

Letters to the Editor

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On Pair Correlation in the Theory of Atomic Structure

E. U. CONDON

*Joint Institute for Laboratory Astrophysics,
Boulder, Colorado 80302*

Most methods in use in the theory of atomic structure are based on the central field approximation with self-consistent field orbitals. In recent years Hartree-Fock orbitals have been obtained both in numerical¹ and analytic² form for a large number of ground and excited atomic states. It is well known that the electron correlation effects that remain contribute significantly to spectra. A number of approaches to electron correlation may be found in two special symposium issues of the *Reviews of Modern Physics* (Vol. 32, April 1960 and Vol. 35, July 1963) which contain considerable material on this and related topics. Revival of interest in the theory of spectra in a number of fields (atomic physics, astrophysics, space science, theoretical chemistry) makes it particularly desirable at this stage to see what types of approaches to correlation have been developed by workers, often from diverse fields, and to compare these.

A particular approach in papers by Sinanoğlu indicates systematic simplifications in the treatment of correlation effects in atoms. Papers with a bearing on this subject by Nesbet, Szász, and several other workers are also of interest. In connection with the rewriting of my book on the theory of atomic spectra, I recently looked into the relation between these various approaches in some detail. Summarized below are observations on these approaches and their relationships.

(1) The traditional method for going beyond the independent-particle model, the configuration-interaction (CI) method, expands the wave function of an N -electron atom as a whole. The Hartree-Fock approximation is often taken as the first term of this expansion. In attempts to calculate atomic energies accurately, as large a number of configurations as possible on the available computer are taken in conventional applications of this method. Aside from special configuration-mixing effects, however, these computations usually seem to have given a fraction of the correlation energy until quite recently due to slow convergence. There are other early approaches, for example, of the type of extensions or variants of Hartree-Fock methods, use of correlation factors, and the like, which again treat each atomic state as an

N -electron system as a whole. These methods have been reviewed, for example, by Löwdin,³ and Nesbet.⁴

(2) In a 1961 paper,⁵ Sinanoğlu solved formally the first-order perturbation equation

$$(H_0 - E_0)\chi_1 = (E_1 - H_1)\phi_0$$

for ground states, taking the ϕ_0 as the Hartree-Fock determinant. He separated the equation into the first-order equations of electron pairs in the HF potential of all the electrons. His solution is such that each electron pair is then separately treated by the variation-perturbation method as if one were applying it to the ground and excited states of the He atom. Sinanoğlu arrived at the basic idea in his preceding paper,⁶ by noting the pairwise additivity of London dispersion forces which as such holds only so long as a set of charge distributions are nonoverlapping. In this 1960 paper, he used rough sum rules to sum parts of the second-order Rayleigh-Schrödinger energy expression and separated this energy into a sum of pair correlation energies and additional exclusion effects.

These 1960 and 1961 papers are the first in the field which suggest the treatment of ground-state N -electron correlations in terms of $N(N-1)/2$ pair correlations independent of each other, to be calculated separately but subject to exclusion effects which he formulates explicitly. The latter allow the energy of each pair to be minimized separately. He suggests that some of the pair correlations may be transferable from system to system semiempirically, provided exclusion effects do not become large.

The method of the Ref. 5 paper has been introduced recently and used also by Byron and Joachain.⁷ These formulations allow use of closed-form pair functions, for example, of the Hylleraas-type, for each pair. Byron and Joachain obtain their functions in terms of $r_{<}$ and $r_{>}$ which seem simpler to use than the r_{12} coordinate. Their procedure seems to be promising for larger systems.

The first-order-perturbation wave function in its usual expanded form starting from Hartree-Fock functions, in particular the vanishing of single-excitation coefficients (Brillouin theorem), has been discussed for quite some time,⁸⁻¹⁰ but these papers do not contain any hint of the basic notion of separate pair-correlation energies to be dealt with individually for calculation or, where applicable, for semiempiricism, as introduced in the Sinanoğlu papers.

(3) Another approach, complementary to the one above, may be mentioned. A different paper by Sinanoğlu¹¹ explores an alternative to "Hartree-Fock-followed-by-correlation." He takes as the starting wave function a determinant of hydrogenic orbitals, then again looks at the formal solution of the first-order Schrödinger equation and second-order energy. This alternative gives corrections to hydrogenic orbitals, as

well as separate pair equations, with the advantage that here everything can be explicit in Z dependence. This alternative has been pursued further more recently by Layzer, Horak, Lewis, and Thompson¹² and by Chisholm and Dalgarno.¹³ Sinanoğlu, himself, seems to have preferred the Hartree-Fock as the initial function and in his later work to have gone on to treat the correlation effects explicitly.

A formal separation of the first-order equation for separate calculation of first-order pair functions has been introduced recently into nuclear theory by Bhaduri, Peierls, and Tomusiak.¹⁴

Another approach, somewhat related to the Z -dependent theory, is that of Bacher and Goudsmit.¹⁵ The well-known Bacher-Goudsmit method is strictly a semiempirical one in which the total energy of an atom with N electrons is expressed in terms of the total energies of its 1, 2, 3, ..., n , ..., $N-1$ electron ions or some combinations of these. In it the Hartree-Fock and correlation energies are not separately considered. The changes in the energies of ions, as those with more electrons are considered, may be the main limitation in the method unless perhaps the energies of a large number of ions of different n are used.

(4) A number of papers on correlation by Sinanoğlu, from 1961 on, (a series entitled "Many Electron Theory of Atoms and Molecules") go beyond perturbation theory and study the relative importance of different correlation effects in the wave function and energy of a many-electron system. He investigates whether the decoupled and separately treated pair correlations introduced in his perturbation papers are a valid and sufficient concept or whether correlations among larger numbers of electrons need to be included. The directions along which his "many-electron theory" proceeds are expressed in a section subtitled "Objectives of the Theory" in his 1962 paper.¹⁶ The important points in this paper, extended and applied in the later papers of the series, are the following:

(a) The nature of the many-particle problems in an infinite electron gas and in nuclear matter are compared with that in atoms and molecules. Sinanoğlu notes major differences in the problem of atoms and proceeds to devise methods tailored to the atomic N -electron problem. He shows with some examples that the potential responsible for correlation between electrons occupying different orbitals is of short range in the case that the orbitals are the Hartree-Fock ones. He discusses the 1, 2, 3... electron correlation functions in the exact wave function individually and by analogy to the Mayer theory of imperfect gases. He writes each n -electron correlation function as a sum of an unfactorable " n -cluster," and of all possible products of fewer electron cluster functions having no orbitals in common. He considers the physical importance of different clusters and demonstrates that, for example,

four electron functions are accounted for, by and large, by all possible products of pair correlation functions. His paper with Tuan¹⁷ studies the one-electron terms in more detail ("effect of correlation on orbitals"), and shows these terms need not be small on the basis of the Brillouin theorem alone, but that they are small in certain types of systems.

Perturbation theory to first order is not sufficient, but these papers make it very plausible that the major part of the wave function of an atom in its ground state consists of all pair correlations and all the possible products of these.

(b) The Sinanoğlu 1962 paper¹⁶ shows that three more electron correlations (his "remainder") arise in the energy even after selecting the pair correlation functions and all their products in the wave function as the major terms. This is a crucial point. If these "remainders" are large, pair correlation energies will not be decoupled. If they are large, then also multiple electron correlations in the wave function may be large as well. The paper argues on the basis of the residual electron-electron potentials, the exclusion effects, and the nature of the matrix elements that the energy remainders should be small, for example in atoms like boron and neon. Sinanoğlu then introduces a method whereby only a major portion of the variational energy expression is minimized to get pieces of the wave function. In particular on pp. 715 and 716 of Ref. 16, he describes a simple configuration-interaction (CI) procedure for obtaining decoupled, individual pair correlations one at a time, followed by ways for estimating the "remainder" effects by carrying out larger CI calculations. The pair correlation energies individually calculated by this pair-at-a-time CI procedure are added together; they provide a good estimate of the total correlation energy if the "remainders" are small.

(5) Two papers have appeared recently by Nesbet^{18a,b} entitled "Atomic Bethe-Goldstone Equations" which carry out CI calculations on the Be and Ne atoms and use the pair-at-a-time CI procedure. The title of these papers, and a number of other recent ones on similar calculations^{19a,b} is given with reference to a 1957 paper²⁰ by Bethe and Goldstone whose contents are not discussed. The Bethe and Goldstone paper with the title "Effect of a Repulsive Core in the Theory of Complex Nuclei" is an important contribution to the theory of infinite nuclear matter. It is concerned with the particular problem of the hard core which has no counterpart in atomic physics. The terminology, "Atomic Bethe-Goldstone equations," "Bethe-Goldstone increments," "Bethe-Goldstone calculations," is confusing. The Bethe and Goldstone paper does not contain the approximations and procedures for atoms introduced and used by a number of authors, therefore this terminology should best be dropped. The possibility of confusion is a real one since several different

approximations and procedures, though differing from one another in crucial aspects, are referred to as "Bethe-Goldstone equations" in a 1965 article²¹ by Nesbet where he first uses this terminology.

Nesbet¹⁸ diagonalizes a separate CI matrix for each electron pair at a time, i.e., over determinants containing excitations from only a given pair of occupied spin orbitals. He adds together the decoupled pair correlation values so obtained to get a total correlation energy quite close to experimental. The derivation and justification of this procedure is given by Sinanoğlu (especially pp. 715 through 717 of Ref. 16; also Ref. 22). The derivation and decoupling depend on the inclusion of possible products of pair functions as well as on the "remainders."

An earlier paper²³ by Nesbet, referred to in Refs. 18(a) and (b) is of interest. It does not refer to the Bethe-Goldstone paper²⁰ but gives an interesting discussion of the difficulties and differences that occur in the application of the Brueckner theory to finite systems. To compare with the Brueckner theory, the conventional configuration-interaction method with excitations from all pairs of spin orbitals in the diagonalization, is reformulated as a set of coupled matrix equations [Eq. (8), (13), and (14)] but decoupled pair correlations each separately calculated^{18,19b} are not discussed.

In the 1965 article²¹ which in part reviews and discusses the Sinanoğlu work, Nesbet (p. 355) states that the sum of decoupled pair correlations between Hartree-Fock spin orbitals would not be adequate in the neon atom and that here the remainder is likely to be especially large. His later calculations in the 1967 and later papers present the opposite conclusion.

Sinanoğlu¹⁶ considered that the "remainders" would be small compared to the sum of pair correlation energies in atoms like boron and neon. Although a number of calculations to test the relative magnitudes of these effects by the several step CI procedure on pp. 715 and 716 of Ref. 16 have been recently carried out, some going beyond the steps used by Nesbet, more such calculations would be worthwhile.

(6) An electron-pair bond type of notion for including correlation has appeared often in the chemical literature following Hurley, Lennard-Jones, and Pople.²⁴ Here correlations are considered to be important only in doubly occupied orbitals. The orbitals considered are often localized ones corresponding to bonds. A trial function, which is a product of N such pair functions, is assumed along with a special strong orthogonality of pairs. The restrictive nature of the assumptions of this approach has been discussed and criticized by Nesbet,²¹ Sinanoğlu,^{6,16} and Szász.²⁵ McKoy and Sinanoğlu,²⁶ Kelly,²⁷ Nesbet,^{18b} and others, in recent atomic correlation calculations, have shown that correlations between different orbitals, omitted in the Hurley, Lennard-Jones, and Pople method, can contribute as much as in doubly occupied orbitals.

(7) A variational procedure and effective equation for calculating the wave function of a pair of electrons moving in the Hartree-Fock potential of other electrons was first derived by Fock, Weselow, and Petrashen.²⁸ This procedure deals with the case of two electrons outside closed shells as in the Ca atom. This case is discussed further by Szász.²⁹ Again for the case of two electrons outside closed shells, Szász and his co-workers have written other interesting papers recently³⁰ on these equations which they refer to as "FWP" equations. They suggest the replacement of the effect of the cores by "pseudopotentials." Nesbet seems to refer also to the FWP procedure as "Bethe-Goldstone equations" in recent papers.

In other work,^{25,18-33} Szász has attempted to generalize the use of r_{ij} coordinates to atoms larger than helium. He does this by multiplying the Hartree-Fock function by an r_{ij} -containing correlation factor for each pair of electrons, then evaluating the expectation value of the total Hamiltonian of the atom. Configuration-interaction versions of such trial functions have occasionally been used also. The Nesbet (1958) paper,²³ mentioned above, also gives a discussion of an over-all CI with this trial function. The trial functions of Szász²⁵ and Nesbet²³ do not include the possible products of pair excitations.

Szász and Nesbet papers prior to those of Sinanoğlu do not deal with the notion of decoupled pair correlations each evaluated by itself by a separate minimization, whether it is with a single r_{ij} in the trial function or double excitations CI from a single pair. These papers do not demonstrate by physical arguments or by calculations the dominance of pair correlations. An efficient CI calculation on an atom like neon diagonalizing the Hamiltonian matrix with a wave function containing excitations from all pairs of electrons and with a sufficiently large basis set would be considerably more difficult than the Sinanoğlu¹⁶ suggestion of carrying out smaller CI calculations each containing double excitations from a given pair of Hartree-Fock spin orbitals at a time. This latter, simpler, procedure is what is carried out in Refs. 18 and 19. The Nesbet 1965 article²¹ passes without discussion from an over-all CI [Eq. (54)] to the Sinanoğlu pair-at-a-time CI [Eq. (61)], in spite of major and crucial differences in the two types of CI approximations.

The detailed discussion given above is intended to clarify possible confusion in the literature, on a subject which is of significance for the extension of theories of atomic spectra and other properties to include correlation effects. The Sinanoğlu papers^{5,6,16,22,26} originate and develop the simple and useful concept of treating an atom in its ground state in terms of $N(N-1)/2$ separate pair correlation energies each calculable by itself. These papers also provide mathematical and physical bases for the approximations involved as well as procedures for systematically going to higher effects. In more recent work, Sinanoğlu and co-workers

extend these methods to excited states and have indicated how additional effects may be taken into account. It would be worthwhile to test and develop these methods further, and to see to what extent a more quantitative theory of atomic spectra may be possible.

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