(5d) = \frac{4\pi}{15} \alpha \alpha_0^2 (k - \epsilon_{5d}) k (2d_{21}^2 + 3d_{23}^2), \quad (13a)$$

$$\beta(5d) = \frac{\frac{2}{5}(d_{21}^2 + 6d_{23}^2 - 18d_{21}d_{23}\cos\Delta\eta)}{2d_{21}^2 - 3d_{23}^2}, \quad (13b)$$

$$\Delta\eta = \sigma_1 + \eta_1 - \sigma_3 - \eta_3, \quad (13c)$$

where the phase shifts and radial dipole amplitudes of Eqs. (13) are defined analogously to Eqs. (2), (3), and (6). In Eq. (13a), $-\epsilon_{5d}$ is replaced by the experimental ionization potential.¹⁴

For $\sigma(6p)$ we have used the two-parameter polarization potential of Norcross²⁹ in order to obtain good agreement with the data of Nygaard *et al.*³⁰ Ortho-

gonalization of the s and d waves to the Cs occupied orbitals of the same symmetry was found to be negligible, as was the deviation from orthonormality of the Cs⁺ and Cs orbitals.³¹

For σ ($5d$) we note the unimportance of exchange near threshold. As in σ ($2p$) for Li, this is due to the dominance of the $(l_0 + 1)$ -wave dipole amplitude (where l_0 is the angular momentum of the initial orbital). Exchange is of minimal importance at low energies in the f wave (and in the d wave for Li) because the centrifugal barrier tends to push the radial wave outside the range of the exchange potential. Thus the big defect of the Slater model is its too attractive exchange, leading to the spurious 0.16 Ry resonance (Figs. 8 and 9). In the range of energies studied a resonance does not appear in the static-approximation cross section, presumably owing to the weakness of static-potential attraction in the region of r in which a "potential" or "shape" resonance can be supported. Use of the other exchange potentials causes a shift of the resonance from 0.16 Ry to a range from about 0.9 to 1.1 Ry, in qualitatively better agreement with Dirac-Fock (DF) results.³² The resonance causes a minimum in the cross section (Fig. 8), according to all of the calculations. The f -wave amplitude passes rapidly through zero with energy. This causes the entire cross section at the minimum to be due to the small p -wave amplitude.

Near the resonance, neither of the improved exchange models shows quantitative agreement with the DF results, and their mutual agreement is poor. On the far low-energy side of the resonance their mutual agreement is good. (The relative importance of relativistic and exact exchange effects has not been unraveled in the DF

calculation; thus an exact HF calculation would provide a more apt comparison.) The poor mutual agreement of the exchange models leads us to be pessimistic that any approximation to exchange is likely to be reliable for resonant cross sections, especially if the resonance appears as a deep minimum in the cross section. Presumably it is the smallness of the different cross sections of Fig. 8 at their respective minima which causes inherent errors belonging to the different exchange approximations to be greatly magnified.

Schmidt orthogonalization of the p wave to Cs orbitals was significant only for Cs $5p$ (although all were included in the calculations). The f -wave dominance near threshold thus causes orthogonalization to be negligible; however, at higher energies, when the p -wave contribution becomes appreciable, orthogonalization is important. Near the minimum, where the f -wave amplitude passes through a zero and the p wave gives the entire contribution, the orthogonalization can cause differences of a factor of 2 or more. However, as suggested above, it is unlikely that any independent-electron theory, including the DF, is likely to be very accurate for calculating such small cross sections.

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