Simple Atomic Model and its Associated Wave Function[*][†]

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A simple atomic model, with features characteristic of the screening-theory approach, is constructed and provides simple analytic trial wave functions ψ_t which describe the motion of the inner electrons particularly well. Basing our model on the energy-extremum principle, in contrast to a semiempirical or phenomenological approach, we can judge improvements in the model in a consistent manner. The single-particle orbitals from which ψ_t is constructed are taken to be *orthogonal* hydrogenlike functions with effective nuclear charges $\bar{Z}_l$ which depend on the quantum number l; the $\bar{Z}_l$ serve as variational parameters. By a succession of reasonably good upper bounds the evaluation of the expectation value of the $1/r_{ij}$ interelectronic terms is reduced to trivial algebraic expressions involving only the occupation number of electrons for each of the (n,l) subshells; no numerical work is necessary to determine the energy-optimized set of $\bar{Z}_l$. With the resulting ψ_t, which is most appropriate for closed-shell atoms, a variety of atomic entities can be obtained directly in analytic form. This model is considered physically more realistic than the Thomas-Fermi model, yielding results of greater accuracy in general. (For large Z, the results obtained yield the usual Thomas-Fermi scaling laws.) Much more importantly, these wave functions will be shown elsewhere to be very useful in exploratory analytic studies to judge the effectiveness of variational techniques in the evaluation of the expectation values of various atomic operators. Also, a straightforward adaptation of the present approach will be shown elsewhere to provide a much better understanding of atomic structure in the presence of the intense magnetic fields characteristic of pulsars, a regime in which studies of the heavier atoms have been limited to a statistical Thomas-Fermi-like approach.

I. INTRODUCTION

Simple atomic models providing reasonably accurate estimates for a variety of atomic properties have been and continue to be quite useful in the study of atoms and ions. At present this is particularly evident in astrophysical applications, where often the prime concerns are simplicity and a knowledge of the analytic dependence on the atomic parameters, while order-of-magnitude numerical results may suffice. Over the years a number of general classes of simple atomic models have gained wide acceptance; these include the statistical Thomas-Fermi (TF) model[1,2] and the screening theory of atomic structure.[3-7] Yet surprisingly, neither approach, to the best of our knowledge, has provided simple means for generating simple analytic reasonably accurate atomic wave functions, derived from a first-principles approach, which are suitable for our purposes (detailed below).

The TF model does not, of course, directly generate an atomic wave function. Moreover, the semiclassical TF electronic charge density, in addition to being applicable only for large atomic numbers, is seriously handicapped by unphysical features in the regions close to the nucleus and near the edge of the atom—regions where there is a breakdown in the fundamental TF assumption of a slowly varying potential. This reflects itself in grossly inaccurate estimates for atomic entities

that heavily weight either region of the atom. Recently, attention has been focused on methods to remove these unphysical features.[2]

Screening theories which provide approximate atomic wave functions have, of course, been advanced. The single-particle orbital functions are generally taken to be either hydrogenlike functions or Slater-type functions. The relevant point for our purposes, however, is that generally the parameters in the orbital functions are fixed either semiempirically or by fitting them to certain experimental data. The Slater screening model,[3] for example, is essentially based on a set of empirically determined rules. As a second example, we should also like to refer to certain recent work in which the screening parameters have been determined in more precise fashion by fitting them to existing x-ray data on energy levels taking proper account of the effects of inner and outer shielding.[7] Wave functions derived in this manner continue to prove their utility by providing reasonable first estimates of many atomic processes.[7] Yet, for our purposes, a serious drawback to such wave functions is that, generally, the resultant single-particle orbital functions which differ solely in the principal quantum number n will no longer be orthogonal; other orbitals will, of course, still be orthogonal by virtue of their angular or spin parts. The orbital functions need then to be subsequently orthogonalized, reducing not only their simplicity

but also their accuracy; one would otherwise be forced, in the evaluation of matrix elements, to calculate a large number of overlap integrals.

Our intention is to derive simple atomic wave functions based on the energy-extremum principle. This also forms the basis for the general screening theory, which is advanced by Layzer and co-workers[4] and is directed principally toward developing a theoretical scheme for correctly describing complex atomic energy spectra. Since the approach is that of Rayleigh-Ritz, one can always systematically improve results simply by including more variational parameters in the wave function. We shall assume a trial wave function which is a product of hydrogenlike orbitals with different effective nuclear charges; the effective charges, which serve as the variational parameters, will a priori be restricted so as to maintain an orthogonal set of functions. The "best" set of effective charges is defined to be that set which minimizes the total energy. This generally leads to coupled equations for the effective charges.[4] In the interest of simplicity, we will introduce certain upper bounds on the $1/r_{ij}$ interelectronic terms which decouple the equations for the effective charges and eliminate any serious calculational work. These resulting hydrogenlike wave functions can be used directly to predict atomic properties, generally with greater accuracy than the TF model. Moreover, the results, in the limit of large Z, often exhibit the scaling laws characteristic of TF theory. The results for the energy and other properties will generally not be as accurate as those derived from the phenomenological or semiempirical screening approaches, where parameters are tailored to fit more detailed studies of atomic structure. Also, in view of the fact that accurate self-consistent field calculations for most atomic properties are now available,[8] their utility on these grounds would perhaps be rather limited. Yet they have proved to be extremely useful for reasons discussed below.

One of our concerns has been to judge the utility of applying variational principles in the evaluation of matrix elements of arbitrary operators, for different atomic properties. By invoking such variational principles, one may ultimately be able to derive accurate estimates of atomic properties within the context of simpler atomic models. Presently such variational estimates have been limited to helium, though the accuracy of the results in this case have been quite encouraging.[9] In large measure this can be attributed to the fact that appropriate trial wave functions for heavier atoms are not readily available. Simple analytic trial wave functions applicable to any atom, even though inaccurate in certain respects, would be particularly

well suited for an exploratory investigation of such variational principles, since the calculations involved would generally be limited and, moreover, the systematics of the results would not be obscured by numerical work. By basing these trial wave functions on the energy-extremum principle, one could then judge in a consistent manner the effects of improvements in the wave functions upon the variational estimates for the matrix elements of other operators. The hydrogenlike trial wave functions derived in this paper are extremely useful in this regard. In fact, we have been able to carry through analytic variational calculations for the operators $\sum_i r_i^n$ for atoms up through argon.[10]

We have also been concerned with developing simple atomic models applicable to atoms in the intense magnetic field regime ($B \sim 10^{10}$–10^{13} gauss). This range of magnetic field strengths is of great interest, since such magnetic fields presumably exist on the surface of neutron stars. We have used an adaptation of the present approach, suitably modified to include the effects of the magnetic field, to generate simple atomic trial wave functions applicable in this regime. In this case the results obtained with the use of such trial wave functions[11] are quite useful directly, since more detailed studies for heavier atoms do not exist. For atoms with $Z > 10$, essentially the only approach used thus far[12] has been a statistical model with features characteristic of the TF model.

It may be important to stress, with regard to the purposes of this paper, the requirements that are to be imposed on the trial wave function ψ_t for atoms in intense magnetic fields. One seeks rough results for the energy, dimensions, polarizability, photoelectric cross section, etc., for a wide range of atoms. One therefore seeks simple analytic wave functions, and it is almost essential to have some objective criterion, such as energy minimization, to determine the variational parameters contained in ψ_t, since one has essentially nothing in the way of experimental data or theoretical calculations to rely upon.

II. HYDROGENLIKE MODEL OF THE ATOM

The Rayleigh-Ritz variational principle, providing a variational upper bound on the energy with the sign of the error thereby known, is to be used to determine the "best" set of effective charges in the trial wave function. As is characteristic of this approach, however, the resulting wave function will inherently be less accurate than the energy estimate and may, in fact, be rather poor in certain respects even if the energy estimate is quite good. (This is particularly evident in the description of the outermost electrons which only negligibly contribute to the energy.) Moreover, it is not trivial

to estimate the magnitude of the error either in the energy or the wave function. One does at least have a consistent means of improving the results by simply including more variational parameters in the trial wave function.

One can readily obtain a crude but rigorous lower bound on the energy; this is taken up in the Appendix. Although of limited utility by itself, it is of interest because, in the limit of large Z, it reproduces the TF scaling laws for the characteristic size of the atom and the energy. These results, combined with similar scaling laws to be derived for the upper-bound approach, confirm that these scaling laws are not uniquely associated with the specific assumptions of TF theory. Essentially the same scaling $Z^{7/3}$ dependence for the leading term in the energy has been confirmed previously[5,6] within the context of different atomic models. An accurate lower bound on the energy, however, is always relatively difficult to obtain and we will not attempt to improve this lower bound.

Let E be the total ground-state energy of the atom, V_{ee} the electron-electron (e-e) interaction energy, V_{en} the electron-nucleus (e-n) interaction energy, and T the kinetic energy contribution to E. The trial wave function ψ_t is taken to be an anti-symmetrized product of Z different hydrogenlike orbitals with different effective nuclear charges which serve as the variational parameters. In order to simplify matters, however, all the negative exchange e-e contributions to E, which arise because ψ_t is a determinant, are dropped from the calculation. This, of course, still preserves the upper bound on E. (We note that this approach is not quite the same, however, as starting directly with a Hartree product of Z *different* orbitals, since antisymmetrizing ψ_t ensures its proper boundary conditions in the calculation of other atomic properties. Also, we will show later on that one can crudely estimate the exchange interaction energy within the context of this model.) For reasons of orthogonality, the effective charges are taken to be independent of the principal quantum number n; moreover, in order to preserve the spherical symmetry of the electronic subshells and thereby simplify the estimate of the contributions to the energy of the $1/r_{ij}$ terms, the effective charges are also taken to be independent of m_l. Finally, on physical grounds and for purposes of simplicity, the effective charges are taken to be independent of m_s. (Note that within the context of the upper-bound approximations to the $1/r_{ij}$ terms, which we shall introduce in a moment, we *can* lower the estimate for the total energy slightly by arbitrarily distinguishing between effective charges for the two spin states. This procedure is analogous to that used in the unrestricted Hartree-Fock method.) The ef-

fective charges depend only on the quantum number l and are denoted by $\tilde{Z}_l$. Thus, we have

$$\psi_t(\tilde{Z}_l) = \prod_{i=1}^{z} \phi_{nlm_l m_s}(\tilde{Z}_l; \vec{r}_i) , \qquad (2.1)$$

where, with χ_{m_s} a spin function and R_{nl} a hydrogenic function,

$$\phi_{nlm_l m_s}(\tilde{Z}_l; \vec{r}_i) = R_{nl}(\tilde{Z}_l; r_i) Y_{lm_l}(\hat{r}_i) \chi_{m_s}(i) .$$

Adding and subtracting a term, the Hamiltonian can be written as $H = H_0 + H'$, where

$$H_0 = \sum_i T_i - \sum_i \tilde{Z}_l e^2/r_i ,$$

$$H' = -\sum_i (Z - \tilde{Z}_l) e^2/r_i + \frac{1}{2}\sum_{i \neq j}\sum e^2/r_{ij} . \qquad (2.2)$$

The effective charges $\tilde{Z}_l$ implicitly depend on the electronic index i.

We now carry out the estimate of the upper bound on E. The expectation value of H_0 reduces trivially to a sum of single-electron terms for hydrogenic systems of nuclear charges $\tilde{Z}_l$ and thus

$$(\psi_t(\tilde{Z}_l), H_0\psi_t(\tilde{Z}_l)) = - (e^2/2a_0)\sum_{nl} \nu(nl) (\tilde{Z}_l^2/n^2) , \qquad (2.3)$$

where $\nu(nl)$ is the number of electrons in the (nl) subshell and satisfies $0 \leq \nu(nl) \leq 2(2l+1)$. Also, utilizing the virial theorem for each of the hydrogenic orbitals, we have

$$- (Z - \tilde{Z}_l) \left(\psi_t(\tilde{Z}_l), \sum_i \frac{e^2}{r_i} \psi_t(\tilde{Z}_l)\right)$$

$$= -\frac{e^2}{a_0} \sum_{nl}{}' \nu(nl) \frac{Z\tilde{Z}_l - \tilde{Z}_l^2}{n^2} . \qquad (2.4)$$

Finally, we must evaluate V_{ee}, or, more precisely, the "direct" e-e interactions, which we shall denote by V_{ee}^D. As is well known,[13] the contribution to V_{ee}^D from the direct interaction of electrons in two distinct (nl) subshells obtained by summing over the m_l quantum numbers simplifies greatly if at least one of the subshells is complete or doubly complete (that is, all values of m_l are occupied either once or twice, respectively). It reduces to the product of an occupation factor detailing the number of independent pair interactions multiplied by the so-called F^0 Slater integral, defined as

$$F^0(\tilde{Z}_l \tilde{Z}_{l'}; nl, n'l') = e^2 \int \int R_{nl}^2(\tilde{Z}_l; r) R_{n'l'}^2(\tilde{Z}_{l'}; r')$$

$$\times (1/r_>) r^2 r'^2 \, dr \, dr'; \qquad (2.5)$$

$r_>$ is the larger of r and r'. If neither of the sub-

shells is complete, F^0 can be shown to represent an upper bound to the average interaction energy between a pair of electrons. Hence an upper bound for the total contribution to V_{ee}^D from the two subshells is simply

$$\nu(nl)\nu(n'l')\, F^0(\tilde{Z}_i \tilde{Z}_{i'}\,;nl,n'l')\ .$$

Analogous results apply to the direct e-e interactions within an (nl) subshell, except that certain of the diagonal terms $m_l = m_l'$ must be deleted for electrons with the same spin configuration. Since these terms are certainly positive (and small), the upper bound on the energy can be maintained by simply dropping them; however, we can do somewhat better by including at least the spherically symmetric parts of these terms which are also proportional to the F^0 Slater integrals. An upper bound on this occupation factor is therefore $\frac{1}{2}[\nu^2(nl) - \nu(nl)]$, the number of independent pairs of electrons within the subshell.

The exact evaluation of the F^0 Slater integrals with hydrogenic functions can readily be carried out and, in fact, tables exist for certain of these integrals.[14] We would have to extend these results somewhat since here, in general, the orbitals may have different effective charges. Such an approach would, however, be contrary to the spirit of this paper and, moreover, the resulting set of coupled algebraic equations defining the "best" set of effective charges would be quite complicated and generally solvable only by numerical techniques. Alternatively, we note that a simple but reasonable *upper bound* for these integrals (which therefore maintains the upper bound for the energy E) can be obtained if we replace $1/r_>$ by either $1/r$ or $1/r'$. This essentially corresponds to the case of no external screening discussed by Layzer[4] and others and is similar to work done by Goodisman.[5] Normally we replace $r_>$ by either r or r', whichever variable corresponds to the "larger" set of quantum numbers (nl) according to the hydrogenic scheme, whereby shells are ordered according to increasing n and within each n according to increasing l. However, using the hydrogenic scheme, it may happen that the set of $\tilde{Z}_l$, determined by minimizing the energy, are such that there is an inversion of the ordering of two particular subshells. This does not invalidate the results of the calculation, since we can maintain the upper bound by replacing $r_>$ by either r or r'; but it does mean that we can improve the results for the energy by starting off with the inverted order, as will be discussed later. Assuming normal hydrogenic ordering, F^0 is therefore bounded by $(e^2/a_0)(\tilde{Z}_{l_>}/n_>^2)$, where $n_>$ is the larger of n and n', and $l_>$ is the quantum number associated with $n_>$. This upper-bound replacement is not of high accuracy,

particularly for $n = n'$, as is shown in Table I for several of the subshells; the total energies calculated will, however, be much better than these numbers might at first suggest, because the variational estimation of the $\tilde{Z}_l$ provides partial compensation for the error generated by this replacement, and because the approximation is not nearly so bad for $n \neq n'$.

Collecting all terms, we therefore have the upper-bound estimate for the energy

$$E \leq \frac{e^2}{a_0}\sum_l\left(\tilde{Z}_l(\tilde{Z}_l - 2Z)\sum_{n=l+1}^{s}\frac{\nu(nl)}{2n^2} + \tilde{Z}_l\sum_{n=l+1}^{s}\frac{\nu(nl)^2 - \nu(nl)}{2n^2}\right.$$
$$\left. + \tilde{Z}_l\sum_{n=l+1}^{s}\frac{\nu(nl)N(nl)}{n^2}\right)\ , \qquad (2.6)$$

where s is the maximum value of n. The first term in the above expression is the familiar $T + V_{en}$. The next is the interaction energy for electrons within a given (nl) subshell. The last term is the interaction of the electrons in the (nl) subshell with all the electrons that lie within the orbit defined by (nl), a quantity we represent by $N(nl)$. Only the electrons within a particular subshell need be considered, because the interaction with the ones above occur with the smaller $\tilde{Z}_l$ corresponding to them. The essential feature of this energy expression, which makes calculations no more complicated than for the case with just one $\tilde{Z}$ value, is the fact that it does not contain any cross terms between the different $\tilde{Z}_l$. Thus, in minimizing the energy, separate equations result for each of the effective charges. In fact, we have

$$\tilde{Z}_l^{\min} = Z - \frac{\sum_{n=l+1}^{s}\nu(nl)[N(nl) + \frac{1}{2}\nu(nl) - \frac{1}{2}]/n^2}{\sum_{n=l+1}^{s}\nu(nl)/n^2}\ . \quad (2.7)$$

The best set of $\tilde{Z}_l$ also has the feature, previously noted by Slater,[3] that the expectation value of the "perturbation" H' is zero for this set of $\tilde{Z}_l$ (as can easily be shown by direct substitution). Thus the bound on the energy minimized with respect to $\tilde{Z}_l$ can be written simply, using (2.3), as

$$E \leq -\frac{e^2}{a_0}\sum_l (\tilde{Z}_l^{\min})^2\sum_n\frac{\nu(nl)}{2n^2}\ . \qquad (2.8)$$

Note that for configurations consisting only of

TABLE I. Comparison of the exact value of $a_0 F^0(\tilde{Z}_l, \tilde{Z}_l; nl, nl)/\tilde{Z}_l e^2$ and its upper bound $1/n^2$ for a few subshells.

(nl)	$a_0 F^0/\tilde{Z}_l e^2$ upper bound	$a_0 F^0/\tilde{Z}_l e^2$ exact
$2s$	0.250	0.1504
$2p$	0.250	0.1816
$3s$	0.111	0.0663
$3p$	0.111	0.0719
$3d$	0.111	0.0860

closed subshells, for which $\nu(n, l) = 2(2l + 1)$, Eq. (2.7) reduces to

$$\bar{Z}_l^{\min} = Z - (2l + \tfrac{1}{2}) - \left(\sum_{n=l+1}^{s} \frac{N(nl)}{n^2} \right) \bigg/ \left(\sum_{n=l+1}^{s} \frac{1}{n^2} \right) \quad . \quad (2.9)$$

In an actual calculation, we must search for the set of $\nu(nl)$ which minimizes the energy, by performing exactly the sums in Eqs. (2.7) and (2.8). Once the configuration is chosen the $N(nl)$ can be written down by inspection. Tables II and III present detailed results for several atomic numbers along with the TF estimates and improved TF estimates as well as the "exact" nonrelativistic energies.[15] In spite of the fact that there is not very much work involved, the results for E are seen to be quantitatively superior to the TF results, though, as mentioned previously, the results for E will *not* generally be as good as those obtainable via the phenomenological screening approach.

We turn now from considerations of the total energy to considerations of the accuracy of the description for the innermost and outermost electrons. In the first place, even though some of the outermost electrons must be placed in subshells with unrealistically large values of (nl) (Table II cites several examples), all of the electrons are nevertheless bound to the atom with orbital energies which we will see are quite realistic for the configuration that minimizes the total energy. This is an interesting result in itself for two reasons. First,

the requirement that the effective charge be a function of l only places severe constraints on the flexibility of the model, and has a particularly adverse effect on the outermost electrons, since they contribute only negligibly to the total energy. One could well imagine that a good description of the inner electrons with quantum number l, which largely determine the energy, would lead to a very inaccurate description of the outermost electrons with quantum number l. This is indeed the case, to a certain extent, and is responsible for the fact that certain of the outermost electrons must be placed in subshells with high values of (nl) in order to gain a new value of the l quantum number and, hence, a new effective charge. At a later stage, when we further restrict the effective charges for *all* electrons to be the same, we will find that the minimum total energy is achieved for 40% of the electrons unbound.

The second point is that in spite of the fact that the e-e interactions have been overestimated, which is especially relevant for the outermost electrons, the orbital energies for these electrons vary qualitatively in the appropriate manner as the subshells are completed, though the actual values remain somewhat unrealistic. Consider the case where the outermost electrons are in the doubly complete subshell (sl') and this value of l' is being used for the first time. (We should note that although this situation is characteristic of the hydrogenlike

TABLE II. Total ground-state binding energies of some neutral atoms, in units of $e^2/a_0 = 27.21$ eV. The single-parameter variational upper bound, Eq. (3.2), and the many-parameter variational upper bound, Eq. (2.8), are compared with Thomas-Fermi results, improved Thomas-Fermi results (footnote a), and the "exact" nonrelativistic values extracted from Herman-Skillman (footnote b). For each value of Z considered, the configuration in the bottom row of both variational upper bounds is the physical configuration, and the one in the top row for the many-parameter case is the configuration which minimizes the energy. (In some cases there are a number of configurations which give the same energies to within about 10 eV, an amount which is small compared to the error in the energy. We have not, therefore, put any stress on finding the absolute minimum.) For Eq. (2.8) the minimizing configuration occurs for the outer electrons in states of very high orbital angular momentum. For the results of Eq. (3.2), the configuration specifies the number of electrons with a given value of the principal quantum number n; the value of the variational parameter $\bar{Z}^{\min}$ is also included. For the results of Eq. (2.8) lower values of n, when not indicated, represent completely filled shells. (Note that a variational upper bound on the energy gives a variational lower bound on the binding energy.)

	Thomas-Fermi energy	Improved TF energy[a]	Variational upper bound Eq. (3.2)			Variational upper bound Eq. (2.8)		"Exact" nonrel. energy[b]
Z			Configuration	$\tilde{Z}^{\min}$	Energy	Configuration	Energy	
10	166	151	2, 8	7.0	98	$1s^2 2sp^5 3d^2$	114	128[a]
						$1s^2 2s^2 p^6$	113	
20	834	750	2, 8, 8, 2	14.8	546	$3d^8 4f^2$	611	674[a]
						$3s^2 p^6 4s^2$	572	
40	4210	3760	2, 8, 18, 10, 2	29.2	2860	$4f^{11} 5g$	3240	3535
						$4s^2 p^6 d^2 5s^2$	3040	
60	10830	9700	2, 8, 18, 22, 8, 2	44.2	7570	$4d^{10} f^{14} 5g^7 6h$	8550	9125
						$4s^2 p^6 d^{10} f^4 5s^2 p^6 6s^2$	8080	
80	21200	19000	2, 8, 18, 32, 18, 2	58.4	15000	$5g^{18} 6h^2$	17000	18090
						$5s^2 p^6 d^{10} 6s^2$	16100	

[a]J. Goodisman, Ref. 2.   [b]Reference 15.

model, there is no direct correspondence with the outermost filled subshell of the physical configuration beyond $2p$.) The sums in Eq. (2.7) reduce to just one term and the expression for the effective charge is simply

$$\tilde{Z}_{l'}^{\min} = Z - (2l' + \tfrac{1}{2}) - N(sl') = 2l' + \tfrac{3}{2} = 2s - \tfrac{1}{2} \ .$$

We used the fact that $l' = s - 1$; we specifically put the electrons in this subshell to gain a new value of l' in order to bind the electrons to the atom. Now the orbital energy for an electron in this last subshell will be shown to be approximately

$$\epsilon_{\text{ion}}(sl') \approx - (e^2/a_0)(\tilde{Z}_{l'}^{\min})^2/2s^2 \cong - 2e^2/a_0 \ ,$$

which is consistent with the Slater screening model in which the orbital energy for each electron is approximately equal to the energy of a hydrogenlike system with the corresponding effective charge.[3] This will *not* generally be the case here for electrons in different subshells that share the same effective charge. The ionization energy for this outermost electron is, hence, about 2 a.u. (We note in passing that if the effective charges had been allowed to depend on m_s, this ionization energy would then be 1 a.u., which is closer to the exact values.) We also note that when the last subshell (sl') is incomplete, that is, $\nu(sl') < 2(2l' + 1)$, then $\tilde{Z}_{l'}^{\min} < 2s - \tfrac{1}{2}$. Effectively, each other electron gives a screening of $\tfrac{1}{2}e$. $|\epsilon_{\text{ion}}|$ is, then, < 2 a.u. and gradually increases in value as the subshell fills, reaching 2 a.u. when the subshell is complete, followed by an abrupt drop when the next electron enters the next subshell. This reproduces, at least qualitatively, the behavior of ϵ_{ion} along the Periodic Table.

Single-particle orbital energies can crudely be calculated as follows. Each electron moves in an effective potential given by

$$V_{\text{eff}}(r) = - Ze^2/r + e^2 \sum_{n'l'} \nu(n'l')$$

$$\times \int R_{n'l'}^2(\tilde{Z}_{l'}; r')(1/r_>)r'^2 dr' \ . \quad (2.10)$$

We make a slight error here in that we include all Z electrons instead of $Z - 1$; moreover, if a particular $(n'l')$ subshell is incomplete we replace its contribution to $V_{\text{eff}}(r)$ by a spherical average, thus making it possible to replace $|\vec{r} - \vec{r}'|^{-1}$ by $r_>^{-1}$. Rough estimates of the orbital energies can then be made by evaluating the expectation value of $(T + V_{\text{eff}})$ using the ground-state orbitals $\phi_{nlm_lm_s}(\tilde{Z}_l; r)$. It is clear from the form of $V_{\text{eff}}(r)$ that the orbital energies will only depend on the electron's principal quantum number n, since we always replace $1/r_>$ by either $1/r$ or $1/r'$. One can see from this that the innermost electron, which is in the subshell $(1,0)$, has an

orbital energy corresponding to an effective charge nearly equal to Z. In fact, most of the orbital energies (all of those with $n - l$ greater than perhaps 2, for which $\tilde{Z}_l$ is largely determined by the $n - l = 1$ orbital) are now in good agreement with the exact values. Table IV illustrates, for atomic number 60, the energies for the lower orbitals; these have been obtained not by using V_{eff} but simply by taking the difference between the total energy computed with and without an electron in the orbital under consideration. Also, we note that the radius of the atom, taken to be the radius of the last occupied subshell, increases slightly with Z, being given by

$$R = s^2 a_0/\tilde{Z}_{l'}^{\min} = s^2 a_0/(2s - \tfrac{1}{2}) \approx Z^{1/3} a_0 \ ,$$

since for a closed shell atom $s \approx (3Z/2)^{1/3}$. Empirically, as determined from ionic radii, the radius of a heavy atom is found[1] to increase as $Z^{1/6}$.

In the above discussion, we have considered the electrons to fill subshells in such a way as to get the lowest possible energy. We find that, in many cases, instead of filling in electrons according to the hydrogenic sequence of (nl) subshells, one can get lower energy by inverting certain subshells. Thus, for instance, the $(4s)$ fills in before the $(3d)$. This is a reflection of the Madelung rule[16] for the filling of subshells across the Periodic Table, where a shell with lower $(n + l)$ fills before one with a higher value for this sum, even though this might entail a higher value for n being occupied first. Though it is heartening that our model is sufficiently accurate to reproduce this semiempirical Madelung rule, the result is not to be taken too literally because often the lowest energy is achieved for a choice of subshells which does not correspond to

TABLE III. Effective charge $\tilde{Z}_l^{\min}$ for the different subshells evaluated from Eq. (2.7). For each value of Z considered, the values of the variational parameters $\tilde{Z}_l$ along the top row correspond to the configuration which minimizes the energy; those along the bottom row are for the physical configuration. Both configurations are as in Table II.

Z	Effective charge $\tilde{Z}_l^{\min}$					
	s	p	d	f	g	h
10	9.33	5.0	1.5			
	9.1	3.5				
20	19.1	13.5	6.5	1.5		
	17.6	11.0				
40	38.3	31.0	17.5	7.0	1.0	
	36.7	27.6	14.1			
60	58.3	5.10	33.9	15.5	5.0	1.0
	55.7	44.3	29.0	2.5		
80	77.6	67.5	49.7	27.5	11.5	1.5
	75.7	64.3	40.9	7.5		

the subshells in the actual atom. We note, however, that the gain in the total energy by looking for the best sequence is relatively small and hence, when considering other properties of the atom, it seems most convenient to use a more physical configuration. Though there is a slight loss in the total energy, computations are much simpler and it is not likely that computation of most atomic properties will be changed appreciably by this simplification. This is particularly relevant for applications of these wave functions in the variational estimates for other atomic properties for which we always restrict ψ_t to the physical configuration.

III. STILL SIMPLER HYDROGENLIKE MODEL

It will be interesting to consider briefly the case for which $\tilde{Z}_l$ is chosen to be independent of l; all electrons then "see" the same effective charge $\tilde{Z}$ which is now the only variational parameter. Applications of the model are now particularly simple.

The expressions for both the effective charge and total energy simplify; we drop the (small) term $-\tilde{Z}_l\sum\nu(nl)/n^2$ in (2.6), which preserves the bound, and replace $\nu(nl)$ by $\nu(n)$ and $N(nl)$ by the sum over n' for $n' < n$ of $\nu(n')$, and obtain

$$\tilde{Z}^{\min} = Z - \frac{1}{2}\sum_{n,n'}\frac{\nu(n)\nu(n')}{n_>^2}\Big/\sum_n\frac{\nu(n)}{n^2} \quad , \qquad (3.1)$$

$$E \le -(\tilde{Z}^{\min})^2(e^2/2a_0)\sum_n\frac{\nu(n)}{n^2} \quad , \qquad (3.2)$$

where $\nu(n)$ is the total number of electrons in the nth shell. Table II presents results for the energy from Eqs. (3.1) and (3.2) using the physical configuration. It should be noted, however, that the minimum energy for a fixed Z is achieved within this model for a configuration in which 40% of the

TABLE IV. Orbital energies for a neutral atom of atomic number $Z = 60$ in units of (e^2/a_0). The orbital energies are calculated as the difference between the energy computed from Eq. (2.8) with and without an electron in the orbital under consideration.

Subshell (nl)	Orbital energies for $Z=60$ from (2.8)	"Exact" nonrel.[a]
$1s$	1511	1519
$2s$	209	240
$2p$	205	228
$3s$	20	102
$3p$	24	47
$3d$	25	37

[a]Reference 15.

electrons are unbound; the improvement in E is about 10% over that obtained with the physical configuration. However, it is clear that in the calculations of most atomic properties, one must restrict oneself to the use of more physically meaningful configurations.

In order to compare the scaling aspects of this method with the lower-bound result and with the TF result, we consider closed shells (from $n = 1$ to $n = s$), approximate the sums by integrals, and drop the last term in V_{ee}. The energy bound becomes

$$E \le (\tilde{Z}^2 - 2Z\tilde{Z})s\frac{e^2}{a_0} + 2\tilde{Z}\frac{e^2}{a_0}\sum_{n,n'}n_<^2$$

$$\simeq (3N/2)^{1/3}(\tilde{Z}^2 - 2Z\tilde{Z} + \tfrac{1}{2}N\tilde{Z})(e^2/a_0) \quad , \qquad (3.3)$$

where successive terms represent T, V_{en}, and V_{ee}, respectively. We note that this upper-bound calculation gives, for the case of a neutral atom, $V_{ee}/V_{en} = -\tfrac{1}{4}$, which is to be compared with the TF result of $-\tfrac{1}{7}$ and more exact calculations[5,17] which give a value somewhat greater in magnitude than $\tfrac{1}{7}$. Minimizing the energy expression with respect to $\tilde{Z}$, with N fixed at Z, yields $\tilde{Z}^{\min} = \tfrac{3}{4}Z$ and the expression for the energy becomes $E \le -17.4\,Z^{7/3}$ eV. (For an ion, we would simply minimize E with respect to $\tilde{Z}$ for N and Z fixed and different.) [The energy result of this paragraph also follows, more directly, from Eqs. (3.1) and (3.2).]

In a comparison directed principally at the TF model, we should now like to indicate how one can develop, by a further rather crude approximation of the hydrogenlike model, an electronic number density which is not only trivial to derive, but generally represents an improvement over the characteristic TF behavior. Again we consider the case of a single effective charge $\tilde{Z}$ and closed subshells. It is clear, of course, that the number density appropriate to the hydrogenlike model can generally be expressed as $\rho(r) = \sum_{nlm_lm_s}|\phi_{nlm_lm_s}|^2$, which has the proper physical behavior both at the origin and at infinity, namely, it goes to a constant value for $r \to 0$ and falls off exponentially for large r. However, if, for simplicity, we consider each of these (nl) subshells to be rather sharply defined at a radius given by $r = (n^2a_0/\tilde{Z})$, compute the number $N(r)$ of electrons within the radius r, and determine $\rho(r)$ from

$$\rho(r) = \frac{1}{4\pi r^2}\frac{dN(r)}{dr} \quad ,$$

we find

$$\rho(r) = (1/4\pi)(\tilde{Z}/a_0 r)^{3/2}, \quad r < R$$

$$= 0, \qquad\qquad r > R \quad , \qquad (3.4)$$

where R, of course, is the radius of the last filled

subshell and is defined by

$$R = s^2 a_0 / \tilde{Z} \simeq (\tfrac{3}{2}Z)^{2/3} a_0 / \tilde{Z} \quad .$$

We note that this approximate number density has the same $r^{-3/2}$ behavior near the origin as the TF distribution. However, as opposed to the TF density, which stretches out to infinity, this $\rho(r)$ cuts off at a certain finite R. In similar fashion we can generate an approximate effective potential $V_{eff}(r)$ either by using this expression for $\rho(r)$ in the derivation of Eq. (2.10) or by applying the same simplifying assumptions in Eq. (2.10), namely, $r_{>}$ is to be replaced by r' for $n' > n$ and by r for $n' < n$. This gives

$$V_{eff}(r) = -Ze^2/r + e^2(\tilde{Z}/a_0)^{3/2}(-\tfrac{4}{3}r^{1/2} + 2R^{1/2}),$$

$$r < R \quad (3.5)$$

and 0 for $r > R$.

Though admittedly rather approximate, even within the context of the hydrogenlike model, we should like to illustrate how useful this simple analytic form is by a sample calculation of an atomic property. The scattering amplitude, $f_B(\theta)$, for the elastic scattering of electrons by atoms is formally given in the Born approximation,[18] where θ is the scattering angle. With $q\hbar = 2k\hbar \sin(\tfrac{1}{2}\theta)$ the momentum transfer, and k the wave number of the electron, and using the above expression for V_{eff} with $\tilde{Z} = \tfrac{3}{4}Z$, for example, we find

$$f_B(\theta) = -(2Z/a_0q^2)[1 - h(qZ^{-1/3})], \quad (3.6)$$

where

$$h(qZ^{-1/3}) = (2\pi)^{1/2}(\tfrac{4}{3}a_0qZ^{-1/3})^{-3/2} S_2(qR)$$

and where we have noted that R scales as $Z^{-1/3}$. $S_2(qR)$ is the Fresnel sine integral.[19] We stress the fact that here the universal function is arrived at analytically. It must be stressed again that we here are making a comparison only with the Thomas-Fermi approach. Having made an approximation which leads to an artificial singular r dependence at the origin, we cannot expect truly accurate results to follow from our $\rho(r)$. We could easily give a prescription for eliminating the singularity—we might, for example, choose $\rho(r) = $ const. for $r < a_0/Z$, the radius of the $1s$ state—but this would be a semiphenomenological approach and contrary to the spirit of the paper.

As a final consideration, we obtain approximate expressions for the exchange contribution V_{ee}^{ex} and for the relativistic correction $\Delta E(\text{rel})$ to the total energy; these bring results for E much closer to the exact values, though it must be noted that since they are "patched on" to the energy calculation, they do not directly serve to improve the number density. Moreover, the upper-bound nature of E

will no longer strictly apply to these results. It is important to estimate these corrections, however, so that we can have some idea of the accuracy attainable with our trial function. First, using the well-known Slater approximation for exchange[20] in conjunction with the charge density, Eq. (3.4) yields $V_{ee}^{ex} \approx -\tfrac{1}{3}Z^{5/3}(e^2/a_0)$. Alternatively, we can estimate it more directly. Since, in our model, wave functions for different (nl) subshells are considered effectively nonoverlapping, V_{ee}^{ex} arises only from electrons in the same subshell. Also, since the orbit corresponding to a subshell is thought of as being very narrow, we have that $F^* \approx F^0$ and hence, using the upper bound for F^0, we obtain $V_{ee}^{ex} \approx -\tfrac{2}{3}(\tfrac{3}{2}Z)^{2/3}(\tilde{Z}e^2/a_0)$ which is of the same form as above. (As for the direct interactions, diagonal-term contributions for electrons in the same spin state are deleted from the sum.) Both estimates are expected to overestimate the exchange correction. Roughly speaking, estimates of this exchange contribution are of the order of several percent of the corresponding ground-state energy, though decreasing sharply for larger values of Z.

The spin-orbit correction vanishes to first order for closed shells, and we restrict our consideration to the relativistic correction for spinless particles. This can be estimated by applying to each electron the relativistic virial theorem which, after making the approximation of replacing $\langle v^4/c^4 \rangle$ by $\langle v^2/c^2 \rangle^2$ and summing over all electrons, leads to a relativistic correction of the form

$$\Delta E(\text{rel}) = -\tfrac{5}{4}\mu c^2 (\alpha\tilde{Z})^4 \sum (1/n^2) ,$$

where α is the fine-structure constant and μ is the electron mass.

We conclude by noting that although these wave functions have certain interesting features and have proved quite useful for the purposes outlined in Sec. I, they have obvious drawbacks. The most serious difficulty, of course, involves our decision to choose the effective charges to be independent of n, thereby greatly reducing the accuracy of the description of the outer electrons. Other approximations, such as using a simple Hartree expansion, or retaining only F^0, the simplest of the Slater integrals, and replacing it by an upper bound, may be removed, with some effort, if the particular application warrants it. We will not dwell on these points further, however, since they are reported on separately.

APPENDIX: LOWER-BOUND APPROACH

If the (non-negative) e-e repulsion interactions are dropped altogether, we are led to a rigorous lower bound on E. One might expect in this way to at least obtain the correct leading-term Z dependence for E, since all the interactions scale in the

same way with distance and since TF theory and more precise considerations[5,17] indicate that the magnitude of the ratio V_{ee}/V_{en} is only around $\frac{1}{7}$. The electrons then fill in successive hydrogenic states, and since there is no screening each "feels" the full nuclear charge Z. If, for simplicity, we assume a neutral atom with complete shells from $n = 1$ to $n = s$ and note that s, which is fixed through normalization, is given approximately for heavy atoms by $s \approx (\frac{3}{2}Z)^{1/3}$, then the result $E \gtrsim -30Z^{7/3}$ eV follows immediately. Similarly the size of the last filled shell is seen to be proportional to $Z^{-1/3}$.

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