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Ab Initio Computations in Atoms and Molecules*

Abstract: The present status of *ab initio* computations for atomic and molecular wave functions is analyzed in this paper, with special emphasis on the work done at the IBM Research Laboratory, San Jose. The Roothaan-Hartree-Fock method has been described in detail for atomic systems. A systematic tabulation of atomic Hartree-Fock functions has been made available in an extended supplement to this paper.† Techniques for computing many-center, two-electron matrix elements have been discussed for Slater or Gaussian basis sets. It is concluded that the two possibilities are comparable in efficiency. We have advanced a few suggestions for the extension of the self-consistent field technique to macromolecules. The validity of the suggestions have not been tested.

Following the Bethe and Salpeter formalism, the relativistic correction has been discussed and illustrated with numerical results for closed-shell atoms. A brief analysis of the relativistic correction for molecular systems shows that the relativistic effects cannot be neglected in ionic systems containing third-row atoms.

The correlation energy is discussed from an experimental starting point. The relativistic and Hartree-Fock energies are used for determining the correlation energy for the elements of the first three periods of the atomic system. A preliminary analysis of the data brings about a "simple pairing" model. Data from the third period force us to consider the "simple pairing" model as a first-order approximation to the "complex pairing" model. The latter model is compared with the geminals method and limitations of the latter are pointed out.

A semiempirical model, where use is made of a pseudopotential that represents a coulomb hole, is advanced and preliminary results are presented. This model gives reason to some hope for the practical formulation of a Coulomb-Hartree-Fock technique where the correlation effects are accounted for and the one-particle approximation is retained.

Introduction

The aim of this paper is to analyze the present status of *ab initio* quantum-chemical calculations with emphasis primarily on the recent work done at the IBM Research Laboratory, San Jose. By "quantum chemistry" we mean those aspects of atomic and molecular chemistry and physics which have been, and likely will be, quantitatively explained by quantum theory. There are many additional phenomena which are qualitatively explainable by quantum theory, but those will not be dealt with in this work since the emphasis here is on computations. We shall restrict this paper to computation of wave functions and total energies, and only brief mention will be made of computations of different expectation values. As is known, the prerequisite to an expectation value computation is the availability of functions and energies. Since the computational complexity in obtaining a wave function by far exceeds the complexity of computing other properties of a system, and since we are aiming at exact wave functions, which by definition provide exact expectation values, we feel that our restriction is justified.

The fact that the field of quantum-chemical computations is undergoing a revolutionary change due to the availability of high speed computers is too well known to be emphasized here. I shall show that this field is now at its beginning after several years of probing. We have now reached the "mass production" stage in some simple aspects of it—atomic and diatomic computations—and there is very promising work in progress in order to extend this situation to more complicated systems.

It is customary to divide quantum-chemical computations into "ab initio" and "semiempirical" types.[1] The first refers to computations where one uses the correct Hamiltonian for the problem[2] and operates with such a Hamiltonian on a function which satisfies some physical model.

The second type is essentially a curve fitting method.

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† The supplement, entitled "Tables of Atomic Functions," is available upon request to the Editor.

In many instances one is not interested in why and how a molecular binding energy, or a given spectroscopic constant, can be computed from exact models but only in its value. Therefore, all that is desired is to obtain these values by a reliable fitting procedure. These calculations are usually called "semiempirical", and in the author's opinion should be simply called "fitting formulas" since they are no more than this. Their practical and even theoretical value, however, is unquestionable.

Another type of semiempirical computation is obtained by substituting given quantities (which can be obtained correctly, but most laboriously) with equivalent quantities that can be obtained by much simpler techniques. An example of this is the Mulliken approximation of the many-center integrals, where it is known from experimental data that they are accurate to within 15-20%, and are obtained by an extremely simple technique. This type of "semiempirical work", if used carefully, can subtract very little information from an *a priori* computation. Indeed, it can often make the latter feasible.

For particularly simple problems one can attempt a direct solution of the Schrödinger equation. The recent work of Conroy[3] for the He, H_2^+, Li systems is a most interesting step in this direction. How much the formalism of Conroy can be extended to more complicated systems seems to depend directly upon the availability of extra fast and large electronic computers. We shall not comment further on this direct approach since it seems to be somewhat premature.

For a more complex system a basic model is provided by the one-electron approximation. In this approximation taken in its simplest form one assumes that the total wave function of N particles is a product of one-electron functions called "orbitals" (atomic or molecular, according to the system). In order to satisfy the correct statistics for the electron, the product is antisymmetrized. There are good experimental grounds for the one-electron approximation, i.e., that the total energy of the system is very largely accounted for by simply adding up the one-electron energies obtained by *neglecting the electron-electron interaction.* Indeed, if one uses the one-electron approximation *in this strict sense*, and adopts conveniently selected orbital exponents, one can obtain as exact an energy as he wishes.[4] The reason is that variation of the orbital exponent, as suggested here, is equivalent to a variation of the screening constants, and this in turn is equivalent to introducing electron-electron interaction.

A more refined method of obtaining one-electron functions is provided by the Hartree-Fock model. In this model[5] the electron-electron interaction is conceived as the interaction of a given electron with the average field of the remaining electrons. Clearly this picture is not fully correct because the electrons act on themselves as individual interacting particles, as well as a collective system. Therefore, the fine details of electronic structure that are essential in the spectroscopy of molecules and atoms, as well as in the binding energy of molecules and many ions, are poorly explained by the Hartree-Fock model.

In the following, we shall discuss several problems related to the Hartree-Fock method in molecular computations. Then we shall present numerical results for the relativistic correction in atoms, and we shall present arguments which predict that the relativistic correction should not be ignored in quantum-chemical computations. Finally, we shall analyze the correlation energy problem. As is known, the traditional approach to the correlation energy problem is to propose, from the outset, models, techniques, and formalism without reference to experimental data. In the author's opinion, this approach has not furnished a practical and satisfactory solution to the correlation energy problem, and a different starting point will be adopted in this paper. Namely, we shall first derive correlation energies, based on experimental data, for a large sample of atomic systems and configurations. Then we shall analyze these data and derive models and techniques which explain quantitatively the correlation energy previously derived from experimental information.

The Hartree-Fock method

• *Unsolved computational problems for atoms and molecules*

In this section we shall deal with several problems which have not received sufficient attention in the past literature, or which have been considered by many but have not yet been satisfactorily solved.

The first problem to be discussed is related to the computation of Hartree-Fock functions for heavy elements. For the moment, we shall neglect the basic difficulties related to the formulation of an accurate relativistic Hartree-Fock technique, since we shall deal with the relativistic correction in the following section of this paper.

We restrict the discussion to the atomic elements with Z from 37 to 103 since for elements $Z = 2$ to $Z = 36$ we have available Hartree-Fock solutions. Let us assume that we are interested in a systematic collection of the Hartree-Fock functions for the remaining elements.

As is known, the time-consuming part in atomic computations made by the Hartree-Fock method are in the optimization of the orbital exponents[6] of the basis set. The slow variation of the inner-shell orbital exponents with successive ionizations, and the possibility of interpolation, should be the two main criteria for the construction of a "control program". This program should automatically (a) establish the optimal order of the states to be computed, (b) optimize only those orbital exponents which are needed and decide the order of the optimization and (c) interpolate data and automatically create inputs for new cases to be computed. For additional comments

on this point, we will refer to some recent work where the above suggestion has been analyzed in more detail.

In addition, it might be useful to consider in advance (a) whether or not one should proceed with the analytical Hartree-Fock method or whether it is useful to compute numerical Hartree-Fock functions (which can be expressed later as linear combinations of a basis set of functions) in view of the cost involved in the optimization of the orbital exponents of the basis set, and (b) whether it is possible to retain sufficient accuracy in the calculation, especially in the total energy. (It is noted in this regard that ten-figure accuracy is needed in the very heavy elements if one wishes to have the total energy accurate to the order of a few hundredths of an eV.)

In the supplement to this paper[7] we have extensively reported on the Hartree-Fock technique, the main emphasis being on the atomic problem; the situation for the molecular systems is quite similar from a conceptual standpoint. This is true because (a) both in atoms and molecules one can express the orbitals as linear combinations of a suitable basis set of functions,[8] and (b) the Hartree-Fock equations are formally identical for the atomic and molecular cases.

However, from the computational point of view, there are differences because the matrix elements in the molecular cases involve more than one center; in the atomic case, of course, only one center is needed.

For molecular cases the main difficulty arises in the solution of matrix elements of the type

$$\langle \chi_a \chi_b \mid \chi_c \chi_d \rangle \equiv \iint dv_1\, dv_2 \tilde{\chi}_a^{(1)} \chi_b^{(1)} \frac{1}{r_{12}} \tilde{\chi}_c^{(2)} \chi_d^{(2)}, \qquad (1)$$

where a, b, c, d may wholly or in part be different centers (atoms), χ_i is an analytical function centered on the i^{th} center, 1 and 2 refer to electrons 1 and 2. The above integral is a two-electron, in general four-center matrix element where the centers can be arbitrarily arranged in space. The solution of the problem is further complicated by two prerequisites: (a) the integrals must be solved in an extremely short time, in order to obtain a Hartree-Fock molecular function in a reasonable amount of computer time and (b) the integral should be computed with high accuracy. The simultaneous satisfaction of the above two prerequisites is not a trivial problem; indeed it is one of the main difficulties in quantum-mechanical computations for molecular systems.

Table 1 Number of two-electron integrals in typical computation (*Slater set*)

System	Slater orbitals basis		Number of integrals	IBM 7094 time (hrs)
Si	$7(s)$,	$5(p)$	1.8×10^3	$\sim .05$
CO	$18(\sigma)$,	$8(\pi)$	1.7×10^4	$\sim .5$
CO_2	$27(\sigma)$,	$12(\pi)$	1.0×10^5	~ 3.5
C_2N_2	$36(\sigma)$,	$16(\pi)$	2.5×10^5	~ 8.0

In order to demonstrate the reason for the first prerequisite we provide the data in Table 1, where we have indicated how many two-electron integrals must be computed in order to obtain a Hartree-Fock solution for the following systems: Si(atom), CO, CO_2, C_2N_2 (linear molecules). The assumptions are made that the basis set consists of Slater-type orbitals,[6] (the size of the basis set is given in the table), and we have assumed the $C_{\infty v}$ symmetry for the systems[9] (except for the Si atom). The total estimated time for the computation is based on previous experience and is given for the IBM 7094 computer.[10]

Several techniques have been put forward in the last decade for the solution of these integrals.[11] It is noted that the interest is not in computing a single integral at a time but rather in computation of large numbers of integrals.

In the following we shall summarize A. D. McLean's method[12] for computation of integrals between Slater-type orbitals. This method has been used extensively in linear molecules and is now being extended by A. D. McLean and M. Yoshimine for molecules of arbitrary geometry. The analysis which is given here is not yet available in the literature, but has been reported at several meetings. I shall follow closely the analysis reported by McLean at the Symposium on Molecular Structure and Spectroscopy at Columbus, Ohio, June 1958.

The computation for the general four-center integral can be usefully divided into two stages, first the integration over the coordinates of electron 1, and second the integration over the coordinates of electron 2.

• *Integration over electron 1 coordinates*

The result of this integration, because of the r_{12} in the integrand, will be a function of the coordinates of electron 2, and in fact will be the potential felt by electron 2 due to the average field of electron 1.

There are two possible types of potential, depending on whether a and b refer to the same nuclei or not, giving rise to a one-center (spherical) or two-center (spheroidal) potential.

The radial part of the one-center potential is evaluated in terms of the simple functions $A_\lambda(x)$ and $e_\lambda(x)$ where $x = (\zeta_a + \zeta'_a) r_{a_2}$. The quantities ζ_a and ζ'_a are the two orbital exponents involved and

$$A_\lambda(x) = \lambda!\, x^{-\lambda-1} e^{-x} \sum_{k=0}^{\lambda} \frac{x^k}{k!} \qquad (2)$$

$$e_\lambda(x) = \lambda!\, x^{-\lambda-1} (1 - e^{-x}) \sum_{k=0}^{\lambda} \frac{x^k}{k!} \qquad (3)$$

The angular part of the one-center potential is a linear combination of spherical harmonics with nucleus a as the center.

The two-center potential V is evaluated in terms of spheroidal coordinates ξ and η with a and b as foci from the formula

$$V = C \sum_{l=|m|}^{\infty} P_l^{|m|}(\eta_2)e^{im\phi_2}(2l + 1)[(l - |m|)!] \cdot [(l + |m|)!]^{-1}[P_l^{|m|}(\xi_2)k_l^{|m|}(\xi_2) + Q_l^{|m|}(\xi_2)k_l'^{|m|}(\xi_2)], \tag{4}$$

where C is a constant depending on the orbitals involved and the internuclear distance $m = -m_a + m_b$; m_a and m_b are the axial quantum numbers of χ_a and χ_b; $P_l^{|m|}$ and $Q_l^{|m|}$ are the associated Legendre functions of first and second kinds

$$k_l^{|m|}(\xi_2) = \int_{\xi_2}^{\infty} dx e^{\alpha x}(x^2 - 1)^{\frac{1}{2}|m|}Q_l^{|m|}(x) \cdot \sum_{\eta,j} \omega_{\eta j} b_j^{|m|l}(-\beta)x^n \tag{5}$$

$$k_l'^{|m|}(\xi_2) = \int_{1}^{\xi_2} dx e^{-\alpha x}(x^2 - 1)^{\frac{1}{2}|m|}P_l^{|m|}(x) \cdot \sum_{\eta,j} \omega_{\eta j} b_j^{|m|l}(-\beta)x^n \tag{6}$$

$$b_j^{|m|l}(\beta) = \frac{1}{2}\frac{(l - |m|)!}{(l + |m|)!} \cdot \int_{-1}^{1} d\eta P_l^{|m|}(\eta)(1 - \eta^2)^{\frac{1}{2}m}e^{-\beta\eta}\eta^j. \tag{7}$$

The ω_{nj} are numerical coefficients arising from the expansion of the orbital product in terms of the spheroidal coordinates. These are finite summations. The quantities α and β are defined by

$$\alpha = (\zeta_a + \zeta_b)R_{ab}/2 \tag{8}$$

$$\beta = (\zeta_a - \zeta_b)R_{ab}/2. \tag{9}$$

The most efficient way of computing the potential is by using an equal-spacing type of integration formula for computing $k_l^{|m|}(\xi_2)$ and $k_l'^{|m|}(\xi_2)$.

• *Integration over electron 2 coordinates*

For a linear configuration of nuclei, the ϕ integration can be done very simply, and in the current method the integrations over the other two coordinates are done numerically. Gaussian-type integration formulas have been found very useful in this regard.

The method has been tested for linear molecules. However, little has been done on the case where the nuclei are not in a linear configuration. From recent work by A. D. McLean and M. Yoshimine it seems that this problem can be solved with reasonable speed.

The advantage of McLean's analysis is in its complete generality, where no restrictions are imposed on the quantum numbers. It is known that the method works with high speed and accuracy. Indeed, the large fraction of accurate functions for polyatomic molecules available today in the literature has been obtained with the McLean method. Many alternatives to the McLean many-center integral techniques have been proposed in the literature,[11] but we shall not deal with them since these have not been tested sufficiently in complex molecular computations. In this respect, it is noted that for this type of numerical application a given analysis can be proven convenient only *after* the complete coding and testing is done. The reason is in the speed requirement. For example, the time factors alone will decide whether it is convenient to replace the elegance of an analytical expansion in an integration by the convenience of a direct numerical integration.

In the search for practical methods for solving the many-center-integral problem a different technique should be mentioned, i.e., the one which uses a Gaussian basis set instead of a Slater-type basis set. The suggestion of using Gaussian orbitals goes back to the original work of Boys,[13] and has been exploited almost entirely by Boys and his coworkers.[13] After many years it is still difficult to assess the relative merits of the two integration techniques. The main difficulty arises from the fact that no exhaustive attempt has been made in order to compare the two techniques. For this reason, Huzinaga has recently undertaken the first systematic comparison.[14] The obvious starting point is the atomic systems. It is noted that the problem is purely one of deciding between two different methods of integration. The advantage of Gaussian functions is that the product of two Gaussians G_a and G_b, centered on a and b, is a new Gaussian function G_e centered on e. Therefore the four-center problem $\langle G_a G_b \mid G_c G_d \rangle$ reduces to the two-center problem $\langle G_e \mid G_f \rangle$. The latter integral can be computed up to a few hundred times faster than the integral $\langle \chi_a \chi_b \mid \chi_c \chi_d \rangle$ with a Slater basis set. On the other hand, one needs a much larger basis set in order to obtain with equal accuracy a given energy, say the Hartree-Fock energy, by using Gaussian as compared with Slater-type orbitals. The need of a larger basis set offsets part or nearly all of the speed advantages. In order to be more quantitative about this point, let us first consider Huzinaga's results for atomic computations. In Table 2 the size of the Gaussian basis set is given for some computations on first row atoms. The computed energy is compared with two different sizes of basis sets for Slater type orbitals obtained by the author.[15,16]

Clearly, one obtains better energies with a limited Slater basis set (set A[15]) than with a considerably larger Gaussian set. Indeed with the extended Gaussian basis set used, one has by no means reached the energy obtained with the Slater set B.[16] Since the set B gives very closely a

Table 2 Comparison of Gaussian and Slater basis sets (*Energies in a.u.*)

Element and state	Gaussian* 9(*s*), 5(*p*)	Slater (set *A*)** 4(*s*), 2(*p*)	Slater (set *B*)*** 5(*s*), 4(*p*)
Li (^2S)	−7.432279	−7.432718	−7.432726
Be (^1S)	−14.57207	−14.57237	−14.57301
B (^2P)	−24.52713	−24.52789	−24.52905
C (^3P)	−37.68525	−37.68668	−37.68858
N (^4S)	−54.39534	−54.39787	−54.40090
O (^3P)	−74.80029	−74.80476	−74.80935
O (^1D)	−74.72010	...	−74.72920
O (^1S)	−74.60159	...	−74.61094
F (^2P)	−99.39559	−99.40116	−99.40921
Ne (^1S)	−128.5267	−128.53480	−128.5470

* Huzinaga set (Ref. 14).
** Double ζ set (Ref. 15).
*** Hartree-Fock set (Ref. 16).

Table 3 Number of two-election integrals in typical computations (*Gaussian set*)

System	Gaussian basis	Number of integrals
Si	15(*s*), 9(*p*)	1.4×10^4
CO	30(σ), 12(π)	2.3×10^5
CO_2	45(σ), 18(π)	1.1×10^6
C_2N_2	60(σ), 24(π)	3.6×10^6

Hartree-Fock energy, one can be disappointed by the performance of the Gaussian basis. On the other hand, if we are interested in spectral differences, the results with Gaussian orbitals are as good as the results with Slater orbitals. Indeed the Gaussian set gives the energy differences $O(^3P) - O(^1D)$ and $O(^3P) - O(^1S)$ as 0.080187 a.u. and 0.198699 a.u. which compares well with the equivalent values of 0.080147 a.u. and 0.198415 a.u. for the Hartree-Fock functions (set *B*). In addition, it should be pointed out emphatically that the correct results are 0.072283 a.u. and 0.153949 a.u., respectively, and therefore the difference between the Gaussian set and the Slater set is of relatively little importance if we are interested in exact calculations.

Let us proceed to molecular computations, and give the equivalent of Table 1, this time using a Gaussian basis set instead of a Slater basis set. Again we wish to obtain Hartree-Fock energies for the systems Si, CO, CO_2 and C_2N_2 (Table 3). The examples given are not yet computed and are presented only as a comparison. The basis set selected for this sample computation likely will not give a good Hartree-Fock wave-function whereas the best basis set in Table 1 will. On the other hand, the Gaussian set will give an energy which will differ from the Hartree-Fock energy by no more than about one eV for the above molecules.

Comparison between Tables 1 and 3 indicates that the number of integrals needed in a Gaussian set is certainly much larger than the number of integrals needed in comparable Slater basis sets, and that Gaussian integrals can be computed up to 100 times faster than the Slater integrals. On the other hand, the Hartree-Fock matrix dimension in the Gaussian case is larger than the matrix dimension for a Slater basis and thus requires additional computer time. The net conclusion of these conflicting factors is that probably the two techniques are comparable, and it will be difficult to positively state which method is better until actual program performance can be compared. I feel at present, however, that the use of Gaussian orbitals for many-center integrals might offer some advantage over the Slater set. One could consider the possibility of a mixed set where Slater orbitals of 1*s* type are used with Gaussian sets. This possibility, if practical, would eliminate the poor behavior of the 1*s* Gaussian functions at the origin. It is noted that this behavior is the reason for the unsatisfactory performance (Table 2) of the Gaussian functions for the atomic systems.

With molecular problems of the size we have been mentioning, and especially for systems much larger than C_2N_2, one should look for new methods within the Hartree-Fock technique. Up to now one constructs the Hartree-Fock orbitals by obtaining the best linear combination of a given basis set. For large molecules (which require very large basis sets) it might be convenient to work with larger blocks than the initial basis set of Gaussian or Slater functions, for example, with Hartree-Fock atomic orbitals. This will reduce the computational difficulty in the solution of the Hartree-Fock equation. As an alternative, one could use Hartree-Fock orbitals for the inner shells and Slater (or Gaussian) orbitals for the valence electrons. This might be useful not only for molecular cases but also for atoms with many electrons (say more than 80 electrons).

For large systems one might be compelled to resort to a much more drastic departure from the present standard technique. Let us consider, for example, the porphyrin system (see Fig. 1). In order to simplify the problem, one could consider the pyrrole group as starting blocks. In this case, the porphyrin symmetry orbitals will be a linear combination of the pyrrole radical symmetry orbitals, and the self-consistent technique will optimize the expansion coefficients of the basis set of pyrrole symmetry orbitals. This is equivalent to introducing a perturbation (or polarization) on the original pyrrole symmetry orbitals.[17] In turn the pyrrole symmetry orbitals can be obtained by using a symmetry-adapted set where the basis is not in terms of Slater orbitals, but of Hartree-Fock orbitals.

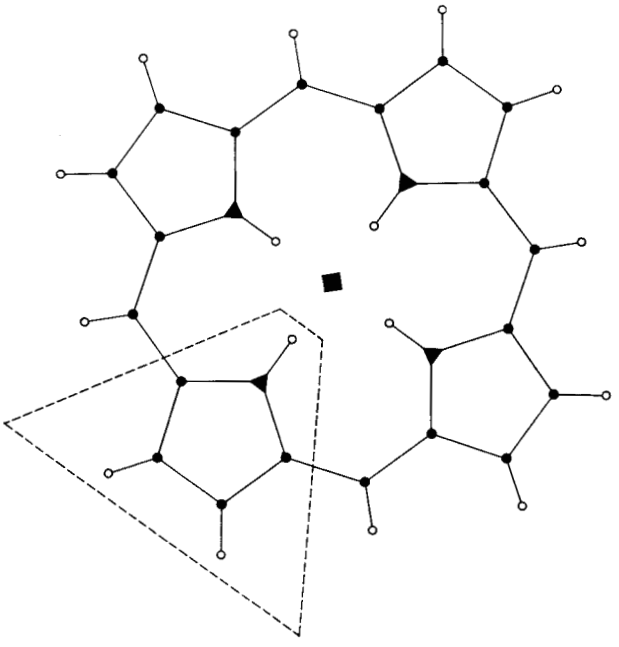

Figure 1 The pyrrole molecule is part of the metal-porphyrin and is indicated inside the area limited by dashed lines. Key: ○ hydrogen atoms, ● carbon atoms, ▲ nitrogen atoms, ■ a metal atom of the II or III period.

The proposal essentially is to do a repetitive set of self-consistent computations. First for the atoms as such; this will freeze the coefficient for the Slater-type orbitals into atomic Hartree-Fock orbitals. Then for the symmetry adapted orbitals of the pyrrole group; this will freeze the linear combination of the Hartree-Fock orbitals into the pyrrole radical symmetry-adapted orbitals. Finally, the porphyrin symmetry-adapted orbital will be obtained by the SCF technique as an expansion of pyrrole orbitals. Schematically, if φ_P indicates a porphyrin orbital, φ_p a pyrrole orbital, φ_A a Hartree-Fock orbital for atom A, φ_s^A a Slater (or Gaussian) type orbital on atom A, we shall have

$$\varphi_A = \sum_s c_s^A \varphi_s^A \quad \text{First SCF cycle for atoms}$$

$$\varphi_p = \sum_A d_A \varphi_A \quad \text{Second SCF cycle for groups of atoms}$$

$$\varphi_P = \sum_p e_p \varphi_p + \sum_A{}' d'_A \varphi'_A \quad \text{Third SCF cycle for the whole system,}$$

where c, d, e and d' are the expansion coefficient (with proper symmetry), and φ'_A represent those additional atoms in the porphyrin molecule not accounted for in the pyrrole molecules.

Since much time is required for computing the integrals in a macro-molecular computation, we shall mention two possibilities that should reduce the amount of computer time.

First, many four-center integrals have exceedingly small values, such that two- to three-figure accuracy is all that is needed. Most of the past programs compute all the integrals, small or large, with the same method. It seems that this could amount to a waste of computer time and one should test, by some approximation (for example the Mulliken approximation) the value of the integral beforehand, and compute it accurately only if its value exceeds a certain threshold, whereas the integral would be computed approximately if the value is below the same threshold. Alternatively, if electron 1 is located on centers far removed from the center of electron 2, then we can use the dipole-dipole approximation in the $1/r_{12}$ expansion, since then $r_1 \ll R$ and $r_2 \ll R$ where R is the distance between the two centers for electrons 1 and 2, and r_1, r_2 are the distances of electrons 1 and 2 from their origin. The decision on when to shift from the usual calculation to the dipole-dipole approximation can be left up to the computer, which is provided with simple testing rules involving the value of R and the values of $\langle r_1 \rangle$ and $\langle r_2 \rangle$.

Second, for large molecules (or even for atoms with many electrons), it seems more likely that one could do a set of computations on the same system in different excited states or various geometrical configurations. For example, one could be interested in several electronic states or in analogous systems where new atoms or chemical groups are added or removed from the original system. In this case it seems to be wasteful to compute repeatedly for each individual computation a large number of integrals, which could and should be saved from one computation to the next.

The practicality of most of the suggestions put forward in this section has not yet been tested. On the other hand, it seems to us that the "traditional" setup of past programs should not be merely extended for large molecules, but the above points should be carefully considered, unless one wishes to perform computations at a very exorbitant cost.

• *Atomic Hartree-Fock computations*

Up to now the first three periods of the periodic table have been carefully studied by the Hartree-Fock techniques. Results on the positive, negative and neutral elements from He to Kr are available in the literature.[14,18] The collection of the functions computed at our laboratory is given in the supplement to this paper.[7] It has given reliable functions, ionization potentials, electron affinities, screening constants,[19] and basis sets very useful for molecular and solid state calculations. From a theoretical point of view, the main value of this work has been in providing a large series of accurate data on atomic correlation energies, totally absent from the available literature. For a detailed analysis of the atomic Hartree-Fock method we refer to the introduction to the supplement of this paper.[7]

• *Molecular Hartree-Fock computations*

Most of the molecular computations obtained up to date have been performed as "test" computations. There is a considerable number of functions which have been done in the self-consistent-field framework, but have not reached the Hartree-Fock limit. For a complete bibliography we refer to Allen and Karo's review paper[20] and to the Slater volume on molecular structure.[21] Recently, we have reached the stage of mass production of Hartree-Fock diatomic functions; this work, done at the Laboratory of Molecular Structure and Spectroscopy (University of Chicago), is not yet published, but preliminary information can be obtained from their technical reports.[22]

Previous computations which obtained an approximate Hartree-Fock solution[23] for a few diatomic molecules have clearly demonstrated that: (a) the computed electronic charge distribution well represents the experimental electric multiple moments, (b) the computed equilibrium internuclear distances are within a few percent of the experimental distances, (c) the computed vibrational and rotational constants are accurate to approximately 15%, and (d) the directly computed binding energies are generally very poor (see the discussion on the molecular correlation energy at the end of this paper). The new data, now available from Chicago, confirm the above conclusions.

For molecular systems with more than two atoms, the progress has been limited by the difficulty in the many-center integral computations, and by the lack of sufficiently fast and large computers. In view of the progress made in computer technology in the last few years, it is now feasible to consider computations at the Hartree-Fock level for systems much larger than diatomic molecules. The greatest remaining difficulty is in the treatment of the correlation energy.[24] This will be discussed later in the paper.

The relativistic correction

For the He atom ($Z = 2$) the relativistic energy is 10^{-5} smaller than the Hartree-Fock energy, but for the Zn atom ($Z = 30$) is only 10^{-2} smaller than the Hartree-Fock energy. This is due to the well known high-Z dependency of the relativistic effects. Therefore, for high Z the relativistic correction cannot be any longer considered as a simple perturbation and $L \cdot S$ coupling is no longer a satisfactory quantization scheme for the system. All this is known, but there are still several problems of theoretical nature. The essential point is that, at present, the many-electron relativistic Hamiltonian is only partially known and very few numerical computations have been made to verify the accuracy of the approximated Hamiltonian proposed. This seems to be the main difficulty that lies ahead in the computation of systems containing heavy elements. In the following we shall present some results of computed relativistic energies. Since we have considered low-Z cases, the perturbation technique is adequate.

The relativistic energy has been defined in the literature in a number of different ways and for the purpose of this paper the formulation and notation given by Bethe and Salpeter[25] of the relativistic energy of a two-electron system based on the Breit equation is extended to the N-electron system. The Breit equation describes the interaction of two relativistic electrons with each other and with an external electromagnetic field. The Hamiltonian of this system can be expanded in powers of $(Z\alpha)$ (Pauli's approximation, where Z is the nuclear charge and α is the fine structure constant) and consists of both one-particle and two-particle operators. We assume that the Hamiltonian for an N-electron system can be obtained by summing all one-particle operators over all N electrons and summing all two-particle operators over all pairs of electrons in the system. A great simplification occurs for closed-shell atomic systems. Up to and including the order of α^2, the relativistic correction to the Hamiltonian for such a system depends on three terms:

$$H_{\text{rel}} = H_1 + H_4 + H_5, \tag{10}$$

where

$$H_1 = \frac{-1}{8m^3c^2} \sum_{i=1} p_i^4, \tag{11}$$

and

$$H_4 = \frac{e\hbar^2}{(2\ mc)^2} \sum_{i=1} (\nabla^2 V_i + \nabla V_i \cdot \nabla_i), \tag{12}$$

$$H_5 = 4\left(\frac{e\hbar}{2\ mc}\right)^2 \frac{1}{2} \sum_{i \neq j} S_i \cdot S_j \left(\frac{-8\pi}{3}\right) \delta^3(r_{ij})$$

$$= \left(\frac{e\hbar}{mc}\right)^2 \left(\frac{-8\pi}{3}\right) \sum_{i>j} S_i \cdot S_j \delta^3(r_{ij}) \tag{13}$$

Here e is the absolute value of the electronic charge.

The Hartree-Fock orbitals are taken in the form of

$$\psi(x) = \sum_i U_i(x), \tag{14}$$

where $U_i(x)$'s are the single-particle wave functions of the type

$$U_i(x) = \sum_j C_{i,j} \frac{f_{nl}(r)}{r} Y_{lm}(\theta, \phi)\eta(\zeta). \tag{15}$$

η is the spin wave function α or β. The value i runs from 1 to N = the number of electrons. Y_{lm} = normalized spherical harmonics and $f_{nl}(r)/r$ is the radial part of the exponential function in the form proposed by Slater.[26] The coefficient of the expansion of the Slater-type basis set, $C_{i,j}$, is determined by the self-consistent field technique.

If we define

$$I_1(nl) = \int f_{nl}'^2\, dr,$$

Table 4 Relativistic energies (*in a.u.*) for closed-shell systems

Atom	$E(1s)$	$E(2s)$	$E(2p)$	$E(3s)$	$E(3p)$	$E(4s)$	$E(3d)$	E(REL)	E(Hartree-Fock)
He	−0.000070							−0.000070	−2.8616801
Be	−0.002033	−0.000165						−0.002198	−14.573021
Ne	−0.106628	−0.013845	−0.010737					−0.131210	−128.54701
Mg	−0.228050	−0.034385	−0.031252	−0.001363				−0.295049	−199.61458
Ar	−1.220578	−0.235288	−0.257411	−0.025311				−1.760981	−526.81730
Ca	−1.884626	−0.380956	−0.428731	−0.051217	−0.051264	−0.002907		−2.798701	−676.75801
Zn	−9.900744	−2.284792	−2.802329	−0.368432	−0.447182	−0.015103	−0.100389	−15.918970	−1777.8471

$$I_2(nl) = \int \frac{1}{r^2} f_{nl}^4 \, dr,$$

$$I_3(nl) = \int \frac{1}{r^2} f_{nl}' f_{nl} \, dr,$$

$$I_4(nl) = \int \frac{1}{r^4} f_{nl}^2 \, dr, \tag{16}$$

and

$$I_5(nl) = Z\left[\frac{1}{r} f_{no}^2\right]_{r=o}, \tag{17}$$

where f' and f'' are the first and second derivatives of $f_{nl}(r)$ then one can show that

$$E_1 = \tfrac{1}{4} \sum_{nl} (2l+1)[I_1(nl) - 2l(l+1)I_3(nl) + l^2(l+1)^2 I_4(nl)] \tag{18}$$

and

$$E_4 + E_5 = \tfrac{1}{4} \sum_{n} I_5(n0) + \tfrac{1}{4} \sum_{nl} (2l+1) I_2(nl) \tag{19}$$

and, in general,

$$E_{\text{rel}} = E_1 + E_4 + E_5 = -\tfrac{1}{4} \sum_{n,l,i} d_{nli} I_i(nl), \quad i = 1, 2, 3, 4, 5. \tag{20}$$

The coefficients d_{nli} that are needed for the computation of the relativistic energies of closed shell states of 2, 4, 10, 12, and 18 electron systems are available from Hartmann and Clementi.[27]

The error in the computed relativistic energy can be estimated by computing the next higher-order correction, that is, the Lamb shift, of orders $Z^2\alpha^3$ and $Z\alpha^3 \ln \alpha$. For a two-electron atom in its ground state, the lowest order Lamb shift is given in a.u. by[28]

$$E_{L,2} + E_{L,2'} = \frac{4Z}{3} \alpha^3 \langle \delta(r_1) + \delta(r_2) \rangle_{00} \cdot \left[2 \ln (1/\alpha) - \ln \frac{k_o}{ry} + \frac{19}{30}\right] - \frac{14}{3} \alpha^3 \langle \delta(r_{12}) \rangle_{00} \ln (1/\alpha) \text{ a.u.}, \tag{21}$$

where k_0 is the average excitation energy.

Estimates of the Lamb shift can be obtained by using[28]

$$\begin{aligned} k_0 &= 80.5 \text{ Ry} \quad \text{for} \quad Z = 2, \\ &= 191.6 \text{ Ry} \quad \text{for} \quad Z = 3, \\ &= 19.77Z^2 \quad \text{for} \quad Z \geq 4, \end{aligned} \tag{22}$$

and

$$\langle \delta(r_1) + \delta(r_2) \rangle_{00} \frac{2Z^3}{\pi} \left[1 - \frac{0.653}{Z} + \frac{0.138}{Z^2}\right] \tag{23}$$

$$\langle \delta(r_{12}) \rangle_{00} = \frac{Z^3}{8\pi} \left[1 - \frac{1.877}{Z} + \frac{1.189}{Z^2}\right]. \tag{24}$$

The relativistic energy corrections for the Hartree-Fock functions for He, Be, Ne, Mg, and Ar atoms are presented in Table 4. The relativistic energy corrections are computed for each subshell of electrons $E(1s)$, $E(2s)$, etc., and then summed to give the total relativistic energy E_{rel}.

The lowest order Lamb shifts are computed, using Eqs. (23) and (24), for the two-electron isoelectronic series and tabulated in Table 5.

Because of the quasiadditivity of the $E(nl)$ contributions to the relativistic energy (Eq. 20) it is not difficult to improve the computed values of the relativistic energy in the following manner: Instead of using the computed values of $E(1s)$ from the Hartree-Fock functions, one could use the $E(1s)$ obtained from the exact function of Pekeris[29] and add to it the $E(nl)$ for $n \geq 1$ from our computations. Pekeris' relativistic energies are available up to $Z = 10$ and have been extrapolated by Scherr et al.[30] to $Z = 20$. These values have been tabulated in Table 6 along with our computed values. The difference between our values for $E(1s)$ and those of Pekeris and Scherr are tabulated in the third column of the table and can then be used as a correction to all the terms in Table 4. It should be noted that if this correction is used, the results for 4, 10, 12, and 18 electron systems will include Lamb-shift corrections for the $1s$ electrons, but not for the other electrons. This is justified because the Lamb-shift corrections are small compared with the main relativistic

Table 5 Lowest-order Lamb shifts for two-electron atoms (*In a.u.*)

Z	$E_{L,2} + E_{L,2'}$	Z	$E_{L,2} + E_{L,2'}$
2	0.000022	19	0.064270
3	0.000106	20	0.073933
4	0.000323	21	0.084081
5	0.000740	22	0.094600
6	0.001439	23	0.105350
7	0.002500	24	0.116174
8	0.004000	25	0.126887
9	0.006015	26	0.137283
10	0.008614	27	0.147130
11	0.011856	28	0.156165
12	0.015791	29	0.164110
13	0.020460	30	0.170665
14	0.025887	31	0.175480
15	0.032085	32	0.178194
16	0.039051	33	0.178422
17	0.046765	34	0.175742
18	0.055190	35	0.169699

Table 6 Relativistic correction for a two-electron system

Z	a	b	Δ
2	−0.000049	−0.000060	−0.000011
3	−0.000433	−0.000500	−0.000067
4	−0.001767	−0.001878	−0.000111
5	−0.004914	−0.005092	−0.000178
6	−0.011086	−0.011345	−0.000259
7	−0.021807	−0.022166	−0.000359
8	−0.038918	−0.039395	−0.000477
9	−0.064576	−0.065202	−0.000626
10	−0.101276	−0.102075	−0.000799
11	−0.151820	−0.152847	−0.001027
12	−0.219385	−0.220655	−0.001270
13	−0.307451	−0.308996	−0.001545
14	−0.419797	−0.421671	−0.001874
15	−0.560656	−0.562833	−0.002177
16	−0.734444	−0.736965	−0.002521
17	−0.946076	−0.948891	−0.002815
18	−1.200515	−1.203750	−0.003235
19	−1.503578	−1.507060	−0.003482
20	−1.860704	−1.864620	−0.003916

[a] Our results including $E(\text{rel}) + E_{L,2} + E_{L,2'}$.
[b] Pekeris' relativistic energies up to $Z = 10$ and their extrapolations by Scherr et al. for $Z > 10$.

contribution, (compare Tables 4 and 5), and the main contribution to the Lamb shifts should come from the 1*s* electrons. Table 6 indicates that the estimates of Scherr et al. agree with our theoretical computations within 1% except for low Z, where the discrepancy is larger.

The above analysis has been made by direct extension of the Bethe and Salpeter two-electron Hamiltonian. This is certainly an oversimplification of the problem. Unfortunately, a "correct" Hamiltonian for N-particle systems in a central field is not available. For additional references on the relativistic correction we refer to the work of Hirschfelder et al.,[31] Slater,[26] Brown,[32] Breit,[33] and Grant.[34]

I should add that the quantum-chemical literature on the relativistic correction is practically nonexistent, despite the importance of the correction in those molecular systems with heavy atoms.

The correlation energy

• *Atomic correlation energy from spectral data*

The correlation energy is commonly defined as the difference between the exact nonrelativistic energy and the Hartree-Fock energy.[24,25]

It is worth while to note that there are several Hartree-Fock schemes,[35] each leading to a somewhat different energy and, consequently, to different values of the correlation energy. For this reason we state from the beginning that in the following, when we refer to the Hartree-Fock energy, we refer to the best energy one can obtain by the analytical self-consistent field method as put forward by Roothaan.[8] The reason for this choice is simply that by now this method has been used to obtain many atomic functions and energies and a large number of molecular functions and energies.

From a conceptual point of view one might prefer to define the correlation energy as the difference between the exact nonrelativistic energy and the Hartree energy, since the Hartree-Fock method presents an unbalanced situation when we look at the way in which electrons with like spins and those with different spins are considered.[36] The Hartree-Fock method partially correlates electrons with the same spins. This correlation present in the Hartree-Fock method will be hereafter referred to as *precorrelation*, where we define the precorrelation energy as the difference between the Hartree-Fock energy and the Hartree energy. This energy difference is a correlation energy, but in view of the accepted definition of correlation, we might say that it is a correlation energy *ante literam*.

We note that the emphasis on the nonrelativistic exact energy in the definition of the correlation energy has mainly a practical value. The relativistic energy itself can be partitioned into a correlated and an uncorrelated relativistic energy.

It is well known that there are, in principle, several methods available in order to obtain correlated wave functions.[23, 35, 36, 37] At present it seems that a common characteristic of these methods is that they are not easily applicable and are often outside of today's computational capabilities. For these reasons, it is of interest to give

estimates of the correlation energy for the isoelectronic series of atomic systems with 2 to 22 electrons.

Since electrons with parallel spins are somewhat correlated in the Hartree-Fock method and since parallel spins occur to a varying extent in the low energy states of atoms, one can expect that the correlation energy in the ground states of neutral atoms is not a linear function of the number of electrons. The Hartree-Fock method uses antisymmetrized wave functions; this is done to satisfy the Pauli principle, and brings about the exchange energy which is the origin of the precorrelation energy. Electrons with the *same* spin find themselves encircled by a Fermi hole which prevents electrons with the same spin from approaching each other.

We can expect a large correlation energy for pairs of electrons of the same shell (intrashell correlation), a smaller correlation energy between electrons of different shells (intershell correlation), and a quasi-constancy for the correlation of given types of pairs of electrons with opposite spin.

With the Fröman[38] and Linderberg-Shull[39] work in mind, one will predict that the correlation energy of the ground-state first-row atoms will behave as follows: There is a given correlation for the pair of electrons in the He atom. For the Be atom, the correlation is about twice that of helium. Lithium will have an intermediate correlation energy between He and Be. Since the extra electron (compared with He) is a $2s$ electron, which has a maximum radial probability far from the $1s$ electrons, its correlation with the $1s$ electrons is certainly small. In fact, from the Linderberg and Shull[39] values, we know it to be very small (the intershell correlation for $1s$-$2s$ is *much smaller* than for the $1s$ (or $2s$) intrashell correlation). The correlation energy of B, C, and N in their ground states can be estimated by keeping in mind that the $2p$ electrons have all parallel spins and consequently the precorrelation existing in the Hartree-Fock energy will take care of most of the correlation for the $2p$ electrons. There will certainly be some intershell correlation of $1s$-$2p$ type and $2s$-$2p$ type. Since the $2s$ electrons are in the same spatial neighborhood as the $2p$ electrons, one is tempted to assume that ($1s$-$2p$) intershell correlation $\ll$($2s$-$2p$) intershell correlation.

The correlation energy for O, F, and Ne should increase sharply. With those atoms we build one, two, and respectively, three pairs of unparallel spin electrons in the same shell (the $2p$ shell). The sharp increase is due to the lack of precorrelation for those newly added electrons.

It is fairly simple to be more quantitative about all the above reasoning. Accurate Hartree-Fock energies are available.[18] The necessary relativistic energies were available from our work;[27] and the total energy can be obtained experimentally by adding the ionization potentials from Moore.[40] Then the correlation energy is simply the total energy minus the Hartree-Fock energy minus the relativistic energy.

With these data we obtain an accurate estimate of the correlation energy for 2 to 10 electrons in atoms and in positive ions with Z from 2 to 10. The results are condensed into a diagram (Fig. 1) where the correlation energy is plotted against Z.

This diagram, we feel, reveals the essential features of the correlation energy problems for atomic systems in the $L \cdot S$ coupling. In order to compute the correlation energy of excited states we again make use of Moore's tables or of an extrapolation of the data of Moore by means of a power expansion in Z, and we can calculate the total energies of excited states. Thus, we have the total energy, E(TOT), the relativistic energy, E(REL), and the Hartree-Fock energy, E(HF), for the ground and the excited states. We note that the Hartree-Fock energy is computed in the approximation of infinite nuclear mass. Consequently, the Hartree-Fock energies must be mass corrected. (See for example, Bethe and Salpeter, Reference 25, page 253.) The correlation energy is simply $E(\mathrm{COR}) = E(\mathrm{TOT}) - E(\mathrm{REL}) - E(\mathrm{HF})$. A sample of the results we have obtained is given in Table 7 (in atomic units; one atomic unit equals 27.2097 eV). The Hartree-Fock energies are computed with seven significant figures and the relativistic and the total energies are computed with the same number of figures. In Table 7 the correlation is given to the number of figures we feel are correct (*plus one in order not to introduce roundoff error*). One can notice that the number of significant figures we give varies from four to two. This is done in view of the uncertainty in the relativistic energy and the extrapolations of the total energy.

In Figure 2 we have also given the correlation energy for excited states of the ground-state configuration for neutral atoms. The correlation energy for excited states of the positive ions was not indicated, to avoid confusion on the diagram. The dot-dash lines connect states with the same multiplicity and total angular momentum. Linear dependency on the number of electrons for the correlation energy of ^1S(Be), ^1S(Ne), excited ^1S(C), and ^1S(O) was obtained. The same is true for the ^2P(B), ^2P(F), and excited ^2P(N).

There are cases in which the correlation is directly known from computations of the Hartree-Fock and correlated functions. For the two-electron cases, the data of Weiss[41] and those of Pekeris[29] give us accurate correlation energies up to Ne^{8+}. The computations by Weiss[41] and Kelly[42] of three- and four-electron systems up to O^{5+} and O^{4+}, respectively, give us data for the correlation energies for three and four electrons. There are no other data of comparable accuracy available. In Table 8 the Pekeris, Weiss and Kelly data for two, three and four electrons are given. It is noted that for the three- and

Table 7 Experimental correlation energy for atomic isolectronic series with 2 to 22 electrons (*In a.u.*)

Z	$2-{}^1S_0$	$3-{}^2S_{1/2}$	$4-{}^1S_0$	$5-{}^2P_{1/2}$	$6-{}^3P_0$	$7-{}^4S_{1/2}$	$8-{}^3P_2$
2	−0.0421						
3	−0.0435	−0.0453					
4	−0.0443	−0.0475	−0.0944				
5	−0.0448	−0.0489	−0.1123	−0.125			
6	−0.0451	−0.0498	−0.1268	−0.139	−0.158		
7	−0.0453	−0.0505	−0.1412	−0.151	−0.167	−0.188	
8	−0.0455	−0.0510	−0.1551	−0.162	−0.175	−0.193	−0.258
9	−0.0456	−0.0513	−0.1684	−0.173	−0.182	−0.197	−0.260
10	−0.0457	−0.0516	−0.1814	−0.182	−0.188	−0.200	−0.267
11	−0.0458	−0.0519	−0.1941	−0.191	−0.193	−0.203	−0.274
12	−0.0459	−0.0521	−0.2066	−0.200	−0.199	−0.205	−0.279
13	−0.0459	−0.0523	−0.2190	−0.208	−0.204	−0.207	−0.285
14	−0.0460	−0.0524	−0.2313	−0.216	−0.209	−0.209	−0.291
15	−0.0461	−0.0525	−0.2435	−0.225	−0.214	−0.211	−0.296
16	−0.0461	−0.0527	−0.2556	−0.232	−0.218	−0.213	−0.301
17	−0.0462	−0.0528	−0.2677	−0.240	−0.222	−0.214	−0.305
18	−0.0463	−0.0529	−0.2797	−0.248	−0.227	−0.215	−0.309
19	−0.0463	−0.0529	−0.2917	−0.2555	−0.231	−0.217	−0.313
20	−0.0463	−0.0530	−0.3037	−0.263	−0.235	−0.218	−0.317
21	−0.046	−0.053	−0.316	−0.270	−0.24	−0.22	−0.32
22	−0.046	−0.053	−0.327	−0.278	−0.24	−0.22	−0.32
23	−0.047	−0.053	−0.339	−0.285	−0.25	−0.22	−0.33
24	−0.047	−0.053	−0.351	−0.293	−0.25	−0.22	−0.33
25	−0.047	−0.053	−0.363	−0.300	−0.25	−0.22	−0.34
26	−0.047	−0.053	−0.375	−0.31	−0.26	−0.23	−0.34
27	−0.047	−0.053	−0.387	−0.32	−0.26	−0.23	−0.34
28	−0.047	−0.053	−0.398	−0.32	−0.26	−0.23	−0.35
29	−0.047	−0.053	−0.411	−0.33	−0.27	−0.23	−0.35
30	−0.047	−0.053	−0.423	−0.34	−0.27	−0.24	−0.35

Z	$9-{}^2P$	$10-{}^1S$	$11-{}^2S$	$12-{}^1S$	$13-{}^2P$	$14-{}^3P$	$15-{}^4S$
9	−0.324						
10	−0.328	−0.393					
11	−0.336	−0.396	−0.403				
12	−0.344	−0.402	−0.411	−0.451			
13	−0.350	−0.409	−0.420	−0.464	−0.482		
14	−0.358	−0.417	−0.429	−0.482	−0.504	−0.522	
15	−0.366	−0.426	−0.438	−0.499	−0.523	−0.54	−0.561

Z	$16-{}^3P$	$17-{}^2P$	$18-{}^1S$	$19-{}^2S$	$20-{}^1S$	$21-{}^2D$	$22-{}^3F$
16	−0.60						
17		−0.71					
18			−0.79				
19				−0.82			
20					−0.84		
21						−0.85	
22							−0.86

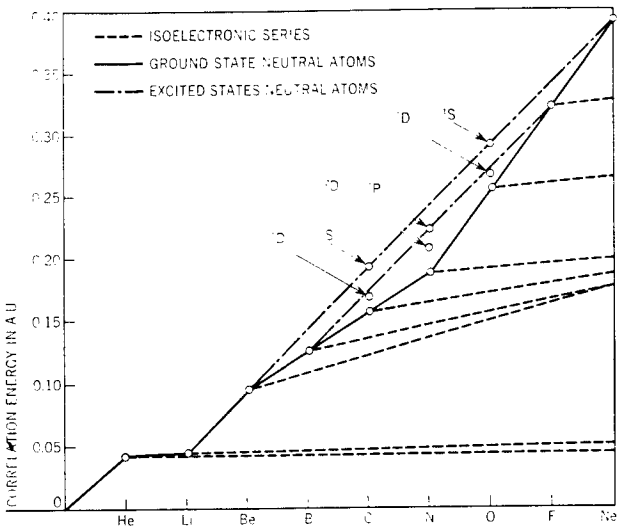

Figure 2 Correlation energy for the first row elements. The dashed lines connect isoelectronic series in the ground state; the solid lines connect ground states of the first row neutral elements; the dot-dashed lines connect excited states of neutral elements with some symmetry. The ground states for the neutral elements from He to Ne are ^1S, ^2S, S, ^2P, ^3P, ^4S, ^3P, ^2P and ^1S, respectively.

four-electron cases the Weiss computations give only a lower limit of the correlation energy since the exact nonrelativistic energy was not fully obtained.

It is quite interesting to note that not only the $1s^22s^2$ isoelectronic series has a strong Z dependency, but also the $2p(n)$ isoelectronic series shows large Z dependency. One notices that the Z dependency is pronounced in the Be(^1S) series, and progressively less in B(^2P), C(^3P), and N(^4S) series. In the series from O(^3P) to Ne(^1S) the dependency is about constant. We note that Linderberg and Shull[39] have discussed the Z dependency of the $1s^22s^2$ configuration in terms of $2s$, $2p$ near degeneracy.

We can comment on the excited states correlation energies somewhat further than that done earlier. The correlation energy for the multiplet components of a given term is approximately the same. The difference in correlation energy, for example, between B($^2P_{1/2}$) and B($^2P_{3/2}$) is very small and within the error of the estimate. For this reason no such data are reported.

For different states of the same electronic configuration the correlation energy has the following characteristics. *First, the lowest correlation energy is for the state of highest spin multiplicity.* For example, in the ^3P, ^1D, and ^1S series beginning at C (or O), $E(\text{COR. } ^3P) < E(\text{COR. } ^1D)$ and $E(\text{COR. } ^3P) < E(\text{COR. } ^1S)$. This is, as mentioned previously at length, a consequence of the spin precorrelation in the Hartree-Fock method. *Second, for states with the same spin multiplicity the correlation energy is smaller for the states of highest angular momentum.* For example, $E(\text{COR. } ^1D) < E(\text{COR. } ^1S)$ for the carbon and the oxygen series, and $E(\text{COR. } ^2D) < E(\text{COR. } ^2P)$ for the nitrogen series. Since states with the same spin multiplicity but different angular momenta do not have the same correlation energy (for given Z and number of electrons), one concludes that in the Hartree-Fock method we have not only spin-related precorrelation but also angular precorrelation. The angular precorrelation being in the sense that the higher the angular momentum (total angular momentum) the higher the angular precorrelation. This is quite interesting because it tells us that we cannot obtain excitation energies of the correct magnitude with the Hartree-Fock method even for states of the same multiplicity. A simple explanation of the differences of the correlation energies between states of the same multiplicity but different total angular momentum is that the larger the angular momentum, the more "preferential" is the electron's motion about the nucleus.

- *The two-particle model*

Up to now the results we have obtained for the correlation energy in the first,[43] second,[44] and third[45] row have indicated a remarkably simple picture, where one can simply divide the correlation energy into "strong" and "weak" pairs, the former for intrashell electron pairs, the latter for intershell electron pairs. In addition, for the first and second row, the "weak pairs" have much smaller correlation where the electrons in the pair have different principal quantum numbers, for example, the $1s$-$2s$ pair correlation is smaller than the $2s$-$2p$ correlation.

There seems to be evidence that the above *simple pairing model*[46] is only the limit of a more complex situation, which we have called the *complex pairing model.* For this we mean that the simple division between "strong" and "weak" pairs is inadequate, that the "weak" interactions increase not only in number (simply because

Table 8 Correlation energies from *ab initio* computations

Case	Pekeris*	Case	Weiss**	Case	Weiss**
He	−0.0424	Li	−0.0444	Be	−0.0869
Li^+	−0.0453	Be^{+1}	−0.0462	B^{+1}	−0.1038
Be^{+2}	−0.04427	B^{+2}	−0.0472	C^{+2}	−0.1177
B^{+3}	−0.04474	C^{+3}	−0.0479	N^{+3}	−0.1305
C^{+4}	−0.04506	N^{+4}	−0.0483	O^{+4}	−0.1424
N^{+5}	−0.04529	O^{+5}	−0.0486		Kelly***
O^{+6}	−0.04546			Be	−0.92
F^{+7}	−0.04558				
Ne^{+8}	−0.04570				

* See Ref. 29.
** See Ref. 41.
*** See Ref. 42.

there are more electrons in the systems) but also in strength. In other words, the new situation is that the correlation energy to a first approximation is not the simple sum of the "strong" pairs correlation, but, one should add to this the contribution of the intershell correlation; this contribution is comparable in value to that of the "strong" pairs. One reason for this behavior is that the n, l, m, and s quantum numbers (L-S coupling) do not describe adequately the atomic system. If the atomic system under examination is partially described by j-j coupling, then this prevents assigning strong and weak pairs to the valence electron configuration. This point can be simply stated in the following way: "If a system is, for example, not a pure singlet, but a mixture of singlet, triplet and quintet states, then why consider the correlation as due entirely to its singlet component? Further, if the system does not possess a well-defined total orbital or spin angular momentum, what is the meaning of pairs based on the assumption of a well-defined total orbital or spin angular momentum?" A second reason is that the number of subshells is more important, for example, in the third group we have $4s$, $4p$, $4d$ and $4f$ degeneracy as compared with only $2s$ and $2p$, the case for the first period. These two reasons affect the correlation energy picture in the same way, namely, they emphasize the role of the "weak pairs" of the "simple pair model". We might say that the larger the number of electrons, the more linear the correlation behavior becomes with respect to the number of all possible strong and weak pairs. This is tantamount to saying that we see the emerging of a *statistical picture* which is very likely the final limit of the *complex pairing model.*

Let us examine, for example, the scandium atom,[45] and consider the correlation energy for the $Sc(^2D)$, $Sc^+(^3F)$, $Sc^{+2}(^2D)$ and $Sc^{+3}(^1S)$, with corresponding configuration ..... $4s^23d^1$, $4s^03d^2$, $4s^03d^1$ and $4s^03d^0$. The correlation energy difference from Sc to Sc^+, from Sc^+ to Sc^{++} and from Sc^{+2} to Sc^{+3} are 0.037, 0.034 and 0.031 a.u., respectively. In the first step, Sc to Sc^+, a "strong pair" is destroyed and the $4s$ electron promoted to the $3d$ shell can bring about only "weak pairs". In the second and third steps, we leave unaltered the number of "strong pairs" and we vary only the number of "weak pairs". But the correlation energy is very insensitive to such distinction of "weak" and "strong" pairs and behaves as if the $4s$ and $3d$ electrons do not depend on the n, l, m, and s quantum numbers at all. (The remarkable linearity of the computed values 0.037, 0.034, 0.031 a.u., should not be taken too literally, because of the angular momenta, near degeneracy, uncertainty in ionization potentials, lack of accuracy in the computation of the relativistic effects, etc.) Unfortunately, the lack of reliable data for higher ionization potentials for many cases prevents a final conclusion. It is noted that the highest ionization potentials available in the literature are likely to be in error, because of the heavy reliance on extrapolation and analogy which characterizes the determination of the high order ionization potentials for the third group.

The net outcome of the analysis of these data is that we see the emerging of the "complex pairing model" and the collapse of the "simple pairing model".

The above considerations on the two-particle model are obtained by analyzing the correlation energy data. It should be pointed out that the two-particle method has been proposed and analyzed by Hurley, Lennard-Jones and Pople,[47] and later by others.[48] Their analysis is not within the self-consistent framework. Recently, Huzinaga[49] derived a set of coupled Hartree-Fock type equations to determine the two-electron geminals.

Presently there are no numerical computations to prove that the two-particle model functions (called *geminals*)[48] represent a general answer to the correlation problem. However, the numerical results on the correlation energy which we have reported seem to indicate that this model will work well for the Be atom, less well for the Ne atom, and poorly for atoms with more than 20 electrons. The reason is the large amount of correlation energy due to the intershell correlation. In addition, we note that the model at present makes no provision for those cases where one should work in terms of j-j coupling. On the other hand, it is expected that the two-particle model will give a satisfactory answer for saturated molecules with strongly localized bonds.

- *Coulomb hole and correlation energy*

The Hartree-Fock (HF) models assume that each electron experiences the average field of all the remaining electrons and that the total wave function can be expressed as an antisymmetrized product of one-electron orbitals. Thus, the exact function is replaced by a single determinant of one-electron orbitals (at least for closed shell systems) and the $1/r_{i,j}$ operator of the exact Hamiltonian is replaced by Coulomb and exchange operators, representing the average field interaction.

Formally, the Hartree-Fock model can be equated to an "unperturbed system" and the difference between the exact and the average electron-electron interaction will be a "perturbation potential". This much is well-known from the Möller and Plesset[50] analysis of the correlation problem. As a consequence, one can attempt to obtain the exact function by taking the HF function as a zero-order function and then add some correction via perturbation and/or variation techniques.

Physically, one can equate the Hartree-Fock model to a system where the "Coulomb hole" for electron pairs with antiparallel spin is not accounted for. We refer to Wigner's work on this point.[51]

We shall attempt to introduce in the Hartree-Fock

potential an additional term which directly represents the "Coulomb hole". Since we are interested in the quantum chemistry of molecular systems, *we are concerned with not increasing the mathematical complexity of the problem beyond the Hartree-Fock formalism.*

The "Coulomb hole" is introduced directly as a modification of the Coulomb integrals $J_{\lambda pq,\mu rs}$.[6,7] This modification consists in replacing the integration range of the first electron from zero to r and from r to infinity, (the usual limits of the $J_{\lambda pq,\mu rs}$ elements) with the integration range from zero to $(r - \delta)$ and from $(r + \delta)$ to infinity. Since at the integration limit r the two electrons of the Coulomb element occupy the *same* radial position, the effect of replacing r by $(r - \delta)$ and $(r + \delta)$ introduces a discontinuity in the potential. Thus, we have a "Coulomb hole". In our method there are as many δ as J integrals, thus δ is designated as $\delta_{\lambda pq,\mu rs}$.

It is not difficult to obtain an expression for the $\delta_{\lambda pq,\mu rs}$. In our work[52] we have made use of two empirical parameters, one for the case of δ with $\lambda = \mu$ and the second for the case δ with $\lambda \neq \mu$. The first parameter has been obtained by fitting the He atom (^1S state), the second by fitting the Ne atom (^1S state).

With these two fittings we have analytically computed the $J'_{\lambda pq,\mu rs}$ elements which differ from the standard $J_{\lambda pq,\mu rs}$ because of the discontinuity in the integration range.

In summary, the technique of computation is as follows: (a) compute a Hartree-Fock function, (b) compute the $\delta_{\lambda pq,\mu rs}$ and then the $J'_{\lambda pq,\mu rs}$ matrix elements, and (c) compute again the self-consistent field function, but with the newly obtained J' matrix elements.

The resultant energies (in a.u.) for the first and second period are given in Table 9. The first column gives the Hartree-Fock energy for the functions we have used as a starting point; the second column gives the Coulomb-Hartree-Fock (CHF) energies (we shall call this the Coulomb-Hartree-Fock method, CHF). The third column gives the difference between the CHF and HF energies (i.e., the correlation energy computed by the CHF method). The results are in substantial agreement with the "experimental correlation energies" presented in Table 7 (see Fig. 3).

We note that the CHF functions may represent an improvement or a step backward as compared with the HF functions. In order to test this important point, we have computed the dipole polarizability of the Be atom. The Hartree-Fock dipole polarizability[53] is 9.94×10^{-24} cm^3, the Coulomb-Hartree-Fock dipole polarizability[52] is 4.5×10^{-24} cm^3, the latter agrees well with the correct value[54] of 4.5×10^{-24} cm^3. We are presently testing more extensively the validity of the CHF functions. The same improvement over the Hartree-Fock functions has been obtained for the polarizability of Li, F^-, Ne, Na, Mg and Ar.

The main results of this work seem to indicate that:

Table 9 Correlation energy from the CHF method (*In a.u.*)

System	Hartree-Fock	CHF	EC(comp)*	EC(exp)**
He(^1S)	−2.86166801	−2.9037222	−0.0420421	−0.0421
Li(^2S)	−7.4327257	−7.4850509	−0.0523252	−0.0453
Be(^1S)	−14.649920	−14.573070	−0.076860	−0.0944
B(^2P)	−24.529052	−24.632040	−0.102988	−0.125
C(^3P)	−37.688611	−37.829531	−0.140920	−0.158
N(^4S)	−54.400911	−54.590641	−0.189730	−0.188
O(^3P)	−74.809359	−75.055357	−0.245998	−0.258
F(^2P)	−99.409284	−99.725809	−0.316521	−0.324
Ne(^1S)	−128.54636	−128.94431	−0.39795	−0.393
Na(^2S)	−161.85734	−162.26045	−0.40311	−0.403
Mg(^1S)	−199.61430	−200.05139	−0.43709	−0.451
Al(^2P)	−241.87625	−242.35842	−0.48217	−0.482
Si(^3P)	−288.85109	−288.38888	−0.53779	−0.522
P(^4S)	−340.71846	−341.30388	−0.58538	−0.561
S(^3P)	−397.50460	−398.14259	−0.63799	−0.60
Cl(^2P)	−459.48169	−460.20544	−0.72375	−0.71
Ar(^1S)	−526.81703	−527.64943	−0.83240	−0.79
Be^{+2}(^1S)	−13.611256	−13.654058	−0.042802	−0.0443
C^{+4}(^1S)	−32.361154	−32.404169	−0.043015	−0.0451
O^{+6}(^1S)	−59.111119	−59.154215	−0.043096	−0.0455
Ne^{+8}(^1S)	−93.861103	−93.904409	−0.043306	−0.0457
Kr^{+34}(^1S)	−1273.6110	−1273.6543	−0.0433	−0.047

* Difference of E(CHF) − E(HF).
** From Table 7.

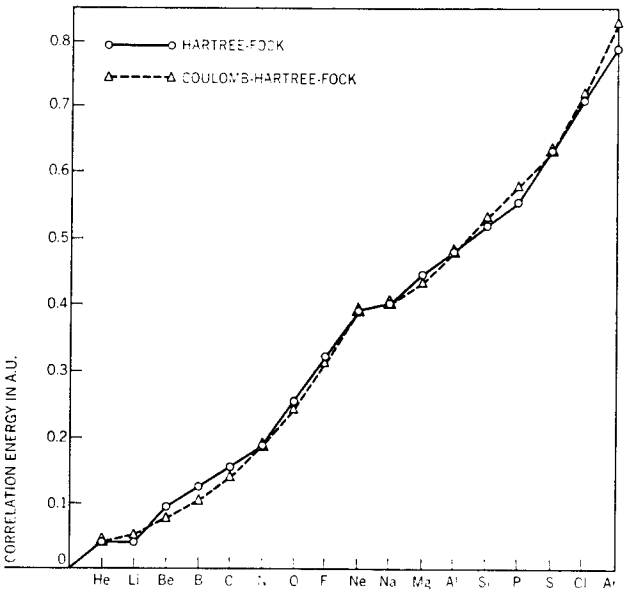

Figure 3 Comparison of the correlation energy obtained from Hartree-Fock energies (see Table 7) with the correlation energy computed directly in the Coulomb-Hartree-Fock semi-empirical method (see Table 9).

(a) *the HF method can be improved within the spirit of the one-electron approximation* (notice that the HF model is a direct extension of the Hartree model, via introduction of the Fermi hole; in an analogous way the CHF model is an extension of the HF model, via introduction of the Coulomb hole); (b) the CHF semiempirical method *proposed* and *tested* here gives correlation energies in rough agreement with the experimental values; and (c) the empirical CHF functions seem to be as good as the HF functions, but this point must be studied further.

At present we are expanding our analysis[52] and we are attempting to obtain the δ's directly from some physical model without making use of empirical parameters. Simultaneously, we are attempting to extend the CHF method to molecular systems.

We note that the CHF method could be reformulated by referring to the F integrals, (introduced by Slater[18a]) in place of the J integrals (as defined by Roothaan[8]).

- *Molecular correlation energy*

From the previous discussion one could be led to the hurried conclusion that the "simple pairing model" should hold well for those molecules with component atoms of low Z value (say, Z less than 15). Indeed, for such molecules the spin-orbit effect (at least at the equilibrium distances) is small and the complications due to the near-degeneracy in the atoms are removed, because of symmetry requirements in the molecule. It is noted that the above conclusion might be in error because in multiple-bonded molecules the intershell effect can be substantial.

In the following, we shall clear up a few points about the relations of atomic correlation and molecular correlation energies. Up to a few years ago, there had been sufficient numerical computations in atomic systems that one could advance the hypothesis that the correlation energy in atoms is simply a function of the number of electrons. For molecular computations, the situation was such as to predict molecular correlation incorrect even in the order of magnitude (for example the correlation energy per bond in CH was estimated to be a few tenths of an eV instead of somewhat more than one eV). With improved accuracy in molecular computations and the increasing number of accurate atomic computations, a somewhat better situation started to emerge. Roothaan and Kolos[55] pointed out the equality of the correlation energy in the He, H^- and H_2 problems. Karo and Allen[56] made use of approximate atomic correlation for the fluorine neutral atom (^2P) and negative ion (^1S) in order to estimate a limit for the molecular extra correlation energy of the HF molecule. Since their computation is somewhat far from an Hartree-Fock function, any definite answer on the possibility of computed dissociation energy was prevented. Most puzzling was the suggestion that the correlation energy for a $2p$ pair in F^- should be at least 1.5 eV (later from our work, it turned out to be a correct suggestion) about one-third more than expected from previous available atomic work. A new calculation by the author on the HF molecule[57] approximately reached the Hartree-Fock function. The molecular correlation energy was, therefore, defined within about 0.1 eV and the concept of molecular extra correlation energy was first defined and its value determined within 0.1 eV. This was done by explicitly using the known value of the dissociation energy. Since the computed function was not an accurate Hartree-Fock function, and since we were lacking accurate data on atomic correlation energy, it was concluded that the problem of computing exact dissociation energies was not yet under control. A later computation on the HF molecule was reported by Nesbet.[58] However, this new work did not improve our computed total energy despite the use of a larger basis set. The dissociation energy was estimated, following the same argument presented by Allen and Karo.[56] The net correlation energy contribution was put between 2.0 eV and 1.6 eV, and the hope was expressed that the correlation energy for simple atoms and molecules would behave very regularly as a function of the number of electrons.[58]

The availability of the correlation energies for the first three periods of the atomic system proved that we can use atomic correlation data for predicting the correlation energy in molecules. This was done first in our works on LiF (Ref. 59) and CH_4, (Ref. 60) then in A. D. McLean's

work on LiF (Ref. 61) and subsequently in the CH_4 computations by Carlson and Skancke,[62] the N_2, CO, BF analysis by Nesbet,[63] and the BeO analysis of Yoshimine.[64]

It seems worthwhile to define a few quantities somewhat more critically than was previously done.[57] First, we shall partition the correlation energy. The total correlation energy in a molecule is defined in the same way as for the atoms, namely, it is that energy needed to reach the exact energy in a molecular system, as an addition to the Hartree-Fock energy and to the relativistic energy.

As a practical first step, we shall assume for now that the relativistic energy in the molecule is the same as in the constituent atoms. But this needs some judgment. Namely, if we have a molecular compound built up of atom A and atom B, with resulting molecule A-B, we shall use the atomic data on the relativistic energy, with attention to the fact that if the compound is of type A^+B^-, then the relativistic data for the separated atoms A and B must be that for the ions A^+ and B^-. However, since very few compounds are totally ionic, the relativistic energy of the ions should be corrected by some appropriate weighed factor. It is noted that the relativistic energy difference between A and A^+ is up to 5 kilocalories in the third row elements.

The total molecular correlation energy as was defined is clearly a function of the internuclear separation and we shall use the notation TMCE(r) to indicate this fact in diatomic molecules, where (r) is the internuclear distance. For polyatomic molecules, TMCE will be a function not only of the internuclear distances, but also of the bond angles, in addition. In this regard, we refer the reader to the numerical results obtained by A. D. McLean for the H_2 and LiF molecules. We finally are in a position of partitioning TMCE(r). If we have a system of N atoms designated as $A_1, \cdots, A_n$, then the first partition is

$$\mathrm{TMCE}(r) = \sum_i^n (\mathrm{AC})_i + \mathrm{MECE}(r).$$

Namely, TMCE is the sum of the correlation energy of the component atoms, $AC_1 \cdots AC_n$ plus a remainder which was called the molecular extra correlation energy, MECE. It is important to point out the need of having exact Hartree-Fock functions in order to make any meaningful analysis of the molecular correlation energy. Naively, one could assume that an approximate self-consistent field computation on a molecule and an approximate self-consistent field computation on the separated atoms are sufficient in order to determine the molecular correlation energy. However, this is not the case, since the above assumption can bring about up to several tenths of one eV of error in the estimate of the binding energy.

In Table 10 we present the value of the molecular extracorrelation energy for several diatomic molecules. The Hartree-Fock energies at the equilibrium internuclear distance are available from the L.M.S.S. Technical Reports.[22] The quantity denoted as D_e(HF) is the Hartree-Fock dissociation energy; the last column of Table 10 gives the experimental dissociation energy. By simple inspection of the MECE data given in the table, one realizes that there are several regularities. For example, the LiH value is approximately the same as expected for the creation of a new s-type pair, the HF value is approximately the same as expected for the creation of a new p-type pair. The four new pairs needed to obtain the CH_4 molecule from $C(^3P)$ and four $H(^1S)$ atoms are 1.3 eV, again approximately the value for the formation of an s-type pair.

With some ingenuity one can account for a large percent of the MECE, and build up empirical rules which should help in predicting the MECE as was done in several cases. However, it is still an open question as to how reliable these empirical rules will be.

The possibility of extending the Coulomb-Hartree-Fock method to molecular cases seems to be a more attractive technique, than building up empirical rules as previously done.[59-64]

On the other hand a limited amount of configuration interaction might provide somewhat better energies and a close agreement with experiments for vibrational and rotational constants. But configuration interaction will not provide an adequate answer to the molecular quantum chemistry computations, nor will the Hartree-Fock method alone. Configuration interaction applied to the geminals could in principle, give very accurate results, but at present no such formalism is available and the computational difficulties could be very substantial.

The recent work by Sinanoglu[24] is now in the testing

Table 10 Molecular extra correlation energy, MECE, and dissociation energy, D_e, for diatomic heteronuclear molecules (*In eV*)

		MECE	D_e(HF)*	D_e(exp)
CO	$^1\Sigma^+$	3.406	7.836	11.242
BF	$^1\Sigma^+$	2.397	6.183	~8.58
LiH	$^1\Sigma^+$	1.040	1.476	2.516
FH	$^1\Sigma^+$	1.682	4.378	~6.06
CH_4	$^1A_{1g}$	~5.20	~13.0	~18.20
N_2	$^1\Sigma_g$	4.631	5.271	9.902
Li_2	$^1\Sigma^+_g$	0.884	0.169	1.050
C_2	$^1\Sigma^+_g$	5.469	0.781	~6.25
N_2	$^1\Sigma^+_g$	4.631	5.271	9.902
O_2	$^3\Sigma^-_g$	4.910	1.227	5.178
O_2	$^1\Delta_g$	4.171	−0.520	4.171
O_2	$^1\Sigma^+_g$	3.951	−1.392	3.518
F_2	$^1\Sigma^+_g$	3.047	−1.374	1.679

* The Hartree-Fock function for diatomic molecules have been obtained at the University of Chicago. The value of this column is the computed Hartree-Fock dissociation energy.

stage for atomic systems but it is not of simple applicability even for closed shell atoms. In the author's opinion this method will not provide a practical working solution for chemical systems. Perhaps it is too optimistic to think of present and past techniques as being practical and satisfactory methods for molecular computations when these same techniques fail for simple atomic cases.

In the author's opinion, we shall have to resort to semiempirical methods for several years. On an extremely crude basis, for example the Hückel theory, one can obtain a remarkable insight for spectral assignment in complex molecules. With quite simple theoretical computations, one can understand and sometimes make reliable predictions in such complex systems as the charge-transfer complex. Most of the theory of the molecular structure, available to date, has been provided with much intuition and little computation by R. S. Mulliken.

It is not difficult to extend the list of these cases which all have one common factor: much of the chemistry can be explained and, to some extent predicted, without exact wave functions. On the other hand, exact quantitative understanding of chemistry can be achieved only via exact computations. The net conclusion of these contrasting comments is, in the author's opinion, that exact computations should be done whenever technically and economically feasible. "Testing" computations of exact nature should be done for very complex systems only in order to provide models for "routine" semiempirical computations, or in order to prove or disprove theories and models based on experimental or empirical evidence.

These "test" computations possibly will provide the prototypes of routine computation, if the computer technology continues at the present astonishing pace.

Conclusions

In the past ten years we have seen the realization of the computation, with some accuracy, of atomic and small molecular systems. Hartree-Fock functions for atoms and diatomic molecules are now mass produced. There still remain the correlation energy problem, which is a formidable and practical one for macromolecular computations but has been fairly accurately understood. Few exact computations are available for atomic systems but a large number of accurate estimates have been presented in recent literature. The next few years will probably see equivalent development for small molecular systems and a few pilot computations for large molecules.

In this paper we have not underestimated the existing difficulties. On the other hand, the progress in quantum-mechanical computations has been extremely rapid and this gives hope for the future.

In this work we have made little attempt to present the entire development of *ab initio* computations in a systematic fashion, and we have made no attempt to offer a complete set of references. A recent review of the field has been made by R. Parr[65], where heavy emphasis has been put on semiempirical methods and on the Sinanoglu pairing theory.[24] We refer the reader to this work for such subjects. Promising attempts have been made at the Wisconsin University and at Upsala University to obtain good functions via perturbation methods. These are additional examples of very interesting approaches, not covered in this paper, since here our emphasis is on the Hartree-Fock technique.

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