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## SYSTEMATICS OF ATOMIC CORRELATION ENERGIES

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**Résumé.** — Les énergies de corrélations des niveaux les plus bas des atomes de la première rangée et de leurs ions sont classées de façon commode suivant les diverses approximations qui permettent de dépasser le modèle Hartree-Fock. On examine plus particulièrement *la fonction de polarisation* définie par l'interaction de configuration incluant la fonction Hartree-Fock et toutes les configurations obtenues à partir de cette dernière par l'excitation d'une seule orbitale, et *la fonction d'onde du premier ordre*, qui en plus tient compte des effets dus à la présence d'orbitales de valence non occupées. Ces fonctions d'onde sont définies en termes d'excitation d'orbitales (plutôt que de spin-orbitales) et font intervenir des configurations dont chacune est une fonction propre à plusieurs électrons d'un moment angulaire. La fonction d'onde de polarisation est particulièrement utile dans l'estimation des paramètres de structure hyperfine. Les fonctions d'onde du premier ordre décrivent l'énergie de corrélation associée au mode d'occupation des orbitales. Nous appelons celle-ci énergie de corrélation *orbitale*. Le reste, ou énergie de corrélation *non orbitale*, peut être estimé empiriquement pour donner une bonne estimation des affinités électro-niques. Une évaluation directe de la plus grande part de l'énergie de corrélation non orbitale peut être obtenue à partir d'une *fonction d'onde du second ordre* ou des énergies de corrélation de paires calculées, comme le fait Nesbet, à partir des équations de Bethe-Goldstone. Les énergies de paires obtenues sont pratiquement cohérentes avec les énergies des fonctions d'onde du second ordre si on utilise des paires de *symétrie adaptée* c'est-à-dire, si les paires sont décrites par des fonctions propres du moment angulaire contenant deux orbitales excitées. Les énergies de paires de symétrie adaptée peuvent être aussi décomposées en incréments associés aux valeurs successives des nombres quantiques de moment angulaire orbital et ces incréments peuvent être utilisés pour étudier si la base des orbitales est angulairement complète.

**Abstract.** — The correlation energies of the low-lying states of first-row atoms and their ions are conveniently systematized in terms of various approximations beyond the restricted Hartree-Fock model. Of particular interest are the *polarization wavefunction*, defined by the configuration interaction including the Hartree-Fock function and all configurations which are orbitally singly-excited therefrom, and the *first-order wavefunction*, which in addition includes effects due to the presence of unoccupied valence orbitals. These wavefunctions are defined in terms of orbital (rather than spinorbital) excitation, and involve configurations each of which is an appropriate many-electron angular momentum eigenfunction. The polarization wavefunction is particularly useful in estimating hyperfine structure parameters. First order wavefunctions describe the correlation energy associated with orbital-occupancy patterns; we call this the *orbital* correlation energy. The remaining, or *nonorbital* correlation energy may be estimated empirically to give close estimates of electron affinities. Direct evaluation of most of the nonorbital correlation energy may be obtained from a *second-order wavefunction* or from pair correlation energies calculated, following Nesbet, from Bethe-Goldstone equations. The pair energies are very nearly consistent with the energies of second-order wavefunctions if *symmetry-adapted* pairs are used, i. e. if the pairs are described by angular-momentum eigenfunctions containing two excited orbitals. Symmetry-adapted pair energies can also be decomposed into increments associated with successive orbital angular momentum quantum numbers, and these increments can be used to study the angular completeness of orbital basis sets.

**Introduction.** — Although the conventional restricted Hartree-Fock (RHF) model can be very successful in providing a nearly quantitative description of atomic charge distributions, it is necessary to consider electron-correlation effects to obtain consistently good values for the energies of atomic states. Electron correlation has been treated both by perturbation — theoretic and direct configuration — interaction (CI) methods, and at least for light atoms both approaches seem capable of yielding satisfactory results. A part of the correlation

energy can be obtained by removing some of the restrictions of the usual RHF model [1]. Calculations indicate, however, that near-quantitative accuracy is not reached in this way [2].

This communication will be primarily concerned with both direct and perturbative methods based on configuration-interaction calculations. It will seek to indicate the relationships and accuracy of various procedures, and to survey the current situation. In particular, it will examine the approaches of Sinanoglu [3] and of Nesbet [4] and the calculations

of these investigators, the author's group, and others. The discussion will omit one area of considerable current interest, namely the use of Brueckner-Goldstone perturbation-theoretic methods which has been pioneered by Kelly [5] and extensively utilized by his group and that of Das [6].

A main conclusion of this paper is that the best results are obtained from procedures which are systematic and which exhibit a well-defined degree of approximation. It is shown to be of particular value to maintain the symmetry of states throughout a calculation. It is also illustrated how the results of *ab initio* calculations can be supplemented by the judicious incorporation of relevant experimental results.

**CI wavefunctions.** — As indicated in the introduction, all the work referred to in this paper is based on various configuration-interaction calculations. The CI wavefunctions used in these calculations all contain as a dominant part the RHF function, which for most atomic states can be represented as an antisymmetrized product of spinorbitals, i. e. as a single Slater determinant. There are two main possibilities for the further definition of a CI wavefunction, of which the older and more used is to identify its remaining terms as the determinants formed by spin-orbital excitations from the RHF determinant. This identification requires for each term a specification as to which RHF spinorbitals have become unoccupied and as to the additional spinorbitals which are occupied in their stead.

The determinants forming a CI wavefunction are not all individually eigenfunctions of the orbital and spin angular momenta  $L^2$  and  $S^2$ , and in some of the more recent work CI wavefunctions have been constructed using angular-momentum eigenfunctions produced by *LS*-projection of determinants. The projection causes all possible  $m_l$  and  $m_s$  values to be associated with each spatial orbital, so that it no longer makes sense to identify CI terms by their spin-orbital excitations, and the angular symmetry describing excitations must be limited to the  $l$  quantum numbers. The *LS*-projected determinants are referred to as *configurations* [7], and the excited configurations will in general consist of linear combinations of determinants. The use of configurations guarantees that a CI wavefunction will maintain the necessary angular symmetry.

It is of course possible to construct CI wavefunctions starting from independent-electron functions which are better than the RHF function. In particular, one might start from projected Hartree-Fock calculations in which maximum double occupancy of spatial orbitals is no longer required. The wavefunctions resulting from such calculations are not built from orthogonal orbitals and this introduces practical difficulties which make the RHF function a more attractive starting point. The main improvements

obtainable by improved independent-electron methods are easily recovered in CI, so no serious drawback is associated with starting from the RHF function.

The accuracy of a CI wavefunction depends upon the kinds of configurations which are included and upon the choice of the orbital basis set. The choice of configurations is one of the main topics of the present discussion and will be treated later at length. For CI calculations to yield definitive results, it is necessary that the orbital basis set be in a practical sense complete. This is achieved by starting with the RHF orbitals (obtained by direct calculation or from published results), and adding to the basis set additional Slater-type orbitals of a comparable scale but with increasing numbers of nodes, both radial and angular. The orbitals added in this way bear little resemblance to excited-state orbitals, as their function is to enable correlation of electrons which are spatially well described by the RHF orbitals. Orbital with additional radial nodes automatically result from orthogonalization of the added basis functions to each other and to the RHF orbitals. It is not of particular importance to increase the principal quantum number but is more vital to avoid near linear dependence. One good way to obtain appropriate orbitals is to choose their exponential screening parameters  $[\zeta \text{ in } \exp(-\zeta r)]$  so that their maximum radial densities are equally spaced and in the region of significant density for the orbital whose correlation they are expected to help describe. Experience indicates that orbitals containing up to four additional radial nodes suffice for a nearly quantitative description of the largest correlation effects; smaller correlation effects are adequately handled with about two extra radial nodes. About three extra angular nodes are needed for high accuracy; this point is illustrated by results to be quoted later. Thus, for an atom whose RHF function contains  $s$  electrons the basis set should contain  $s$ ,  $p$ ,  $d$  and  $f$  orbitals; if  $p$  orbitals are present in the RHF function the basis should really contain  $g$  orbitals as well.

The simplest well-defined CI wavefunction of proper symmetry consists of the RHF function and all *configurations* which are singly-excited therefrom. According to Brillouin's theorem, singly-excited configurations which maintain the orbital symmetries will not mix with the RHF function, so that the configurations of importance here are those in which an orbital symmetry changes. Such configurations will only exist for open-shell atomic states. For such states, these configurations enable the description of spin polarization and other effects associated with the removal of orbital symmetry restrictions, and for that reason this CI function has been called the *polarization* wavefunction [7]. Just as for the RHF function, it is implicit in the discussion that the basis set will be complete enough that further additions will not produce significant changes. The extent to which this completeness is achieved determines the closeness to

which the polarization wavefunction is approximated. The polarization wavefunction will in general contain determinants in which more than one spinorbital is occupied differently than in the RHF function, as such spinorbital assignments can result from the action of the LS projector. In fact, such determinants are essential to the effectiveness of the polarization wavefunction. For example, in the ground state of boron, whose RHF configuration can be described as  $1s^2 2s^2 2p^2 P$ , the polarization wavefunction contains configurations such as  $1s^2 2s 2pd^2 P$ , which consists of several determinants differing among other things in the  $m_l$  value of the  $2p$  orbital. The  $s \rightarrow d$  promotion in boron makes an important contribution to the correlation energy, as it removes the inappropriate restriction of the individual orbitals to pure angular symmetry.

More complete CI functions than the polarization wavefunction may be obtained by including configurations involving those multiple excitations which may be expected to be most important. The smallest group of such configurations are those in which the multiple excitations are among nearly degenerate orbitals, as illustrated by the excitation from the  $1s^2 2s^2 {}^1S$  ground state of beryllium to the configuration  $1s^2 2p^2 {}^1S$ . Such effects are provided for by defining a *first-order wavefunction* [8] consisting of the RHF function, all configurations involving excitations to unoccupied orbitals within the atom's valence shell, and all configurations singly-excited from those previously enumerated.

The first-order wavefunction contains all the configurations whose existence depends directly on the atomic shell structure and orbital symmetry assignments, and therefore presumably would yield results of comparable accuracy for both open and closed-shell atomic states. The correlation energy associated with the first-order wavefunction has accordingly been called the *orbital* correlation energy, with the remainder of the correlation energy referred to as *nonorbital*.

The logical extension of the first-order wavefunction is to include all configurations involving double excitations beyond an atom's valence shell. The wavefunction thereby produced is called the *second-order* wavefunction. Second-order wavefunctions should describe the bulk of the electron correlation, including both structure-dependent and other contributions.

In the actual execution of second-order calculations, it is found that the number of possible configurations can easily outstrip the capacities of even the largest computers. It is therefore necessary in practice to limit the number of configurations by truncation of the orbital basis set. This can be done without compromising the quality of the calculations by using pseudo-natural orbitals (PNO's) [9]. Such techniques have been pioneered by Bunge and Bunge [10]. The PNO's are found by transforming the orbital

basis to the most efficient form for describing the correlation of a particular pair of electrons, and nearly the entire correlation energy of that electron pair can be reproduced from relatively few PNO's. By using PNO's appropriate to electron pairs from each atomic shell, a good second-order calculation can be made using a relatively small basis. The completeness of the calculation is assured by having a sufficient basis prior to the PNO transformations.

**Perturbation calculations.** — The perturbation calculations to be examined here are of the Bethe-Goldstone type, in which the total correlation energy is partitioned into single-electron, two-electron, ... contributions which are assumed to be additive. Following in a general way the approach of Nesbet [4], there results a hierarchy of Bethe-Goldstone calculations of which the last, involving the contribution of all electrons together to the correlation energy, is exact. In practice the hierarchy is almost always carried only through the two-electron contribution, and it then describes a situation in which electron-pair correlations are assumed to be additive.

A single-electron or electron-pair Bethe-Goldstone calculation can be carried out by making a CI in which only the electron (s) under consideration are excited out of the RHF orbitals. As in ordinary CI calculations there are two ways in which these CI's have been defined. In the original work of Nesbet, the excitations were of specific spinorbitals to form singly or doubly excited determinants, and this leads to what will be called here *standard* Bethe-Goldstone calculations. The alternative is to use singly or doubly excited configurations, leading to what will be called here *symmetry-adapted* Bethe-Goldstone calculations [11].

The standard and symmetry-adapted calculations differ in two significant ways. First, the number of standard contributions of given order is larger than the number of symmetry-adapted contributions of the same order, thereby placing more strain upon the additivity assumption. Secondly, the CI calculations for the standard calculations do not produce LS eigenfunctions, in contrast to the symmetry-adapted calculations. The first of these differences is well illustrated by the pair calculations for neon. There are 45 standard pairs ( $1s\alpha 1s\beta$ ,  $1s\alpha 2s\alpha$ ,  $1s\alpha 2s\beta$ ,  $1s\alpha 2p_0\alpha$ ,  $1s\alpha 2p_0\beta$ , ...), while there are only six, symmetry-adapted pairs ( $1s 1s$ ,  $1s 2s$ ,  $1s 2p$ ,  $2s 2s$ ,  $2s 2p$ ,  $2p 2p$ ). An example of the second difference is provided by the  $1s\alpha 2s\beta$  pair, which cannot yield an LS eigenfunction without configurations coming from the  $1s\beta 2s\alpha$  pair.

**Results and discussion.** — It is well known that nonsystematic CI calculations can give erratic results for many physical properties, with variations arising from the choice of both basis set and configurations. A main advantage of the systematic CI formulations

described here is that, if carried out adequately, they are free of any dependence on basis set choice and represent a degree of approximation dependent only on the classes of configurations which are included or excluded. It is for this reason that even the simpler of the CI wavefunctions defined here are sufficient for a number of uses. Polarization wavefunctions, though totally incapable of describing electron-electron interactions, are relatively effective in correcting some defects of the RHF model. They give good values of hyperfine structure parameters, including qualitatively satisfactory spin densities [7]. For such uses, first-order wavefunctions do not produce much improvement over polarization wavefunctions, but the first-order functions provide a more systematic starting point for correlation studies.

As already indicated, first-order wavefunctions yield the directly structure-dependent, or *orbital* correlation energy. The possibility of identifying this part of the correlation energy was also noticed by Sinanoglu and Öksüz [12], who gave the names «internal» and «semi-external» to determinants involving zero or one excitation beyond the valence shell. However, the numerical results obtained by Sinanoglu and Öksüz are not directly comparable with those to be cited here because those workers made no serious attempt to approach basis set completeness.

TABLE I  
*Orbital and nonorbital correlation energies (hartrees)*  
*Data from Reference [13]*

State	Orbital Correlation Energy	Nonorbital Correlation Energy
C( <sup>3</sup> P)	- 0.062 1	- 0.091 6
N( <sup>4</sup> S)	- 0.055 7	- 0.127 9
N( <sup>2</sup> P)	- 0.066 2	- 0.158 7
O <sup>+</sup> ( <sup>4</sup> S)	- 0.061 1	- 0.125 1
O <sup>+</sup> ( <sup>2</sup> P)	- 0.076 2	- 0.156 1
O( <sup>3</sup> P)	- 0.049 6	- 0.200 3
F( <sup>2</sup> P)	- 0.030 4	- 0.279 6

The original hope motivating the classification of correlation energy into orbital and nonorbital parts was that the latter would be relatively free of dependence on the details of the structure of the atomic state, but would depend smoothly upon the nuclear charge and the number of electrons. This hypothesis can be checked, as the total correlation energies of many first-row atoms and ions are experimentally known and the corresponding orbital correlations can be readily calculated. Such calculations have now been carried out [13], giving results of the sort illustrated in Table I. The data show that the nonorbital correlation energy does not at all conform to the hoped-for behavior. Instead, the nonorbital correlation energy is seen to be strongly and irre-

regularly dependent upon the symmetry of the state and the number of electrons, and in many cases exhibits more dependence on these quantities than does the supposedly more structure-dependent orbital correlation energy. However, the nonorbital correlation energy does have an useful regularity, namely its dependence (for a particular state) on the nuclear charge.

The fact that the nonorbital correlation energy has a weak and slowly-varying nuclear-charge dependence has been used as a starting point for the semi-empirical estimation of electron affinities [13]. The nonorbital correlation energy of a negative ion is estimated by extrapolation from the known values for the isoelectronic neutral atom and positive ion, while the negative ion's orbital correlation energy is directly calculated. This method leads to electron affinities as listed in Table II. The agreement with known affinities is quantitative, suggesting a high degree of reliability for the other estimated affinities.

TABLE II

*Electron Affinities (eV) predicted from calculated orbital and estimated nonorbital correlation energies*  
*Data from Reference [13]*

	Predicted	Experimental
F( <sup>2</sup> P) → F <sup>-</sup> ( <sup>1</sup> S)	+ 3.453	3.448 ± 0.005
O( <sup>3</sup> P) → O <sup>-</sup> ( <sup>2</sup> P)	+ 1.461	1.465 ± 0.005
C( <sup>3</sup> P) → C <sup>-</sup> ( <sup>4</sup> S)	+ 1.242	1.25 ± 0.03
N( <sup>4</sup> S) → N <sup>-</sup> ( <sup>3</sup> P)	- 0.213	—
N( <sup>2</sup> D) → N <sup>-</sup> ( <sup>1</sup> D)	+ 0.844	—
B( <sup>2</sup> P) → B <sup>-</sup> ( <sup>3</sup> P)	+ 0.187	—

Logically better than an estimation of nonorbital correlation energies would be their calculation, and a large step towards so doing would be to use second-order wavefunctions. The few second-order calculations thus far carried out do yield almost all the nonorbital correlation, but because of the size of the calculations it makes sense to search for alternatives such as are provided by perturbation approaches. The perturbation studies which are comparable to the second-order wavefunction are the pair calculations, and accordingly both the direct second-order and the pair CI's will now be discussed together.

As first shown by Nesbet [4], pair CI's produce energies which very nearly add to the full correlation energy. This conclusion applies whether standard or symmetry-adapted pairs are used. However, the different types of pair calculation do yield slightly different results, and, as pointed out by Barr and Davidson [14], the results can also be altered by taking the pair excitations from any orbitals produced by a unitary transformation among the standard RHF orbitals (this does not change the RHF function). The ambiguity with respect to unitary transformation may be rather important in molecules where the RHF

orbitals can often be transformed to far more localized forms, but is minimal in practice for lighter atoms, where symmetry considerations remove much of the orbital arbitrariness.

The difference between standard and symmetry-adapted pair calculations can be definitively studied only if both calculations are done using the same basis. Such a study has been carried out for neon [15], where the symmetry-adapted pairs were found to give about 10 % less correlation energy than the standard pairs. The significance of these results becomes clearer if both are compared with the direct second-order calculation, which shows that the pair correlations deviate from additivity by about 2 % for the symmetry-adapted pairs and by about 12 % for the standard pairs. The standard pairs exhibit the larger deviation for reasons already cited, namely that more contributions must be assumed to be independent, including contributions which should be strongly coupled because of angular symmetry.

Comparison of pair and second-order calculations with experiment can also produce information as to the importance of triple and higher excitations. The calculations used for the discussion of the preceding paragraph are not quite complete enough to give authoritative comparisons with experiment, and for this purpose it is appropriate to turn to the recent calculations of Barr and Davidson [14] and Bunge and Peixoto [16]. Both these authors, after exhaustive comparison of pair, second-order, and more complete CI studies among themselves and with experiment, come to the conclusion that the standard pair calculations in neon may overestimate the correlation energy by as much as 10 %, and that a good second-order calculation should yield all but about 2 % of the

correlation energy. This leads to the further conclusion that a complete symmetry-adapted pair calculation would give almost the exact experimental energy, with its deviations from pair additivity fortuitously cancelling almost the entire effect of triple and higher excitations. It is not yet known how precisely these conclusions apply to open-shell atoms.

In analyzing the various CI-based calculations, it is also important to be systematic in determining the effective degree of completeness of the basis set, particularly with respect to the angular quantum numbers. One way of investigating this question is to break down the various pair energies into s, p, d, ... contributions. After an initial irregularity related to the angular symmetries of the orbitals being excited from, the pair energy increments from higher angular quantum numbers decrease regularly and it becomes possible to estimate truncation errors. This point is well illustrated by the recent neon calculations [14, 16], and Bunge and Peixoto have been particularly thorough in their analysis. They conclude that about 9 % of the neon correlation energy comes from orbitals of g and higher orbital angular momentum; their methods indicate a probable uncertainty of up to about 1.5 %.

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#### References

- [1] POPLE (J. A.) and NESBET (R. K.), *J. Chem. Phys.*, 1954, **22**, 571 ; LÖWDIN (P. O.), *Phys. Rev.*, 1955, **97**, 1509.
- [2] See, for example, KALDOR (U.), *J. Chem. Phys.*, 1968, **48**, 835 ; *Phys. Rev.*, 1968, **176**, 19 ; GODDARD (W. A.), *Phys. Rev.*, 1969, **182**, 48 ; KALDOR (U.) and HARRIS (F. E.), *Phys. Rev.*, 1969, **183**, 1.
- [3] SINANOĞLU (O.), *J. Chem. Phys.*, 1962, **36**, 706.
- [4] NESBET (R. K.), *Phys. Rev.*, 1967, **155**, 51 ; 1967, **155**, 56 ; 1968, **175**, 2.
- [5] KELLY (H. P.), *Phys. Rev.*, 1963, **131**, 684 ; 1964, **136**, B 896 ; 1966, **144**, 39.
- [6] See, for example, DUTTA (N. C.), MATSUBARA (C.), PU (R. T.) and DAS (T. P.), *Phys. Rev. Letters*, 1968, **21**, 1139.
- [7] SCHAEFER (H. F.), KLEMM (R. A.) and HARRIS (F. E.), *Phys. Rev.*, 1968, **176**, 49.
- [8] SCHAEFER (H. F.), KLEMM (R. A.) and HARRIS (F. E.), *Phys. Rev.*, 1969, **181**, 137.
- [9] EDMISTON (C.) and KRAUSS (M.), *J. Chem. Phys.*, 1966, **45**, 1833.
- [10] BUNGE (A. V.), THESIS (Ph. D.), U. of Florida 1968 ; BUNGE (A.) and BUNGE (C. F.), *Phys. Rev.*, 1970, **A 1**, 1599.
- [11] SCHAEFER (H. F.) and HARRIS (F. E.), *Phys. Rev.*, 1968, **167**, 67.
- [12] SINANOĞLU (O.) and ÖKSÜZ (I.), *Phys. Rev. Letters*, 1968, **21**, 507.
- [13] SCHAEFER (H. F.), KLEMM (R. A.) and HARRIS (F. E.), *J. Chem. Phys.*, 1969, **51**, 4643.
- [14] BARR (T. L.) and DAVIDSON (E. R.), *Phys. Rev.*, 1970, **A 1**, 644.
- [15] VIERS (J. W.), HARRIS (F. E.) and SCHAEFER (H. F.), *Phys. Rev.*, 1970, **A 1**, 24.
- [16] BUNGE (C. F.) and PEIXOTO (E. M. A.), *Phys. Rev.*, 1970, **A 1**, 1277.