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Energies and wave functions for many-electron atoms

Young-Dae Jung and Robert J. Gould
Department of Physics, 0319, University of California, San Diego, La Jolla, California 92093-0319
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Screening constants σ are given for one-electron basis-set radial wave functions for atomic systems with $2 \leq Z \leq 18$. The parameters σ for an individual screened electron (i) are dependent on the states of the screening electron (j), and the matrix of values σ_{ij} is different from that suggested long ago by Slater [Phys. Rev. **36**, 57 (1930)]. The matrix is slightly more complicated than Slater's, but the results for individual electron binding energies are much more accurate—even comparable in accuracy with Hartree-Fock (HF) values. The procedure is applied to compute both inner- and outer-shell binding energies, and a comparison is made with other similar calculations as well as with the HF and experimental values. The K-shell binding energies E_K calculated with the new screening constants are in particularly close agreement with the results of HF calculations and with experimental values for elements for which accurate measurements can be made for gaseous atomic species. The quantities E_K computed for C, N, and O atoms by the screening-constant method, while in agreement with HF calculations, differ from the values now being employed to evaluate the x-ray opacity of the interstellar gas. These currently used K threshold energies have not been measured for gaseous monatomic matter and are off by 2–6%; the theoretical E_K are very likely more accurate and should be adopted. A simple prescription is suggested for modifying the screening-constant wave functions for $2p$ states. Uncorrected, these functions, which are hydrogenic, fall off too fast at large r. Adding a single additional exponential term gives a much better fit to the HF functions, and a universal coefficient is suggested for this term. The prescription yields good agreement with HF values for $\langle r \rangle$ and $\langle r^2 \rangle$ for the species B to Ne; the computed diamagnetic susceptibility for Ne using the simple modified wave function agrees well with the experimental value.

I. INTRODUCTION

The description of the states of many-electron atoms requires simplifying approximations. One general approach that works well is the Hartree-Fock (HF) or self-consistent-field method, which, however, requires numerical procedures and generates wave functions in tabular form. The numerical wave functions can be expressed in terms of a sum of exponential terms with certain exponents and coefficients, but these are different for each atomic system. The HF method has been used extensively to compute wave functions and energies for atomic systems and for the evaluation of dynamical processes such as rates of transitions involving these systems. Even with the amount of work involved, the method still has its limitations in the accuracy of the results. For example, the HF calculation of the ionization energy of atomic oxygen is in error by about 13%. This is because there are approximations involved in the HF method, such as the independent-particle approximation (IPA) and the central-field approximation (CFA). The error introduced depends on the system involved, and the above example (13%) is perhaps an extreme case since it involves an atomic system with a half-filled outer shell. For most applications the HF method yields very accurate results, especially for the calculation of energies and especially for the description of inner-shell states for which the inherent approximations IPA and CFA are very good.

Sometimes highly accurate wave functions are not required for a description of an atomic state. For example, it may be that a certain problem or application calls for only an approximate representation of the wave function. A very simple set of prescriptions for this purpose was suggested long ago by Slater [1] to give approximate wave functions and energies for many-electron atoms of low to moderate atomic number. Slater gave simple rules for determining an effective Coulomb field seen by an individual electron in a particular one-particle state. Because of their basic simplicity and the reasonable accuracy of the results, the Slater rules are still employed today. Other authors have given modified rules to improve the accuracy of the wave functions and energies and a comparison of the various results will be summarized later in this paper.

For the case of an atomic system stripped of some of its electrons, a description by means of screened hydrogenic states or screened hydrogenic basis functions is particularly accurate and convenient. In fact, even if only one or two electrons are removed the IPA and CFA approximations are much better than in the neutral-atom case. Also, the representation of the total Hamiltonian in terms of a sum of independent effective Coulomb potentials is a better approximation (see following section). Thus the criteria for the applicability of the screening-constant and HF approaches are essentially the same although the latter makes less drastic approximations and should *a priori* be expected to yield more accurate results. In fact, the former method can be made to yield values for the energies of *comparable* accuracy, even for the outer-shell states and even for neutral atoms; the accuracy of calculations for ionized species can be expected to be even better. In many areas of astrophysics and plasma physics the ionized atomic systems are of particular interest. The establishment of effective screening constants, energies, and wave functions is then very useful, since the procedure is a general one and the treatment is analytical rather than numerical as in the HF approach. The screening-constant analytical functions can also be used as starting input functions in the HF calculations. A simple and quantitative understanding of atomic shell structure is also attained, especially for low-Z species for which there is less overlap in the wave functions for states of different principal quantum number n. What is most unexpected and encouraging, however, is the high accuracy of the results in the screening-constant formulation. The accuracy approaches that in the HF calculations and the procedure has the advantage of applicability to any atomic system.

The screening-constant formulation and derivation of their values is outlined in Sec. II. Comparison with previous work, HF calculations, and experimental results for energies is also given there. Section III is concerned with certain aspects of the associated wave functions, with a special application to the calculation of the diamagnetic susceptibility of neon as a test of their accuracy. For the calculation of this quantity the $2p$ wave function must be modified to give a more accurate representation in the large-r tail.

II. SCREENING CONSTANTS AND ENERGIES

A. Formulation

Neglecting spin-orbit and relativistic effects, the Hamiltonian for a many-electron atomic system consists of terms from the electron's kinetic energy, their attraction to the central nucleus, and the Coulomb repulsion between the electrons; in atomic units ($e=\hbar=m=1$),

$$H=-\tfrac{1}{2}\sum_i \nabla_i^2 - Z\sum_i \frac{1}{r_i}+\sum_{i>j}\frac{1}{r_{ij}} . \tag{1}$$

For a system with N electrons $i,j=1,2,\ldots,N$, and the solution to the many-electron Schrödinger equation

$$Hu=Eu \tag{2}$$

is a function of $3N$ variables: $u=u(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$. This is, of course, an impossible task because of the $1/r_{ij}$ terms in the Hamiltonian that introduce correlation effects and prevent factorization in the wave function u. If the Hamiltonian is approximated by

$$H\approx\sum_i H_i , \tag{3}$$

with, moreover,

$$H_i=-\tfrac{1}{2}\nabla_i^2-\frac{Z-S_i}{r_i} , \tag{4}$$

where the S_i are constants, the problem is greatly simplified. In this extreme version of the IPA and CFA each electron is taken to move in an effective Coulomb field. The total and one-electron energies are then, in this approximation.

$$E\approx\sum_i E_i , \tag{5}$$

$$E_i=-(Z-S_i)^2/2n_i^2 , \tag{6}$$

where n_i is the principal quantum number for the one-electron state. The individual wave functions are the hydrogenic functions

$$u_{nlm}(\mathbf{r})=R_{nl}(r)Y_{lm}(\theta,\phi) , \tag{7}$$

in terms of the radial function and spherical harmonics. The symmetrized many-electron wave function constructed from the one-electron states would be the Slater determinant

$$u=\frac{1}{\sqrt{N!}}\sum_P \epsilon_P \prod_{i=1}^{N} u_{Pi}(i) , \tag{8}$$

in which P is the permutation operator and ϵ_P is $+1$ or -1 depending on whether the reordering is an even $(+)$ or odd $(-)$ permutation of $1,2,\ldots,N$.

In the drastic approximation (3) with the individual terms (4) and the resulting energies (5) and (6), there will be no multiplet splitting, which occurs for many-electron systems with incompleted shells. Multiplet splitting arises from the $1/r_{ij}$ terms in the accurate Hamiltonian (1) and these terms are absorbed into S_i/r_i for the individual H_i. These terms in H_i then represent the electron-electron Coulomb energy *per electron,* such that the sum over i is the same as the sum over pairs in the total Hamiltonian (1). However, because of the separable form for the Hamiltonian the energies are given by (5) and (6) and represent an average over the multiplet. Multiplet splitting would result if we evaluated the *difference* between the Hamiltonians (1) and (3). Even without the calculation of this difference, the present description is very useful and can be employed to give, with appropriate choices for the screening constants S_i, approximate results for energies and wave functions.

B. Screening-constant matrix

Screening constants for low-Z atomic systems ($N\le 18$) were first suggested by Slater [1]. For each screened electron (i) in a particular nlm state there would be a contribution σ_{ij} to S_i from each of the other screening (j) electrons:

$$S_i=\sum_j \sigma_{ij} . \tag{9}$$

There is then a matrix of screening parameters with the row i and column j designating, respectively, the screened and screening electrons. Slater's values [2] for the σ_{ij} are reproduced in Table I. Obviously, there has been some simplification and rounding off in coming up with this set of parameters, and revised values can be obtained that provided a better description of energy level structure.

For example, variations on the two numbers 0.85 and 0.35 at points in the matrix can be introduced, and there are good reasons for doing this aside from fitting experimental data.

In the Slater rules the screening of the 2*s* and 2*p* electrons by the 1*s* electron is the same, and this should not be the case. The 2*s* wave function has a "1*s* part," being larger than the 2*p* function at small *r* where screening by the inner electron takes place. Screening is then less complete for the 2*s* state and we expect

$$\sigma_{2s1s} < \sigma_{2p1s} \; . \tag{10}$$

Further, consider the 2×2 submatrices σ'_{ij} in which i,j are 2*s* and 2*p* and also 3*s* and 3*p*. In the Slater rules this has the simple form

$$\sigma'_{ij} = \begin{bmatrix} u & u \\ u & u \end{bmatrix} , \tag{11}$$

with $u = 0.35$. This, too, is an approximation, made in the interest of simplicity, that can be modified. In principle, all four elements of this matrix should be different and be different for the 2*s*,2*p* and 3*s*,3*p* cases. However, in modifying the Slater rules we want to retain the element of simplicity and also provide some physical basis and insight for the new results. Modifications of σ'_{ij} that could be attempted are, for example, the two-parameter forms

$$\sigma'_{ij} \to \sigma''_{ij} = \begin{bmatrix} u & v \\ u & v \end{bmatrix} , \begin{bmatrix} u & u \\ v & v \end{bmatrix} , \begin{bmatrix} u & v \\ v & u \end{bmatrix} \; . \tag{12}$$

In fact, we find that the first form on the right works best and we shall try to provide some explanation for why this should be so. Moreover, we find that $u < v$, and this too can be understood.

There have been other attempts to obtain screening constants since the original work of Slater in 1930; the work of Clementi and Raimondi [3] and Burns [4] can be cited and the results in this paper will be compared with theirs. Both Slater and Burns assume, as we do, that the energy levels are related to the screening constants by means of relations (5), (6), and (9); that is, the electrons are regarded as moving in effective Coulomb fields. This is not assumed by Clementi and Raimondi, in whose work the corresponding screening parameters are meant to go with exponents in nodeless basis-set functions in analytic forms for one-electron functions in HF calculations. The approach in the present work is most closely related to that of Slater. However, our parameters are different and the resulting energy values are more accurate.

TABLE I. Slater screening matrix (σ_{ij}).

	Screening				
Screened	1*s*	2*s*	2*p*	3*s*	3*p*
1*s*	0.30	0	0	0	0
2*s*	0.85	0.35	0.35	0	0
2*p*	0.85	0.35	0.35	0	0
3*s*	1.00	0.85	0.85	0.35	0.35
3*p*	1.00	0.85	0.85	0.35	0.35

For our modified matrix σ_{ij}, in the interest of simplicity, we retain the 0's and 1's of the Slater matrix in Table I, and we include only two digits in all the other values. The constant σ_{1s1s} is set equal to the "theoretical" value of 0.31; this is just $\frac{5}{16}$ obtained in a one-parameter variational calculation for bare two-electron systems. This is found to be quite accurate for *K*-shell electrons and would be approached as *Z* becomes increasingly larger than 2. The corresponding variational wave function corresponds, moreover, to an effective Coulomb field description. The two parameters of Eq. (10) are to be determined by comparison with experimental data and accurate HF calculations, and the best fit does yield the inequality as suggested. In the submatrix σ''_{ij} we take, at first for *i* and *j* equal to 2*s*,2*p*, the first two-parameter form on the right side of Eq. (12); that is,

$$u = \sigma_{2s2s} = \sigma_{2p2s}, \quad v = \sigma_{2s2p} = \sigma_{2p2p} \; . \tag{13}$$

Physically, this can be taken to imply, if electron *i* is described by a wave function having a characteristic radial extent r_i that is roughly the same for 2*s* and 2*p* states [5], that screening *by* the same electron is equal. This would then be so for electrons in the same *n* shell, for screening by electrons in inner shells the situation is different, since $\sigma_{2s1s} \neq \sigma_{2p1s}$. In the usual notation for radial wave functions, in terms of

$$P_{nl}(r) = rR_{nl}(r) \; , \tag{14}$$

a measure of the screening by electron *j* would be the charge interior to *r*:

$$N_j(r) = \int_0^r P_j^2(r) dr \; . \tag{15}$$

The ratio $N_{2s}(r)/N_{2p}(r)$ can be computed easily for hydrogenic wave functions; it goes asymptotically to unity at $r = \infty$, and for very small *r* it is much greater than unity. On the other hand, for a range of *r*, including the "characteristic" *r* of about $4/Z$ (effective *Z*) the ratio is in the neighborhood of 0.7, similar to the value of u/v that is found for the screening constants.

To determine the elements of the 3×3 submatrix with *i* and *j* equal to 1,2,3, we consider the neutral atomic species with $Z = 3-10$. The problem is the evaluation of four parameters in this submatrix, and there are experimental data and results of HF calculations for 1*s*, 2*s*, and 2*p* binding energies for these eight elements. We have used only the higher-*Z* end (F and Ne), since these species have the maximum number of 2*p* electrons and since only Ne has an accurate experimental measurement of the 1*s* binding energy. As a confirmation of the accuracy of the parameters—and of the effective Coulomb field approach—the resulting approximate calculations of binding energies at the lower *Z* are found to give good results. For the most weakly bound electrons we have relied on the work of Clementi and Roetti [6], who calculate HF ionization energies for the basic Hamiltonian (1); they have given results for all multiplet levels (when there is multiplet splitting) for neutral and singly ionized species. For more general results for individual one-electron binding energies for 1*s*, 2*s*, and 2*p* electrons, the relaxed-orbital relativistic HF results of Huang *et al.* [7] are used, these calculations include a number of small corrections, such as fine-structure splitting (for *p* electrons), and values quoted here are for both corresponding *j* levels. Comparison is made with the less accurate HF calculations of Mann [8], which are in the "frozen orbital" (Koopmans's theorem) approximation.

The values found for the 3×3 submatrix are given in the upper left of Table II; the inequality (10) occurs and $u/v \approx 0.74$. For individual one-electron states the parameters (10) for neutral oxygen are compared with previous results in Table III and it is seen that the values are close to those of Slater; however, the differences are significant. Burns's values are very different and hard to understand. Note that we have carried the submatrix σ''_{ij} in Table II down into the lower right for the 3*s* and 3*p* states; the column with 0.90 and 0.95 has been retained as well for screening in these states by 2*s* and 2*p* electrons. Although we have tried other values for the elements of σ_{ij} in the lower right, the numbers adopted give equally good results for binding energies for the *K* and *M* shells for Na to Ar; the values for the 2*p* binding energies for these species are not quite as good, but there is a reason for this. The matrix in Table II could be modified further, of course, and this is not the only combination of numbers that can yield accurate binding energies. However, the simplicity of the original Slater approach has been retained and the revision of the screening constants has a physical basis.

Finally, concerning the screening constants and energies, it may be well to emphasize here that the one-electron values E_i in (6) are different from eigenvalues that would be obtained in a HF calculation. In particular, the latter one-electron energies would be associated with the Coulomb interaction of, say, electron *i* with all of the other electrons. In the formulation given in this work the E_i represent the energy *per electron* such that the sum over *i* yields the total energy of the system. In the total energy the sum of $1/r_{ij}$ over pairs is, of course, meant to be counted only once. These same remarks apply for the meaning of the screening parameters S_i and σ_{ij}; that is, they are essentially defined in terms of the form (6) and the total (5). This definition is the same as in the original Slater treatment. Our σ_{ij} are determined phenomenologically, except for the 1*s*-1*s* value which is that associated with the one-parameter variational treatment of the two-electron problem. The result of that elementary calculation is consistent with our general approach, since it gives $-(Z-\frac{5}{16})^2$ for the energy. This energy is the same as if we were to take H_1+H_2 [as in (3)] for the two-electron Hamiltonian with each electron being affected by a Coulomb field of charge $Z-\frac{5}{16}$. That is, the Coulomb repulsion energy is essentially divided between electrons 1 and 2.

TABLE II. Modified screening matrix (σ_{ij}).

Screened	Screening 1*s*	2*s*	2*p*	3*s*	3*p*
1*s*	0.31	0	0	0	0
2*s*	0.90	0.25	0.34	0	0
2*p*	0.95	0.25	0.34	0	0
3*s*	1.00	0.90	0.90	0.25	0.34
3*p*	1.00	0.95	0.95	0.25	0.34

TABLE III. Comparison of screening ($Z-S_i$) for states of neutral oxygen. The designations S, CR, and B refer to the work of Slater (Ref. [1]), Clementi and Raimondi (Ref. [3]), and Burns (Ref. [4]); JG designates the present work (Jung and Gould).

State	S	CR	B	JG
1*s*	7.70	7.66	7.65	7.69
2*s*	4.55	4.48	5.15	4.59
2*p*	4.55	4.42	3.95	4.58

The individual energies E_i computed from (6) are, moreover, different from the actual binding energies for the associated states. The binding energies, discussed in the following subsections, are obtained by taking the difference between the *total* energy of the system with and without the particular electron.

C. *K*-shell energies

Results for *K*-shell binding energies for the 16 neutral atoms Li to Ar are given in Table IV. The first three columns of numbers compare values for E_K computed from the screening constants suggested by Slater, Burns, and this work. We do not compute E_K from the screening constants given by Clementi and Raimondi [3], since they do not imply the existence of Eqs. (5) and (6) to be used with their parameters. Two sets of HF calculations are given for comparison; here the results of Huang *et al.* should be considered as much more accurate than those of Mann, for the reasons already stated. In Sevier's compilation [9] of experimental data, as stated in that work, the numbers for Be, B, Si, P, S, and Cl are suspect; we feel, in particular, that the values for Be and B must be in error. For these elements and many others, the HF results of Huang *et al.* [denoted by HF (H) in Table IV] and our results (labeled in the table as JG for Jung and Gould) should be considered as more accurate. That is, the E_K can be calculated better than they can be measured for elements that do not exist normally in gaseous atomic form. The value 64.39±0.03 eV for Li should be considered as accurate, however, and this is important as a test of the HF(H) and JG results. The experimental number is based on the spectroscopic work of Ederer, Lucatorto, and Madden [10] on lithium vapor. The agreement with experiment for the HF(H) and JG results for Li and Ne (870.1±0.2 eV) suggests that the theoretical calculations are preferable to the experimental values for the elements in between. The *CRC Handbook of Chemistry and Physics* [13] and Lotz [14] compilations of experimental data are listed in Table IV for comparison, partly

TABLE IV. K-shell binding energies (eV). The designations S, B, and JG refer to Slater (Ref. [1]), Burns (Ref. [4]), and the present work. Two HF results are listed [Huang *et al.* (Ref. [7]) and Mann (Ref. [8])]. The compilation of experimental data on atomic species by Sevier (Ref. [9]), is designated by "Expt." HCP is the *CRC Handbook of Chemistry and Physics* (Ref. [13]) and L refers to the compilation by Lotz (Ref. [14]). The column labeled DC gives results from the extrapolation formula of Daltabuit and Cox (Ref. [11]).

Atom	S	B	JG	HF(H)	HF(M)	Expt.	HCP	L	DC
Li	65.95	58.67	64.35	63.85	67.42	64.39	54.7	58	59
Be	127.37	117.37	123.43	123.22	128.78	119.3	111.5	115	113
B	208.48	194.51	201.06	200.82	209.40	194	188	192	186
C	309.29	290.02	297.37	296.94	308.54		284.2	288	280
N	429.80	403.91	412.36	411.88	426.31		409.9	403	395
O	570.00	536.15	546.02	545.37	562.76		543.1	538	533
F	729.89	686.77	698.37	697.59	717.92		696.7	694	694
Ne	909.48	855.75	869.40	869.15	891.79	870.1	870.2	870.1	878
Na	1124.45	1064.38	1080.28	1078.19	1101.48	1079.1	1070.8	1075	1088
Mg	1362.70	1296.28	1313.83	1310.58	1334.23	1311.2	1303	1308	1322
Al	1624.24	1549.20	1571.81	1567.87	1591.90	1567.0	1562.3	1564	1581
Si	1909.05	1825.39	1853.01	1848.62	1872.68	1846	1839	1844	1867
P	2217.15	2124.87	2157.43	2152.32	2176.62	2154	2149	2148	2179
S	2548.53	2447.63	2485.48	2479.91	2503.75	2477	2472	2476	2517
Cl	2903.18	2793.67	2835.94	2830.93	2854.06	2830	2823	2829	2884
Ar	3281.12	3163.00	3210.02	3205.39	3227.56	3202.9	3205.9	3206.3	3277

to show the differences that exist among the various references. The last column gives the values suggested by Daltabuit and Cox [11] (DC). The DC values are perhaps the most erroneous, not that it is their fault, however, since they just adopted the "best" values at the time. Unfortunately, though, the DC K thresholds are currently being used for the important application to interstellar x-ray absorption [12]. Erroneous E_K (error$\approx$6% for C, 4% for N, 2% for O, etc.) have been employed in countless papers in x-ray astronomy, even before the work of DC.

For the elements Li to Ne the agreement between the JG and HF(H) values for E_K is remarkable. Given the inherent approximations in the HF method there is essentially no difference in the collection of values. In fact, sine there is actually better agreement in the JG results when comparison is made with the reliable experimental results for Li and Ne, the JG numbers might be slightly preferable to HF(H) for the elements B to F. Certainly the JG energies agree as well as could be hoped for. For one thing, the σ_{ij} have all been rounded to two significant figures; the E_i are proportional to $(Z-S_i)^2$, so that the expected relative uncertainty in the JG energies could be of order $0.02/Z$. The agreement is much better than this—of the order 0.1%. On the other hand, the Slater screening constants yield E_K off by 4–5% for the elements C to Ne; the Burns values are also in error by about this amount.

For the elements Na to Ar there is still good agreement between our values and those of Huang *et al.* values for E_K, with a typical difference of about 0.1–0.2%. Again, this is about as good as can be expected, especially since no new adjusted parameters were introduced in the lower right of the σ_{ij} matrix (Table II). The errors in the Slater and Burns values are much greater, typically about 2–4%. In general, for the elements Na to Ar the Huang *et al.* energies should probably be taken as most accurate, since the IPA and CFA are probably very good approximations. The HF values of Mann [denoted by HF(M)] are less satisfactory but better than for lower Z because of the reduced error from the frozen orbital approximation.

Finally, concerning K-shell binding energies, there is another reason why a simple description must have limited accuracy: there are relativistic corrections to the energy. The correction factor can be written as $1+\eta_r$, and for hydrogenic 1s states

$$\eta_r(1s)=\tfrac{1}{4}Z^2\alpha^2\ , \tag{16}$$

where α is the fine-structure constant. For Ne, $Z\approx10$ (effecive value), and $\eta_r\approx0.0013$; for Ar, $Z\approx18$, and $\eta_r\approx0.0043$. Thus deviations of several tenths of a percent can be expected on this basis alone.

D. Outer- and intermediate-shell energies

Accurate calculation of binding energies for the L and M shells is more difficult than for the K shell, whether by HF or screening-constant methods. In the HF approach there are the IPA and CFA assumptions which, however, are still not as drastic as the approximation in the screening-constant approach which considers the effective field affecting an individual electron as that of a (screened) Coulomb field. Nevertheless, the latter method does seem to work well in explaining the 2s, 2p, 3s, and 3p binding energies for the elements Li to Ar. For example, we now obtain very different values for the 2s and 2p energies as well as for 3s and 3p, while with Slater screening constants the energies would be the same. A comparison of energies is given in Tables

TABLE V. L-shell binding energies (eV) (Li to Ne). The column titles are the same as in Table IV. An additional collection HF(CR) of calculated binding energies is listed, from the work of Clementi and Roetti (Ref. [6]). Their binding energies are associated with the lowest multiplet level of the atom and corresponding ion, that is, the energy listed is the normal ionization energy. The parentheses after some of the $2p$ energies indicate the particular j value ($\frac{1}{2}$ or $\frac{3}{2}$) for the state when it is distinguished in the calculation or measurement.

Atom	nl	S	B	JG	HF(H)	HF(M)	HF(CR)	Expt.
Li	$2s$	5.75	5.75	4.90	5.33	5.34	5.34	5.39
Be	$2s$	7.87	7.87	9.41	7.99	8.42	8.05	9.32
B	$2s$	9.78	11.11	13.89	12.63	13.46		14.05
	$2p$	9.78	5.85	10.13	7.97	8.43	7.93	8.30
C	$2s$	11.46	14.27	19.08	18.11	19.38		19.39
	$2p$	11.46	7.23	12.30	9.48	11.07	10.79	11.26
N	$2s$	12.93	17.36	25.00	24.32	26.22		25.41
	$2p$	12.93	8.38	14.38	11.75$(\frac{1}{2})$	13.84	13.96	14.55
					12.62$(\frac{3}{2})$			
O	$2s$	14.17	20.39	31.64	31.61	34.02		32.31
	$2p$	14.17	9.32	16.37	14.07$(\frac{1}{2})$	16.77	11.89	13.62
					14.71$(\frac{3}{2})$			
F	$2s$	15.19	23.35	38.99	39.73	42.79		40.19
	$2p$	15.19	10.03	18.27	16.59$(\frac{1}{2})$	19.86	15.72	17.42
					16.92$(\frac{3}{2})$			
Ne	$2s$	15.99	26.24	47.06	49.21	52.53		48.47
	$2p$	15.99	10.53	20.08	19.50$(\frac{1}{2})$	23.14	19.85	21.66$(\frac{1}{2})$
					19.40$(\frac{3}{2})$			21.56$(\frac{3}{2})$

V–VII, and we now discuss the results in the various energy classes and for the elements Li to Ar. Basically, as for the K-shell energies, the comparison of our (JG) values should be made with the Slater energies, the various HF calculations, and with the experimental (Expt.) results.

First, considering the $2s$ binding energies, the JG values are much better than the other screening-constant results of Slater and Burns. Comparing with experiment (Expt.), they are, on the whole, better than the HF results for Li to Ne but not quite as good as HF for Na to Ar. The $3s$ JG energies are much better than the Slater values and the Burns energies are completely erroneous, actually being negative. Comparing with experiment, the JG $3s$ values are even better than those from HF calculations, this is surprising and encouraging, since the lower-right submatrix in Table II was simply taken down from that for the $2s$-$2p$ part of the matrix with no new adjusted parameters.

The story on the $2p$ and $3p$ binding energies is more complex and, for several reasons, the simplified methods of screening constants cannot hope to give results with high accuracy for a large range of elements. For one thing, in our effective Coulomb field approximation (3), as in the original Slater approach, there is no multiplet splitting that arises from electron-electron repulsion terms $1/r_{ij}$ in the Hamiltonian. These effects could, of course, be evaluated in the usual perturbation approach by computing the difference between the exact and approximate Hamiltonians. Still, on the whole, the JG results for binding energies are fairly good as can be seen from the tables. For the $2p$ energies, the JG values are comparable in accuracy to HF and better than Slater's results for the elements N to Ne. For Na to Ar the JG $2p$ energies are not as good as HF, but this is to be expected. With our simplified matrix we have not accounted for screening of $2p$ states by M-shell electrons; that is, there really should be some small components $\sigma_{34} \approx \sigma_{35} = \epsilon$ in the matrix in Table II. As a result, without these components the JG $2p$ binding energies are too large by about 10% for the elements Na to Ar. These effects are larger for $2p$ states than $2s$ states because of the more significant large-r tail in the former's radial wave function. The JG $3p$ energies seem to be comparable in accuracy to HF values, except at the upper end (Ar). As for the $3s$ energies, this should be seen as a successful set of results, since no new adjustable parameters were introduced to the σ_{ij} matrix for the M shell. Again except for Ar, the JG $3p$ energies are, on the whole, considerably better than the older Slater values. As in the $3s$ case, the Burns $3p$ energies are not at all accurate.

For outer-shell $2p$ and $3p$ electrons, perhaps the best HF energies are the Clementi-Roetti [6] (CR) results. Their values given in Tables V and VII are for the lowest level of the multiplet, when there is splitting, and would then correspond to the experimental energies. Although these HF energies are quite good in most cases, the agreement with experiment is not always to high accuracy. As noted earlier, for example, the computed oxygen value (11.89 eV) differs from the experimental number (13.62

TABLE VI. *L*-shell binding energies (eV) (Na to Ar). The column headings are the same as in Table IV.

Atom	*nl*	S	B	JG	HF(H)	HF(M)	Expt.
Na	2*s*	35.77	46.00	72.64	71.85	76.11	70.9
	2*p*	35.77	23.18	41.30	36.60($\frac{1}{2}$)	41.31	38.38($\frac{1}{2}$)
					36.43($\frac{3}{2}$)		38.02($\frac{3}{2}$)
Mg	2*s*	59.02	69.23	100.94	97.57	102.53	95
	2*p*	59.02	38.20	65.25	56.40($\frac{1}{2}$)	62.10	55.0($\frac{1}{2}$)
					56.13($\frac{3}{2}$)		54.8($\frac{3}{2}$)
Al	2*s*	85.73	93.27	132.96	127.85	133.63	125.6
	2*p*	85.73	60.22	92.92	81.12($\frac{1}{2}$)	87.58	80.7($\frac{1}{2}$)
					80.37($\frac{3}{2}$)		80.3($\frac{3}{2}$)
Si	2*s*	115.90	120.19	167.99	161.24	167.70	156
	2*p*	115.90	85.64	123.60	109.00($\frac{1}{2}$)	115.99	107($\frac{1}{2}$)
					107.58($\frac{3}{2}$)		106($\frac{3}{2}$)
P	2*s*	149.53	149.98	206.04	197.77	204.87	194
	2*p*	149.53	114.14	157.29	139.58($\frac{1}{2}$)	147.44	141($\frac{1}{2}$)
					138.01($\frac{3}{2}$)		140($\frac{3}{2}$)
S	2*s*	186.63	182.64	247.09	237.54	245.17	235
	2*p*	186.63	146.63	193.99	173.29($\frac{1}{2}$)	181.99	171($\frac{1}{2}$)
					171.55($\frac{3}{2}$)		170($\frac{3}{2}$)
Cl	2*s*	227.18	218.17	291.16	280.41	288.64	278
	2*p*	227.18	182.21	233.70	209.99($\frac{1}{2}$)	219.66	210($\frac{1}{2}$)
					208.06($\frac{3}{2}$)		208($\frac{3}{2}$)
Ar	2*s*	271.20	258.58	338.24	326.66	335.30	326.0
	2*p*	271.20	221.18	276.43	249.95($\frac{1}{2}$)	260.45	250.55($\frac{1}{2}$)
					247.80($\frac{3}{2}$)		248.50($\frac{3}{2}$)

TABLE VII. *M*-shell binding energies (eV) (Na to Ar). The column headings are the same as in Table V.

Atom	*nl*	S	B	JG	HF(H)	HF(M)	HF(CR)	Expt.
Na	3*s*	7.32	−20.33	4.90	4.86	4.96	4.95	5.14
Mg	3*s*	9.08	−22.96	7.81	6.57	6.89	6.61	7.65
Al	3*s*	10.74	−24.71	10.77	10.17	10.71		11.33
	3*p*	10.74	−0.33	5.76	5.51	5.71	5.50	5.99
Si	3*s*	12.31	−26.76	14.05	14.04	14.79		15.17
	3*p*	12.31	−0.02	7.02	6.78	7.59	7.66	8.18
P	3*s*	13.77	−28.84	17.65	18.13	19.22		20.17
	3*p*	13.77	0.18	8.23	8.53($\frac{1}{2}$)	9.54	10.04	10.53
					9.04($\frac{3}{2}$)			
S	3*s*	15.14	−30.96	21.57	22.88	24.02		21.30
	3*p*	15.14	0.29	9.41	10.26($\frac{1}{2}$)	11.60	9.03	10.34
					10.60($\frac{3}{2}$)			
Cl	3*s*	16.41	−33.10	25.80	27.91	29.20		25.31
	3*p*	16.41	0.30	10.54	12.54($\frac{1}{2}$)	13.78	11.79	12.97
					12.65($\frac{3}{2}$)			
Ar	3*s*	17.58	−35.27	30.37	33.20	34.76		29.24
	3*p*	17.58	0.22	11.64	14.76($\frac{1}{2}$)	16.08	14.77	15.81
					14.58($\frac{3}{2}$)			

eV) by 13%. The difference is probably due to the inherent IPA and CFA approximations in the HF method. In neutral oxygen the $2p$ electrons interact with a half-filled shell, a condition where the approximations should be least accurate. Compare, also, the CR result for sulfur (Table VII) which is again off by 13% (and in the same direction—too small).

Concerning the general experimental values for outer-shell electrons, they have, with a few exceptions, been taken from the compilation by Sevier [9]; in some case experimental errors are listed therein and these have been omitted here. Also, in some rare cases, in the interest of simplicity for our tables, an average over several experimental numbers has been taken. Our aim is mainly to provide a general comparison of theoretical descriptions of outer-shell level structure. Very precise experimental energy values are not of prime interest for these purposes; actually, some experimental energies are not determined to high accuracy (see Table VI).

III. WAVE FUNCTIONS

A. Construction from single-term basis functions

The formulation in Sec. II A approximates the many-electron Hamiltonian (1) by a sum of hydrogenic forms (3), yielding the associated energies (5) and (6). However, the individual S_i are different for each individual one-electron state; with the modified screening constants, even the $2s$ and $2p$ states have different S_i. The values for $1s$ states are very different from those for the L and M shells. As a result, the hydrogenic functions (7) are not orthogonal, except for the cases where the angular quantum numbers l and m differ from another pair (l' and m'). For example, the hydrogenic $1s$ and $2s$ functions would not be orthogonal because $Z-S_{1s}>Z-S_{2s}$. A completely hydrogenic function using $Z-S_{2s}$ as the effective Z value is not a bad representation of radial wave function, but a simple procedure leads to a much improved analytic form for the state. An illustration of this for atomic oxygen is provided by Fig. 1 of a previous paper [15]. In this figure h-S designates a completely hydrogenic function using an effective Z value $Z-S_{2s}$ and S_{2s} evaluated from Slater screening constants; with our modified parameters the corresponding function would be very similar. The function S in the figure refers to a slightly different radial wave function, constructed from single-term basis functions as outlined below. As emphasized in that work, this wave function is almost identical to a number of other wave functions, such as HF forms, that are determined by more elaborate methods. Moreover, the basic reason for the accuracy is the imposition of the $2s$-$1s$ orthogonality condition which, because of the high accuracy of the $1s$ function, imprints some of this accuracy onto the $2s$ state. The resulting $2s$ radial wave function is very close to a HF function except at large r where it falls off a little too rapidly.

The Slater $2p$ function for atomic oxygen was compared with a HF function in Fig. 2 of the Gould [15] paper. This function has no orthogonality condition to benefit from and is not as good as the HF result. However, it can be modified in a simple way so that it falls off less rapidly at large r (like the HF function). The corresponding prescription (see below) seems to work reasonably well and has a generality to make it useful in applications to an arbitrary atomic system.

Analytic forms for single-electron wave functions for many electrons are generally constructed from single-term basis functions of the form

$$\chi_\beta(r,\theta,\phi)=\frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}}r^{n-1}e^{-\zeta r}Y_{lm}(\theta,\phi) . \tag{17}$$

Here β designates the three quantum numbers, n, l, and m which have the same meaning as in hydrogenic functions, and ζ is a parameter which, in terms of the screened or reduced Z, is given by

$$\zeta=(Z-S_{nl})/n . \tag{18}$$

The function (17) is normalized, that is,

$$\int |\chi_\beta|^2 d\mathbf{r}=1 , \tag{19}$$

but the functions are orthogonal only for differing values of l and m. Specifically,

$$\int \chi_\beta^* \chi_{\beta'} d\mathbf{r}=I_{\beta\beta'}\delta_{ll'}\delta_{mm'} , \tag{20}$$

with

$$I_{\beta\beta'}=\frac{(2\zeta)^{n+1/2}(2\zeta')^{n'+1/2}}{(\zeta+\zeta')^{n+n'+1}}\frac{(n+n')!}{[(2n)!(2n')!]^{1/2}} . \tag{21}$$

The form (17) is similar to a hydrogenic function in having, in addition to the spherical harmonic, a power r^{n-1} and an exponential term. For a particular nlm state the single term gives the dominant contribution or major peak to the wave function. Although single-term forms are actually used to represent electron states, much better wave functions are constructed from linear combinations of these terms. For a particular state σ, the (nonhydrogenic) wave function can be written as

$$U_\sigma=\sum_\beta C_{\sigma\beta}\chi_\beta , \tag{22}$$

in terms of constant coefficients $C_{\sigma\beta}$. Each term in the sum has the same angular part Y_{lm}, since an effective central potential is assumed, so that in terms of the radial part

$$\lambda_\beta(r)=\frac{(2\zeta_\beta)^{n+1/2}}{[(2n)!]^{1/2}}r^n e^{-\zeta_\beta r} , \tag{23}$$

the function (22) can be written

$$U_\sigma=U_{nlm}=r^{-1}\left[\sum_\beta C_{\sigma\beta}\lambda_\beta(r)\right]Y_{lm}(\theta,\phi) . \tag{24}$$

This is all very standard procedure. In the various functions $\lambda_\beta(r)$ the parameters ζ_β would be evaluated from the appropriate screening constants by means of Eqs. (18) and (9). The individual functions are built up in this manner; for example,

TABLE VIII. Diamagnetic susceptibility of atomic neon. HF(M) denotes the HF results of Mann (Ref. [8]), HF(SN), the results of Saxena and Narasimhan (Ref. [17]). JG labels are our results using analytic wave functions with $\rho=0$ and 0.045.

	HF(M)	HF(SN)	JG		Expt.
			$\rho=0$	$\rho=0.045$	
$\langle r^2\rangle_{1s}$ (a.u.)	0.0335	0.0331	0.0320	0.0320	
$\langle r^2\rangle_{2s}$ (a.u.)	0.9671	0.9380	0.9000	0.9000	
$\langle r^2\rangle_{2p}$ (a.u.)	1.2285	1.1680	0.8618	1.1539	
$\sum_k\langle r^2\rangle_k$ (a.u.)	9.3722	8.9502	7.0348	8.7874	
$-N_0\chi_d$ (10^{-6} cm^3/mol)	7.419	7.085	5.569	6.960	6.96±0.14

$$U_{1s}=r^{-1}\lambda_{1s}(r)Y_{00}\ ,$$

$$U_{2s}=r^{-1}[C_1\lambda_{1s}(r)+C_2\lambda_{2s}(r)]Y_{00}\ , \qquad (25)$$

$$U_{3s}=r^{-1}[C_1'\lambda_{1s}(r)+C_2'\lambda_{2s}(r)+C_3'\lambda_{3s}(r)]Y_{00}\ ,$$

with, in this case, $Y_{00}=(4\pi)^{-1/2}$. In the functions U_{1s}, U_{2s}, and U_{3s} the various C's are fixed by normalizing the functions and by making them orthogonal to one another. In the integrals involved the radial functions satisfy

$$\int_0^\infty \lambda_\beta(r)\lambda_{\beta'}(r)dr=I_{\beta\beta'}\ , \qquad (26)$$

given by formula (21).

B. Modification of the 2*p* function

As mentioned above, the single-term 2*p* wave function is not as accurate as the 2*s* function. In terms of the screening parameter ζ, the function has the simple form

$$\lambda_{2p}(r)=(2/3^{1/2})\zeta^{5/2}r^2e^{-\zeta r}\ , \qquad (27)$$

and falls off too fast at large *r*. We have tried various modifications for this function to follow the more accurate HF forms. One modified form has a single added term with an exponent half as large; normalized, in terms of a parameter ρ, this function is

$$\lambda_{2p}'(r)=\frac{2\zeta^{5/2}}{3^{1/2}}r^2\frac{e^{-\zeta r}+\rho e^{-\zeta r/2}}{(1+2^{11}\rho/3^5+2^5\rho)^{1/2}}\ . \qquad (28)$$

The averages $\langle r\rangle$ and $\langle r^2\rangle$ with this 2*p* wave function are given by ($C=2^{11}/3^5$)

$$\langle r\rangle_{2p}=\frac{5}{2\zeta}\frac{1+4C\rho/3+64\rho^2}{1+C\rho+32\rho^2}\ , \qquad (29)$$

$$\langle r^2\rangle_{2p}=\frac{15}{2\zeta^2}\frac{1+16C\rho/9+128\rho^2}{1+C\rho+32\rho^2}\ . \qquad (30)$$

We have fixed ρ by comparing the function λ_{2p}' with the Hartree-Fock-Slater (HFS) function for neutral atomic oxygen as given in the work of Herman and Skillman [16]. With

$$\rho=0.045\ , \qquad (31)$$

λ_{2p}' passes through the HFS 2*p* at the latter's peak (as well as further out on the tail). In fact, we suggest the form (28) with the value (31) as a *universal* approximation to HF 2*p* wave functions for the elements B to Ne. For these atoms, we have evaluated $\langle r\rangle_{2p}$ and $\langle r^2\rangle_{2p}$ and compared the results with values given by Mann [8]. The analytical expressions (29) and (30), for the corresponding values of ζ with our modified screening constants, yield a good description for the averages for B to Ne using the simple number (31) for the parameter ρ. Specifically, the ratio of the averages (29) to the Mann values ranges from 0.99 to 1.00 for these six elements while the ratio of the $\langle r^2\rangle_{2p}$ to the Mann values ranges from 0.94 to 0.97.

An experimental test of the single-electron averages $\langle r^2\rangle$ is provided by a measurement of diamagnetic susceptibility. For a monoatomic gas the molar value of this quantity is given by

$$-N_0\chi_d=\tfrac{1}{6}N_0\alpha^2a_0\sum_k\langle r^2\rangle_k\ , \qquad (32)$$

where N_0 is Avogadro's number, α is the fine-structure constant, a_0 is the Bohr radius, and the sum is over the atomic bound electrons. For Ne,

$$\sum_k\langle r^2\rangle_{k(\mathrm{Ne})}=2\langle r^2\rangle_{1s}+2\langle r^2\rangle_{2s}+6\langle r^2\rangle_{2p}\ , \qquad (33)$$

so that a large contribution comes from the 2*p* electrons. Moreover, since the effect gives weight to the large-*r* tails of the electron states, the modification (28) of the single-term basis function is necessary to give a calculted χ_d in agreement with experiment. Table VIII gives results of such a calculation, including the HF results of Mann [8] and of Saxena and Narasimhan [17]; our results using analytical wave functions with $\rho=0$ and 0.045 are also given; "Expt." refers to the experimental result of Barter, Meisenheimer, and Stevenson [18]. Listed in the table are individual results for the 1*s*, 2*s*, and 2*p* states in atomic units (a_0^2), with the JG values computed using the screening constants from Table II. The computed $\langle r^2\rangle_{2s}$ employed a U_{2s} made orthogonal to U_{1s} as described in Eq. (25). The exact agreement of our $\rho=0.045$ susceptibility with experiment is fortuitous, since we did not pick the ρ value (31) to accomplish this. What should be noted, however, is the necessity of introducing such a correction to the analytic single-term 2*p* function. Without the correction our calculated $\rho=0$ value for χ_d is not in good agreement with experiment, being 20% too small.

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