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Electron-impact ionization cross sections for excited states of the rare gases (Ne, Ar, Kr, Xe), cadmium, and mercury

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Cross sections have been calculated for electron-impact ionization of singly excited states of the rare gases (neon, argon, krypton, xenon), cadmium, and mercury. The calculations are based upon the symmetric binary-encounter model, together with a semiempirically determined momentum distribution function for the bound, excited electron. Good agreement is obtained with the available experimental data, as well as with existing theoretical results, in the low- to intermediate-energy range.

I. INTRODUCTION

Electron-impact ionization of excited atomic states can play an important role in determining the characteristics of laser plasmas. For example, an understanding of discharge stability in high-power electronic transition lasers[1] requires a knowledge of excited-state ionization cross sections, as does the ability to model the detailed kinetics of the laser medium. Calculations have therefore been carried out to obtain the relevant ionization cross sections for a number of atomic species of current interest, specifically the rare gases (neon, argon, krypton, xenon), cadmium, and mercury.

The calculations are based upon the symmetric binary-encounter model.[2] The cross section is averaged over the quantum-mechanical momentum distribution function of the initially bound, excited electron, with the required configuration-space wave function determined from a semiempirical "scaled-effective-charge" method.[3,4] The present theoretical results are found to be in good agreement with the available experimental data, as well as with existing calculations, in the low- to intermediate-energy range.

II. THEORETICAL METHOD

It is convenient to introduce the dimensionless variables[5,6]

$$s^2 = v_i^2/u\,, \quad t^2 = v_b^2/u\,, \tag{1}$$

where v_i and v_b are the velocities, in atomic units, of the incident and bound electrons, respectively, and u is the ionization or binding energy in rydbergs. The cross section, in the symmetric binary-encounter approximation, for ionization of a bound electron with energy ut^2 is then given by[2,6]

$$Q(s,t) = \frac{4}{u^2}\frac{1}{s^2+t^2+1} \times \left(\frac{s^2-1}{s^2} + \frac{2}{3}t^2\frac{s^4-1}{s^4} - \frac{\phi'}{s^2+1}\ln s^2\right)\pi a_0^2\,. \tag{2}$$

The value of ϕ' lies between zero and unity, and is expected to be small for ionization from excited states.[2] We have, in fact, found that the choice $\phi' = 0$ gives the best agreement with experiment for the processes of interest and therefore the last term in the large parentheses of Eq. (2) is neglected for the calculations described below. The final cross section is obtained by averaging expression (2) over the velocity or momentum distribution of the bound electron:

$$\bar{Q}(s) = \int_0^\infty f(t)Q(s,t)u^{1/2}\,dt\,, \tag{3}$$

where $f(t)$ is the momentum distribution function and is thus related to the Fourier transform of the configuration-space wave function. $f(t)$ can be written

$$f(t) = \frac{2}{\pi}ut^2\left|\int_0^\infty r\,dr\,j_l(u^{1/2}tr)\,P_{nl}(r)\right|^2, \tag{4}$$

with $j_l(x)$ the spherical Bessel function and $P_{nl}(r)$ the radial part of the spatial wave function, normalized according to

$$\int_0^\infty P_{nl}^2(r)dr = 1\,. \tag{5}$$

In order to calculate the wave function, $P_{nl}(r)$, we have used a semiempirical method,[3,4] in which the radial Schrödinger equation for the excited electron is written

$$\left[\frac{d}{dr^2} - \frac{l(l+1)}{r^2} + \frac{2}{r}\zeta\left(\frac{r}{\alpha_{nl}}\right) + \tilde{E}_{nl}\right]P_{nl}(r) = 0\,; \tag{6}$$

$\zeta(\rho)$ is the "effective charge" of the atomic core and is given by

$$\zeta(\rho) = (Z-N) + \sum_{j=1}^{N}\int_\rho^\infty \left(1 - \frac{\rho}{\rho'}\right)P_j^2(\rho')d\rho'\,, \tag{7}$$

where Z is the nuclear charge, N is the number of core electrons, and $P_j(\rho)$ are the radial wave functions of the core electrons. For the calculations discussed below, the core functions are taken to be either Hartree-Fock or Hartree-Fock-Slater wave functions for the relaxed ion. The parameter α_{nl} acts as a radial scaling factor, which allows the atomic core to expand or contract slightly to compensate for effects not included in the theory (i.e., exchange, core polarization, etc.); the present method is thus similar in spirit to the scaled Thomas-Fermi approximation.[7] The method is semiempirical in that we choose $\tilde{E}_{nl}$ to be the *experimental* binding energy, thereby ensuring a good representation for the wave function at large r, where the bulk of the charge density is located for the excited electron. Equation (6), together with the boundary conditions $P_{nl}(0)=P_{nl}(\infty)=0$, is then solved numerically for the eigenvalue α_{nl} and the corresponding eigenfunction $P_{nl}(r)$ which is used in Eq. (4) to determine the momentum distribution function.

III. RESULTS AND DISCUSSION

A. Wave functions

It is of interest to compare radial wave functions obtained from the present scaled-effective-charge (SEC) model with those determined from more extensive self-consistent-field methods. We consider first the $\mathrm{Ar}^*(3p^5 4s\,^3P)$ state, for which a fully self-consistent solution to the Hartree-Fock (HF) equations has been obtained by Knox,[8] who has given a tabulation of the $4s$ wave function which is plotted as the solid curve in Fig. 1. In order to simulate the HF function with the SEC method, we set $\tilde{E}_{nl}$ in Eq. (6) equal to the HF eigenvalue[8] ($\epsilon_{\mathrm{HF}}=0.285$ Ry). The core wave functions are taken to be the analytic Hartree-Fock functions for the relaxed Ar^+ $(3p^5)$ ion, as given by Clementi and Roetti.[9] The computed value for the scaling parameter for this case is $\alpha=1.192$, and the corresponding eigenfunction for the $4s$ orbital is shown as the dashed curve in Fig. 1. The two wave functions are seen to agree very well over the entire radial range, including the core region ($r \lesssim 1.6a_0$).

As a second example, we consider the excited mercury atom. We are not aware of any published excited-state wave functions for mercury, and have therefore calculated a self-consistent solution to the coupled Hartree-Fock-Slater (HFS) equations for the Hg^* $(5d^{10}6s6p)$ state, using the Herman-Skillman computer program.[10] The eigenvalue for the $6p$ electron is $\epsilon_{\mathrm{HFS}}=0.2952$ Ry, and the eigenfunction is given as the solid curve in Fig. 2. As before, for the SEC calculation, we set $\tilde{E}_n=\epsilon_{\mathrm{HFS}}$. The core wave functions are taken to the HFS wave functions for the Hg^+ $(5d^{10}6s)$ ion, again computed with the Herman-Skillman program.[10] Solving Eq. (6) gives $\alpha=1.170$, and the wave function is shown as the dashed curve in Fig. 2. The two curves agree reasonably well, although the agreement is not as good as for the Ar^* case. This is due to the fact that the spatial separation between the core and the excited electron for the Hg^* $(5d^{10}6s6p)$ state is not as well defined as for the Ar^* $(3p^5 4s\,^3P)$ state. In particular, there is considerable overlap between the $6s$ electron (nominally in the core) and the excited $6p$ electron.

It is apparent from the preceding discussion that the SEC method can indeed satisfactorily simulate

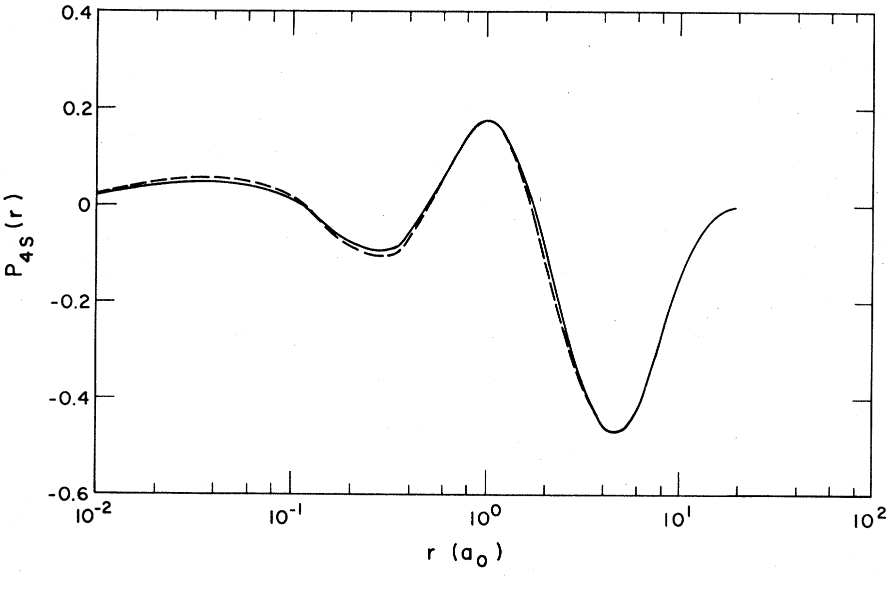

FIG. 1. Radial wave function for the $4s$ orbital of the $\mathrm{Ar}^*(3p^5 4s\,^3P)$ state. Solid curve, Hartree-Fock (HF) theory; dashed curve, scaled effective charge (SEC) theory.

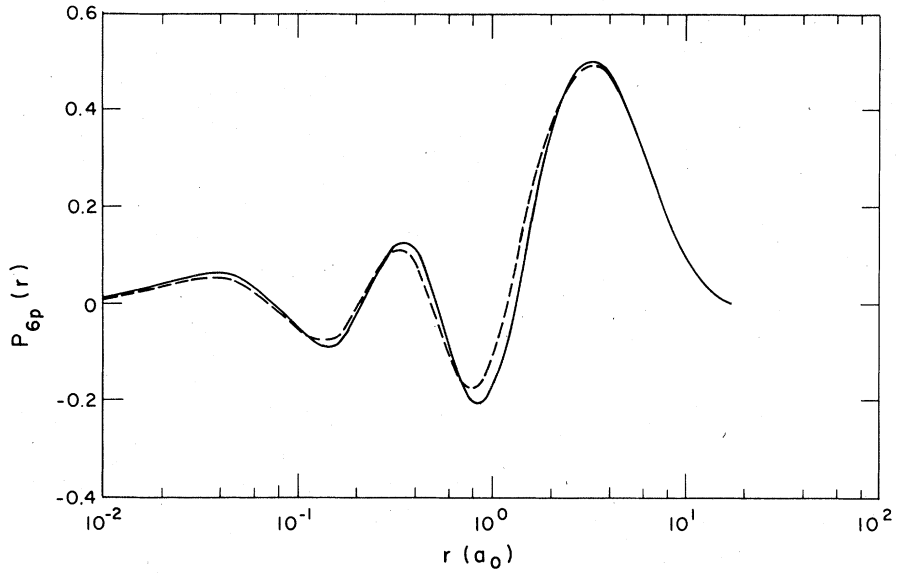

FIG. 2. Radial wave function for the $6p$ orbital of the Hg*($5d^{10}6s6p$) state. Solid curve, Hartree-Fock-Slater (HFS) theory; dashed curve, scaled effective charge (SEC) theory.

wave functions obtained from more elaborate self-consistent-field methods for excited states of complex atoms. It should be emphasized, however, that the Hartree-Fock and Hartree-Fock-Slater theories do not yield particularly accurate binding energies for heavy atoms, and both methods tend to produce wave functions which are spatially too diffuse. This results from the fact that neither theory includes core polarization, relativistic effects, etc. The *semiempirical* SEC method, through the use of the experimental binding energy, attempts to include all of these effects in an approximate way, and is thus better-suited to the problem of interest.

B. Ionization cross sections

Table I lists the excited atomic states for which we have calculated ionization cross sections. Experimental energies for the individual J levels of each configuration or term are taken from the U. S. Natl. Bur. Stand. tables,[11] and a statistically weighted average is carried out to arrive at the average ionization energies listed in column 3. These are the values used in Eq. (6) for $\tilde{E}_{nl}$ (since we are using experimental energies, we also take $u=\tilde{E}_{nl}$). To construct the effective charge $\zeta(\rho)$, the core functions are chosen to be analytic Hartree-Fock wave functions for the relaxed ion, which for Ne$^+$, Ar$^+$, Kr$^+$, Xe$^+$, and Cd$^+$ have been tabulated by Clementi and Roetti.[9] The tables of Ref. 9 do not include mercury and for this case we use HFS wave functions for the Hg$^+$ ion. The calculated eigenvalues of Eq. (6) (i.e., the radial scaling parameters, α_{nl}) are given in the last column of the table. All of the values are reasonably close to unity, which indicates that the corrections to the excited states due to exchange, core polarization, etc., are not too large.

The ionization cross sections, in units of 10^{-16} cm^2, versus incident electron energy in eV are shown in Figs. 3–5, where the solid curves represent the present work and are labeled by the orbital of the excited electron. Our calculations do not include the effects of inner-shell ionization. Electron-impact ionization cross sections for metastable neon and argon have been measured by Dixon *et al.*[12]; their results are shown as the closed circles in Fig. 3 and are in good agreement with our cross sections in the low- to intermediate-energy range. It should be noted that we have not

TABLE I. Ionization energies and scaling parameters.

Atom	State	Average ionization energy (Ry)	Scaling parameter (α_{nl})
Ne	$2p^53s$	0.3601	1.305
	$3p$	0.2186	1.253
Ar	$3p^54s$	0.3063	1.272
	$4p$	0.1946	1.234
Kr	$4p^55s$	0.2970	1.224
	$5p$	0.1859	1.192
Xe	$5p^56s$	0.2802	1.213
	$6p$	0.1761	1.174
Cd	$4d^{10}5s5p\ ^3P$	0.3763	1.223
	$6s\ ^3S$	0.1919	1.217
	$6p\ ^3P$	0.1275	1.198
	$5d\ ^3D$	0.1188	1.296
Hg	$5d^{10}6s6p\ ^3P$	0.3863	1.228
	$7s\ ^3S$	0.1990	1.238
	$7p\ ^3P$	0.1246	1.194
	$6d\ ^3D$	0.1165	1.266

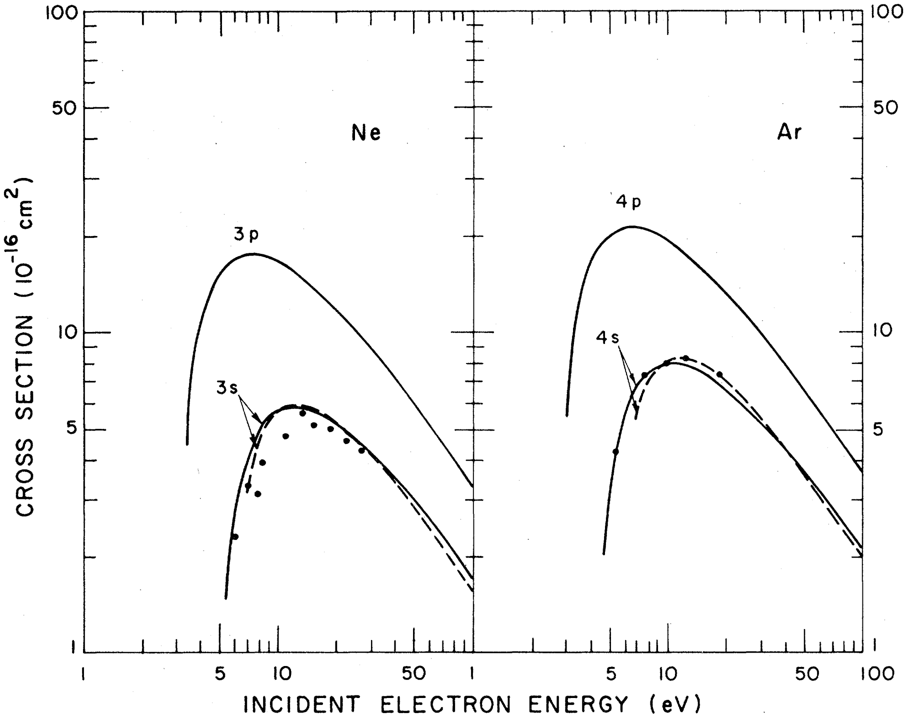

FIG. 3. Electron-impact ionization cross sections for excited states of neon and argon. Solid curves, present theory; dashed curves, Born half-range theory (Ref. 13); closed circles, experimental data (Ref. 12).

included data for incident energies beyond ~30 eV for Ne* and ~20 eV for Ar*, since above these energies inner-shell ionization begins to occur and direct comparison with our theoretical excited-state cross sections becomes invalid. Ton-That and Flannery[13] have calculated ionization cross sections for the metastable rare gases using several different methods. Their Born half-range

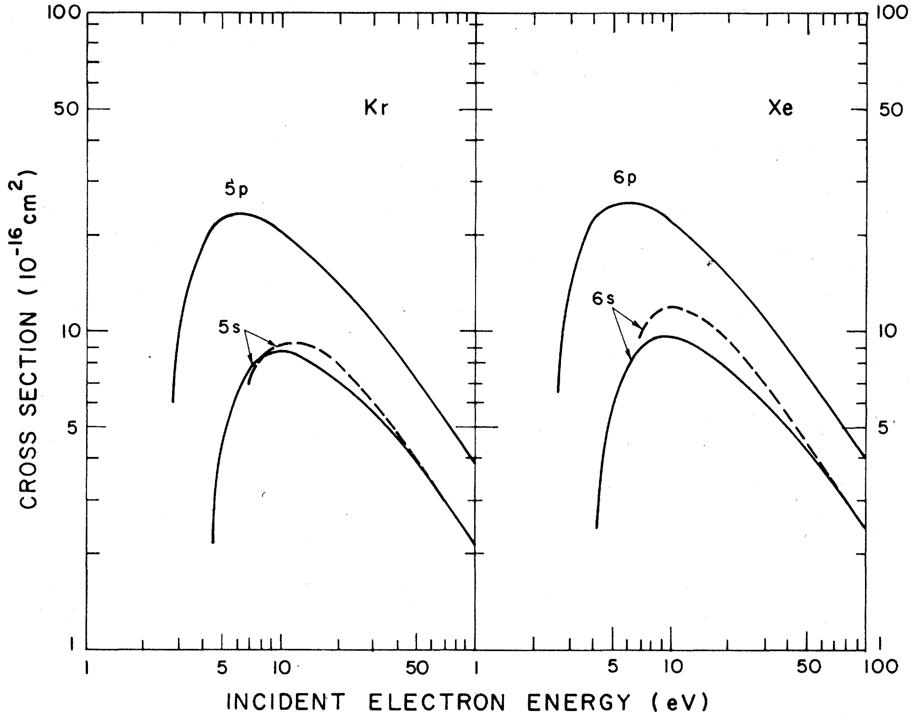

FIG. 4. Electron-impact ionization cross sections for excited states of krypton and xenon. Solid curves, present theory; dashed curves, Born half-range theory (Ref. 13).

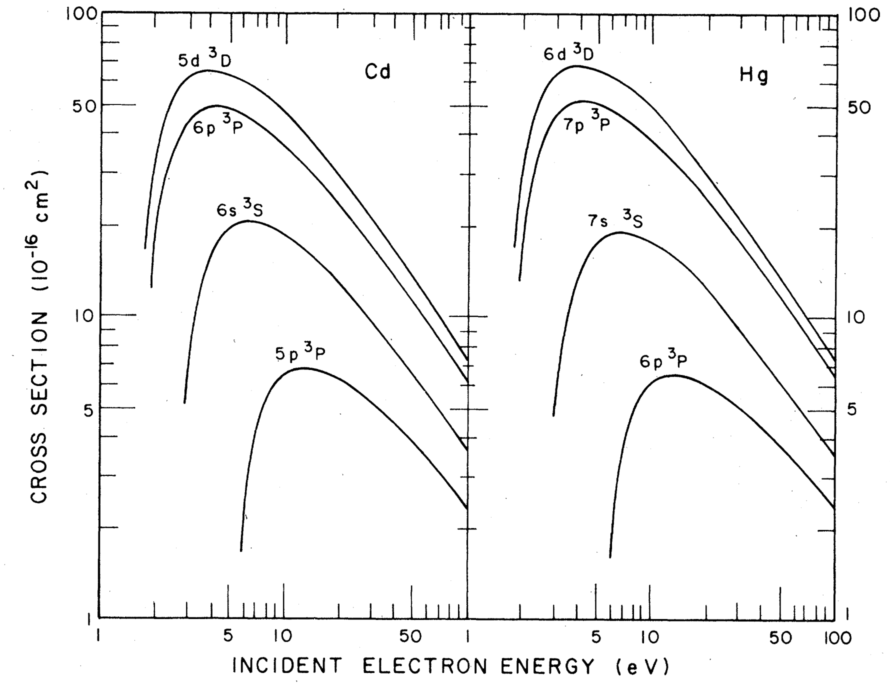

FIG. 5. Electron-impact ionization cross sections for excited states of cadmium and mercury.

results, which gave the best agreement with experiment for Ne* and Ar*, are shown as the dashed curves in Figs. 3 and 4. The present symmetric-binary-encounter theory is in generally good agreement with the Born half-range approximation, although the difference between the two sets of cross sections tends to increase in going from the lighter to the heavier rare gases. In Figs. 3 and 4 we also give the ionization cross sections for the higher-lying np^5 $(n+1)p$ states, which are strongly connected by electron collisions to the np^5 $(n+1)s$ metastable levels.[4] Finally, the results for excited states of cadmium and mercury, which are of importance for understanding certain metal-vapor laser discharges,[1] are shown in Fig. 5. The cross sections for the higher-lying ^3P and ^3D states of Cd* and Hg* are very large due to the small ionization potentials (~1–2 eV) of these levels.

The symmetric binary-encounter theory, together with a semiempirically determined momentum distribution function, appears to be a fairly simple, effective method for obtaining ionization cross sections for excited states of complex atoms, and should thus be useful for a variety of applications.

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