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A Comparative Study of Atomic Variational Wave Functions

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Rayleigh–Schrödinger perturbation theory and the variational principle combined furnish simple criteria for investigating and predicting the accuracy of arbitrary variational wave functions computed with a perturbed Hamiltonian operator. This permits the *a priori* classification of all perturbed variational wave functions into three broad categories which differ in their asymptotic behavior as the perturbation approaches zero. Wave functions belonging to one of these categories have the desirable characteristics of yielding variational energies correct at least through first order and other expectation values correct at least in zero order. These conditions are not fulfilled in the other two categories. The classification scheme is used to survey a wide variety of variational wave functions for atomic isoelectronic sequences. The construction of these wave functions determines their asymptotic category. A more systematic treatment of correlation energy is proposed and various methods of introducing correlation are discussed. Some recommendations are made for future progress in the calculation of accurate atomic wave functions.

I. INTRODUCTION

At present there are available a large variety of approximate solutions to Schrödinger's nonrelativistic time-independent equation for atomic or molecular systems. Many of these approximate wave functions are obtained by application of the variational principle.[1] Regardless of how they are obtained, all approximate solutions for a given system can be arranged by the variational principle in the order of increasing energetic superiority. Such a classification is essentially an *a posteriori* process, as, unless approximate wave functions of the same or of a related form and structure are considered, the variational principle gives no *a priori* information as to the superiority of one wave function over another. As a corollary deficiency, the variational principle offers no *a priori* guidance as to the most effective way of modifying a given approximate solution to improve its accuracy, i.e., which additional parameters, terms, etc. would have the greatest effect. Thus, for example, it follows from the variational principle that the single-configuration, closed-shell[2] Hartree-Fock solution must be the best energetic function of all independent-particle, single-configuration, closed-shell functions. On the other hand, it is not possible to predict from this the relative superiority of this Hartree–Fock solution and, say, a corresponding open-shell[2] function in which the Hartree–Fock orbitals have been replaced with simpler analytic orbitals.

An additional complication arises in the common case where the Hamiltonian operator may be treated as a function of an external perturbing parameter which may assume discrete or continuous values over some range. Here the relative order of energetic superiority of a group of different approximate wave functions may be a function of the perturbing parameter, but the variational principle, taken alone, affords no insight into this. We focus our attention upon an important illustration, namely, atomic isoelectronic sequences for which the variable perturbing parameter may be taken as the inverse nuclear charge, Z^{-1}.

A first step toward resolving some of these difficulties is presented in this comparative study of variational wave functions for atomic isoelectronic sequences. The combination of Rayleigh–Schrödinger perturbation theory and the variational principle furnishes a simple but powerful tool for investigating and predicting the accuracy of variationally obtained wave functions computed with a perturbed Hamiltonian operator. The variational wave functions, as well as expectation values computed with these wave functions, are obtained in the form of expansions in powers of the perturbation parameter. These expansions afford a natural, general scheme for the *a priori* classification of all perturbed variational wave functions into three categories which differ in their asymptotic behavior as the perturbing parameter approaches zero. A theoretical ambiguity in connection with the accuracy of arbitrary approximate wave functions is then resolved by this classification scheme.

This method is illustrated by application to a number of independent-particle model wave functions for various atomic isoelectronic sequences. In particular, a number of simple closed- and open-shell variational wave functions for the ground state of the boron isoelectronic sequence are examined in detail and several apparently anomalous energy trends as a function of increasing Z are noted. These energy trends are interpreted by obtaining the perturbation expansions of the various energies through the third order. It is shown how the choice of orbitals and configurations in these wave functions determine their asymptotic category. Some peculiarities which arise from the use of Slater-type orbitals are discussed.

A similar but less quantitative study is made of the

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[1] It is assumed throughout that the variational principle is applicable. For the application of the variational principle to excited states, see E. A. Hylleraas and B. Undheim, Z. Physik **65**, 759 (1930); J. K. L. MacDonald, Phys. Rev. **43**, 830 (1933); H. Shull and P. -O. Löwdin, Phys. Rev. **110**, 1466 (1958); E. R. Davidson, J. Chem. Phys. **41**, 656 (1964); J. F. Perkins, *ibid.* **42**, 3927 (1965).

[2] These terms are defined in Sec. III.

effect on approximate calculations of increasing the number of electrons N while holding Z fixed. For this purpose, comparative closed- and open-shell ground-state energy data for the isonucleic sequence $F^{7+}-F$ are studied and interpreted. The limitations of the various types of functions are discussed from the standpoint of their Z and N dependency. An estimate is made of the anticipated effectiveness with increasing N of several types of open-shell calculations as compared to the conventional Hartree–Fock solutions.

The Hartree–Fock solutions are examined from the standpoint of their asymptotic classification. A deficiency in the usual definition of correlation energy is noted, an alternate definition is proposed, and numerical examples are given.

More elaborate atomic wave functions are then discussed and compared. The advantages and disadvantages of various methods of introducing correlation are contrasted.

One of the three previously mentioned categories of perturbed variational wave functions is selected as having the most desirable characteristics. It is recommended that, as a minimum requirement, all atomic wave functions be constructed so as to belong to this category. This can always be achieved by a suitable choice of orbitals and configurations. Such wave functions automatically yield a variational energy correct at least through first order, and other expectation values correct at least in zero order; these conditions are not fulfilled for the other two categories.

Some recommendations are made for future progress in the calculation of accurate atomic wave functions.

II. THE PERTURBATION ANALYSIS OF THE VARIATIONAL WAVE FUNCTIONS AND ENERGIES

We use modified atomic units[3] of the type first introduced by Hylleraas[4] in his classic application of perturbation theory to the He isoelectronic sequence.

A. The Perturbation Expansions

According to Rayleigh–Schrödinger perturbation theory,[4,5] the eigenfunctions ψ and eigenvalues ϵ of the nonrelativistic Schrödinger equation,

$$(H-\epsilon)\psi=0, \tag{1}$$

for an atomic isoelectronic sequence with N electrons about a nucleus of charge Z can be obtained as expansions in powers of $\lambda=Z^{-1}$:

$$\psi(N,\lambda)=\sum_{j=0}^{\infty}\psi_j(N)\lambda^j, \tag{2a}$$

$$\epsilon(N,\lambda)=\sum_{j=0}^{\infty}\epsilon_j(N)\lambda^j, \tag{2b}$$

where the $\psi_j(N)$ and $\epsilon_j(N)$ depend only on N and the state of the system. These expansions correspond to the decomposition of the total Hamiltonian H,

$$H=H_0+\lambda H_1, \tag{3}$$

where the perturbing term H_1 represents the Coulombic electronic interaction. The zero-order functions, $\psi_0(N)$, solutions of the unperturbed equation,

$$(H_0-\epsilon_0)\psi_0=0, \tag{4}$$

are known, antisymmetrized products of normalized hydrogenic orbitals. For normalized ψ_0, the zero- and first-order energy terms are given by

$$\epsilon_0=\langle\psi_0\mid H_0\mid\psi_0\rangle, \tag{5a}$$

and

$$\epsilon_1=\langle\psi_0\mid H_1\mid\psi_0\rangle, \tag{5b}$$

respectively, so these quantities can be evaluated analytically[6] for all N and for all states.

The analytic determination of the higher-order ψ_j and ϵ_j is difficult, although highly accurate results have been obtained for $N=2$ by a variational-perturbation method developed by Hylleraas[4] for the determination of ψ_1 and ϵ_2 and recently generalized to higher orders by Knight and Scherr.[7] There have been as yet relatively few applications[8] of this method to systems with more than two electrons. A simple numerical procedure based on a differencing technique has been devised for the direct recovery of the leading terms of the ϵ expansion from experimental energy data, and has been used to determine good estimates of ϵ_2 and ϵ_3 for the ground states of atomic sequences with $3\leq N\leq 10$ electrons.[9]

Consider now an arbitrary, variationally optimized, normalized wave function, $\bar{\varphi}(N,\lambda)$, and the corresponding optimized energy, $\bar{\eta}(N,\lambda)$, for a given isoelectronic sequence.[10] The Taylor expansions of

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[3] The modified atomic units are obtained from the atomic units of footnote 49 by replacing the electronic charge e with $eZ^{\frac{1}{2}}$; thus, the energy expressions in this section are to be multiplied by Z^2 to convert to atomic units. See H. Shull and G. G. Hall, Nature **184**, 1559 (1959).

[4] E. A. Hylleraas, Z. Physik **65**, 209 (1930); E. A. Hylleraas and J. Midtdal, Phys. Rev. **103**, 829 (1956); **109**, 1013 (1958).

[5] See, for example, A. Dalgarno, *Quantum Theory I, Elements*, D. R. Bates, Ed. (Academic Press Inc., New York, 1961), pp. 171–209.

[6] See, for example, D. Layzer, Ann. Phys. (N.Y.) **8**, 271 (1959); J. Linderberg and H. Shull, J. Mol. Spectry. **5**, 1 (1960); and F. C. Sanders and C. W. Scherr, J. Chem. Phys. **42**, 4314 (1965), for such calculations for $2\leq N\leq 10$.

[7] R. E. Knight and C. W. Scherr, J. Chem, Phys. **37**, 2503 (1962); Phys. Rev. **128**, 2675 (1962); Rev. Mod. Phys. **35**, 431 and 436 (1963); see also, J. Midtdal, Phys. Rev. **138**, A1010 (1965) for a recent application of this procedure.

[8] J. Linderberg, J. Mol. Spectry. **9**, 95 (1962), has computed variational approximations to ψ_1 and ϵ_2 for several states of atomic sequences with $N=2$, 4, and 6 by this method.

[9] C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. **127**, 830 (1962).

[10] In this notation, which corresponds to that of Refs. 16 and 18, the use of a superior bar denotes a variationally optimized quantity; the omission of the bar indicates an unoptimized quantity.

these approximate quantities about $\lambda=0$, i.e.,

$$\bar{\varphi}(N,\lambda)=\sum_{j=0}^{\infty}\bar{\varphi}_j(N)\lambda^j, \tag{6a}$$

$$\bar{\eta}(N,\lambda)=\langle\bar{\varphi}(N,\lambda)\mid H\mid\bar{\varphi}(N,\lambda)\rangle=\sum_{j=0}^{\infty}\bar{\eta}_j(N)\lambda^j, \tag{6b}$$

may be compared with the analogous perturbation expansions of the exact quantities ψ and ϵ in Eqs. (2). Similarly, the expansion of an expectation value computed with the variationally optimized wave function,

$$\langle\bar{A}\rangle=\langle\bar{\varphi}\mid A\mid\bar{\varphi}\rangle=\sum_{j=0}^{\infty}\langle\bar{A}\rangle_j\lambda^j, \tag{7a}$$

where

$$\langle\bar{A}\rangle_j=\sum_{l=0}^{j}\langle\bar{\varphi}_l\mid A\mid\bar{\varphi}_{j-l}\rangle, \tag{7b}$$

and A is an arbitrary operator independent of λ, may be compared with the corresponding expansion of the exact quantity.[11] Such comparisons afford a useful measure of the degree of convergence of the approximate wave function in question toward the exact solution. Various approximate solutions may be compared with one another in this manner to determine their relative accuracy.

If the optimized $\bar{\varphi}$ and $\bar{\eta}$ are known analytic functions of λ, the expansions (6) and (7) may be obtained by straightforward evaluation of the Taylor coefficients. Two particularly simple examples of such variational functions with theoretically known expansions have been discussed by Kohn.[12] In one, $\bar{\varphi}$ is taken as the appropriate ψ_0, which of course yields $\bar{\eta}=\epsilon_0+\epsilon_1\lambda$. In the other, $\bar{\varphi}$ is again taken as ψ_0 but the accuracy of the function is improved by the introduction of a variationally optimized scaling parameter which insures that the virial theorem[13] is satisfied; this yields

$$\bar{\eta}=\epsilon_0+\epsilon_1\lambda+\bar{\eta}_2\lambda^2, \tag{8a}$$

where in this particular case, the second-order approximate energy, $\bar{\eta}_2$, is given by

$$\bar{\eta}_2=\epsilon_1^2/4\epsilon_0\geq\epsilon_2. \tag{8b}$$

In all but such simple cases, however, it is impossible or impracticable to obtain the $\bar{\varphi}$ and $\bar{\eta}$ in closed form as functions of λ, so an explicit Taylor expansion cannot usually be performed. On the other hand, Scherr and Silverman[14] have determined the $\bar{\eta}$ expansions through second order for a number of variational wave functions for the He sequence by a limiting algebraic process and Machacek and Scherr[15] have made similar calculations for the Li sequence. Recently, Silverman and van Leuven[16] have developed a general variational-perturbation procedure for the term-by-term calculation and optimization of the $\bar{\varphi}$ and $\bar{\eta}$ expansions, Eqs. (6), as well as for the calculation of the $\langle\bar{A}\rangle$ expansion, Eqs. (7), to any desired order for arbitrary analytic φ. Thus, for example, the zero- and first-order approximate energies, $\bar{\eta}_0$ and $\bar{\eta}_1$, are given by Eqs. (5a) and (5b), respectively, in which ψ_0 is replaced by $\bar{\varphi}_0$.[17] This method has been applied[18] to a variety of variational wave functions for several atomic isoelectronic sequences. The procedure is not limited to atomic sequences, however, as it may be applied in the case of a more general Hamiltonian, $H(\lambda)$, with the expansion,

$$H=H(\lambda)=\sum_{j=0}^{\infty}H_j\lambda^j, \tag{3$'$}$$

where λ is any external perturbing parameter.

The important special case of Hartree–Fock functions and energies has previously been discussed by Löwdin,[13] and Dalgarno[19] has developed a general analytic method for the determination of the $\bar{\varphi}_{\mathrm{HF}}$ and $\bar{\eta}_{\mathrm{HF}}$ as expansions in λ. This method has been applied by several authors[20] to Hartree–Fock calculations for various isoelectronic sequences.

A valuable supplementary method for the determination of the first few terms of the $\bar{\eta}$ expansion, or of an arbitrary $\langle\bar{A}\rangle$ expansion, is the previously mentioned numerical differencing technique[9] which can be employed if the $\bar{\eta}$ or $\langle\bar{A}\rangle$ values are accurately known for several successive members of a given isoelectronic sequence. Recently, Scherr and Silverman[21] applied this numerical procedure to variational data for the $2\leq N\leq 4$ sequences and obtained accurate results as evidenced by comparison[7,11] with theoretically known or directly computed values.

B. The Asymptotic Classification

In general there is no requirement that the $\bar{\varphi}$ and $\bar{\eta}$ expansions, Eqs. (6), derived from the optimization of an arbitrary variational φ should agree term-by-

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[11] C. W. Scherr and R. E. Knight, J. Chem. Phys. **40**, 3034 (1964), have computed a large number of expectation values correct through sixth order for the ground state of the He sequence. See, also, A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. (London) **A247**, 245 (1958); **A257**, 534 (1960); W. A. Sanders and J. O. Hirschfelder, J. Chem Phys. **42**, 2904 (1965).

[12] W. Kohn, Phys. Rev. **71**, 635 (1947); see also Refs. 9 and 13.

[13] P.-O. Löwdin, J. Mol. Spectry. **3**, 46 (1959).

[14] C. W. Scherr and J. N. Silverman, J. Chem. Phys. **32**, 1407 (1960).

[15] M. Machacek and C. W. Scherr, J. Chem. Phys. **33**, 242 (1960).

[16] J. N. Silverman and J. C. van Leuven, Bull. Am. Phys. Soc. **8**, 615 (1963); extended manuscript in preparation.

[17] The simplicity of this expression for $\bar{\eta}_1$ depends upon the fact that $\langle\bar{\varphi}_0\mid H_0\mid\bar{\varphi}_1\rangle+\langle\bar{\varphi}_1\mid H_0\mid\bar{\varphi}_0\rangle$ vanishes. This is true in general only for optimized $\bar{\varphi}_0$ or the exact ψ_0; see Ref. 16.

[18] J. N. Silverman, unpublished calculations; J. N. Silverman and J. C. van Leuven (to be published); J. N. Silverman and D. N. Peden (to be published).

[19] A. Dalgarno, Proc. Phys. Soc. (London) **75**, 439 (1960).

[20] J. Linderberg, Phys. Rev. **121**, 816 (1961); M. Cohen and A. Dalgarno, Proc. Phys. Soc. (London) **77**, 165 (1961); C. S. Sharma and C. A. Coulson, *ibid.* **80**, 81 (1962); C. S. Sharma, *ibid.* **80**, 839 (1962); M. Cohen, *ibid.* **82**, 778 (1963); M. Cohen and P. S. Kelly, Can. J. Phys. **43**, 1867 (1965).

[21] C. W. Scherr and J. N. Silverman, J. Chem. Phys. **37**, 1154 (1962).

term with the corresponding exact ψ and ϵ expansions, Eqs. (2). It is possible, however, to classify variational wave functions into different categories, depending upon the agreement or lack of agreement of corresponding terms in the exact and variational expansions. As this paper is primarily concerned with asymptotic trends, it is sufficient here to deal in detail only with the zero-order wave function and the zero- and first-order energies.

By definition,

$$\bar{\varphi}_0 \equiv (\bar{\varphi})_{\lambda=0}, \tag{9}$$

where $\bar{\varphi}_0$ may be obtained by optimization of the integral,

$$\eta_0 \equiv (\eta)_{\lambda=0} = \langle \varphi \mid H \mid \varphi \rangle_{\lambda=0} = \langle \varphi \mid H_0 \mid \varphi \rangle. \tag{10}$$

Thus, if the form of φ is such that φ becomes equal to ψ_0 for special values of the variational parameters contained in the function, then in accordance with the variational principle, the optimization of Eq. (10) with respect to all these parameters will generate just those special values as the optimum parameters. Consequently, for such φ,[22]

$$\bar{\varphi}_0 = \psi_0, \tag{11a}$$

and from Eqs. (5),

$$\bar{\eta}_0 = \epsilon_0, \tag{11b}$$

$$\bar{\eta}_1 = \epsilon_1, \tag{11c}$$

so the energies computed with these functions are correct, at least through first order.

If the form of φ is such that for no values of the variational parameters can φ become equal to ψ_0, then the optimization of Eq. (10) will merely produce the variational approximation function $\bar{\varphi}_0$. Here,

$$\bar{\varphi}_0 \neq \psi_0, \tag{12a}$$

$$\bar{\eta}_0 \geq \epsilon_0, \tag{12b}$$

$$\bar{\eta}_1 \neq \epsilon_1; \tag{12c}$$

thus, in general, energies computed with these functions are *incorrect*, at least through first order. Although there is no theoretical basis at present, it has been found in all previous calculations[18] with inexact, but scaled $\bar{\varphi}_0$, that Eq. (12c) may be replaced by the stronger relationship,

$$\bar{\eta}_1 \leq \epsilon_1. \tag{12c$'$}$$

The third category, in a sense intermediate to those of Eqs. (11) and (12), arises when there is zero-order degeneracy. According to degenerate perturbation theory,[5,6] the correct ψ_0 may be obtained by diagonalizing the matrix of the degenerate zero-order functions, the $\psi_0^{(i)}$ corresponding to the degenerate configurations, over the perturbation operator. This is equivalent to variationally optimizing the linear coefficients of the configuration–interaction function, formed from a linear combination of the $\psi_0^{(i)}$, in respect to the total Hamiltonian H. Thus, if $\bar{\varphi}_0$ is given by an *arbitrary* linear combination of the $\psi_0^{(i)}$ or in particular by any single $\psi_0^{(i)}$,

$$\bar{\varphi}_0 = \psi_0^{(i)} \neq \psi_0, \tag{13a}$$

then

$$\bar{\eta}_0 = \epsilon_0, \tag{13b}$$

but from the variational principle,

$$\bar{\eta}_1 \geq \epsilon_1. \tag{13c}$$

Consequently, the energies computed with these functions are correct, in general, *only in zero order.*

The statement is often made[23] that the energy of any state may be calculated correct through first order with *any* arbitrary approximate wave function. Thus, let

$$\psi = M(\bar{\varphi} + \chi), \tag{14}$$

where $\bar{\varphi}$ is an arbitrary, normalized, variationally optimized approximation to ψ, χ is a correction function and M is an over-all normalization factor for ψ. There is no requirement that χ be normalized or orthogonal to $\bar{\varphi}$. Then, from Eqs. (6b) and (14),

$$\begin{aligned}\bar{\eta} - \epsilon = \langle \bar{\varphi} \mid H - \epsilon \mid \bar{\varphi} \rangle = M^{-2} \langle \psi \mid H - \epsilon \mid \psi \rangle \\ - M^{-1} [\langle \psi \mid H - \epsilon \mid \chi \rangle + \langle \chi \mid H - \epsilon \mid \psi \rangle] \\ + \langle \chi \mid H - \epsilon \mid \chi \rangle,\end{aligned} \tag{15a}$$

so from Eq. (1) for Hermitian H,

$$\bar{\eta} - \epsilon = \langle \chi \mid H - \epsilon \mid \chi \rangle. \tag{15b}$$

Equation (15b) is the usual formulation of the stationary quality of $(\bar{\eta} - \epsilon)$ through first order in the sense that it is second order in the correction function, χ. This interpretation requires qualification when literally applied to the terms of a perturbation expansion. For H given by Eq. (3) or (3′), and in analogy with Eqs. (2) and (6), χ may be expanded as

$$\chi = \sum_{j=0}^{\infty} \chi_j \lambda^j. \tag{16}$$

In general, if

$$\chi_j = 0, \qquad 0 \leq j \leq p, \tag{17a}$$

then, from Eq. (15b),

$$(\bar{\eta} - \epsilon) = O(\lambda^{2p+2}). \tag{17b}$$

Equation (17b) corresponds to a well-known theorem[5] which, in this formulation, states that if the expansions

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[22] In general, φ may be a much more elaborate function than ψ_0, containing many more terms and parameters. For example, φ may be an analytic HF function, an open-shell function, configuration-interaction function, Hylleraas-type correlated function, or some combination of these. Nevertheless, the conditions of Eqs. (11) will be satisfied if ψ_0 is contained at least implicitly in φ, as then the optimization of φ over H_0, Eq. (10), will project out ψ_0.

[23] See, for example, J. Goodisman and W. Klemperer, J. Chem. Phys. **38**, 721 (1963); these authors essentially limit their discussion to the case where $\bar{\varphi}_0 = \psi_0$.

of $\bar{\varphi}$ and ψ should agree through the pth order, the expansions of $\bar{\eta}$ and ϵ would then agree through the $(2p+1)$th order. In particular, for normalized ψ_0 and $\bar{\varphi}_0$, if

$$\chi_0=0, \qquad \chi_j\neq 0 \quad \text{for} \quad j\geq 1, \tag{18a}$$

then

$$\psi_0=\bar{\varphi}_0, \qquad \psi_j\neq\bar{\varphi}_j \quad \text{for} \quad j\geq 1, \tag{18b}$$

a special case[23] of Eqs. (11). If, on the other hand,

$$\chi_j\neq 0, \qquad j\geq 0, \tag{19a}$$

then,

$$\psi_0=M_0(\bar{\varphi}_0+\chi_0)\neq\bar{\varphi}_0, \tag{19b}$$

and the conditions of Eqs. (12) are fulfilled. In the case of zero-order degeneracy, a similar argument may be used to derive the conditions of Eqs. (13). These and related matters pertaining to the expansions of arbitrary $\bar{\varphi}$ and $\bar{\eta}$ are discussed in greater detail elsewhere.[16]

The three asymptotic categories of approximate wave functions described by Eqs. (11)–(13) include all possible types of perturbed variational solutions to *any* Hamiltonian which may be written in the form of Eq. (3) or (3′), where H_0 is independent of λ and λ is a parameter governing the strength of the perturbing term or terms. In particular, the analysis is used here to provide a natural scheme for classifying variational wave functions for atomic isoelectronic sequences.

III. SIMPLE CLOSED- AND OPEN-SHELL VARIATIONAL WAVE FUNCTIONS

In general, both closed- and open-shell variational wave functions are based on the independent-particle model and are constructed with antisymmetrized sums of products of space-spin orbitals with the proper multiplet symmetry for the system considered. In the closed-shell functions, the radial orbitals of spin-paired electrons are constrained to be identical, while in the open-shell functions some radial correlation[24] is introduced by relaxing this constraint. The proper symmetry can often be obtained in the closed-shell procedure with a single-determinantal wave function, but in the open-shell procedure, a multideterminantal wave function is always required. The Hartree–Fock functions obtained in the conventional manner represent closed-shell or, as they are sometimes termed, restricted Hartree–Fock (HF) solutions.[25] Open-shell, also termed unrestricted, Hartree–Fock (UHF) functions have been discussed by Nesbet,[25] Pratt,[26] and Löwdin,[27] and various approximate UHF solutions have been derived by several authors.[28] As yet no full-scale UHF calculation has been performed because of the attendant difficulties, although Stewart[29] has recently shown how a perturbation expansion approach[19,20] may be used to derive such solutions. On the other hand, if a simple set of analytic orbitals is used as an approximation to the UHF orbital set, open-shell character may be readily achieved by the variational assignment of different parameters to spin-paired orbitals of the same functional form. Such simple analytic, open-shell wave functions were originally introduced by Hylleraas,[30] and, independently, by Eckart[31] for the variational calculation of the energy of He. These calculations were extended by Shull and Löwdin[32] to He-like ions, and subsequently, by Matsen and co-workers to Li,[33] Li-like,[34] Be[35] and Be-like ions[36]; and by Brigman and Silverman[37] to B and B-like ions; in all of these calculations, the open-shell wave functions were constructed with single exponential Slater-type (ST) orbitals. Analogous open-shell calculations have been made for Li and Li-like ions by Ritter *et al.*[38] and by Machacek and Scherr[39] with analytic orbitals somewhat more flexible[40] than the ST orbitals. In these open-shell calculations, the emphasis has been on the use of a single-configuration wave function with highly optimized, nonlinear variational parameters (orbital exponents). For the two- to four-electron systems considered, the initial results were very encouraging, as these open-shell functions are relatively simple and yield energies which are frequently superior to the corresponding closed-shell HF energies. A closer examination, however, reveals that in some cases the HF energies become superior to the open-shell results with increasing Z within an isoelectronic sequence. Thus, recent HF calculations[41,42] have shown that ground-state, open-shell energies computed with ST orbitals are superior for all Z for

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[24] See P.-O. Löwdin, Advan. Chem. Phys. **2**, 207 (1959), for a discussion of electronic correlation energy.

[25] R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955).

[26] G. W. Pratt, Jr., Phys. Rev. **102**, 1303 (1956).

[27] P.-O. Löwdin, Ann. Acad. Sci. Upsaliensis **2**, 127 (1958).

[28] See, for example, J. H. Wood and G. W. Pratt, Jr., Phys. Rev. **107**, 995 (1957); R. K. Nesbet and R. E. Watson, Ann. Phys. (N.Y.) **9**, 260 (1960); L. M. Sach, Phys. Rev. **117**, 1504 (1960); R. E. Watson and A. J. Freeman, *ibid.* **120**, 1125 (1960).

[29] A. L. Stewart, Proc. Phys. Soc. (London) **83**, 1033 (1964); see also, C. Froese, Phys. Rev. **140**, A1489 (1965).

[30] E. A. Hylleraas, Z. Physik **54**, 347 (1929).

[31] C. Eckart, Phys. Rev. **36**, 878 (1930).

[32] H. Shull and P.-O. Löwdin, J. Chem. Phys. **25**, 1035 (1956).

[33] G. H. Brigman and F. A. Matsen, J. Chem. Phys. **27**, 829 (1957).

[34] R. P. Hurst, J. D. Gray, G. H. Brigman, and F. A. Matsen, Mol. Phys. **1**, 189 (1958); see also E. A. Burke and J. E. Mulligan, J. Chem. Phys. **28**, 995 (1958).

[35] G. H. Brigman, R. P. Hurst, J. D. Gray, and F. A. Matsen, J. Chem. Phys. **29**, 251 (1958).

[36] R. P. Hurst and F. A. Matsen, Acta Cryst. **12**, 7 (1959).

[37] G. H. Brigman and J. N. Silverman, J. Chem. Phys. **44**, 3136 (1966).

[38] Z. W. Ritter, R. Pauncz, and K. Appel, J. Chem. Phys. **35**, 571 (1961).

[39] M. Machacek and C. W. Scherr, unpublished calculations (1961).

[40] The more flexible orbitals used in the Li sequence calculations of Ref. 39 were previously used in corresponding closed-shell calculations by E. B. Wilson, Jr., J. Chem. Phys. **1**, 210 (1933); these original closed-shell calculations were refined and extended to larger values of Z by Machacek and Scherr.

[41] See C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960) for accurate, restricted HF calculations for the He, Li, and Be isoelectronic sequences, and E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962) for the extension of these calculations to the neutral first-row atoms.

[42] E. Clementi, J. Chem. Phys. **38**, 996 and 1001 (1962).

Table I. Comparison of ground-state variational energies (in a.u.) for the boron isoelectronic sequence.

Z	Closed-shell				Open-shell	Exact[f]
	SH[a]	ST[b]	MYH[c]	HF[d]	ST[e]	
4	−13.6749			−14.551[g]	−14.5814	−14.6604[g]
5	−23.7223	−24.4984	-24.502_5	−24.5291	−24.5226	−24.6538
6	−36.5198	−37.2528	-37.266_0	−37.2922	−37.2748	−37.4312
7	−52.0673	−52.7614[h]	-52.789_5	−52.8158	−52.7820	−52.9670
8	−70.3648	−71.0195	-71.068_0	−71.0947	−71.0382	−71.2570
9	−91.4122	−92.0245[i]	-92.099_5	−92.1267	−92.0407	−92.2993
10	−115.2097	−115.7758[i]	-115.883_0	−115.9108	−115.7888	−116.0929
15	−275.4471	−275.7093[i]		−276.0957	−275.7168	−276.3203
18	−404.5895			−405.2118	−404.6052	−405.4598
19	−453.1370			−453.7509	−453.0538	−454.0066
20	−504.4344	−504.2554[i]		−505.0402	−504.2541	−505.3034

[a] Computed with Eqs. (8); see Ref. 12.
[b] Unless otherwise indicated, these values are from Ref. 43.
[c] See Ref. 44.
[d] See Ref. 42.
[e] See Ref. 37.
[f] Nonrelativistic energies, Ref. 9.
[g] Estimates; see text and Refs. 9, 47, and 48.
[h] Interpolated.
[i] Incompletely optimized; see Ref. 37.

the He isoelectronic sequence[32,34] and are superior for $Z\leq 4$ but become increasingly inferior for $Z>4$ for the Li[33,34] and Be[35,36] sequences. For the B sequence,[37] the HF energy is not directly available for $Z=4$, but the ST open-shell energies also become increasingly inferior to the HF energies for $Z>4$. On the other hand, the open-shell energies for the Li sequence computed[38,39] with a $2s$ orbital more flexible than the ST $2s$ orbital are superior to the HF energies for all Z.

It is apparent that a straightforward application of the variational principle is inadequate to interpret this anomalous dependence on Z. It is possible, however, to find a simple explanation in terms of the perturbation analysis outlined in Sec. II. To demonstrate the procedure in detail, we select the $^2P^\circ$ ground state of the boron isoelectronic sequence for which there is a wide variety of closed- and open-shell comparative energy data available. The choice of this system has an additional advantage in that all three categories (see Sec. II) of perturbed variational wave functions are represented. In Table I, the single-configuration, closed-shell calculations of Roothaan,[43] Tubis,[44] and Clementi[42] constructed with ST, Morse–Young–Haurwitz[45] (MYH) and HF orbitals, respectively, are compared with the recent corresponding single-configuration, open-shell ST calculations[37] and the exact nonrelativistic energies.[9]

The closed-shell calculations are all based on the configuration $(1s^22s^22p)$ for which there is only one doublet-spin-state function. The open-shell calculation, however, is based on the configuration $(1s1s'2s2s'2p)$ for which there are five linearly independent doublet-spin-state functions.[46] Therefore the most general single-configuration open-shell wave function would have been a linear combination of five independent functions with variationally determined coefficients. Only that doublet-spin function was used,[37] however, which uniquely pairs electrons in the same manner as the closed-shell function because in the analogous open-shell lithium sequence calculations,[33,34] this pairing scheme was found to make the major contribution to the energy.

In order to illustrate the subsequent discussion of the perturbation analysis, the energies computed with the Kohn[12] double-configuration closed-shell function, constructed with scaled hydrogenic (SH) orbitals, are also presented in Table I; this function, which is based on a linear combination of the configurations $(1s^22s^22p)$ and $(1s^22p^3)$, is obtained from the zero-order perturbation wave function by introduction of a variationally optimized scaling parameter. The entries in Table I for the HF and exact energy values for $Z=4$ are estimates obtained from the exact energy for Be[9] and the estimates of correlation energy by Clementi[47] and of electron affinity by Edlén.[48] Unless otherwise specified, all energy data here and elsewhere are in atomic units[49] (a.u.).

Inspection of the energy data in Table I reveals the following significant asymptotic trends with in-

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[43] C. C. J. Roothaan, Technical Report, Laboratory of Molecular Structure and Spectra, The University of Chicago, pp. 24 ff (1955). These original closed-shell ST calculations (for $Z=5$, 6, and 8) were extended in Ref. 37 to larger values of Z by an approximate optimization procedure.

[44] A. Tubis, Phys. Rev. **102**, 1049 (1956).

[45] P. M. Morse, L. A. Young, and E. S. Haurwitz, Phys. Rev. **48**, 948 (1935). These MYH orbitals differ from the Wilson orbitals of Refs. 39 and 40 only in that the Wilson $2s$ orbital is slightly more general.

[46] This may be seen from the spin branching diagram; see, for example, E. M. Corson, *Perturbation Methods in The Quantum Mechanics of n-Electron Systems* (Blackie & Son Ltd., London, 1951), p. 189.

[47] E. Clementi, J. Chem. Phys. **38**, 2248 (1963).

[48] B. Edlén, J. Chem. Phys. **33**, 98 (1960).

[49] The atomic unit of energy is defined as $\hbar^{-2}\mu e^4$, where μ is the appropriate reduced electronic mass for the atom or ion in question; see, however, Ref. 3 for the definition of modified atomic units.

TABLE II. Comparison of ground-state variational $\bar{\eta}$ expansions[a] for the boron isoelectronic sequence.

Function	$\bar{\eta}_0$	$\bar{\eta}_1$	$\bar{\eta}_2$	$\bar{\eta}_3$[b]
Closed-shell				
SH[c]	(-1.375)[d]	$(2.32753\cdots)$[d]	$(-0.984978\cdots)$[c]	(0)[c]
ST[e]	$(-1.37202\cdots)$[f]	2.306	−1.545	−0.91
MYH[g]	(-1.375)[d]	$(2.33445\cdots)$[d]	−1.672	−0.50
HF[h]	(-1.375)[d]	$(2.33445\cdots)$[d]	−1.709	−0.38
Open-shell				
ST[i]	−1.373	2.328[j]	−1.764	−0.38
Exact[k]	(-1.375)	$(2.32753\cdots)$	−1.843	−0.18

[a] Entries in parentheses are exact analytical values; entries without parentheses have been determined by numerical differencing.

[b] The numerically obtained values of $\bar{\eta}_3$ should be regarded as little more than empirical fitting parameters; see the relevant discussion in Ref. 9.

[c] See Eqs. (8).

[d] See Ref. 6.

[e] Input energy data from Ref. 43.

[f] J. N. Silverman, unpublished calculations, Ref. 18.

[g] Input energy data from Ref. 44.

[h] Input energy data from Ref. 42.

[i] Input energy data from Ref. 37.

[j] Equation (12c′) applies here in the sense that $\bar{\eta}_1$ is less than the corresponding single-configuration exact value $2.33445\cdots$.

[k] See Ref. 9.

creasing Z:

(1) For smaller Z, the ST open-shell energies display the anticipated improvement of about 0.02 a.u. over the ST closed-shell values found in the analogous calculations for the $2 \leq N \leq 4$ systems; this improvement diminishes until at $Z=20$, the ST closed-shell value, although not fully optimized,[37,43] is apparently slightly superior to the ST open-shell value.

(2) The error in the ST open-shell energies,

$$\Delta E_{\text{ST open}} = E_{\text{exact}} - E_{\text{ST open}},$$

increases rapidly in magnitude, while the quantity $\Delta E_{\text{ST open}}/Z^2$ diminishes in magnitude at first rapidly and then more slowly, apparently approaching a limiting value[37] at larger Z; the ST closed-shell energies display the same general behavior.

(3) For $Z=4$, the ST open-shell energy is superior to the estimated HF energy, while for $Z \geq 5$, the HF energies rapidly become increasingly superior.

(4) For $Z<7$, the ST open-shell energies are superior to the MYH energies, but for $Z \geq 7$, the former become increasingly inferior and eventually even cross to above the SH energies for $Z \geq 19$.

(5) The HF energies retain an approximately constant superiority over the MYH energies throughout; the errors in both of these energies, ΔE_{HF} and ΔE_{MYH}, increase in magnitude, although not as rapidly as $\Delta E_{\text{ST open}}$, while the quantities $\Delta E_{\text{HF}}/Z$ and $\Delta E_{\text{MYH}}/Z$ diminish in magnitude, apparently approaching a limiting value at larger Z.

Some of these trends appear surprising at first glance. It follows from the variational principle that the HF energies must be superior for all Z to any other single-configuration, closed-shell calculation; similarly, as has been pointed out by Slater,[50] the MYH closed-shell energies must be superior to the ST closed-shell results as the latter function is a special case of the former. On the other hand, the ST open-shell function has five variational parameters while the MYH, ST, and SH closed-shell functions have only four, three and one, respectively, so the relative behavior of these energies seems contrary to expectations.

As a guide in interpreting these asymptotic trends, the $\bar{\eta}$ expansions of the variational energy data in Table I have been determined through third order by means of the numerical differencing technique[51] in conjunction with analytically known[6,12,18] expansion terms. The various sets of $\bar{\eta}_j(5)$ so obtained are collected in Table II where they are compared with the exact[9] $\epsilon_j(5)$. Thus, in a.u., both ST energy errors are essentially quadratic in Z,

$$\Delta E_{\text{ST closed}} = -0.003Z^2 + 0.022Z - 0.298 + 0.73Z^{-1} + \cdots, \tag{20}$$

$$\Delta E_{\text{ST open}} = -0.002Z^2 - 0.079 + 0.20Z^{-1} + \cdots, \tag{21}$$

while both ΔE_{MYH} and ΔE_{HF} are essentially linear in Z with the same leading term,

$$\Delta E_{\text{MYH}} = -0.0069Z - 0.171 + 0.32Z^{-1} + \cdots, \tag{22}$$

$$\Delta E_{\text{HF}} = -0.0069Z - 0.134 + 0.20Z^{-1} + \cdots, \tag{23}$$

and only ΔE_{SH} is essentially independent of Z,

$$\Delta E_{\text{SH}} = -0.858 - 0.18Z^{-1} + \cdots. \tag{24}$$

These energy errors, Eqs. (20)–(24), are plotted in

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[50] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Co., Inc., New York, 1960), Vol. I, pp. 332–372; see also, E. B. Wilson, Jr., Ref. 40, for an analogous discussion.

[51] In most cases, the scaled, i.e., shielded, form of the numerical analysis described in Refs. 9 and 21 was used.

Fig. 1 as a function of Z. The important ΔE_{HF} is commonly called the correlation energy,[24] E_{corr}, and Eq. (23) gives numerical results which are in good agreement with the values for the B sequence obtained by Clementi.[47]

The sources of error in the various sets of $\bar{\eta}_j$ may now be determined by classifying these approximate wave functions in the three asymptotic categories of perturbed variational solutions. According to Eqs. (11), the errors in $\bar{\eta}_0$ and $\bar{\eta}_1$ vanish if $\bar{\varphi}_0=\psi_0$. In terms of Schrödinger perturbation theory, the ψ_0 for atomic isoelectronic sequences must be constructed with hydrogenic orbitals. Therefore, only trial wave functions constructed with orbitals sufficiently flexible to become hydrogenic by variation of the parameters can yield the correct ψ_0.[22]

For the ST orbitals defined in the usual manner[50] only the lowest function of each symmetry species has the required hydrogenic form. As a consequence, both the closed- and open-shell ST functions for the B sequence cannot yield the correct ψ_0 due to the presence of the ST 2*s* orbitals, and are thus described by Eqs. (12). In some ST closed-shell calculations,[43] an ST 2*s* orbital has been used which, for convenience, has been orthogonalized to the ST 1*s* orbital. This orthogonal ST 2*s* orbital cannot become hydrogenic despite a superficial resemblance to the hydrogenic 2*s* orbital and, in fact, in these closed-shell calculations yields the identical wave function and energy as would be obtained with the usual nonorthogonal ST 2*s* orbital.[50] In general, then, Eqs. (12) are applicable to *all* single-configuration[52] functions containing one or more ST orbitals other than the lowest orbital of each symmetry species. This explains, for example, why Machacek and Scherr[15] found $\bar{\eta}_0>\epsilon_0$ in their analysis of ST functions for the Li sequence. In all such ST calculations, there will be an energy error essentially increasing with Z^2, as in Eqs. (20) and (21) and Fig. 1. The opening of the shells of these ST functions cannot eliminate the inherent zero-order error but does improve the variational quality of $\bar{\eta}_0$ by introducing more parameters. Thus, as may be seen from Table II, the ST open-shell value of $\bar{\eta}_0$ is superior to the ST closed-shell value. For the same reason, an additional improvement in $\bar{\eta}_0$ would be obtained if the four other linearly independent doublet-spin-state functions were included in the ST open-shell wave function for the B sequence; there is evidence, however, that this effect would be small.[53]

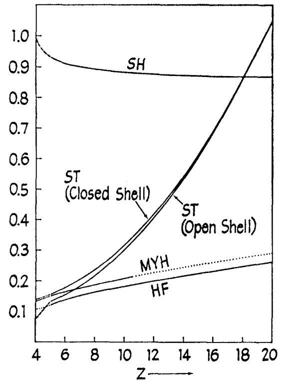

FIG. 1. Variational energy errors as a function of Z for the boron sequence wave functions of Table I. Dotted or dashed lines represent estimated behavior.

The orbitals of the remaining functions considered in Tables I and II, the SH, MYH and the completely flexible HF, all possess the necessary form to become hydrogenic, so therefore $\bar{\eta}_0=\epsilon_0$ for each of these functions. Due to zero-order degeneracy, the correct zero-order function for the ground state of the B sequence is obtained by taking the proper linear combination of the $^2P^\circ$ zero-order functions corresponding to the configurations $(1s^22s^22p)$ and $(1s^22p^3)$. Consequently, the MYH and HF functions, which employ only the former configuration, contain the same $\bar{\varphi}_0=\psi_0^{(i)}$ and generate the same $\bar{\eta}_1(>\epsilon_1)$ in accordance with Eqs. (13). The errors in the energies computed with these functions have therefore the same essential linear dependence on Z, cf. Eqs. (22) and (23) and Fig. 1. The Z dependency of E_{corr} for various states of a number of atomic isoelectronic sequences has previously been discussed from the standpoint of zero-order degeneracy by Linderberg and Shull.[6] The remaining SH function, derived by scaling the correct, double-configuration ψ_0, is the only function to satisfy Eqs. (11); hence the error in the computed energies is essentially independent of Z, cf. Eq. (24) and Fig. 1.

The expansions of Table II and Eqs. (20)–(24) are also sufficient to explain some of the finer details of the energy behavior at moderate values of Z. For example, the comparison of Eqs. (20) and (21), neglecting terms higher than the first order, leads to the prediction that for $Z\approx 22$, the ST closed- and open-shell energies should become equal, and for $Z>22$, the open-shell energies should again become superior; this prediction is in qualitative agreement with the data in Table I which suggests equality somewhere in the range of $15\leq Z\leq 20$, but, as previously mentioned, the ST closed-shell energy is apparently *superior* to the ST open-shell energy at $Z=20$. This anomaly may be understood by suitably interpreting the work of Machacek and Scherr[15] on similar functions. For the Li sequence ST open-shell function, these authors found analytically that at a certain large $Z(Z\approx 34)$, the limiting values of the 1*s* and 1*s'* orbital exponents become equal (and hence the closed- and

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[52] Equations (12) apply also to configuration-interaction functions constructed with ST orbitals provided the choice of configurations is such that the various configuration functions cannot add together to yield ψ_0. For example, the ^2S Li sequence function, $c_1(1s^22s)+c_2(1s^23s)$, is described by Eqs. (12), but the similar function, $c_1(1s^22s)+c_2(1s^21s')$ contains ψ_0 implicitly, due to the properties of determinants, and is described by Eqs. (11); see footnote 80.

[53] For an example of this effect, compare the ST open-shell Li sequence calculations of E. A. Burke and J. F. Mulligan with both linearly independent doublet functions and of R. P. Hurst *et al.* with only one of these functions, Ref. 34.

open-shell energies coincide) and for still larger Z, these optimum parameters become complex conjugates to one another; the complex orbital exponents are required for the open-shell energy to be superior to the closed-shell energy above the critical value of Z. From Eq. (10), it follows that complex orbital exponents can only occur in those $\bar{\varphi}_0$ which satisfy Eqs. (12). Therefore, in this case, the peculiarity arises solely from the use of the ST 2*s* orbital. The energy data in Table I suggests that this also applies to the ST functions for the B sequence, but with the transition to complex parameters occurring at a smaller Z. Since the numerical procedure used[37] for the determination of optimum parameters was restricted to the domain of real numbers, the true open-shell minima could not be located above the critical $Z(Z\approx 17)$. The ST open-shell energies reported in Table I for $18\leq Z\leq 20$ probably represent secondary minima[37] which necessarily lie above the correct open-shell values and which may therefore lie above the optimum closed-shell values.

The greater effectiveness of the ST open-shell calculations at smaller Z is due in part to the peculiarities of functions satisfying Eqs. (12). Thus, from Eqs. (12) it is seen that the errors in $\bar{\eta}_0$ and $\bar{\eta}_1$ occur with opposite sign so partial compensation takes place. In fact, if the ST $\bar{\varphi}_0$ and the exact ψ_0 are compared as variational approximations to the total, exact ψ, the ST $\bar{\varphi}_0$ becomes energetically superior to ψ_0 for

$$Z < -(\epsilon_1 - \bar{\eta}_1)/(\epsilon_0 - \bar{\eta}_0), \tag{25}$$

and inferior to ψ_0 for Z greater than this value. Equation (25) applies in all cases where the inequalities (12b) and (12c′) are valid. For the other types of functions $\bar{\varphi}_0$ is either inferior to ψ_0, Eqs. (13), or equivalent to ψ_0, Eqs. (11), for all Z. Another contributory factor to the greater effectiveness of ST open-shell calculations at small Z is the significant negative contribution of the sum of third- and higher-order terms in the $\bar{\eta}$ expansion as may be seen by comparing the energies summed through the second order with the total energies. As a consequence of these effects, the data in Table I indicate that the ST open-shell energies for the B sequence become increasingly superior with diminishing Z to the corresponding HF closed-shell energies for $Z\leq 4$ in exact analogy with the Li and Be sequences. With increasing Z, however, the inherent Z^2 error in the ST energies rapidly overwhelms the favorable factors.

Since the MYH and HF energies contain the same linear error in Z, the only distinction between these two functions lies in the superior contribution to the total energy of the sum of the second- and higher-order energies obtained with the HF calculations. The superiority of the HF calculations is primarily due to the superior HF second-order energy, since the energy difference between the MYH and HF energies is practically independent of Z and is approximately equal to the difference between the respective second-order energies.

Although the simple SH function yields energies correct through the first order, the error in the second-order energy is so large that this function can compete favorably with the other functions only at very large values of Z. This suggests that the SH function represents a suitable point of departure for the construction of more elaborate wave functions since any improvement in quality would necessarily improve the quality of the second-order energy.

The analysis presented above is perfectly general and may be applied to any group of wave functions for any atomic isoelectronic sequence. The first step in the analysis is to determine the asymptotic behavior of the wave functions with increasing Z by dividing them by inspection into the three categories of Eqs. (11), (12), and (13). For large enough Z, the wave functions of Eqs. (11) must become superior to those of Eqs. (13) which in turn must become superior to those of Eqs. (12). For lower values of Z, this relative order of superiority of the categories may change, resulting in the crossing of energies with varying Z, as is the case for some of the functions considered for the B sequence, e.g., Fig. 1. The second step in the analysis is to compare the functions belonging to a given category. It is anticipated that the relative order of superiority of functions within any one category should in general be independent of Z, as has already been illustrated in the B sequence for the categories of Eqs. (12) and (13). This behavior is particularly clear for the functions of the category of Eqs. (11) for which the second-order energies, $\bar{\eta}_2$, and the first-order wave functions, $\bar{\varphi}_1$,[54] are the dominant factors in determining their relative accuracy. For example, all calculations cited for the He sequence fall in the category of Eqs. (11). In the order of decreasing accuracy of $\bar{\eta}_2$ as well as of $\bar{\eta}$, these calculations are the MYH or ST (the MYH and ST functions are identical for the ground state of the He sequence) open-shell,[14,32] the HF closed-shell[19,41] and the SH closed-shell function[12,55]; this relative order of superiority of $\bar{\eta}$ is found to be independent of Z. Analogously, for the Li sequence, the functions of the category of Eqs. (11), arranged in the order of decreasing superiority, are the open-shell calculations of Ritter *et al.*[38] and of Machacek and Scherr,[39] the HF closed-shell calculations[41] and the closed-shell calculations with the Wilson orbitals[40]; this order of superiority is again found to be independent of Z. On the other hand, the ST open- and closed-shell calculations for the Li[33,34] and Be[35,36] sequences belong to the category of Eqs. (12) so that with increasing Z,

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[54] In general, for a Hamiltonian operator given by Eq. (3), $\bar{\eta}_2 = \langle \bar{\varphi}_0 \,|\, H_1 \,|\, \bar{\varphi}_1 \rangle$; see Ref. 16.

[55] G. W. Kellner, Z. Physik **44,** 91 (1927); the Kellner calculations for He include the first application of an SH closed-shell function and one of the first applications of the method of configuration interaction. See also, J. C. Slater, Proc. Natl. Acad. Sci. (U.S.) **13,** 423 (1927).

TABLE III. Comparison of ground-state variational energies (in a.u.) for $Z=9$ and $2 \leq N \leq 9$.

State	N	System	Closed-shell			Open-shell		Exact[d]
			ST[a]	MYH or Wilson[b]	HF[c]	ST	Wilson	
^1S	2	F^{7+}	−75.473[e]	−75.473[e]	−75.486	−75.497[e]	−75.497[e]	−75.532
^2S	3	F^{6+}	−82.195[e]	−82.266[f]	−82.279	−82.213[e]	−82.290[f]	−82.331
^1S	4	F^{5+}	−87.818[g]	−87.92[h]	−87.934	−87.832[g]		−88.102
$^2P^\circ$	5	F^{4+}	−92.025[i]	−92.100	−92.127	−92.041[i]		−92.299
^3P	6	F^{3+}	−95.208	−95.259	−95.320			−95.501
$^4S^\circ$	7	F^{2+}	−97.454	−97.488	−97.609			−97.806
^3P	8	F^{+}	−98.558	−98.579	−98.832			−99.092
$^2P^\circ$	9	F	−98.942	−98.954	−99.409			−99.734

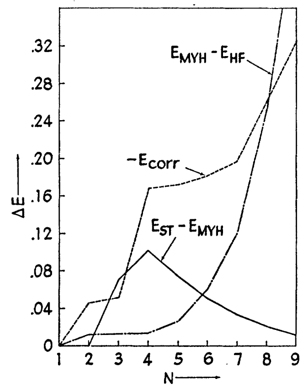
[a] Unless otherwise indicated, these values are from Ref. 43.
[b] Unless otherwise indicated, these values are from Ref. 44.
[c] See Ref. 42.
[d] Nonrelativistic energies, Ref. 9.
[e] See Ref. 34.
[f] See Refs. 39 and 56.
[g] See Ref 36; unpublished data from these calculations.
[h] Interpolated value; see Ref. 56.
[i] See Ref. 37.

the ST open-shell energies rapidly become (for $Z \geq 5$) inferior to the corresponding HF closed-shell energies.

The effect on approximate energy calculations of increasing N while holding Z fixed, may also be examined. In Table III are collected all available single-configuration, ground-state energy calculations with ST, MYH or Wilson,[56] and HF orbitals, as well as the exact nonrelativistic energies for the $2 \leq N \leq 9$ electron atomic sequences at $Z=9$, i.e., for F^{7+}—F. From these data, the quantities $E_{\text{ST closed}}-E_{\text{MYH}}$, $E_{\text{MYH}}-E_{\text{HF}}$, and $-E_{\text{corr}}$ have been determined and are plotted as a function of N in Fig. 2.

In accordance with the variational principle, comparison of the closed-shell ST and MYH (or Wilson) energies shows the latter to be superior for $N>2$. Further, as has been noted by Slater[50] for the similar case of atomic and ionized O, the superiority of the MYH results is slight for the neutral atom, and generally increases with decreasing N. This effect may now be interpreted as it is in parallel trend with the relative number of nonhydrogenic orbitals employed (in this case, the ST 2*s* orbital). For the $3 \leq N \leq 10$ electron atomic systems in their ground state, the ratio of the nonhydrogenic orbitals to the total number of orbitals in ST calculations is a minimum at $N=10$, monotonically reaches a maximum at $N=4$ and decreases again for $N=3$. Therefore, for any fixed Z, it is anticipated that the superiority of the closed-shell MYH (or similar) energies over the corresponding ST energies would be smallest for $N=10$ and *increase* steadily with *diminishing* N to become greatest for $N=4$. The previously discussed dependence on Z of the ST energies may be taken into account by noting that the shift to a smaller, fixed Z, with varying N, would diminish the superiority of the MYH energies for each N, while the shift to a larger, fixed Z would enhance this superiority. As a consequence, the ST open-shell values can compete favorably with the MYH *closed-shell* energies only for negative ions, the neutral atom and the first few positive ions of a given atomic isoelectronic sequence, i.e., for $Z<N$ and $Z \approx N$. These predictions are confirmed in Tables I and III and Figs. 1 and 2, as well as in all other cases where data are available for comparison. There is no difficulty in extending this analysis to excited states and to systems with $N>10$.

FIG. 2. Variational energy differences as a function of N with $Z=9$ for the closed-shell wave functions of Table III.



It is of greater interest to assess the relative accuracy of various open-shell calculations and the corresponding HF closed-shell calculations as a function of Z and N. At the time of revival of interest in open-shell functions, it was hoped that the open-shell technique, when applied to simple, analytic orbitals, would provide a

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[56] Accurate MYH closed-shell energies have been computed for Li and Be by E. Holöien, Proc. Phys. Soc. (London) **A68,** 297 (1955), but do not seem to be available for other members of the three- and four-electron atomic sequences due to errors in the initial calculations of Ref. 45; see W. E. Duncanson and C. A. Coulson, Proc. Phys. Soc. (Edinburgh) **62,** 37 (1944); and Ref. 44. Wilson closed- and open-shell energies, Refs. 39 and 40, are available, however, for the Li sequence and may be expected to differ but slightly from the corresponding MYH results due to the close similarity between both sets of orbitals.

Table IV. Comparison of some ground-state variational single-configuration closed- and open-shell energies[a] (in a.u.).

State	N	Z	Closed-shell				Open-shell	
			MYH or Wilson[b]	Δ_1[c]	HF[d]	Δ_2[c]	MYH or Wilson[e]	$\Delta_1+\Delta_2$[c]
^1S	2	2	−2.8477	−0.0140	−2.8617	−0.0140	−2.8757	−0.0280
		3	−7.2227	−0.0137	−7.2364	−0.0123	−7.2487	−0.0260
		4	−13.5977	−0.0136	−13.6113	−0.0117	−13.6230	−0.0253
		5	−21.9727	−0.0135	−21.9862	−0.0113	−21.9975	−0.0248
		10	−93.8477	−0.0134	−93.8611	−0.0107	−93.8718	−0.0241
		∞	···	−0.0133[f]	···	−0.0101[f]	···	−0.0234[f]
^2S	3	3	−7.4192	−0.0135	−7.4327	−0.0123	−7.4450	−0.0258
		4	−14.2640	−0.0134	−14.2774	−0.0115	−14.2889	−0.0249
		5	−23.3625	−0.0135	−23.3760	−0.0110	−23.3870	−0.0245
		6	−34.7127	−0.0134	−34.7261	−0.0106	−34.7367	−0.0240
		10	−102.6178	−0.0133	−102.6311	−0.0099	−102.6410	−0.0232
		30	−982.1583	−0.0134	−982.1717	−0.0088	−982.1805	−0.0222
^1S	4	4	−14.560[g]	−0.013	−14.5730	(−0.012)	(−14.585)	(−0.025)
		5	(−24.225)	(−0.013)	−24.2376	(−0.011)	(−24.249)	(−0.024)
		6	(−36.396)	(−0.013)	−36.4085	(−0.011)	(−36.420)	(−0.024)
		10	(−110.098)	(−0.013)	−110.1110	(−0.010)	(−110.121)	(−0.023)
$^2P^\circ$	5	5	−24.502	−0.027	−24.5291	(+0.003)	(−24.526)	(−0.024)
		6	−37.266	−0.026	−37.2922	(+0.003)	(−37.289)	(−0.023)
		10	−115.883	−0.028	−115.9108	(+0.005)	(−115.905)	(−0.023)
^3P	6	6	−37.628	−0.061	−37.6886	(+0.037)	(−37.652)	(−0.024)
		10	−120.483	−0.061	−120.5435	(+0.038)	(−120.506)	(−0.023)
$^4S^\circ$	7	7	−54.276	−0.125	−54.4009	(+0.101)	(−54.300)	(−0.024)
		10	−123.982	−0.122	−124.1041	(+0.099)	(−124.005)	(−0.023)

[a] Entries in parentheses are estimates (see text); other entries have been variationally determined.

[b] For $N=2$, see Ref. 34; for $N=3$, see Refs. 39 and 40; for $N=5$, 6, and 7, see Ref. 44.

[c] Δ_1 is the improvement of the HF energies over the closed-shell MYH or Wilson energies; Δ_2 is the improvement of the open-shell MYH or Wilson energies over the HF energies.

[d] See Refs. 41 and 42.

[e] For $N=2$, see Ref. 34; for $N=3$, see Refs. 39 and 40.

[f] These entries are given by the differences in the respective values of $\bar{\eta}_2$; see Refs. 12, 14, and 19.

[g] E. Holöien, Ref. 56.

simple method for computing energies[32–39] and other expectation values[36,57–60] superior to the conventional HF results. From the results of this study, it is now apparent that this promise has not been fulfilled for the ST open-shell energy calculations, aside from the special case of $N=2$. As shown, the relative effectiveness of ST single-configuration open-shell calculations diminishes so rapidly with increasing Z and N that for $Z\geq5$ and $N\geq3$, the corresponding HF energies become superior. For analogous reasons, the expectation values of other properties computed with ST functions necessarily have an incorrect asymptotic behavior but insufficient data are available at the present time for a quantitative study.

It remains to be determined to what extent the effectiveness of open-shell energy calculations can be extended by replacing the ST orbitals with simple orbitals of hydrogenic form. This can be estimated by comparing the MYH or Wilson and the HF closed-shell energies in Table III and Fig. 2. This reveals that the superiority of the HF energies is approximately constant in the range $2\leq N\leq4$ but increases rapidly for $N\geq5$. From this it is evident that the MYH 1s and 2s orbitals are reasonably good approximations to the corresponding HF orbitals but the MYH 2p orbital is not sufficiently flexible to match the HF 2p orbital. Therefore, if the MYH or Wilson orbitals were employed as an improved basis set for single-configuration open-shell calculations, it is anticipated from the data in Tables I and III that the MYH or Wilson open-shell energies would be superior to the corresponding HF closed-shell energies for $2\leq N\leq4$ for all Z but would become increasingly inferior with increasing N for $N\geq5$ and $Z\geq N$.[61] This estimate is based on the observations that the gain in radial correlation energy obtained with open-shell wave functions is derived primarily from opening the first shell[35] and that for a given Z, this energy improvement is relatively insensitive[32–39] to the number of outer-shell electrons. As a consequence, with increasing N, the energy improvement obtained with MYH or Wilson open-shell wave functions can no longer compensate for the superiority of the higher HF orbitals. This situation is illustrated in Table IV for the $2\leq N\leq7$

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[57] R. P. Hurst, J. Miller, and F. A. Matsen, Acta Cryst. **11**, 320 (1958).

[58] F. T. Ormond and F. A. Matsen, J. Chem. Phys. **30**, 368 (1959).

[59] J. N. Silverman, O. R. Platas, and F. A. Matsen, J. Chem. Phys. **32**, 1402 (1960).

[60] O. R. Platas, J. Chem. Phys. **37**, 2755 (1962).

[61] For negative ions with $N\geq5$ and sufficiently low Z, there are indications that the MYH or Wilson open-shell energies would become superior to the HF energies; cf. the entries for $Z=4$ in Table I.

systems by comparing calculated or estimated single-configuration ground-state energy data for the MYH or Wilson closed- and open-shell functions.

In this analysis of MYH (or similar) open-shell and HF closed-shell functions, the influence of zero-order degeneracy has not yet been taken into account. For example, among the $2\leq N\leq 10$ atomic systems, the ground states of the $4\leq N\leq 6$ sequences display such degeneracy.[6] Therefore, single-configuration closed- or open-shell functions for these systems, constructed with generalized hydrogenic orbitals such as the MYH, Wilson, or HF, belong to the category of Eqs. (13) and generate the same first-order errors in the energies, in analogy with Eqs. (22) and (23). In principle, these first-order errors can always be corrected by employing a variational configuration-interaction function containing just those configuration functions required by degenerate perturbation theory; the orbitals used in constructing the various functions must be sufficiently flexible to assume the appropriate hydrogenic form upon variation of the parameters. For convenience, such a configuration-interaction function is designated as the *minimum-configuration* (MC) function. In case of nondegeneracy, the MC function is taken to mean the appropriate single-configuration function. Since the optimization of the MC function (or of a more elaborate configuration-interaction function containing the MC function) in respect to H_0, Eq. (10), would yield ψ_0,[22] such functions necessarily satisfy Eqs. (11). MC calculations could readily be performed with MYH or Wilson open-shell functions and it is estimated that the effectiveness of such simple open-shell functions in surpassing the single-configuration HF closed-shell solutions would be extended in this manner to $N=5$ for all Z. For $N\geq 6$, however, a basis set of orbitals more elaborate than the MYH or Wilson (particularly in respect to the $2p$ and higher) orbitals would be required to construct MC open-shell functions superior to the conventional HF solutions for all Z.[61]

IV. MCHF FUNCTIONS

It has been seen that there are definite advantages in the use of variational wave functions satisfying Eqs. (11). It is of interest to examine HF solutions and the correlation energy in greater detail from this standpoint.

The simplest function satisfying Eqs. (11) is ψ_0. For very large Z, ψ_0 is a sufficient approximation to ψ. With diminishing Z, however, this approximation becomes increasingly inadequate and higher-order terms must be introduced. In the usual variational approach, the higher-order terms are introduced indirectly by constructing a total approximate wave function, φ. There is no difficulty in satisfying Eqs. (11) if ψ_0 is taken as a starting point in constructing φ.[16,22] Thus, ψ_0 can be modified by replacing one or more hydrogenic parameters with variationally determined parameters. For example, within the framework of the closed-shell functional form, the introduction of a single optimum scaling parameter yields the SH[12] function, Eqs. (8), while the successive introduction of additional optimized parameters yields the functions used by Eckart,[31] Green *et al.*,[62] Guillemin and Zener,[63] MYH,[45] Wilson,[40] and Holöien[56] with increasingly accurate results. In the case of nondegenerate ψ_0, which are always represented by a single-configuration function, this process of introducing additional variational parameters and flexibility in the hydrogenic orbitals, subject only to the constraints that the function retain its closed-shell form and that all orbitals remain orthonormal, would ultimately culminate in the single-configuration or conventional Hartree–Fock solution with the maximum accuracy for functions of this form. The HF solutions corresponding to nondegenerate ψ_0 automatically satisfy Eqs. (11) and consequently their correlation energy is a second-order effect. The analytical expansion method devised by Roothaan[64] has provided a powerful and convenient tool for obtaining accurate analytic approximations to single-configuration HF solutions for atomic and molecular systems. The previously mentioned HF calculations[41,42] were performed in this manner and are representative of the rapidly growing number of such calculations for numerous atomic systems by Roothaan, Clementi, and co-workers.[65]

In the event of zero-order degeneracy, ψ_0 cannot be represented by a single-configuration function. In such cases, all single-configuration HF functions which are derived from one of the degenerate configurations, necessarily belong to the category of Eqs. (13) and thus yield energies which are in error at least in first order while other expectation values are in error at least in zero order.[66] Consequently the correlation energy for these HF solutions has the undesirable property of being a first-order rather than a second-order effect, e.g.,

$$E_{\text{corr}}=E_{\text{exact}}-E_{\text{HF}}=(\epsilon_1-\bar{\eta}_{1,\text{HF}})Z+(\epsilon_2-\bar{\eta}_{2,\text{HF}})+O(Z^{-1}). \quad (26)$$

An extreme example is given by the ground state of the Be sequence; here, the simple double-configuration SH function, obtained by scaling the correct ψ_0, yields energies which become increasingly superior for $Z\geq 28$

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[62] L. C. Green, M. M. Mulder, M. N. Lewis, and J. W. Woll, Jr., Phys. Rev. **93**, 757 (1954).

[63] V. Guillemin, Jr., and C. Zener, Z. Physik **61**, 199 (1930); C. Zener, Phys. Rev. **36**, 51 (1930).

[64] C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951); **32**, 179 (1960); C. C. J. Roothaan and P. S. Bagus, *Methods in Computational Physics* (Academic Press Inc., New York, 1963), Vol. 2.

[65] See C. C. J. Roothaan and M. Synek, Phys. Rev. **133**, A1263 (1964); and E. Clementi, J. Chem. Phys. **41**, 303 (1964) for recent Roothaan–Hartree–Fock calculations and for comprehensive references to earlier calculations of this type.

[66] This has been noted by M. Cohen, A. Dalgarno, and J. M. McNamee, Proc. Roy. Soc. (London) **A269**, 550 (1962), who give numerical illustrations for the Be sequence.

to those obtained from the much more elaborate HF function[42] based on the single degenerate configuration $(1s^22s^2)$.

Due to the importance of the HF solutions in providing a "benchmark" for the independent-particle model, one would like to relieve this anomalous behavior for zero-order degeneracy. For example, from the conceptual point of view, it does not seem appropriate to designate the entire energy error in a single-configuration HF calculation as the minimum error due to lack of correlation of the electrons when the first-order portion of this error can always be removed by use of the degeneracy-corrected ψ_0. From this standpoint, a more suitable measure of correlation energy would be to use HF calculations satisfying Eqs. (11) so that the correlation energy would always have the form,

$$E'_{\text{corr}}=E_{\text{exact}}-E'_{\text{HF}}=(\epsilon_2-\bar{\eta}_{2,\text{HF}}')+O(Z^{-1}), \quad (27)$$

where E'_{HF} is the HF energy determined from the MCHF function. In principle, the MCHF function would be obtained from the appropriate ψ_0 by varying to self-consistency not only the orbitals but also all linear configuration-coupling coefficients subject to the constraints that the function retain its closed-shell form, that the orbitals remain orthonormal, and that the total wave function remain normalized. In the case of nondegenerate ψ_0, this procedure reduces to the usual one, i.e., $E_{\text{HF}}=E'_{\text{HF}}$, and the correlation energy is also given by Eq. (27).

At present a general method for obtaining fully self-consistent configuration-interaction wave functions does not seem to be available although an extension of the Roothaan–Hartree–Fock procedure to such calculations appears feasible. Approximate configuration-interaction HF calculations have been discussed by Nesbet[25] and various approximate configuration-interaction HF functions have been derived by Kibartas and Iutsis,[67] Glembotskii *et al.*,[68] Kibartas *et al.*,[69] Nesbet and Watson,[70] Watson,[71] and Donath.[72]

In general, approximate MCHF calculations provide a lower bound for the degeneracy-corrected correlation energy, E'_{corr}.[73] An estimate of E'_{HF} or E'_{corr} can also be obtained via Eqs. (26) and (27), i.e.,

$$E'_{\text{corr}}\approx E_{\text{corr}}-(\epsilon_1-\bar{\eta}_{1,\text{HF}})Z, \quad (28)$$

where ϵ_1 and $\bar{\eta}_{1,\text{HF}}$ can be computed[6,9] from Eqs. (5b) and (13a). Approximate MCHF calculations, as well as Eq. (28), have been used to obtain the entries in Table V in which E_{corr} and E'_{corr} are compared for the degenerate ground states of the neutral atoms for $4\leq N\leq 6$. The degeneracy correction reduces the correlation energy for Be by 48%, for B by 27%, and for C by 12%; with increasing Z within an isoelectronic sequence, the degeneracy correction becomes increasingly important. Tables IV and V also show that MCHF calculations are inferior to MC open-shell calculations with MYH or Wilson orbitals for $N<5$ but become increasingly superior with increasing N for $N\geq 5$ and for all Z.[61]

V. MORE ELABORATE WAVE FUNCTIONS

Although the degeneracy correction provides a more systematic basis for the evaluation of HF solutions, it is well known that, in general, the HF formalism is inadequate for obtaining highly accurate energies and other expectation values. This is demonstrated for energies in Table VI where a comparison is made between E'_{HF} and E_{exact} for the ground states of the neutral atoms with $2\leq N\leq 10$ and for several excited states for $N=2$. There is a real need for wave functions superior to the MCHF functions. We define any wave function which yields energies superior to the MCHF energies as a *correlated* wave function. The previous discussion shows that regardless of how the correlation is introduced, it is always possible to insure[22] that the correlated variational wave function satisfies Eqs. (11). In all subsequent discussion of correlated wave functions, it is assumed that these conditions have been fulfilled, unless otherwise specified. For such functions, correlation may be taken to mean the improvement of the quality of the $\bar{\varphi}_j$, $j\geq 1$, and the $\bar{\eta}_j$, $j\geq 2$, so that these terms become superior to the corresponding degeneracy-corrected HF terms. This common feature permits meaningful comparisons to be made among these functions.

The three "classical" variational methods for introducing correlation in a wave function are the previously discussed open-shell procedure,[25–39] the method of

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[67] V. V. Kibartas and A. P. Iutsis, Zh. Eksperim. i Teor. Fiz. **25**, 264 (1953).

[68] I. I. Glembotskii, V. V. Kibartas, and A. P. Iutsis, Zh. Eksperim. i Teor. Fiz. **29**, 617 (1955) [English transl.: Soviet Phys.—JETP **2**, 476 (1956)]. These authors consider the MCHF function $c_1(1s^22s^22p)+c_2(1s^22p^3)$ for B $(^2P^\circ)$; there appears to be a transposition of digits in Table II of the translation for the one- and two-configuration HF energies as both results are impossibly low, i.e., it is assumed that the computed values are -24.526 and -24.559, respectively, instead of -24.562 and -24.595.

[69] V. V. Kibartas, V. I. Kavetskis, and A. P. Iutsis, Zh. Eksperim. i Teor. Fiz. **29**, 623 (1955) [English transl.: Soviet Phys.—JETP **2**, 481 (1956)].

[70] R. K. Nesbet and R. E. Watson, Phys. Rev. **110**, 1073 (1958).

[71] R. E. Watson, Phys. Rev. **119**, 170 (1960). In these calculations for Be (^1S), successive orthogonalized configurations were added to the single-configuration HF function for $(1s^22s^2)$; as anticipated from degenerate perturbation theory, the greatest single improvement in energy per configuration added resulted from the addition of $(1s^22p^2)$ to form the MC function.

[72] W. E. Donath, J. Chem. Phys. **35**, 817 (1961); **38**, 3032 (1963).

[73] Approximate MCHF functions will satisfy Eqs. (11) exactly, even if complete self-consistency is not attained, provided that each configuration function is fully optimized separately and then held fixed while variationally determining the linear coefficients; such calculations provide an upper bound to $\bar{\eta}'_{2,\text{HF}}$, Eq. (27).

TABLE V. Comparison of E_{corr} and E'_{corr} (in a.u.) for the ground state of some degenerate atomic systems.

State	System	E_{exact}[a]	E_{HF}[b]	$-E_{\text{corr}}$[b]	$-E'_{\text{corr}}$[c]
^1S	Be	-14.66743	-14.57302	0.0944	0.050[d] (0.048)
$^2P^\circ$	B	-24.65379	-24.52905	0.125	0.092[e] (0.090)
^3P	C	-37.8450_3	-37.68861	0.156	··· (0.138)

[a] Nonrelativistic energies, Ref. 9.
[b] Single-configuration HF calculations, Ref. 41.
[c] Entries without parentheses are upper bounds from the indicated, approximate MCHF calculations; entries in parentheses are estimates obtained with Eq. (28).
[d] See Ref. 67.
[e] See Ref. 68.

configuration interaction,[25,55,67–76] and the method of explicitly including interelectronic coordinates[30,77] r_{ij}, in the wave function, all of which were employed by Hylleraas[30,74] in his important early work on the He atom. In what follows, *all* functions explicitly containing terms in r_{ij} are designated as Hylleraas-type functions. In contradistinction to these three indirect methods of improving the quality of higher-order terms in a given variational φ and η, there is the variational-perturbation procedure,[4,7,8] also due to Hylleraas,[4] for the term-by-term calculation of the perturbation expansions of ψ and ϵ; this direct procedure automatically satisfies Eqs. (11). This comparative study is concluded with a survey[78] of these methods and some suggestions as to how future progress may be made.

The open-shell procedure, taken alone, is the most limited in scope of all the methods of correlation since it cannot be extended *per se* to yield any desired degree of accuracy.[79] In general, the effect of open-shell calculations is to improve the corresponding closed-shell energies by an amount approximately independent of N, while, on the other hand, the correlation energy increases rather rapidly with increasing N (cf. Tables III, V, and VI and Fig. 2). Thus it is anticipated that even the best open-shell calculations, i.e., the UHF functions, would prove increasingly inadequate with increasing N. Nevertheless, the open-shell procedure provides a valuable supplementary technique for gaining some correlation energy when used in conjunction with other types of correlated functions. This has been demonstrated for open-shell configuration-interaction functions by the calculations of Taylor and Parr[76] and subsequent authors[14,59] for the He sequence and by the elaborate calculations of Weiss[76,80] for the He, Li, and Be sequences. Analogously, the open-shell technique has been effectively combined with correlating factors containing r_{ij} by Hylleraas,[30] Chandrasekhar,[81] Green *et al.*,[82] and Roothaan and Weiss[83] in calculations for the He sequence. Since most of the improvement in energy results from opening the first shell,[37] it is probably sufficient in such open-shell calculations to split only the 1*s* orbitals.

There are theoretical grounds[78] to believe that the configuration-interaction and the Hylleraas-type procedures are both general methods capable of yielding variational solutions which converge to the exact nonrelativistic solutions with any desired degree of

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[74] E. A. Hylleraas, Z. Physik **48**, 469 (1928).

[75] S. F. Boys, Proc. Roy. Soc. (London) **A200**, 542 (1950) (part I); **A201**, 125 (1950) (part II); M. J. M. Bernal and S. F. Boys, Phil. Trans. Roy. Soc. (London) **A245**, 139 (1952) (part VIII); S. F. Boys, Proc. Roy. Soc. (London) **A217**, 136 (1953) (part IX); **A217**, 235 (1953) (part X); S. F. Boys and V. E. Price, Phil. Trans. Roy. Soc. (London) **A246**, 451 (1954) (part XI) and the other papers in this series.

[76] For additional studies of atomic configuration-interaction functions, see for example, G. R. Taylor and R. G. Parr, Proc. Natl. Acad. Sci. (U.S.) **38**, 154 (1952); L. C. Green, C. D. Chandler, and P. P. Rush, Phys. Rev. **104**, 1593 (1956); L. C. Green, E. K. Kolchin and N. C. Johnson, *ibid.* **139**, A373 (1965) and earlier papers by L. C. Green and collaborators; P.-O. Löwdin, *ibid.* **97**, 1474 (1955); Advan. Phys. **5**, 1 (1956); P.-O. Löwdin and H. Shull, Phys. Rev. **101**, 1730 (1956); H. Shull and P.-O. Löwdin, J. Chem. Phys. **23**, 1362 and 1565 (1955); **30**, 617 (1959); E. Holöien, Phys. Rev. **104**, 1301 (1956); D. H. Tycko, L. H. Thomas, and K. M. King, *ibid.* **109**, 369 (1958); A. W. Weiss, *ibid.* **122**, 1826 (1961); A. L. Davis, J. Chem. Phys. **37**, 1508 (1962); **39**, 1183 and 1827 (1963).

[77] For additional studies of atomic functions containing interelectronic coordinates, see for example, H. M. James and A. S. Coolidge, Phys. Rev. **49**, 688 (1936); L. R. Henrich, Astrophys. J. **99**, 59 (1944); S. Chandrasekhar and G. Herzberg, Phys. Rev. **98**, 1050 (1955); J. F. Hart and G. Herzberg, *ibid.* **106**, 79 (1957); Z. Physik **171**, 83 (1963); T. Kinoshita, Phys. Rev. **105**, 1490 (1957); **115**, 366 (1959); C. L. Pekeris, *ibid.* **112**, 1649 (1958); **115**, 1216 (1959); **126**, 143, 1057, and 1470 (1962); **127**, 509 (1962); W. Kolos, C. C. J. Roothaan, and R. Sack, Rev. Mod. Phys. **32**, 178 (1960); E. A. Burke, Phys. Rev. **130**, 1871 (1963); J. F. Perkins, J. Chem. Phys. **39**, 687 (1963); B. Schiff *et al.*, Phys. Rev. **137**, A1672 (1965); **140**, A1104 (1965).

[78] See J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Co., Inc., New York, 1960), Vol. II, pp. 31–50, for a detailed discussion and comparison of correlated wave functions, and pp. 383–436, for an extensive bibliography.

[79] Open-shell wave functions may be regarded as specialized configuration-interaction expansions; see Refs. 32 and 78.

[80] Although ST orbitals were used to construct the open-shell configuration-interaction functions of A. W. Weiss (which contain the MC functions), Ref. 76, sufficient configurations were included to produce the effect of more flexible orbitals (cf. footnote 52) and thus to satisfy Eqs. (11); this may be verified in a simple manner by noting that the exact zero- and first-order energies were found to be contained in the total variational energies, Ref. 21.

[81] S. Chandrasekhar, Astrophys. J. **100**, 176 (1944).

[82] L. C. Green, M. N. Lewis, M. M. Mulder, C. W. Wyeth, and J. W. Woll, Jr., Phys. Rev. **93**, 273 (1954).

[83] C. C. J. Roothaan and A. W. Weiss, Rev. Mod. Phys. **32**, 194 (1960).

TABLE VI. Comparison of several computed energies (in a.u.) for some light atoms.

N	System	State	$E_1{}^a$	E_1/E_{exact}	$E'_{\text{HF}}{}^b$	$E_3{}^a$	E_{CI}	E_{Hyl}	$E_{\text{exact}}{}^c$
2	He	1^1S	-2.75000	0.947	-2.86168	-2.90332	-2.90344^d	-2.90372^e	-2.90372^e
		2^3S	-2.12414^f	0.977	-2.17425^g	-2.17399^f	-2.17523^h	-2.17523^e	-2.17523^e
		2^1S	-2.03635^f	0.949	-2.14344^g	-2.14612^f	-2.14594^i	-2.14597^e	-2.14597^e
		2^3P	-2.04854^f	0.960	-2.13143^g	-2.12982^f	-2.13313^i	-2.13316^j	-2.13316^j
		2^1P	-1.98026^f	0.932	-2.12246^g	-2.12422^f	-2.12378^i	-2.12384^j	-2.12384^j
3	Li	^2S	-7.05658	0.944	-7.43273	-7.4702	-7.47710^k	$-7.4779_5{}^l$	-7.47807
4	Be	^1S	-13.76290	0.938	-14.619^m	-14.653	-14.66090^k	-14.6337^n	-14.66743
5	B	$^2P^\circ$	-22.73737	0.922	-24.564^m	-24.616	-24.600^o		-24.65379
6	C	^3P	-34.44681	0.910	-37.707^m	-37.781	-37.747^o		-37.8450
7	N	$^4S^\circ$	-49.15027	0.900	-54.40091	-54.49			-54.589
8	O	^3P	-66.70478	0.889	-74.80936	-74.92			-75.068
9	F	$^2P^\circ$	-87.66599	0.879	-99.40929	-99.53			-99.734
10	Ne	^1S	-112.29170	0.871	-128.54701	-128.65	-128.7414^p		-128.94

[a] See Eq. (29) and text; unless otherwise indicated, computed with ϵ_j from Ref. 9.
[b] Unless otherwise indicated, see Ref. 41.
[c] Nonrelativistic energies; unless otherwise indicated, see Ref. 9.
[d] See D. H. Tycko, L. H. Thomas, and K. M. King, Ref. 76.
[e] See C. L. Pekeris, Phys. Rev. **126**, 1470 (1962).
[f] See R. E. Knight and C. W. Scherr (1963), Ref. 7.
[g] See E. R. Davidson, J. Chem. Phys. **42**, 4199 (1965).
[h] See A. L. Davis (1963), Ref. 76.
[i] See L. C. Green *et al.* (1965), Ref. 76.
[j] See C. L. Pekeris *et al.*, Phys. Rev. **126**, 1057 (1962).
[k] See A. W. Weiss, Ref. 76.
[l] See E. A. Burke, Ref. 77.
[m] Computed with Eq. (28); see Table V.
[n] See Ref. 85.
[o] See S. F. Boys (Part X), Ref. 75.
[p] See Ref. 72.

accuracy by the inclusion of sufficient terms. For $N=2$, this has been amply demonstrated by the configuration-interaction calculations[76] of Green and coworkers, Löwdin and Shull, Tycko, Thomas and King, Weiss, Davis, and others, and by the extraordinarily accurate Hylleraas-type calculations[77] of Kinoshita and of Pekeris. These calculations also illustrate the general conclusion that for a given N, the configuration-interaction functions converge much more slowly than the Hylleraas-type functions. Boyd[75] has shown that the configuration-interaction technique can be readily extended to calculations with $N>2$, and a limited number of such calculations in the range $3\leq N\leq 18$ have been performed by Boyd and co-workers,[75] Watson,[71] Donath,[72] Weiss,[76] and others. Unfortunately, as clearly shown by the recent large-scale calculations of Weiss,[76] the already poor rate of convergence of configuration-interaction functions diminishes rapidly with increasing N which necessitates the use of very long expansions for larger N to maintain comparable accuracy. On the other hand, the computational difficulties associated with the extension of the more rapidly convergent Hylleraas-type procedure to $N>2$ have been considered so formidable that few calculations of this type have been attempted. In fact, the only accurate Hylleraas-type calculation presently available for $N>2$ is for the ground state of Li; here the early calculation of James and Coolidge[77] has recently been refined to near spectroscopic accuracy by Burke.[77] In a series of papers, Szasz[84] has considered the general problem of N-electron Hylleraas-type calculations. Contrary to previous opinion, he has concluded that such calculations are feasible for larger N if a large computer is used. In demonstration of this, Szasz[85] has computed the ground-state energy of Be with a Hylleraas-type function and obtained a result superior to the Hartree–Fock energy but considerably inferior to that obtained by Watson[71] and Weiss[76] with configuration-interaction functions. The present perturbation analysis provides a simple explanation for this rather disappointing result. Inspection of the Szasz Be function[85] shows that it is based on the degenerate single-configuration function for $(1s^2 2s^2)$ and thus belongs to the asymptotic category of Eqs. (13). An estimate of the resulting inherent error, computed in a manner analogous to Eq. (28), indicates that if the MC function were used with the Szasz correlating factor, the energy obtained should be superior to the best configuration-interaction result.

The accuracy that has been attained with these

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[84] L. Szasz, Z. Naturforsch. **14A**, 1014 (1959); **15A**, 909 (1960); J. Chem. Phys. **35**, 1072 (1961); Phys. Rev. **126**, 169 (1962); J. Math. Phys. **3**, 1147 (1962); Phys. Rev. **132**, 936 (1963); see also, Y. Öhrn and J. Nordling, J. Chem. Phys. **39**, 1864 (1963); and J. Hinze and K. S. Pitzer, *ibid.* **41**, 3484 (1964).

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correlated functions, as well as the relative paucity of such calculations in general, is illustrated in Table VI where the best available configuration-interaction and Hylleraas-type energies, E_{CI} and E_{Hyl}, are compared with E'_{HF} and E_{exact} for the lighter atoms. All of these results, with the exception of the aforementioned E_{Hyl} for Be,[85] were obtained with wave functions belonging to the category of Eqs. (11). Although, in general, E_{CI} is considerably superior to E'_{HF}, there is much room for improvement with increasing N. The work[76] of Weiss, of Davis, and of Green *et al.* indicates that the convergence problem of configuration-interaction calculations is not as acute for certain excited states (e.g., the 2^3S state of He, Table VI) so such functions may prove adequate for selected excited states for $N>2$. In general the Hylleraas-type functions are clearly superior in those few cases where full-scale calculations have been performed. This is a strong indication of the need for further study and application of the Hylleraas–Szasz procedure.

The direct variational-perturbation procedure[4,7,8] for introducing correlation has as yet received little application. To judge the potential efficacy of this method for systems with larger N, it is convenient to use the truncated perturbation energy expansion, E_n, where in a.u.,

$$E_n=Z^2\sum_{j=0}^{n}\epsilon_j\lambda^j. \tag{29}$$

With the exception of E_1, E_n is not an upper bound[5] to E_{exact} but must converge reasonably rapidly with increasing n if this method is to have any practical value. This type of convergence has been termed perturbational convergence by Knight and Scherr[7] in contradistinction to ordinary variational convergence. In Table VI are collected the values of E_1, E_1/E_{exact}, and E_3, computed with the known values of the ϵ_j.[6,7,9] The simple E_1 furnishes 87% of E_{exact} for $N=10$ and this contribution increases with decreasing N to 98% for 2^3S He. The more rapid, *variational* convergence of configuration-interaction calculations for 2^3S He and other excited states is apparently due in part to the relatively large value of E_1/E_{exact} for such systems. Although the results in Table VI appear promising since in most cases E_3 is superior to E'_{HF} and in some cases to E_{CI}, it is obvious that E_n must be computed to several orders higher in order to surpass the most accurate configuration-interaction calculations. For example, from the data[7] for 1^1S He, $E_5=-2.90367$ and is thus superior to the best E_{CI} while $E_7=-2.90372$ which is equivalent to E_{Hyl} to the same number of significant digits. The need for longer perturbation expansions does not present a serious barrier since the work[7] of Knight and Scherr and of Midtdal indicates that the variational calculation of the successive ψ_j and ϵ_j can be conveniently systematized. The fact that one set of calculations yields the energies[7] and other expectation values[11] for all members of a given isoelectronic sequence to a high degree of accuracy is another advantage which offsets the disadvantage of an expansion formulation. Further, the necessary orthogonality of excited state wave functions[1] to lower states of the same symmetry species is obtained automatically in this procedure.[7] Schwartz[86] and Sommerville and Stewart[87] have shown that the convergence problem of configuration-interaction functions persists when applied to the variational calculation of ψ_j (in particular, ψ_1 of 1^1S He) and that the best results are obtained with Hylleraas-type functions. Thus, the extension of the variational-perturbation procedure as well as of Hylleraas-type calculations to larger N depends to a great extent upon the successful application of the Hylleraas–Szasz or similar method.

The Schrödinger or hydrogenic perturbation expansion discussed in this study corresponds to one arbitrary partition of the Hamiltonian operator [cf. Eq. (3)]. An alternate perturbation approach consists of treating the conventional HF function as the zero-order term in a perturbation expansion of the exact wave function where the perturbing operator is taken as the difference between the total Hamiltonian and the HF operator. This approach was originally proposed by Brillouin[88] and the formalism of this method has been discussed by Møller and Plesset,[89] Peng,[90] Nesbet,[25] Allen,[91] Cohen and Dalgarno,[92] and Sinanoğlu.[93] In the HF expansion, the sum of the zero- and first-order energies is given by E_{HF} while the sum of all higher-order energy terms corresponds to E_{corr}.

In extension of the HF perturbation scheme, Sinanoğlu[94] has developed a theory for the approximate calculation of E_{corr} via a variationally derived, correlated correction function to the HF function; this theory and the approximations involved have been discussed by Krauss and Weiss.[95]

The use of the HF function as a starting point in either of these two approaches does not appear to have any clear-cut practical or theoretical advantages over Hylleraas-type calculations coupled with the hydrogenic perturbation expansion or with a total variational wave function of the category of Eqs. (11). Thus, although E_{HF} is considerably better than the corresponding E_1 in the hydrogenic expansion (cf. Tables V

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and VI), Weiss and Martin[96] found for the ground state of the He sequence that E_3 in the hydrogenic expansion is superior to the corresponding summation in the HF expansion. For some operators, the situation is reversed and expectation values computed through first order in the HF expansion[96] are superior to the hydrogenic first-order expansions. (Indeed, from the Brillouin theorem,[88,89] it follows that the expectation values of any one-electron operator is obtained correct through first order[92] in the HF expansion when computed with the conventional HF function.) On the other hand, the sixth-order hydrogenic expectation values of Scherr and Knight[11] are far more accurate than the first-order HF values[96] and are in good agreement with the "exact" values computed by Pekeris[77] with large-scale Hylleraas-type functions. The results of higher-order HF calculations are not as yet available.[97] Tuan and Sinanoğlu[98] and subsequently, Geller, Taylor, and Levine[99] have applied the Sinanoğlu theory[94] to the calculation of E_{corr} for the ground state of Be with highly accurate results. In view of the approximations[95,99] involved in the theory, it is difficult to evaluate the general significance of these calculations. Two additional objections have been advanced to the HF approaches: (1) the HF zero-order functions are known only approximately[96]; (2) the use of correlating functions containing r_{ij} in either HF approach introduces the same difficult three-electron integrals[95,96,99] as occur in Hylleraas-type calculations for $N>2$.[84] In short, the correlated HF methods are at least as difficult and appear to offer no greater potential accuracy[97] than the Hylleraas-type approach with functions satisfying Eqs. (11).

VI. CONCLUSIONS

On the basis of this study, it is proposed that Eqs. (11) be adopted as the minimum criteria to be satisfied whenever possible in the construction of variational wave functions. These criteria can always be fulfilled for atomic isoelectronic sequences since the exact zero-order wave functions in the Schrödinger perturbation expansion are known for such systems in all states and for all N. Variational wave functions satisfying Eqs. (11) have the desirable characteristic of yielding energies correct at least through first order and other expectation values correct at least in zero order. For all such functions, the variational principle assumes the form,

$$\sum_{j=2}^{\infty}\bar{\eta}_j\lambda^j \geq \sum_{j=2}^{\infty}\epsilon_j\lambda^j, \tag{30a}$$

and correspondingly,

$$\bar{\eta}_2\geq\epsilon_2. \tag{30b}$$

Any improvement in the quality of functions of this category is automatically concentrated where it belongs, namely, in improving the quality of second- and higher-order energy terms. As previously indicated, the absolute error in the energies computed with even very simple functions of this type (e.g., the SH function in Fig. 1) is quite insensitive to Z and is essentially given by $(\epsilon_2-\bar{\eta}_2)$. The relative error in the energies computed with such a function for an isoelectronic sequence diminishes as Z^{-2} while the relative error of other expectation values diminishes in general as Z^{-1}. Thus, if satisfactory results can be obtained with a given variational function of this category for a neutral atom, this asymptotic behavior insures increasingly accurate results for the higher members of the isoelectronic sequence. This is in marked contrast to the asymptotic behavior of the functions satisfying Eqs. (12) and (13) which may yield good results for lower values of Z, where partial cancellation of error among various orders can occur, but which must inevitably yield diverging results with increasing Z.

In calculations where moderate accuracy is sufficient, simple MC closed-shell functions satisfying Eqs. (11) may be employed with the most accurate results for calculations of this type being obtained with the MCHF functions. The accuracy of such MC closed-shell calculations can be improved somewhat by using the corresponding MC open-shell function but the relative effectiveness of the open-shell technique diminishes rapidly with increasing N. For greater accuracy, more drastic methods of correlation must be employed. On the basis of the available evidence, Hylleraas-type functions appear to offer the most promise. It is recommended that the Hylleraas–Szasz or similar procedure be further explored either by combining simple MC functions such as the SH function with correlating factors or via the hydrogenic variational-perturbation expansion. It is evident that the field of atomic calculations is far from being a closed book and that much remains to be done.

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