TABLE III. Intermediate coupling coefficients.

Methods	c_1	c_2	α	β
Fine structure	0.4412	0.8974	0.9874	−0.1582
$^3P_1$ state g_J value	0.4278	0.9038	0.9850	−0.1725
Lifetime ratio	0.4289	0.9033	0.9852	−0.1714
Pure LS coupling	0.5774	0.8165	1	0

Russell-Saunders coupling are related to the values in intermediate coupling by the expression[1]

$$g_J(^3P_1)=\alpha^2[g_J{}^0(^3P_1)]+\beta^2[g_J{}^0(^1P_1)], \qquad (2)$$

where α and β are related to the coupling coefficients c_1 and c_2, and we have taken $g_J{}^0(^3P_1)=1.50096$ and $g_J{}^0(^1P_1)=0.99980$. These values for $g_J{}^0$ include an estimate of −200 ppm for relativistic and diamagnetic corrections. This estimate is obtained as follows: $g_J(^3P_2)=1.50099(10)$. The difference between this value and the theoretical value $g_J=1.501156$ is 170 ppm. From a treatment of the relativistic and diamagnetic corrections similar to the treatment of Abragam and Van Vleck for oxygen,[8] we can show that the corrections to both the $^3P_1$ and the $^1P_1$ g_J values are almost the same and are slightly larger than the correction to the $g_J(^3P_2)$. Hence we make the estimate of −200±40 ppm for the corrections.

In line 3, we have used the $^1P_1$ state lifetime together with the $^3P_1$ state lifetime to calculate the coupling coefficients from the equations

$$\frac{\beta^2}{\alpha^2}=\frac{\tau(^1P_1)}{\tau(^3P_1)}\frac{\lambda^3(^3P_1-{}^1S_0)}{\lambda^3(^1P_1-{}^1S_0)},$$

$$\alpha^2+\beta^2=1.$$

We have taken an average value $\tau=(1.145\pm0.02)\times10^{-7}$ sec for the lifetime of the $^3P_1$ state.

The agreement between all three methods is good and the agreement between the methods of lines 2 and 3 is excellent. This is expected, since the fine structure is more sensitive to configuration interaction than are g_J values or the lifetime ratio.

ACKNOWLEDGMENTS

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[8] A. Abragam and J. H. Van Vleck, Phys. Rev. 92, 1448 (1953).

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Wave Functions and Transition Probabilities in Scaled Thomas-Fermi Ion Potentials[*]

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A semiempirical method for computing atomic and ionic wave functions is described. The method uses a one-electron potential obtained from a scaled Thomas-Fermi ionic charge distribution. The scale factors are chosen to make the one-electron binding energies agree with experimental ionization potentials. A number of oscillator strengths have been evaluated and are found to agree well with results of alternative methods of calculation. The method has a wider range of applicability than that of Bates and Damgaard, and calculations are much shorter than those using the self-consistent-field methods.

I. INTRODUCTION

We consider in this paper an approximate and rapid method for obtaining radial wave functions in many-electron atoms and ions. Our main goal in this work is the calculation of electric-dipole transition probabilities ("oscillator strengths"), although other applications (collision cross sections, spin-orbit parameters, Slater integrals, etc.) suggest themselves. In applications such as opacity calculations, which require many hundreds of wave functions for transition probabilities, speed of computation becomes an important consideration. Our particular concern, therefore, is to evaluate wave functions via some method which circumvents the lengthy "self-consistent-field"

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(SCF) methods, since SCF rapidly gets lengthier as the number of occupied electron orbitals increases, and it becomes prohibitively lengthy if one contemplates evaluating many oscillator strengths in many stages of ionization of many elements. Current methods of computing oscillator strengths are discussed briefly in Sec. II.

Our method may be regarded as a hybrid of the semiempirical method of Bates and Damgaard[1] and the nonempirical method of Thomas[2] and Fermi.[3] The basic approximation we make is that any one-electron wave function can be represented adequately by a solution of the one-electron Schrödinger equation in which the potential is that produced by a Thomas-Fermi ion with the correct nuclear charge, the correct number of electrons, and some value (*not* in general the Thomas-Fermi value) of the mean radius of the charge distribution. The Thomas-Fermi ion, in other words, is uniformly and isotropically dilated or contracted to force some parameter of the radial wave function to have a prescribed value. In the present work, this parameter is the energy parameter in the one-electron wave equation, which we take equal to the experimental ionization potential of the electron in question; other choices are, of course, possible. With this choice the oscillator strength of any transition can be evaluated from a knowledge of the initial and final energy levels referred to the energy of the parent ion, as in the Bates-Damgaard method; unlike their method, however, our method does not neglect the part of the dipole matrix element arising from small radial distances and so is not restricted to initial and final states in which the active electron lies mostly outside the passive electrons. The price paid for this wider range of applicability is a brief machine calculation instead of a hand calculation; the machine calculation, however, is at least an order of magnitude faster than any of the SCF methods known to us. Our method is described in Sec. III.

Our particular choice of potential is based on a number of empirical considerations, besides the obvious one of ease of handling: good numerical fit with potentials obtained from the SCF methods, the resulting close agreement of radial wave functions, and, ultimately, reasonable agreement with the dipole matrix elements obtained by other methods. The comparison with other theoretical and experimental results is exhibited and discussed in Sec. IV. Conclusions and future work are summarized briefly in Sec. V.

II. CURRENT METHODS

Methods for obtaining wave functions of many-electron atoms and ions may be divided into two broad classes: first-principle methods and semiempirical methods. The former class, of which the Hartree,[4] Hartree-Fock,[5] Hartree-Fock-Slater,[6] and "charge-expansion"[7] methods are examples, attempts to find approximate solutions to the many-electron Schrödinger equation which satisfy a criterion of variational optimization within a restricted class of trial functions chosen in advance. The quantity which is optimized is always the total energy of the atom or ion. Although the total energy is usually given quite accurately by the variational methods, it is not ordinarily the quantity which one wishes to evaluate. One usually wants the ionization potential of an outer electron, a transition probability (square of the off-diagonal matrix element of an operator such as the electric-dipole moment), etc. These quantities are usually much more sensitive to the behavior of the wave function in the outer parts of the atom or ion than is the total energy, so that, as has been pointed out many times, approximate wave functions which give excellent total energies need not give even fair transition probabilities.

In contrast to first-principle methods, semiempirical methods require that the approximate wave functions satisfy some constraints taken from experiment, such as one-electron energy levels or ionization potentials. Among the semiempirical methods, the "Coulomb approximation" of Bates and Damgaard[1] (which has been extended to photoelectric transitions by Burgess and Seaton[8]) leads to a relatively simple computational scheme and has been widely applied with considerable success,[9] often yielding oscillator strengths which agree with experiment better than the self-consistent-field values do. The Bates-Damgaard (BD) method utilizes the experimental binding energy of the active electron to construct an approximate radial wave function which is accurate at large radial distances: a Coulomb wave function with the right behavior at infinity and the right energy. The length form of the electric-dipole matrix element, which emphasizes large radial distances, is then evaluated using two such wave functions. The resulting transition probability depends on the initial and final energies and angular momenta of the active electron, but not on the details of the atomic potential at small radii.

The basic postulate of the BD method is that nearly all of the dipole-length matrix element is contributed by the wave function at radii where the active electron is outside the "core" (the charge distribution of the rest of the electrons and the nucleus); the contribution

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[1] D. R. Bates and A. Damgaard, Phil. Trans. Roy. Soc. London **A242**, 101 (1949).

[2] L. H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1927).

[3] E. Fermi, Atti Accad. Nazl. Lincei, Rend., Classe sci. fis., mat. e nat. **6**, 602 (1927); Z. Physik **48**, 73 (1928).

[4] D. R. Hartree, Proc. Cambridge Phil. Soc. **24**, 89 (1928).

[5] See, for example, D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).

[6] J. C. Slater, Phys. Rev. **81**, 385 (1951); J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vols. I and II; see also Ref. 31.

[7] D. Layzer, Ann. Phys. (N. Y.) **8**, 271 (1959); C. M. Varsavsky, Astrophys. J., Suppl. Ser. **6**, No. 53, 75 (1961); A. Naqvi, J. Quant. Spectry. Radiative Transfer **4**, 597 (1964).

[8] A. Burgess and M. J. Seaton, Monthly Notices Roy. Astron. Soc. **120**, 121 (1960).

[9] H. R. Griem, *Plasma Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1964), Chap. 3.

from smaller radii is either neglected (by using a cutoff radius) or severely approximated (by introducing a modifying factor into the approximate wave function, which prevents the radial integral from diverging at the origin). The postulate is violated, and the BD method suspect, in two cases: (a) when the active electron is in an inner orbital with very small amplitude outside the core or (b) when the outer contribution to the matrix element is very small because of cancellation so that the value of the inner contribution is important. The method described in the next section is designed to remain accurate even when the postulate of the BD method is violated.

III. THE SCALED THOMAS-FERMI METHOD

The derivation of the Thomas-Fermi (TF) statistical model for atoms and ions has been treated extensively by Gombás[10] and will not be repeated here. Several authors have evaluated one-electron wave functions and energy levels in the TF potential (or approximations to it); the most comprehensive set of results is due to Latter,[11] who obtained one-electron energies for neutral atoms distributed through the periodic table. The potential experienced by the electron whose wave function is sought (the "valence" electron) is produced by the nucleus and the rest of the electrons (the "core") and reduces at large radii to the Coulomb potential of the core charge. Thus, an approximate potential for all radii is obtained if we replace the core by a TF ion whose net charge is the core charge and whose nucleus has the actual nuclear charge. (Latter used, instead, a neutral TF atom and a somewhat unphysical charge shell to get the asymptotic Coulomb potential.) The one-electron radial wave equation for an electron of angular momentum l and principal quantum number n is then

$$d^2P_{nl}/dr^2+[2Z\psi(r/\mu)/r+E_{nl}-l(l+1)/r^2]P_{nl}(r)=0, \qquad (1)$$

where r is in Bohr radii, E is in Rydbergs, and

$$\psi(x)=\varphi(x)+qx/x_0 \quad (x\leq x_0)$$
$$=q \quad (x\geq x_0);$$

φ is the TF function, which satisfies

$$d^2\varphi/dx^2=\varphi^{3/2}x^{-1/2};$$
$$\varphi(0)=1;$$
$$\varphi(x_0)=0;$$
$$q=-x_0 d\varphi/dx|_{x_0};$$
$$x=r/\mu; \qquad (2)$$
$$\mu=0.8853Z^{-1/3};$$
$$q=z/Z;$$
$$z=\text{core charge};$$
$$Z=\text{atomic number}.$$

The radial wave function $P(r)$ satisfies the usual boundary and normalization conditions:

$$P_{nl}(0)=0;$$
$$P_{nl}(\infty)=0 \quad\text{and}\quad \int_0^\infty P_{nl}^2dr=1, \quad\text{if}\quad E<0; \qquad (3)$$
$$P(r)\xrightarrow[r\to\infty]{}\cos(kr+\delta(r)), \qquad \text{if}\quad E=k^2>0.$$

For bound states, n is defined as $l+1+N$, where N is the number of nodes excluding those at zero and infinity.

If the bound-state energies E_{nl} are determined as eigenvalues of Eq. (1), they do not of course coincide with experimental values. We can render the model semiempirical if we replace μ by $\alpha_{nl}\mu$, where the scale factor α_{nl} plays the role of an eigenvalue to be determined by setting E_{nl} equal to the experimental one-electron binding energy. The introduction of α_{nl} corresponds to a uniform dilatation or contraction of the TF core in an effort to compensate for all the omissions and approximations of the TF model (exchange, correlation, relativity, etc.), and its justification is primarily the quality of the resulting wave functions and oscillator strengths. We note in passing that radial scale factors in the TF model have been employed by Fock[12] in connection with a virial theorem and by March[13] as a variational parameter in an approximate correction for exchange.

With α_{nl} determined as above, the parallel between our method (which we will call the "scaled TF" or STF method) and the BD method is very close—at radii outside the core radius ($r>\alpha\mu x_0$), the STF wave function is, apart from normalization, identical with the BD wave function.

We have found that α_{nl} is a very weak function of the quantum number n (see Table II). It is therefore a simple matter to extrapolate α_{nl} to a value to use in the Schrödinger equation for unknown levels or continuum wave functions. Hence the method is also readily applicable to the calculation of photoionization cross sections, including those for x rays.

With the radial wave functions obtained as above, the dipole absorption oscillator strength for a transition from nl to $n'l'$ is given by the standard relations

$$gf=\tfrac{1}{3}(E'-E)\mathcal{S}(\mathcal{M})\mathcal{S}(\mathcal{L})\sigma^2,$$

$$\sigma^2=\frac{1}{4l_>^2-1}\left|\int_0^\infty P_{nl}P_{n'l'}rdr\right|^2,$$

where $l_>=\max(l,l')$, and the angular factors $\mathcal{S}(\mathcal{M})$ and $\mathcal{S}(\mathcal{L})$ can be obtained from tables computed by Goldberg[14] and reproduced by Allen,[15] or from formulas of

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[10] P. Gombás, *Die Statistische Theorie des Atoms* (Springer-Verlag, Vienna, 1949).

[11] R. Latter, Phys. Rev. **99**, 510 (1955).

[12] V. Fock, Physik Z. Sowjetunion **1**, 747 (1932).

[13] N. H. March, Advan. Phys. **6**, 1 (1957).

[14] L. Goldberg, Astrophys. J. **82**, 1 (1935); **84**, 11 (1936).

[15] C. W. Allen, *Astrophysical Quantities* (The Athlone Press, University of London, London, 1963), 2nd edition.

TABLE I. Oscillator strengths for some atoms and ions.[a]

Z	Atom or ion	Transition	gf_{STF}	gf_{BD}	gf_{Expt}	Other	α^{b}	α'
3	Li I	$2s$-$2p$	1.46	1.49	...	1.49^{c} 1.59^{d}	1.30	1.12
10	Ne I	$(2p^5)2p$-$3s$	0.193	...	...	0.163^{f} 0.188^{e}	0.995	1.027
		$2p$-$4s$	0.031	...	...	0.026^{f} 0.029^{e}	0.995	1.010
		$2p$-$5s$	0.011	...	...	0.009^{f} 0.008^{e}	0.995	1.007
		$2p$-$6s$	0.005	...	...	0.004^{f} 0.003^{e}	0.995	1.006
		$2p$-$3d$	0.052	...	...	0.037^{f} 0.036^{e}	0.995	1.199
		$2p$-$4d$	0.026	...	...	0.020^{f} 0.025^{e}	0.995	1.146
		$2p$-$5d$	0.015	...	...	0.011^{f} 0.018^{e}	0.995	1.154
		$2p$-$6d$	0.009	...	...	0.007^{f} 0.012^{e}	0.995	1.159
11	Na I	$3s$-$3p$	1.95	1.87	...	1.94^{c}	0.95	0.97
19	K I	$4s$-$4p$	2.10	1.98	1.98^{d} 2.1^{g}	2.08^{c}	1.13_5	1.13_5
20	Ca I	$3d4s(^3D_3)$-$3d4p(^3F_4)$	2.70	2.45	1.1^{d} 2.0^{g}	...	1.19	1.24
21	Sc I	$3d^24s(^4F_{9/2})$-$3d^24p(^4G_{11/2})$	3.58	3.20	2.6^{d} 2.3^{g}	...	1.17	1.21
22	Ti I	$3d^34s(^5F_5)$-$3d^34p(^5G_6)$	3.94	3.46	3.8^{d} 3.7^{g}	...	1.14	1.18
23	V I	$3d^44s(^6D_{9/2})$-$3d^44p(^6F_{11/2})$	3.80	3.33	4.0^{d} 3.0^{g}	...	1.11	1.13
24	Cr I	$3d^54s(^7S_3)$-$3d^54p(^7P_4)$	2.73	2.35	0.6^{d} 0.5^{g}	...	1.08	1.11
25	Mn I	$3d^64s(^6D_{9/2})$-$3d^64p(^6F_{11/2})$	3.76	3.24	5.3^{d} 9.3^{g}	...	1.05	1.07
26	Fe I	$3d^74s(^5F_5)$-$3d^74p(^5G_6)$	4.13	3.56	4.1^{d} 4.4^{g}	...	1.02	1.03
27	Co I	$3d^84s(^4F_{9/2})$-$3d^84p(^4G_{11/2})$	3.78	3.29	3.2^{d} 4.6^{g}	...	0.98_5	1.00
28	Ni I	$3d^94s(^3D_3)$-$3d^94p(^3F_4)$	2.68	2.31	0.8^{d} 1.0^{g}	...	0.96	0.99
29	Cu I	$3d^{10}4s(^2S_{1/2})$-$3d^{10}4p(^2P_{3/2})$	1.24	1.08	0.8^{d} 0.64^{g}	...	0.93	0.95
55	Cs I	$6s$-$6p_{1/2}$	0.753	0.697	2.38^{h}	2.26^{c} 0.788^{i}	1.14	1.135
		$6s$-$6p_{3/2}$	1.56	1.50		1.63^{i}	1.14	1.119
		$6s$-$7p_{1/2}$	0.012	0.013	0.032^{h}	0.054^{c} 0.0057^{i}	1.14	1.127
		$6s$-$7p_{3/2}$	0.040	0.034		0.0348^{i}	1.14	1.111
		$6s$-$8p_{1/2}$	0.00233	0.00259	0.00616^{h}	0.013^{c} 0.00063^{i}	1.14	1.125
		$6s$-$8p_{3/2}$	0.00933	0.00982		0.00698^{i}	1.14	1.109
80	Hg I	$6p(^3P)$-$7s(^3S)$	1.41	0.77	0.7^{d} 1.46^{j}		1.00	1.04
		$6p(^3P_1)$-$6d(^3D_1)$ $6p(^3P_1)$-$6d(^3D_2)$	1.46	1.15	0.9^{j}		1.00	1.03

[a] When only one strength is given for a doublet, it is the combined value.
[b] α and α' are the scale factors for the lower and upper states, respectively.
[c] Anderson and Zilitis, Ref. 18.
[d] Allen, Ref. 15.
[e] Kelly, Ref. 19.
[f] Cooper, Ref. 20.
[g] Corliss and Bozman, Ref. 21.
[h] Kvater and Meister, Ref. 22.
[i] Stone, Ref. 23.
[j] Penkin, Ref. 24.

Rohrlich[16] or Kelly.[17] The above expression refers to gf for a spectral line; gf values for multiplets or transition arrays are sums over the gf's of the constituent lines.

For photoionization transitions, the upper-state wave function belongs to the continuum; the cross section per atom in the lower state, in units of $\pi\times$(Bohr radius)^2, is

$$A=\frac{4}{3}\frac{1}{137}(E'-E)\sigma^2\frac{1}{kg}\sum_{L'S'}\mathcal{S}(\mathcal{M}),$$

where $k^2=E'=$kinetic energy of photoelectron, in Rydbergs; g is the statistical weight of the lower state; and σ^2 is as before but with $P_{n'l'}$ replaced by a continuum wave function normalized to asymptotic amplitude unity as in Eq. (3). The above expressions (and all the results of the present paper) neglect configuration mixing, departures from LS coupling, and rearrangement of the core electrons.

IV. RESULTS AND DISCUSSION

In order to make a preliminary assessment of the STF method, we have used it to compute a number of oscillator strengths in various atoms and ions. Our choice of test cases is intended to be representative rather than comprehensive; we have included examples of heavy and light, simple and complex atomic systems. The examples are chosen, in part, for availability of comparison data. In Table I (which cites Refs. 18–24) we have tabulated some values, for neutral atoms, of the quantity gf, where g is the statistical weight of the lower state and f is the absorption oscillator strength. Some of the transitions treated are single lines, others are multiplets, and still others are transition arrays, as indicated by the presence or absence of the quantum numbers L, S, and J. In all cases, the gf values we give are sums over quantum numbers which do not appear explicitly. For each transition, we give in the STF column, our value of gf; in the next column, the BD value; in the "Expt" column, experimental values; in the "Other" column, values calculated by other

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[16] F. Rohrlich, Astrophys. J. **129**, 441 (1959); **129**, 449 (1959).

[17] P. S. Kelly, Astrophys. J. **140**, 1247 (1964).

[18] E. M. Anderson and V. A. Zilitis, Opt. i Spectroskopiya **16**, 382 (1964); **16**, 177 (1964) [English transl.: Opt. Spectry. (USSR) **16**, 211 (1964); **16**, 99 (1964)].

[19] P. S. Kelly, J. Quant. Spectry. Radiative Transfer **4**, 117 (1964).

[20] J. W. Cooper, Phys. Rev. **128**, 681 (1962).

[21] C. H. Corliss and W. R. Bozman, Natl. Bur. Std. (U.S.), Monograph 53 (1962).

[22] G. S. Kvater and T. G. Meister, Vestn. Leningr. Univ., Ser. Fiz. i Khim. **9**, 137 (1952), as referred to in Ref. 18.

[23] P. M. Stone, Phys. Rev. **127**, 1151 (1962).

[24] N. D. Penkin, J. Quant. Spectry. Radiative Transfer **4**, 41 (1964).

semiempirical methods or by the Hartree-Fock-Slater method; and in the last two columns, the values of the scale factors α and α', corresponding respectively to the lower and upper states of the transition. Each scale factor was determined, as described in Sec. III, by setting the energy parameter in the one-electron radial wave equation equal to the experimental ionization potential[25] of the electron which makes the transition (referred to the appropriate parent term); for transition arrays, the ionization potential was taken as a weighted mean over L and S. The same energy parameters were used in the BD calculations shown here.

We consider first the results for the alkali metals (Li, Na, K, Cs) in Table I. The strengths of the resonance lines ($ns \longrightarrow np$) of these elements agree closely with the results of other methods; this is hardly surprising since the large oscillator strengths of these lines are rather insensitive to the details of the wave functions. On the other hand, strengths of the higher lines in the principal series ($ns \longrightarrow n'p$) are extremely sensitive to the wave functions because of strong cancellation in the radial integrals. In particular, we note that in Cs I the computed oscillator strengths of $6s_{1/2}$-$7p_{3/2}$ and $6s_{1/2}$-$7p_{1/2}$ are in the ratio 3.3/1 even though the $7p_{3/2}$ and $7p_{1/2}$ binding energies differ by only 2%. If the radial integrals for these transitions were identical, the strengths would have the ratio 2/1; the departure from this value is observed experimentally.[26] The close agreement of our gf values with those of BD indicates that the contributions from the wave functions inside the core are insignificant in CsI. In the region outside the core, the form of the wave function depends almost entirely on the one-electron binding energy. The radial integral, as we have seen, is very sensitive to changes of the order of 1% in the one-electron binding energy. This accuracy is not often attained by SCF methods.

In Hg, we see that our values differ appreciably from those of BD. This is undoubtedly because the states involved have binding energies large enough to nearly invalidate BD's own criterion that the effective principal quantum number should not be less than about $l+\frac{1}{2}$.

The data for the iron group ($Z=20$ through 29) illustrate the application of the STF method to complex atoms. Throughout this group three low-lying configurations of even parity ($3d^{x+1}$, $3d^x4s$, and $3d^{x-1}4s^2$) are present. Strong configuration mixing is to be expected,[27] and may produce large departures of the line strengths from those computed from any pure-configuration model. Therefore, it is somewhat surprising that the over-all agreement with experiment is as good as it is.

TABLE II. Selected oscillator strengths and scale factors in the sodium isoelectronic sequence.[a]

Z	Ion	Transition	f_{STF}	f_{BD}	α	α'
11	Na I	$3s$-$3p$	0.977	0.934	0.943	0.963
		$3s$-$4p$	0.151(−1)	0.143(−1)		0.958
		$3s$-$5p$	0.236(−2)	0.201(−2)		0.957
12	Mg II	$3s$-$3p$	0.940	0.891	1.008	1.004
		$3s$-$4p$	0.230(−3)	0.124(−3)		0.997
		$3s$-$5p$	0.100(−2)	0.129(−2)		0.995
13	Al III	$3s$-$3p$	0.866	0.826	1.043	1.027
		$3s$-$4p$	0.113(−1)	0.105(−1)		1.019
		$3s$-$5p$	0.681(−2)	0.746(−2)		1.017
14	Si IV	$3s$-$3p$	0.796	0.758	1.067	1.042
		$3s$-$4p$	0.302(−1)	0.286(−1)		1.033
17	Cl VII	$3s$-$3p$	0.627	0.607	1.139	1.093
		$3s$-$4p$	0.102	0.091		1.088
20	Ca X	$3s$-$3p$	0.525	0.507	1.140	1.087
		$3s$-$4p$	0.145	0.143		1.078
23	V XIII	$3s$-$3p$	0.450	0.439	1.217	1.135
		$3s$-$4p$	0.195	0.182		1.126
26	Fe XVI	$3s$-$3p$	0.399	0.394	1.259	1.154
		$3s$-$4p$	0.226	0.210		1.144
29	Cu XIX	$3s$-$3p$	0.363	0.358	1.305	1.173

[a] Note: α and α' are the scale factors for the lower and upper states, respectively.

Neon is included as an example which cannot be treated by the BD method because the effective principal quantum number for the $2p$ orbital is too small; here we obtain generally good agreement with Cooper's[20] simplified self-consistent-field results and with Kelly's[19] Hartree-Fock-Slater results.

In Table II we exhibit the behavior of a few STF oscillator strengths and scale factors along the sodium-like isoelectronic sequence, again based on experimental energy levels. Table II serves to illustrate the smooth behavior of α along such a sequence or along a Rydberg series, and hence the possibility of extrapolating α's to unknown levels. For comparison, the BD oscillator strengths are also shown.

Table III (citing Ref. 28) shows STF photoionization cross sections from the ground state of atomic oxygen. In these calculations the continuum radial wave functions were evaluated using values of α determined from bound states of the corresponding angular momenta. For comparison, cross sections computed from Hartree-Fock wave functions using the length and velocity forms of the dipole matrix elements[28] are quoted.

We have compared the $2p$ orbital of the ground state of oxygen obtained in the STF potential with orbitals obtained by the Hartree,[29] Hartree-Fock,[30] and Hartree-Fock-Slater[31] methods. When the α in the STF method was adjusted to give the same energy parameter as the HF method (1.26 Ry) the HF and STF wave functions

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[25] Charlotte E. Moore, *Atomic Energy Levels*, Natl. Bur. Std. (U. S.), Circ. 467, Vol. I (1949), Vol. II (1952), Vol. III (1958).

[26] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1959), p. 376.

[27] Reference 26, p. 330.

[28] A. Dalgarno, R. J. W. Henry, and A. L. Stewart, Planetary Space Sci. **12**, 235 (1964).

[29] D. R. Hartree and M. M. Black, Proc. Roy. Soc. (London) **A139**, 311 (1933).

[30] D. R. Hartree, W. Hartree, and B. Swirles, Phil. Trans. Roy. Soc. London **A238**, 229 (1939).

[31] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

were found to agree within 5% in the tail ($r>4$ Bohr radii); at smaller radii, the agreement was considerably better. The maxima of both wave functions occurred at 0.85 Bohr radii.

TABLE III. Photoelectric cross sections at various wavelengths from the ground state of atomic oxygen, in units of 10^{-18} cm^2.[a]

λ(Å)	HF$_L$	HF$_V$	STF
550	12.4	10.0	14.3
420	11.4	9.0	11.2
290	7.8	6.0	5.7
175	3.2	2.5	1.9

[a] Note: HF$_L$ and HF$_V$ refer to the use of length and velocity matrix elements, respectively, taken between Hartree-Fock wave functions as reported in Ref. 28.

In Table IV is a comparison of wave functions obtained by the various methods at one point in the tail; the ratios of the wave functions are typical for $4<r<8$. It is important to note that the energy parameter in each case is the one obtained by the respective method. This table is shown to emphasize how sensitive the asymptotic amplitudes of the wave functions are with respect to relatively small changes in the energy. By way of contrast, all these functions are within 5% of one another at 1 Bohr radius.

Since the TF model is a rather simplified picture of the atom, one may well ask to what extent its omissions and approximations can be compensated by introduction of the single parameter α. Our use of the STF, rather than the unmodified TF, potential rests simply on the numerical observation that (in the cases we have examined) the STF gives a reasonably good fit to SCF potentials, and is usually significantly better than the TF. This observation is supported by comparisons of the resulting wave functions and transition probabilities with SCF results.

We consider first the "screening function" ψ which appears in the radial wave equation (1). In the numerical SCF methods this function is replaced by a function $U(r)$ which is constructed from previously estimated wave functions. Specifically, for a configuration with N_i electrons in the ith orbital (n_il_i), the screening function U_i in the ith radial wave equation is[6]

$$U_i(r)=1+\frac{1}{Z}\Bigg\{-\sum_j N_jY_0(jjr)+AY_0(iir)$$

$$+B\frac{3r}{4}\left[\frac{6}{\pi^2r^2}\sum_j N_jP_j^2(r)\right]^{1/3}$$

$$+C\Bigg[Y_0(iir)+\frac{N_i-1}{4l_i+1}\sum_{k\geq 2}c^k(ii)Y_k(iir)$$

$$+\sum_{j\neq i}\frac{N_jP_j(r)}{P_i(r}\Bigg(\frac{\sum_k c^k(ij)Y_k(ijr)}{2[(2l_i+1)(2l_j+1)]^{1/2}}$$

$$-(r/2)\delta_{l_il_j}\lambda_{ij}\Bigg)\Bigg]\Bigg\},$$

where $(A,B,C)=(1,0,0)$ in the H (Hartree) method
$=(0,1,0)$ in the HFS (Hartree-Fock-Slater) method
$=(0,0,1)$ in the HF (Hartree-Fock, configuration average) method;

$$Y_k(ijr)=\int_0^r P_i(r')P_j(r')(r'/r)^k dr'$$

$$+\int_r^\infty P_i(r')P_j(r')(r/r')^{k+1}dr';$$

$$c^k(ij)=c^k(l_i0;l_j0)=\tfrac{1}{2}[(2l_i+1)(2l_j+1)]^{1/2}C_{l_il_jk};$$

(Ref. 32)

$\lambda_{ij}=$ off-diagonal Lagrange multiplier

and, in each case, $-E_i$ is the computed ionization potential in the Koopmans ("unrelaxed-core") approximation. The quantity $(Z-\sum_j N_j+1)/Z$ is, of course, the (core charge/nuclear charge) ratio q.

The potentials corresponding to all of the above screening functions [and to the STF screening function $U_{\mathrm{STF}}(r)=\psi(r/\alpha\mu)$] reduce to the nuclear potential as $r\rightarrow 0$, i.e., $U(0)=1$. As $r\rightarrow\infty$, U_{H} and U_{STF} approach q, and U_{HF} does the same when the ith orbital is the outermost so that $P_j/P_i\rightarrow 0$. The HFS method, which uses an averaged exchange potential obtained from the *local* electron density (as in the Thomas-Fermi-Dirac model), fails to eliminate completely the self-interaction potential. Accordingly, $U_{\mathrm{HFS}}\neq 1$ for one-electron atoms, and in general $U_{\mathrm{HFS}}\rightarrow q-1/Z$ as $r\rightarrow\infty$. In recent extensive applications[31,19] the procedure adopted was to replace U_{HFS} by q whenever $U_{\mathrm{HFS}}<q$; in the rest of this paper the designation HFS implies this replacement.

In the analytic Hartree-Fock (AHF) method,[17,33,34] the orbitals are not obtained as numerical solutions of wave equations with the screening functions U_{HF}, but are restricted to prescribed analytic forms. The wave equation which such an orbital does satisfy can be obtained readily by differentiating the analytic orbital twice. The resulting screening function U_{AHF}, may or

TABLE IV. Comparison of $2p$ orbitals in the ground state of oxygen at $r=6$ obtained by various methods.

Method	$-E_{2p}$(Ry)	$P_{2p}(r=6)$
Hartree-Fock[c]	1.26	0.011
Scaled Thomas-Fermi	1.165[a]	0.013
Hartree-Fock-Slater[d]	1.04	0.016
Hartree[b]	0.94	0.025

[a] This energy parameter is the experimental ionization potential averaged over L and S.
[b] See Ref. 29.
[c] See Ref. 30.
[d] See Ref. 31.

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[32] See Ref. 26, p. 182.

[33] C. C. J. Roothaan and P. S. Bagus, *Methods in Computational Physics* (Academic Press Inc., New York, 1963), Vol. II.

[34] C. C. J. Roothaan and P. S. Kelly, Phys. Rev. 131, 1177 (1963).

may not agree closely with the U_{HF} constructed by integration from the same set of orbitals, depending on the flexibility of the trial functions employed and on the size of the wave function at the point where the comparison is made; the agreement tends to be worst at very small and very large radii where the wave function is small and has little weight in the total energy. Unfortunately these regions may contribute appreciably to transition probabilities.[17] The "charge-expansion" method[7] may be regarded as a rather highly restricted AHF scheme using scaled hydrogenic orbitals, and corresponds to $U_{\mathrm{AHF}}=Z_i/Z$, where the effective charge Z_i is a variationally determined constant for each orbital. This scheme naturally leads, in general, to rather poor wave functions except for inner orbitals or highly stripped ions.

It is illuminating to compare the various screening functions for a specific example. Figure 1 exhibits this comparison for the $2p$ orbital in the $1s^2\,2s^2\,2p$ configuration of O IV; we have used the AHF orbitals of Roothaan and Kelly[34] to construct U_{H}, U_{HFS}, and U_{HF} by integration, and U_{AHF} by differentiation. We also show U_{STF} with $\alpha=1.67$ (which yields the experimental E_{2p}) and with $\alpha=1$ (which yields the unmodified TF potential). Figure 2 shows the corresponding quantities for the $3d$ orbital in the $1s^2\,2s^2\,3d$ configuration, where Kelly's AHF orbitals[17] were used and $\alpha=1.96$. The reason for using the same wave functions throughout is to exhibit directly the HF exchange contribution $(U_{\mathrm{HF}}-U_{\mathrm{H}})$ and its HFS approximation $(U_{\mathrm{HFS}}-U_{\mathrm{H}})$.

Examining Figs. 1 and 2, we see that the STF and HFS potentials appear to be of comparable quality as approximations to the HF potential. Both decrease somewhat too steeply in the outer part of the ion. The Hartree potential, and especially the TF potential, are consistently smaller than the HF potential; a radial scaling of the Hartree potential would bring it quite close to the HF. The AHF potential is indistinguishable (in the graphs) from the HF, except at large radii for the $2p$ orbital and small radii for the $3d$ orbital.

The $2p$ and $3d$ orbitals are nodeless; for orbitals with nodes, the HF and AHF potentials in general have poles at the nodes of the orbital, and so cannot be fitted in detail by any smooth potential such as the STF or HFS. Nevertheless the resulting wave functions can be quite similar, as illustrated by the $4p$ orbitals for neutral krypton[31,35] shown in Fig. 3.

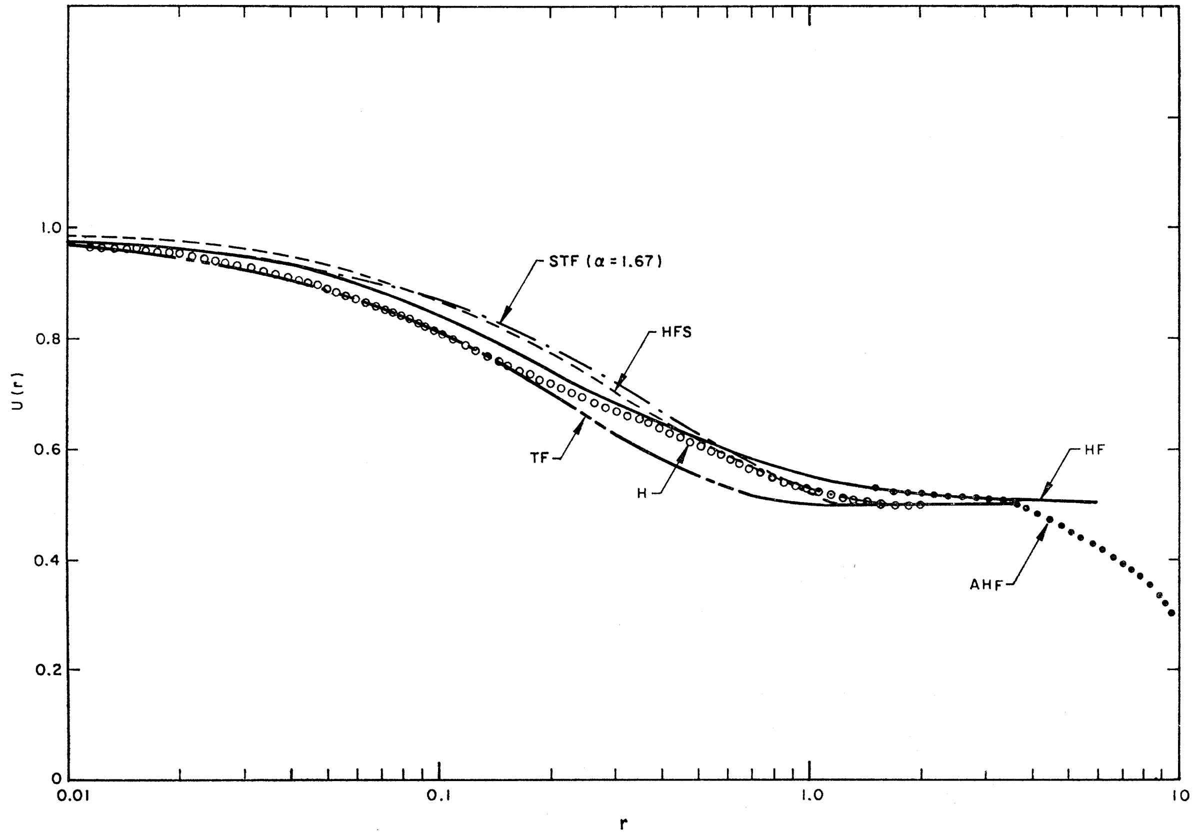

FIG. 1. Screening functions for the $2p$ orbital in the $1s^2\,2s^2\,2p$ configuration of O IV. Where the analytic Hartree-Fock (AHF) function (dotted curve) is not shown, it is indistinguishable from the Hartree-Fock (HF) function.

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[35] B. H. Worsley, Proc. Roy. Soc. (London) A247, 390 (1958).

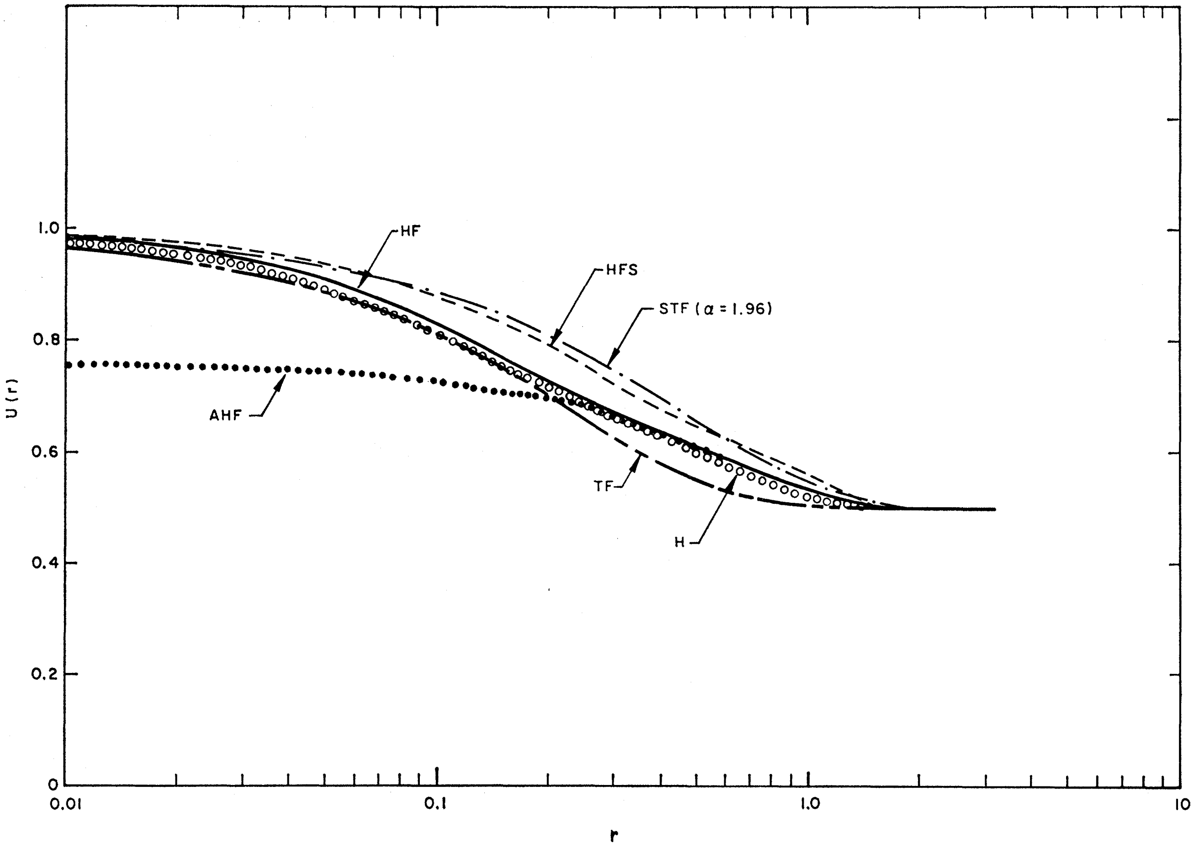

FIG. 2. Screening functions for the $3d$ orbital in the $1s^2\,2s^2\,3d$ configuration of O IV. Where the AHF function (dotted curve) is not shown, it is indistinguishable from the HF function.

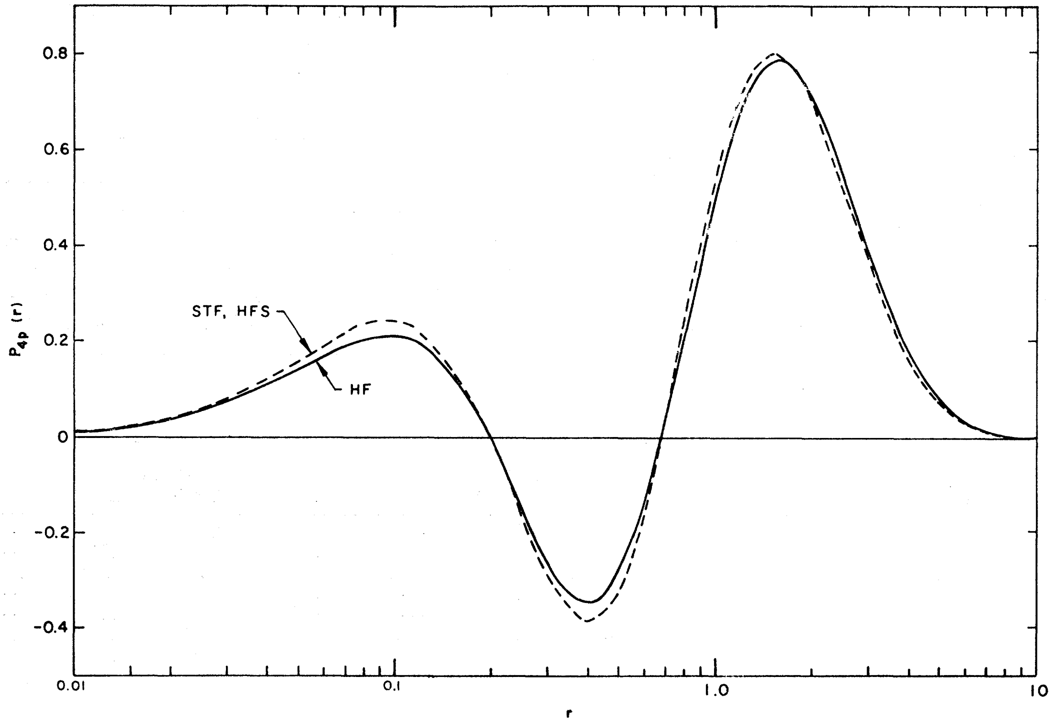

FIG. 3. $4p$ orbital in the ground state of neutral krypton ($Z=36$): Hartree-Fock (HF) by Worsley (Ref. 35), Hartree-Fock-Slater (HFS) by Herman and Skillman (Ref. 31), scaled Thomas-Fermi (STF) with $\alpha=1.02$. The difference between HFS and STF is too small to show on the graph.

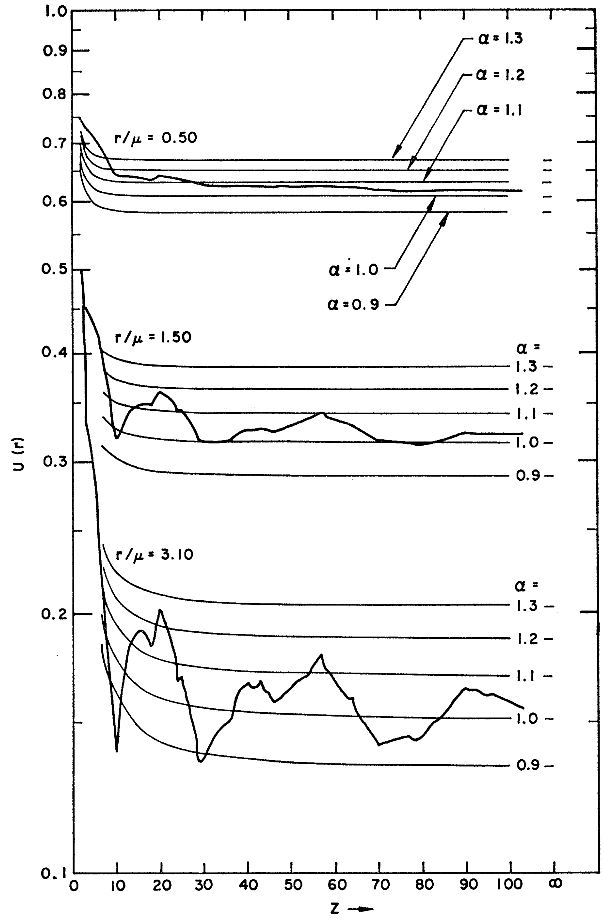

FIG. 4. Hartree-Fock-Slater (HFS) (Ref. 31) and scaled Thomas-Fermi (STF) screening functions for neutral atoms at $r/\mu = 0.50$, 1.50, 3.10. The heavy curves give the HFS values, and the light curves (labeled with values of α) the STF values.

We consider next the comparison of U_{STF} and U_{HFS} for neutral atoms. Although no HF or AHF results are available, to our knowledge, beyond $Z=47$, the HFS potentials and orbitals for the ground states of all neutral atoms have been computed by Herman and Skillman.[31] Their results for U_{HFS} at three selected values of r/μ are plotted against Z in Fig. 4, together with U_{STF} for several values of α. (The neutral TF potential used by Latter corresponds to $\alpha=1$, $Z=\infty$.) The peaks and dips in U_{HFS} as a function of Z, which reflect the influence of shell structure, show the extent to which α must fluctuate if U_{STF} is forced to fit U_{HFS}. The quality of fit obtained in a few cases is shown in Fig. 5. The STF potentials, with α's which correspond to the experimental ionization potential of the outermost electron in each atom, fit the HFS potentials closely except in the vicinity of the HFS cutoff radius.

Finally we consider the transitions $2p$-$3s$ and $2p$-$3d$ in oxygen and nitrogen in several stages of ionization, which have been investigated by Kelly using both AHF[17] and HFS[19] orbitals. Table V lists his values of the radial factor σ^2 for the transition arrays $1s^2\,2s^2\,2p^N$—$1s^2\,2s^2\,2p^{N-1}\,3s$ and $1s^2\,2s^2\,2p^N$—$1s^2\,2s^2\,2p^{N-1}\,3d$, with $N=4$ to 1 in oxygen and $N=3$ to 1 in nitrogen. Each array (except when $N=1$) consists of several multiplets; we have averaged Kelly's AHF results over the multiplets in each array, weighted with the relative multiplet strengths $\mathcal{S}(\mathfrak{M})$. The HFS method yields one value of σ^2 per array. Our STF results were calculated using as one-electron binding energies the appropriately weighted means of the experimental values; the corresponding values of α appear in the table. Some BD values, calculated from the same energies, are also shown; these result from extrapolating the BD tables into the region $l+\frac{1}{2}<n^*<l+1$ [where $n^*=z/\sqrt{(-E)}$], which is considered marginally valid by BD; where no BD values appear, it is because $n^*<l+\frac{1}{2}$ for the $2p$ orbital. Unfortunately, no measured strengths of these ultraviolet transitions are known to us. Using the AHF values as a standard of comparison, we find for every case in Table V that the STF value of σ^2 is closer (though not always much closer) to the AHF than either HFS or BD is.

V. CONCLUSIONS AND FUTURE WORK

The results presented in Sec. IV suggest that the STF method is accurate enough to provide a useful complement to the BD method. Roughly speaking, we may divide the transitions of interest into two classes: those (Class I) to which the BD method is thought to be applicable (because $n^*\geq l+1$ for the initial and final states of the active electron) and those

TABLE V. Radial integrals for nitrogen and oxygen.

				$\sigma^2(2p,3s)$				$\sigma^2(2p,3d)$			
Ion	$\alpha(2p)$	$\alpha(3s)$	$\alpha(3d)$	STF	AHF[a]	HFS[b]	BD	STF	AHF[a]	HFS[b]	BD
N I	1.27	1.40_5	1.53	0.197	0.166	0.243	···	0.0121	0.0071	0.0138	···
N II	1.45	1.64	1.75	0.101	0.112	0.142	···	0.036	0.030	0.043	···
N III	1.65	1.84	1.92_5	0.056	0.069	0.090	0.038	0.044	0.048	0.056	0.040
O I	1.16	1.24	1.28_5	0.137	0.109	0.151	···	0.0050	0.0028	0.0055	···
O II	1.32	1.46	1.50	0.080	0.082	0.098	···	0.021	0.016	0.024	···
O III	1.48	1.65	1.70	0.048	0.056	0.066	0.025	0.030	0.028	0.035	0.024
O IV	1.67	1.88	1.96	0.031	0.037	0.046	0.022	0.033	0.036	0.040	0.032

[a] See Ref. 17.
[b] See Ref. 19.

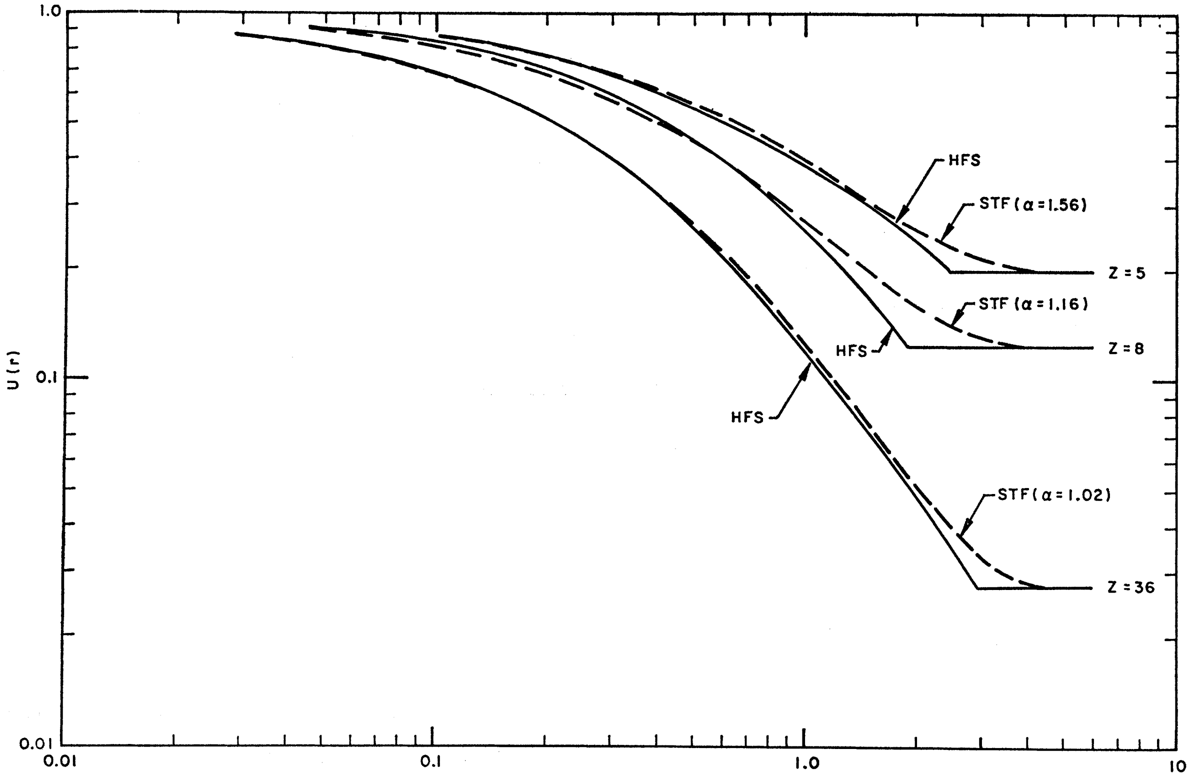

FIG. 5. Hartree-Fock-Slater (HFS) (Ref. 31) and scaled Thomas-Fermi (STF) screening functions for neutral atoms of boron ($Z=5$), oxygen ($Z=8$), and krypton ($Z=36$).

(Class II) to which it is inapplicable or marginally applicable. In Class I the STF and BD methods agree rather closely, as expected; in Class II the STF method appears to be, at least, competitive in accuracy with the HFS method as an approximation to the AHF method.

On the basis of the extensive experience of Herman and Skillman[31] and Clementi,[36] representative computing times (IBM-7090) per configuration may be estimated: about one minute for the HFS method and one hour for the AHF method at moderate atomic number, with a trend toward longer times for higher atomic numbers. In contrast, the STF method takes about five seconds per orbital (ten seconds for a transition probability). In view of these numbers and the fact that applications in astrophysics and plasma physics exist[37] which require very large numbers of oscillator strengths, we cannot regard the speed advantage of the STF method as insignificant for large-scale computation. Its most useful application is probably to Class-II transitions, which ordinarily lie in the experimentally difficult ultraviolet or soft x-ray region and are inaccessible to the BD method. For Class-I transitions the STF method does not seem to offer any advantage over the BD method except perhaps near the class boundary $n^*=l+1$; a simple program we have used which interpolates in the BD tables takes 1/15 second for a transition probability.

The need for experimental energies in the STF method is somewhat alleviated by the observation we have already mentioned: The scale factor α varies smoothly along Rydberg series and isoelectronic sequences and is always of the order of unity, permitting accurate extrapolation. The quantum defect is also smooth but has a far greater range of variation.

We also note from Tables I, II, and V that the α's involved in a transition are usually within a few percent of each other. This suggests that, as a simplifying approximation, the two α's be set equal. We would then be able to produce a universal line-strength table similar to BD but extended in scope. Instead of their parameters n^* and $n^{*\prime}$ for a given l and l', we would use n, n', n^*, and $n^{*\prime}$ for a given l and l'. The extra parameters n and n' are discrete and take on only a few values.

ACKNOWLEDGMENTS

The authors are indebted to Mrs. E. Metzner, Mrs. M. Bryant, and Dr. B. W. Roos for their invaluable aid in the computations.

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[36] E. Clementi, J. Chem. Phys. 41, 303 (1964).

[37] J. Quant. Spectry. Radiative Transfer 4, No. 5 (1964); 5, No. 1 (1965).

APPENDIX

A. Scaled Thomas-Fermi Potential for the Positive Ion

The scaled Thomas-Fermi (STF) potential of a positive ion as seen by an electron is given (in Rydbergs) by

$$\begin{aligned} -V(r) &= (2Z/r)[\varphi(x)+qx/x_0] \quad (x\leq x_0)\,, \\ &= (2Z/r)q \quad (x\geq x_0)\,, \end{aligned} \tag{A1}$$

where r is the distance in Bohr radii and x is the distance in scaled TF units, which is related to the actual distance in Bohr radii by

$$r=\alpha\mu x\,, \tag{A2}$$

with $\mu=\frac{1}{4}(9\pi^2/2Z)^{1/3}=0.88534Z^{-1/3}$. The fractional degree of ionization is $q=(Z-N)/Z$, where Z is the nuclear charge and N is the number of screening electrons in the ion. The factor α in (A2) is the scaling factor for the charge distribution, and the ionic radius in scaled TF units is x_0.

The TF function $\varphi(x)$ in Eq. (A1) satisfies the differential equation

$$\varphi''(x)=x^{-1/2}\varphi(x)^{3/2} \tag{A3}$$

subject to the boundary conditions

$$\varphi(0)=1 \tag{A4}$$

and

$$\varphi(x_0)=0\,,\quad \varphi'(x_0)=-q/x_0\,. \tag{A5}$$

The problem of solving for $\varphi(x)$ is not trivial because x_0 as a function of q is not initially available.

We have made a high-accuracy polynomial fit of $x_0(q)$ which allows the boundary conditions (A5) to be met as initial conditions so that when (A3) is integrated from x_0 back to 0, $\varphi(0)=1$ is automatically satisfied to better than 1 part in 10^5. To eliminate the singularity in (A3) for numerical solution, the substitution $x=y^2$ is made.

TABLE VI. Coefficients for determining the ionic radius x_0 (in TF units) as a function of the fractional degree of ionization q. [See Eqs. (A6)–(A11)].[a]

$n=$	a_n	b_n	c_n
0	9.959960(−9)	2.402529(−1)	2.039856(−2)
1	2.959563	−4.751733	−2.060645
2	1.853800(−1)	−3.441959	−9.042510(−1)
3	7.709556	−6.138401	−3.031483(−1)
4	−5.57687(1)	−7.127922	−3.978742(−2)
5	4.724630(2)	−6.352223	1.407012(−2)
6	−3.063916(3)	−4.261793	8.716138(−3)
7	1.503024(4)	−2.135743	2.182259(−3)
8	−5.522799(4)	−7.861645(−1)	2.367851(−5)
9	1.516092(5)	−2.061712(−1)	7.862225(−7)
10	−3.086518(5)	−3.644020(−2)	0
11	4.587142(5)	−3.888973(−3)	0
12	−4.830562(5)	−1.892519(−4)	0
13	3.412177(5)	0	0
14	−1.449479(5)	0	0
15	2.798640(4)	0	0

[a] The integers in parentheses are the powers of 10 by which the coefficients must be multiplied.

In order to maintain high accuracy throughout the physically interesting range $q=(1,0.01)$, it was found necessary to split the range into three regions: $1.0\geq q>0.5$, $0.5\geq q>0.1$, $0.1\geq q>0.01$. These regions will be identified as I, II, and III, respectively.

In region I, we have

$$x_0^{\mathrm{I}}=\sum_{n=0}^{15} a_n\xi_{\mathrm{I}}^n\,, \tag{A6}$$

where

$$\xi_{\mathrm{I}}=(1-q)^{2/3}; \quad 1.0\geq q>0.5\,. \tag{A7}$$

In region II,

$$x_0^{\mathrm{II}}=\sum_{n=0}^{12} b_n\xi_{\mathrm{II}}^n\,, \tag{A8}$$

where

$$\xi_{\mathrm{II}}=\ln q; \quad 0.5\geq q>0.1\,. \tag{A9}$$

Finally, in region III

$$x_0^{\mathrm{III}}=\exp\Bigl(\sum_{n=0}^{9} c_n\xi_{\mathrm{III}}^n\Bigr)\,, \tag{A10}$$

where

$$\xi_{\mathrm{III}}=\ln q; \quad 0.1\geq q>0.01\,. \tag{A11}$$

The coefficients a_n, b_n, c_n are given in Table VI.

B. Numerical Solution of the Schrödinger Equation

Probably the most efficient way to solve numerically a second-order ordinary differential equation with first derivatives absent is to use Numerov's method.[38] This scheme approximates the solution to the Schrödinger equation:

$$p''(r)=K(r)p(r)\,, \tag{B1}$$

where

$$K(r)=l(l+1)/r^2+V(r)-E\,, \tag{B2}$$

through the recursion relation

$$p_{n+1}=\frac{2+(5h^2/6)K(r_n)}{1-(h^2/12)K(r_{n+1})}p_n - \frac{1-(h^2/12)K(r_{n-1})}{1-(h^2/12)K(r_{n+1})}p_{n-1}\,, \tag{B3}$$

where h is the step size.

There is much to be gained, however, in changing the independent variable to

$$y=\sqrt{r} \tag{B4}$$

since, in the kind of fields we are dealing with, the nodes of the wave function become nearly equally spaced in the y scale so that the step size need not be constantly changed to maintain numerical accuracy.

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[38] R. W. Hamming, *Numerical Methods for Scientists and Engineers* (McGraw-Hill Book Company, Inc., New York, 1962).

The disadvantage to such a change of independent variable is that instead of Eq. (B1) there now appears an equation with a first derivative,

$$p''(y)-y^{-1}p'(y)=4y^2K(y^2)p(y)\,, \tag{B5}$$

which is not amenable to solution by Numerov's method. A change of dependent variable eliminates the first derivative:

$$p(y)=y^{1/2}q(y)\,, \tag{B6}$$

so that we now have

$$q''(y)=\tilde{K}(y)q(y)\,, \tag{B7}$$

where

$$\tilde{K}(y)=[16l(l+1)+3]/4y^2+4y^2[V(y^2)-E]\,, \tag{B8}$$

which is of the required form. Equation (B7) is now solved using the recursion scheme (B3), using $\tilde{K}(y)$ instead of $K(r)$, and the final solution is obtained through the transformation (B6).

C. Normalization of the Continuous Wave Functions

The continuous wave functions are integrated numerically from the origin starting with an arbitrary slope, with the consequence that the amplitude does not reach ± 1 asymptotically, as required. At energies of several Rydbergs, this is not a problem since the wave function quickly reaches its asymptotic amplitude and could be renormalized by inspection. At a fraction of a Rydberg, however, the asymptotic amplitude is not attained except at distances which are prohibitively distant for numerical integration.

We have found, using recently published tables of Coulomb wave functions[39] as a check, that it is possible to apply the WKB approximation to normalize our continuum wave functions with sufficient accuracy.

Let $r_0=\alpha\mu x_0$ be the ionic radius. At distances $r>r_0$, continuous wave functions must be a linear combination of $F(r)$ and $G(r)$, the regular and irregular Coulomb wave functions, respectively:

$$P(r)=\alpha F(r)+\beta G(r)\,. \tag{C1}$$

Since we require that $P(r)$ reach unit amplitude at infinity, and since $F(r)$ and $G(r)$ are already normalized to behave asymptotically like sine and cosine, $P(r)$ will be properly normalized by dividing it by

$$(\alpha^2+\beta^2)^{1/2}.$$

To find $\alpha^2+\beta^2$, a point $R>r_0$ is found, by interpolating between points of the numerical solution if necessary, where

$$P(R)=\alpha F(R)+\beta G(R)=0\,. \tag{C2}$$

The derivative (with respect to r) is found here also:

$$D(R)\equiv\alpha F'(R)+\beta G'(R)\,. \tag{C3}$$

We make use of the Wronskian, $FG'-GF'=\sqrt{E}$, to find that

$$\alpha^2+\beta^2=D^2(F^2+G^2)/E\,. \tag{C4}$$

We have found that the WKB approximation

$$F^2(R)+G^2(R)\approx\left[\frac{E}{E+(2z/R)-[l(l+1)/R^2]}\right]^{1/2} \tag{C5}$$

holds extremely well, provided

$$R>\max\{r_0,\,(l+1)^2/z,\,5/z\}\,. \tag{C6}$$

These are modest requirements. Equation (C5) is then accurate to better than 1% even in the limit $E\rightarrow 0$.

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[39] A. R. Curtis, *Royal Society Mathematical Tables* (University Press, Cambridge, England, 1964), Vol. 11.