In addition to this g type of in-out correlation, there is an additional in-out correlation provided by additional terms of the σ_u type after the first one. This is, however, essentially impossible to separate from left–right correlation energy since it is not clear whether the energy improvement occurs from the off-diagonal interaction with the major σ_g terms (left-right correlation) or the interaction with the major σ_u term (in-out correlation) or both. It seems most likely to be the former, however, and we lump it together with that type in the following.

The next interesting case is the limiting best function which retains only axially symmetric orbitals for basis functions. That is, the $(\sigma_g + \sigma_u)$, or Σ limit. This is the function which James and Coolidge[11] identified as the best function using only four essential coordinates [omitting r_{12} in their case, $(\varphi_2 - \varphi_1)$ in ours]. Whereas James and Coolidge reported -1.1577 H for this limit, we find -1.160876 H for our best function of this type (No. 20). The total Σ correlation energy in III is, therefore, 0.0276 H, somewhat higher than but still close to the figure of 0.0239 H predicted from a symmetrical division of correlation energy of the He atom.[10] Actually, the total Σ correlation energy is probably somewhat greater than this ($\sim$0.0286 H) since it seems clear that the chief deficiency of function III is in the $\sigma\sigma$ terms. DJ[7] report a Σ-type function with energy -1.161695 H.

Comparing calculations No. 20 and No. 26, we find an improvement in adding π_u terms of 0.0110 H. An additional contribution of 0.00085 H results from adding π_g terms (No. 26–No. 28), for a total π correlation energy contribution of about 0.012 compared to 0.015 suggested from He.[10] Clearly left-right correlation in H_2 is more important than is computed from the united atom description of the molecule, and correspondingly up-down or axial correlation is less important. This is a not unreasonable result considering the increasing importance that left-right correlation has with increasing internuclear distance and the decreasing importance of angular correlation for large distances.

Finally, we should mention the Δ term (28–30) of 0.000535 H. DJ obtained an improvement of 0.000477 H upon adding their first δ_g term. In He, terms of this type contribute 0.00116 to the correlation energy, so once again we see the decreased importance of axial correlation in H_2 as compared to the same type of correlation in He. It should be noted, however, that the total correlation energy is very nearly the same in the two cases, and He may still be retained as a very good model for H_2.[12]

As Davidson and Jones point out, there is a noticeable break in the energy contribution produced by additional natural orbitals after the fourth term has been added. This four term function (No. 22) in our case had an energy of -1.169785 H. DJ report a slightly better limiting energy of -1.169969, which is a remarkably good result for such a simple function.

In conclusion, it can be said that the present calculations have confirmed in detail previous surmises about (a) the invariance of the natural orbital expansion, (b) its utility in wave-function comparison, (c) the similarities between He and H_2, (d) the rough additivity of correlation energies of different types. The calculations provide detailed natural orbitals which should be useful in a variety of other calculations in which one is primarily exploring the effects of a systematic rapidly convergent improvement in the nature of the wave-function expansion.

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[11] H. M. James and A. S. Coolidge, J. Chem. Phys. 1, 825 (1933).

[12] Hagstrom (reference 3) has also considered the effect of adding φ_u basis orbitals and found that a single (φ_u, φ_u) term added to the 33-term function of Case III gave an improvement of <0.00001 H.

Discussion on Natural Expansions and Properties of the Chemical Bond

F. Harris, *Chairman*

Nesbet: What are the symmetry properties of the natural spin-orbitals?

Löwdin: A theorem was presented at the Madison Symposium in 1956 about the symmetry properties of the natural spin-orbitals stating that they are symmetry-adapted. [See P. O. Löwdin, J. Phys. Chem. **61**, 55 (1957).] The basic theorem says that, if there is a normal constant of motion Λ commuting with the total Hamiltonian $\mathcal{H}$ which is built up from one-electron operators $\Lambda(i)$ by means of the sum

$$\Lambda = \textstyle\sum_i \Lambda(i)\ , \tag{1}$$

or by means of any other fundamental symmetric function of the one-electron operators, including the product $\Lambda(1)\Lambda(2)\cdots\Lambda(N)$, then the natural spin-orbitals associated with an exact or approximate eigenfunction Ψ to $\mathcal{H}$ are always eigenfunctions to $\Lambda(1)$ or (in the case of degenerate occupation numbers) can be chosen that way, provided Ψ is an exact eigenfunction to Λ.

The proof has been given every year at the summer and winter institutes and is very simple. The total wave function Ψ may be written as a superposition of Slater determinants D_K formed from a complete basis of one-electron functions which are chosen as eigenfunctions to $\Lambda(1)$. Such a basis is simply constructed from any complete basis by means of projection technique. Each determinant is then also an eigenfunction to Λ associated with the eigenvalue under consideration. Since this total eigenvalue is a linear, symmetric function of the one-electron eigenvalues, it is clear that two determinants have either the same set of one-electron eigenvalues or differ in at least two eigenvalues. In the latter case, the combination of the two determinants will not give any contribution to the first-order density matrix depending on orthogonality, and this means that this matrix is already partly diagonalized in the representation chosen. Any further diagonalizing will not change the fact that the orbitals are already eigenfunctions to the one-electron operator $\Lambda(1)$.

This proof is directly applicable to angular momenta, translations, cyclic operators, and abelian groups, whereas, for the point groups, the terminology and the proof have to be slightly modified by letting the complete basis introduced instead transform properly corresponding to the irreducible representations. Again, one finds that the natural spin-orbitals are symmetry adapted.

This theorem is of importance, since it tells us that certain one-electron properties connected with $\Lambda(1)$ will be preserved and have a meaning even in the exact many-electron theory. It tells us that, if S_z is a good quantum number, the natural spin-orbitals will be of either α- or β-type. In a conjugated system with planar symmetry and the reflection σ_z as a constant of motion, the natural spin-orbitals will necessarily be either σ-orbitals or π-orbitals, and the total number of π-electrons is, for instance, a well defined quantity, even if it may differ from being an integer. Finally, in solid-state physics, the reduced wave vector k represents a one-electron property which will be preserved also in the exact theory together with such concepts as "effective mass," etc. which is very important. [See P.-O. Löwdin, J. Appl. Phys., Suppl. **33**, 251 (1962)].

DAVIDSON: The natural expansion of the Kolos and Roothaan wave function for H_2 illustrates the utility of natural orbitals for a two-electron system. The natural expansion of Ψ has the form

$$\Psi = \sum_i C_i^1 \alpha_i(1)\bar{\alpha}_i(2) ,$$

where, if C_1^1 is chosen positive, C_i^1 is negative for $i > 1$. The occupation numbers for the first five orbitals are in surprisingly close agreement with those obtained by Shull for simpler wave functions.

In this expansion, it turns out that two logical levels of approximation appear. The first of these involves one configuration and gives virtually the SCF energy. The next involves three additional configurations describing correlation in the three space coordinates and gives 90% of the correlation energy. Beyond this point the expansion converges more slowly and involves terms designed mostly to fit the local correlation hole.

The natural orbitals can also be found from the eigenvalue equation

$$[(\mathbf{1} \otimes X^T)(H + HTH)(\mathbf{1} \otimes X)]\, X = EX ,$$

where X is the coefficient vector for a natural orbital. Here,

$$H = \int \phi(1) \otimes \phi(2)\mathcal{H}_{\mathrm{op}}\phi^T(\cdots)(1) \otimes \phi^T(\cdots)(2)dT_1dT_2 ,$$

and T is the matrix defined by Löwdin with $0 = XX^T$. This method was tried at the Theoretical Chemistry Institute, University of Wisconsin, with only 4 basis functions and was found to give rapid convergence. Unfortunately, with a basis set of N functions the calculation of T involves inverting an $N^2 \times N^2$ matrix iteratively. [F. R. Davidson and L. L. Jones, J. Chem. Phys. **37**, 1616 (1962)].