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SYSTEMATICS OF ATOMIC CORRELATION ENERGIES

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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-Gold-
stone 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 intro-
duction, 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 possi-
bilities 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 specifi-
cation 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 con-
structed using angular-momentum eigenfunctions pro-
duced by \( LS \)-projection of determinants. The projec-
tion causes all possible \( m_l \) and \( m_s \) values to be asso-
ciated with each spatial orbital, so that it no longer
makes sense to identify CI terms by their spinorbi-
tal excitations, and the angular symmetry describ-
ing 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 deter-
minants. 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 calcula-
tions 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 method
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 practica-
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 lit-
lar resemblance to excited-state orbitals, as their func-
tion is to enable correlation of electrons which are spa-
tially 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 particu-
lar importance to increase the principal quantum
but is more vital to avoid near linear dependence.
One good way to obtain appropriate orbitals is to
choose their exponential screening parameters \( [c_i\mathrm{e}^{\xi r}] \) so that their maximum radial density
are equally spaced and in the region of significan-
density for the orbital whose correlation they are
expected to help describe. Experience indicates that
orbitals containing up to four additional radial node
suffice for a nearly quantitative description of the
largest correlation effects; smaller correlation effects
are adequately handled with about two extra radi-

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 \( s, p, \delta \) and \( f \) orbitals; if \( p \) orbitals are presen-
in the RHF function the basis should really contain \( f \)
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 con-
figurations 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 this
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 
ls² 2s² 2p² 2p, the polarization wavefunction 
contains configurations such as Is² 2s 2p½ 2p, which 
consists of several determinants differing among other 
things in the m½ value of the 2p orbital. The s → d 
promotion in boron makes an important contribution 
to the correlation energy, as it removes the inappro-
priate restriction of the individual orbitals to pure 
angular symmetry. 

More complete CI functions than the polarization 
wavefunction may be obtained by including config-
urations 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 
ls² 2s² ½S ground state of beryllium to the configu-
ration ls² 2p² ½S. Such effects are provided for by 
defining a first-order wavefunction [8] consisting of 
the RHF function, all configurations involving exci-
tations 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 config-
urations whose existence depends directly on the 
atomic shell structure and orbital symmetry assign-
ments, 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 exci-
tations beyond an atom’s valence shell. The wave-
function 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 calcula-

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 calcula-
tions 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 (1s½ 1s½, 1s½ 2s½, 1s½ 
2p½, 1s½ 2p½z, 1s½ 2p½y, ...), while there are only six, 
symmetry-adapted pairs (1s 1s, 1s 2s, 1s 2p, 2s 2s 
2p 2p). An example of the second difference is 
provided by the 1s½ 2p½ pair, which cannot yield 
an LS eigenfunction without configurations coming 
from the 1s½ 2s½ pair. 

Results and discussion. — It is well known that 
systematic 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] |

<table>
<thead>
<tr>
<th>State</th>
<th>Orbital Correlation Energy</th>
<th>Nonorbital Correlation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(2P)</td>
<td>-0.062</td>
<td>-0.091</td>
</tr>
<tr>
<td>N(2S)</td>
<td>-0.055</td>
<td>-0.127</td>
</tr>
<tr>
<td>N(2P)</td>
<td>-0.066</td>
<td>-0.158</td>
</tr>
<tr>
<td>O*(2S)</td>
<td>-0.061</td>
<td>-0.125</td>
</tr>
<tr>
<td>O*(2P)</td>
<td>-0.076</td>
<td>-0.156</td>
</tr>
<tr>
<td>O(3P)</td>
<td>-0.049</td>
<td>-0.200</td>
</tr>
<tr>
<td>F(2P)</td>
<td>-0.030</td>
<td>-0.279</td>
</tr>
</tbody>
</table>

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 energies 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 irregularly 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 energy |
| Data from Reference [13] |

<table>
<thead>
<tr>
<th>Predicted</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(2P) $\rightarrow$ F$^-$(2S)</td>
<td>+ 3.453</td>
</tr>
<tr>
<td>O(2P) $\rightarrow$ O$^-$(2P)</td>
<td>+ 1.461</td>
</tr>
<tr>
<td>C(2P) $\rightarrow$ C$^-$(2S)</td>
<td>+ 1.242</td>
</tr>
<tr>
<td>N(2S) $\rightarrow$ N$^-$(2P)</td>
<td>- 0.213</td>
</tr>
<tr>
<td>N(2D) $\rightarrow$ N$^-$(2D)</td>
<td>+ 0.844</td>
</tr>
<tr>
<td>B(2P) $\rightarrow$ B$^-$(2P)</td>
<td>+ 0.187</td>
</tr>
</tbody>
</table>

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 Nesbitt [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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