Electron-impact excitation of atomic copper

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Cross sections are calculated for excitation of Cu for elastic scattering of electrons from the $4s$ ground state and for excitation to excited states $3d^9 4s^2$, $4p$, and $4d$. A three-state close-coupling approximation is used for the energy range $3.8 < E < 10$ eV, and a four-state one for $6 < E < 100$ eV. Accurate target functions are used in the expansion. Poor agreement is obtained with renormalized experimental data of Trajmar *et al.*

I. INTRODUCTION

The scattering of electrons by atomic copper is studied for a range of energies between 6 and 100 eV for elastic scattering and for excitation of the laser levels $3d^9 4s^2\,{}^2D$ and $3d^{10}4p\,{}^2P^o$. Copper is predicted[1] to have a high efficiency and to exhibit scalability for use as a metal-vapor laser. A pulsed copper laser is expected to be at least ten times more efficient than the cw argon laser. These predictions come from a laser model[2] which is constructed to reproduce results of a small prototype copper laser. The model requires energy levels, oscillator strengths and excitation, and deexcitation cross sections. However, only conflicting information on the electron-impact excitation cross sections is available due to the difficulty of performing quantitative measurements or reliable calculations.

Normalized electron-collision data for Cu have been obtained by Trajmar *et al.*[3] in a crossed-beam experiment in which they obtain energy-loss spectra at fixed impact energies and scattering angles. Due to the difficulty in determining the metal atom densities in the beam, they devised a four-stage calibration procedure for their experiment. The fourth step depended on the calculated elastic 40° differential cross section at 100 eV of Winter,[4] who used a static exchange approximation.

Borozdin *et al.*[5] measured the cross sections of copper atoms for excitation by electron impact in a crossed-beam experiment. The relative error claimed is 35—40% for $4s$-$4p$ spectral lines at 324.8 and 327.4 nm and for $3d^9 4s^2$-$4p$ spectral lines at 510.6, 570.0, and 578.2 nm. Cross sections were made absolute by comparing the radiation with that of lines of nitrogen which was present as a residual gas of known density.

Absolute effective electron-impact excitation cross sections have also been measured by Aleksakhin *et al.*[6] in a crossed-beam experiment. The relative error claimed is no more than 40% for $4s$-$4p$ spectral lines at 324.8 and 327.4 nm and no more than 30% for $3d^9 4s^2$-$4p$ spectral line at 510.6 nm. Cross sections were made absolute by comparing the radiation with that of a standard source, a ribbon-filament lamp (in the visible spectral region) and a hydrogen lamp (in the ultraviolet).

Neither Ref. 5 nor Ref. 6 gives an estimate of the reliability of their determination of the density of copper atoms. Borozdin *et al.* determine this density by weighing the layer deposited on the surface of the atomic collector during a specified time interval. Aleksakhin *et al.* use a radioengineering method.

Previous calculations include elastic differential cross sections at energies ≥ 100 eV obtained by Fink and Ingram[7] who described the ground-state target atom by a Hartree-Fock-Slater wave function and the scattered electron was obtained in a relativistic nonexchange approximation. Calculations for excitation of ^2D and $^2P^o$ were carried out by Leonard,[8] who used a classical Gryzinsky model, and by Trainor *et al.*,[9] who used an impact parameter model. Winter[4] used a Born approximation and, for excitation of ^2D only, Smith and Wade[10] presented preliminary close coupling calculations in which the ground state and the two lasing states were included. Peterkop and Liepinsh[11] used a Born approximation to calculate excitation to several excited states at incident-electron energies up to 600 eV. Atomic functions were determined by an analytical independent particle model of Green *et al.*[12] Winter and Hazi[13] used experimental transitional energies and oscillator strengths in an impact parameter formula, in which the minimum impact parameter is determined so that the Born and impact parameter method give the same $4s \rightarrow 4p$ cross section at 200 eV.

The two major limiting factors on the accuracy achieved by a close-coupling approximation are the number of states included in the close coupling expansion and the choice of atomic states to be used in the expansion. We use an accurate description of the target wave function. Electron-impact excitation cross sections are calculated in three-state and four-state close-coupling approximations for elastic scattering and for excitation of the states $3d^9 4s^2$, $4p$, and $4d$. In our calculation, orbitals are used to describe the target which yield reliable oscillator strengths, f, for the resonance transition $4s$-$4p$. The wave function detailed in Sec. II gives an oscillator strength of $f=0.644$ in both the dipole length and the dipole velocity approximations.

Since cross sections at large values of angular momen-

tum L are directly proportional to the oscillator strength calculated in the dipole length approximation, and inversely proportional to the energy difference between the states, we anticipate that in the high energy limit, where the Bethe approximation is valid, we would obtain a $4s$-$4p$ excitation cross section accurate to 10%. At low electron-impact energies, we investigate the effect of adding $3d^{10}4d$ state to the close-coupling expansion. Further, we are encouraged by the very good agreement between theory and experiment for copperlike Zn^+ for the energy range $15 < E < 100$ eV. Absolute emission cross sections were obtained by Rogers *et al.*[14] in a crossed-beam experiment. When cascade contributions are included in a calculation, very good agreement is obtained with a close-coupling approximation of Msezane and Henry,[15] who included the states $4s$, $4p$, $3d^9 4s^2$, $5s$, and $4d$.

In Sec. III, we compare our close-coupling results with the Born approximation calculations of Peterkop and Liepinsh,[11] the static exchange and Born calculations of Winter,[4] and the impact parameter calculations of Winter and Hazi.[13] Also, comparison is made with the measurements of Trajmar *et al.*,[3] and Aleksakhin *et al.*[6]

II. WAVE FUNCTIONS

We construct target wave functions for Cu such that the oscillator strengths for $(4^2S$-$4^2P^o)$ calculated in the dipole length (f_L) and dipole velocity (f_v) approximations are the same and are close to the experimental values of 0.65 ± 0.065 (Bieniewski and Krueger[16]) and 0.633 (Ashenfelter[17]) and compare well with the multiconfiguration Hartree-Fock (MCHF) calculated value of 0.624 by Froese Fischer.[18] In addition, we require that the energy splitting between the ground state and various excited states be reasonably close to observed splittings.[19] Table I indicates that these conditions are satisfied very well. The value we obtain for both f_L and f_v is 0.644.

We use a configuration-interaction wave function to represent the ground ^2S state as

$$0.9918\ 3d^{10}4s + 0.1270\ 3d^9 4s\,4d + 0.0108\ 3d^9 4p\,4f + 0.0074\ 3d^9 4p^2 + 0.0050\ 3d^9 4s\,5d\,.$$

The excited ^2D states are represented by

$$-0.9995\ 3d^9 4s^2 + 0.0300\ 3d^{10}4d + 0.0005\ 3d^{10}5d$$

and

$$0.0300\ 3d^9 4s^2 + 0.9994\ 3d^{10}4d + 0.0153\ 3d^{10}5d\,.$$

TABLE I. Energy levels (in a.u.) and oscillator strengths for Cu I, relative to the ground state.

	Calculation	Experiment (Ref. 19)
$3d^{10}4s$	0	0
$3d^9 4s^2$	0.0660	0.0510
$3d^{10}4p$	0.1306	0.1391
$3d^{10}4d$	0.2180	0.2275
$3d^{10}4s$-$3d^{10}4p$	f_L 0.644	0.65 ± 0.065[a]
	f_v 0.644	0.633[b]

[a]Bieniewski and Krueger (Ref. 16).
[b]Ashenfelter (Ref. 17).

The excited $^2P^o$ state is represented by a single configuration $3d^{10}4p$. In the above, the inert core $1s^2 2s^2 2p^6 3s^2 3p^6$ has been omitted for conciseness in notation. The $4d$, $4f$, and $5d$ orbitals may be considered as contracted functions or correlation-type, whereas $4s$ and $4p$ are spectroscopic-type orbitals. Froese Fischer[18] observed that since there are ten $(3d,4l)$ pairs compared to six $(3p,4l)$ pairs, correlation with the $3d^{10}$ group contributes the major correlation effect. Thus, the $3d^{10}$ is expressed as a combination of $3d^{10}$ and $3d^9 4d$ and we obtain the configuration interaction wave functions given above. Correlation effects are significant in that they reduce Hartree-Fock values by more than 50% from $f = 1.16$ to 0.624.

The orbitals required to describe the wave functions are given in Table II. To generate them we start with the Clementi and Roetti[20] $1s$, $2s$, $2p$, $3s$, $3p$, $3d$, and $4s$ exponents and coefficients for Cu. Due to a dimension constraint in our version of the Clementi computer code, we reduce the basis set of s-type symmetry from 11 to 10 and then reoptimize the exponents with respect to the $4s^2\,^2D$ state. The total energy for Cu is evaluated and found to be approximately the same as given by Clementi and Roetti. Final optimization is achieved by slight adjustment of the last exponent of the $3d$ orbital to which the energy of the $4s^2\,^2D$ state is very sensitive. The resultant optimized exponents and coefficients of the orbitals from $1s$ through $4s$ are then used as input to the program CIV3 of Hibbert.[21] Excited orbitals $4p$, $4d$, $5d$, and $4f$ are obtained and optimized one at a time in this order.

The desired excited orbitals $4p$ and $4d$ are fixed and the remaining excited orbitals $5d$ and $4f$ are treated as correlation-type orbitals which are to be varied. Initially, a large number of configurations is added on both the

TABLE II. Coefficients and exponents for some orbitals for Cu I.

$$P_{nl}(r) = r^l \sum_{i=1}^{n-l} a_i r^i e^{-\alpha_i r}$$

nl	a_1	a_2	a_3	α_1	α_2	α_3
$4p$	32.018 93	−66.717 57	0.024 12	13.523 88	9.960 58	0.710 04
$4d$	10.572 98	−0.040 04	0	4.484 92	0.795 47	0
$4f$	12.785 69	0	0	2.861 76	0	0
$5d$	1951.526	−195.314	0.000 06	10.784 92	5.785 47	0.870 00

$4s\ ^2S$ and the $4p\ ^2P^o$ states without varying the $5d$ and $4f$ orbitals. The total energy of Cu decreased but f_L and f_V remained unequal. The exponents of the $5d$ and $4f$ orbitals are then adjusted and important configurations arising from these correlation-type orbitals are identified. The final number of configurations retained on the $4s\ ^2S$ and $4p\ ^2P^o$ states to ensure the equality of f_L and f_V and the appropriate energy spacing is 5 and 1, respectively. Additional configurations on the $4p\ ^2P^o$ state have insignificant effect on f_L and f_V and so they are omitted. (Note, we could not obtain a reasonable energy splitting between the ground $4s\ ^2S$ and the various excited states, particularly the $4s^2\ ^2D$ state, when we optimized on the $4s\ ^2S$ state even with a very large number of configurations, nor could we obtain reasonable agreement between f_L and f_V).

III. CROSS SECTIONS

The integro-differential equations which arise in the close-coupling approximation are solved using a noniterative integral-equation method[22] (NIEM). The basic step size at small values of the radial distance r is $0.0017a_0$. Exchange terms are neglected at $r=19.9a_0$, where the longest-ranged orbital has fallen to less than 10^{-3}.

Partial cross sections for the forbidden ^2S-^2D transition fall off rapidly with increasing total angular momentum L and truncation of the partial sum at $L=18$ is sufficient to achieve a cross-section sum accurate to 1% at the highest energy considered. For the optically allowed ^2S-$^2P^o$ cross section, values of L up to 50 are retained to converge the sum to within 1%. For $L \geq 9$, the nonexchange close-coupling equations are solved by the NIEM method. For $L \geq 20$, a unitarized Born approximation is used. At the highest energies, where $L \geq 40$ is needed, the Bethe approximation is used to obtain the contribution from the highest partial waves.

Table III gives cross sections for elastic scattering and for excitation of $4p$, $3d^9 4s^2$, and $4d$ as a function of incident energy E (eV). Calculations are made in a four-state close-coupling approximation with the target wave function described in Sec. II. Optically forbidden cross sections $4s \rightarrow 3d^9 4s^2$ and $4s \rightarrow 4d$ are found to depend approximately inversely with energy for large energies. The optically allowed cross section $4s \rightarrow 4p$ increases with increasing energy as $E^{-1} \ln E$.

Figure 1 gives cross sections for $4s \rightarrow 4p$ as a function of incident energy. Curves A and B represent Born approximation calculations of Winter[4] and Peterkop and Liepinsh,[11] respectively. A semiclassical impact parameter calculation of Winter and Hazi[13] is given as curve C. Curves D and E represent present three-state and four-state close-coupling calculations. Renormalized measurements of Trajmar *et al.*[3] are given by the open circles. This renormalization is obtained by requiring the measured differential cross sections below 15° to follow the shape of our calculated four-state close-coupling approximation results.[23] In addition, an energy independent normalization factor of 0.36 has been applied to each measured point. This factor was obtained by Msezane and Henry[24] on comparing generalized oscillator strengths obtained in their calculations with those measured. Measurements of Aleksakhin *et al.*[6] are represented by open triangles.

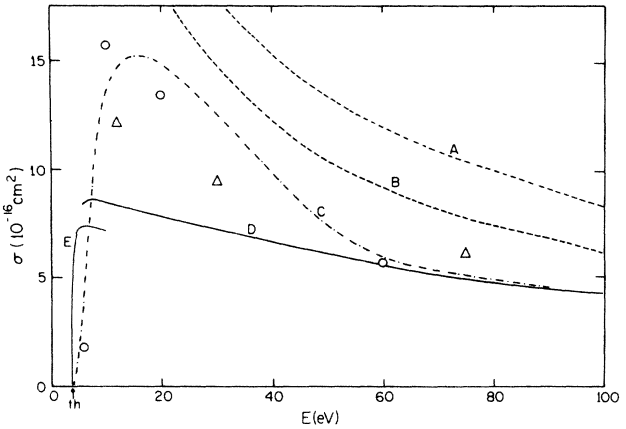

FIG. 1. $\sigma(4s \rightarrow 4p)$ vs E for Cu. Curve A: Born approximation (Ref. 4); Curve B: Born approximation (Ref. 11); Curve C: impact parameter approximation (Ref. 13); Curve D: four-state close-coupling approximation; Curve E: three-state close-coupling approximation; △: Aleksakhin *et al.* (Ref. 6); ○: renormalized measurements of Trajmar *et al.* (Ref. 3) (see text).

Winter[4] and Peterkop and Liepinsh[11] used different descriptions of the target wave functions in their Born approximation calculations. Winter used Wachters's Gaussian basis set[25] which gave 1.257 for the optical oscillator strength. Peterkop and Liepinsh used atomic wave functions which were determined by a semiempirical method using an analytical atomic potential. These functions gave 0.92 for the optical oscillator strength. Since at higher energies the excitation cross section is directly proportional to the oscillator strength, cross sections obtained by Winter are found to be larger than those of Peterkop and Liepinsh. Similarly, Born approximation results obtained with the present wave functions which give an oscillator strength of 0.64, would be expected to be lower than those of Peterkop and Liepinsh. The semiclassical impact parameter calculations[13] and our close-coupling calculations agree well for energies above 50 eV. Both calculations have similar transition energies and oscillator

TABLE III. Cross sections (in πa_0^2) for Cu.

Energy (eV)	6	10	20	60	100
σ (elastic)	22.07	6.39	2.59	4.54	5.24
$\sigma(4s \rightarrow 4p)$	9.63	9.66	8.88	6.44	4.85
$\sigma(4s \rightarrow 3d^9 4s^2)$	0.760	0.597	0.270	0.040	0.023
$\sigma(4s \rightarrow 4d)$	1.69	3.65	2.31	0.86	0.48

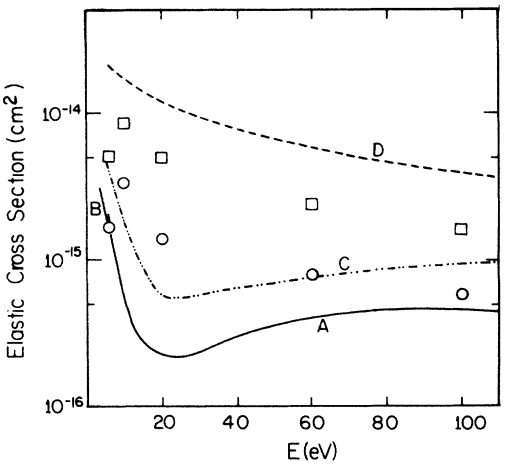

FIG. 2. σ (elastic) vs E for Cu. Curve A: four-state close-coupling approximation; Curve B: three-state close-coupling approximation; Curve C: static exchange approximation (Ref. 4); Curve D: Born approximation (Ref. 4); □: Trajmar *et al.* (Ref. 3); ○: renormalized measurements of Trajmar *et al.*

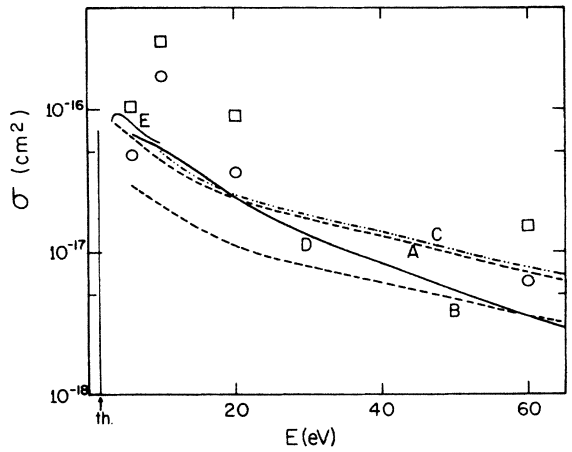

FIG. 3. $\sigma(4s \rightarrow 3d^9 4s^2)$ vs E for Cu. Notation as in Fig. 1, □: Trajmar *et al.* (Ref. 3).

strengths.

The addition of the $3d^{10}4d$ state in the close-coupling expansion produces a 15% change in the excitation cross section $4s \rightarrow 4p$. The reactance matrix elements which couple the $4s,4d$ and $4p,4d$ states are found to be large, whereas the $3d^9 4s^2$ state is only weakly coupled to the other states. Hence the differences between curves D and E in the 6–10 eV range where they overlap in energy. Test calculations in which we include other states in the close-coupling expansion such as $3d^{10}5s$ and $3d^{10}5p$ do not produce a significant change in the cross section for the dominant partial waves at 10 eV.

The crossed-beam experiment of Aleksakhin *et al.*[6] detects the radiation for $4s\,^2S - 4p\,^2P$ and $3d^9 4s^2\,^2D - 4p\,^2P$ plus many other transitions. No correction has been made to the measurements for cascade effects and so they should represent upper limits to the $4s \rightarrow 4p$ excitation cross section.

Figure 2 gives cross sections for elastic scattering of electrons from Cu as a function of incident energy. Curves A, B, C, and D represent calculations in a four-state close-coupling, three-state close-coupling, static exchange,[4] and Born[4] approximations, respectively. Squares give experimentally derived integral cross sections of Trajmar *et al.*,[3] where normalization was to 100 eV, 40° elastic scattering static exchange calculations of Winter. Circles represent renormalized experimental data. Since Trajmar *et al.* measured relative differential cross sections for elastic scattering and ^2S-^2P transitions, we assume that their data for elastic scattering should be renormalized by the same energy-independent factor[24] of 0.36 as for the resonance transition. For elastic scattering the experimental and theoretical differential cross sections are similar for $\theta < 20°$ and so no additional correction is applied.

There is little agreement between theory and experiment. The measurements indicate a maximum in the cross section at 12 eV whereas the close-coupling calculations and those in a static exchange approximation give a minimum at 22 eV and then a monotonic increase to at least 100 eV. The shape of the cross section with energy is the same for the static exchange and close-coupling calculations. The difference in magnitude is due to both a different description of the target wave functions and to additional terms being included in the close-coupling expansion. The static exchange approximation is equivalent to a one-state close-coupling approximation.

Figure 3 gives cross sections for excitation $^2S - 3d^9 4s^2\,^2D$ as a function of energy. Born approximation calculations of Winter[4] and Peterkop and Liepinsh,[11] respectively, are given by curves A and B. Curve C depicts a semiclassical impact parameter calculations of Winter and Hazi.[13] Curves D and E represent present three-state and four-state close-coupling calculations. Squares and circles give measurements of Trajmar *et al.*[3] with two different normalizations. Original results are given by squares. Circles represent a renormalization based on a renormalization of ^2S-$^2P^o$ cross sections as described above. Since Trajmar *et al.* measured relative differential cross sections for ^2S-^2D and ^2S-$^2P^o$ transitions, we assume that their data for the metastable level should be renormalized by the same energy-independent factor of 0.36 as for the resonance transition. However, additional correction factors are invoked since the shape of the differential cross section for ^2S-^2D is radically different from that assumed by Trajmar *et al.* for $\theta < 20°$. In particular, the theoretical differential cross section[23] has an unanticipated maximum at 6°. Thus, the extrapolation to 0° was overestimated as was the integral cross section for the metastable level. The additional correction factors are obtained by requiring the measured differential cross sections below 20° to follow the shape of our calculated four-state close-coupling approximation results.

The effect of coupling to $3d^{10}4d$ is relatively small. Differences between the two Born calculations reflects the differences in descriptions of the target wave functions. Again, the theoretical and experimental cross-section shapes with energy do not agree, at least for $E < 20$ eV. The measurements show a maximum at 12 eV whereas a theory maximum is evident in the three-state close-coupling approximation calculation at 4 eV.

IV. CONCLUSION

There is a consistency among various calculations on the energy shape of integral cross sections which is not borne out by the measurements of Trajmar *et al.*[3] For elastic scattering of electrons by atomic copper, static exchange, and four-state close-coupling calculations give a minimum at 22 eV for the cross section whereas the measurements indicate a maximum at 12 eV. For excitation $4s\,^2S \rightarrow 3d^9 4s^2\,^2D$ theory and experiment do not agree for low energies. The measurements show a maximum at 12 eV in contrast to a theoretically predicted maximum at 4 eV. Agreement in shape is reasonable for excitation $4s\,^2S \rightarrow 4p\,^2P^o$. However, the measurements of Trajmar *et al.* are approximately a factor of 2 larger than close-coupling results for energies below 30 eV *even after* reducing the values by a factor of 3 due to renormalization considerations. Trajmar *et al.*[3] performed a difficult experiment on Cu in 1977. In view of the importance of copper, the existing disagreements with theory, and advances in technology, further experiments are encouraged.

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[1]W. T. Walter, N. Solimene, M. Piltch, and G. Gould, IEEE J. Quantum Electr. **2**, 474 (1966).
[2]M. J. Kushner and B. E. Warner (private communication).
[3]S. Trajmar, W. Williams, and S. K. Srivastava, J. Phys. B **10**, 3323 (1977).
[4]N. W. Winter, quoted in Ref. 3.
[5]V. S. Borozdin, Yu. M. Smirnov, and Yu. D. Sharonov, Opt. Spektrosk. **43**, 384 (1977).
[6]I. S. Aleksakhin, A. A. Borovik, V. P. Starodub, and I. I. Shafranjosh, Zh. Prik. Spektrosk. **30**, 236 (1979).
[7]M. Fink and J. Ingram, Atom. Data **4**, 129 (1972).
[8]D. A. Leonard, IEEE J. Quantum Electron. **3**, 380 (1967).
[9]D. Trainor, A. Mandl, and H. Heyman, quoted in Ref. 3.
[10]K. Smith and S. J. Wade, in *Proceedings of the Tenth International Conference on the Physics of Electronic and Atomic Collisions, Paris, 1977,* edited by G. Watel (North-Holland, Amsterdam, 1978), p. A.8.
[11]R. Peterkop and A. Liepinsh, Latv. PSR Zinat. Vestis Fiz. Teh. Zinat. **2**, 3 (1979).
[12]A. E. S. Green, D. L. Sellin, and A. S. Zachor, Phys. Rev. **184**, 1 (1969).
[13]N. W. Winter and A. U. Hazi, Lawrence Livermore Laboratory, Report No. UCID 19314, 1982 (unpublished).
[14]W. T. Rogers, G. H. Dunn, J. O. Olsen, M. Reading, and G Stefani, Phys. Rev. A **25**, 681 (1982).
[15]A. Z. Msezane and R. J. W. Henry, Phys. Rev. A **25**, 692 (1982).
[16]T. M. Bieniewski and T. K. Krueger, Aerospace Research Laboratories, Report No. ARL 71-0135, Project No. 7114, 1971 (unpublished).
[17]R. C. Ashenfelter, Dissertation Abstracts B **28**, 2982 (1968).
[18]C. Froese Fischer, J. Phys. B **10**, 1241 (1977).
[19]C. E. Moore, *Atomic Energy Levels,* NBS Circular No. 467 (Washington, D.C., U.S. GPO, 1952).
[20]E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).
[21]A. Hibbert, Comput. Phys. Commun. **9**, 141 (1975).
[22]E. R. Smith and R. J. W. Henry, Phys. Rev. A **7**, 1585 (1973); R. J. W. Henry, S. P. Rountree, and E. R. Smith, Comput. Phys. Commun. **23**, 233 (1981).
[23]A. Z. Msezane and R. J. W. Henry, following paper, Phys. Rev. A **33**, 1636 (1986).
[24]A. Z. Msezane and R. J. W. Henry, Phys. Rev. Lett. **55**, 2277 (1985).
[25]A. J. H. Wachters, J. Chem. Phys. **32**, 1033 (1970).