Theor Chem Acc (2000) 103:228–230
DOI 10.1007/s002149900076

Theoretical
Chemistry Accounts

Perspective

Perspective on "Quantum theory of many-particle systems I, II, and III"

Löwdin P-O (1955) Phys Rev 97:1474–1520

Björn O. Roos

Department of Theoretical Chemistry, Chemical Center, P.O. Box 124, S-221 00 Lund, Sweden

Received: 26 February 1999 / Accepted: 1 July 1999 / Published online: 4 October 1999

Abstract. The title paper is reviewed in perspective of the later development of computational methods in quantum chemistry. The importance of the concept of natural spin orbitals is discussed and its implication for the future development of multiconfigurational self-consistent-field theories is illustrated.

Key words: Natural orbitals – Configuration interaction – Multiconfigurational self-consistent-field

---

1 Introduction

The material we see first, the first books we read, and the first articles we encounter, will probably have a strong and may be decisive influence on how we develop our attitude to the scientific field we are working in. One of the first things I did as a young student was to travel the 70 km to Uppsala and take part in the 1961 summer school in quantum chemistry organized by Per-Olov Löwdin and the Uppsala Quantum Chemistry Group. It was in many ways an overwhelming experience. Löwdin was an excellent lecturer and to listen to his explanations of the foundations of quantum chemistry made you believe that it was all very simple, logical, and straightforward. When I therefore half a year later saw the green reprint of the title article(s) on the desk of my supervisor in Stockholm, I borrowed it from him. I have not yet returned it.

What Löwdin published in 1955 (the manuscripts were received in July that year) was a series of three articles under a common heading: *Quantum theory of many-particle systems*. The three parts had the following subtitles: I. Physical interpretation by means of density matrices, natural spin-orbitals, and convergence problems in the method of configuration interaction; II. Study of the ordinary Hartree–Fock approximation; and III. Extension of the Hartree–Fock scheme to include degenerate systems and correlation effects. Without doubt the first article has had the greatest impact, but also in the two others is it possible to find little pearls that act as precursors for later developments of computational strategies in quantum chemistry. These articles had a profound influence on my own development, especially on the way I came to think about the molecular orbital (MO) concept in conjunction with accurate wave functions and configuration interaction (CI).

2 Natural spin orbitals

The single concept, which is defined and discussed in these articles, that without doubt has had the most penetrating impact on the whole field of quantum chemistry, is the concept of the natural spin orbitals. This concept is, in principle, very simple: the set of MOs that makes the first-order density matrix diagonal. Löwdin starts out by defining a hierarchy of reduced density matrices for a general wave function:

$$\Gamma^{(p)}(x_1'x_2'\ldots x_p'|x_1x_2\ldots x_p) = \binom{N}{p}\int \Psi(1'2'\ldots p'\ldots N)\Psi(12\ldots p\ldots N)\,\mathrm{d}x_{1'2'\ldots p'} \quad (1) .$$

He goes on to show that for the description of the energy it is sufficient to know the second-order reduced density matrix $\Gamma(x_1'x_2'|x_1x_2)$. This was a favorite subject when he was lecturing and led to speculations about the possibility to compute the second-order density matrix directly, and discussions of the so called N-representability problem. In spite of several attempts, this way of attacking the quantum chemical many-particle problem has so far been unsuccessful. Of special interest was the first-order reduced density matrix, $\gamma(x_1'|x_1)$, which when expanded in a complete one-electron basis, ψ, is obtained as

$$\gamma(x_1'|x_1) = \sum_{k,l}\psi_k^*(x_1')\psi_l(x_1)\gamma(l|k) \ , \qquad (2)$$

where we use Löwdin's own notation. The matrix $\gamma(l|k)$ was identified as the charge and bond order matrix used earlier by Coulson and Longuet-Higgins (I will not repeat all the references given by Löwdin. They can be found in the article). The diagonal elements were interpreted as a measure of the occupation of a given spin orbital and it was shown that this always lies between 0 and 1, or more generally

$$0 \leq \gamma(k|k) \leq 1; \quad Tr(\gamma) = N \ . \tag{3}$$

2.1 Configuration interaction

Löwdin now makes a detour to discuss the method of CI. He expands the wave function in the set of Slater determinants that can be formed from the one-electron basis, ψ. He introduces the word complete CI to emphasize that the expansion is, in principle, exact. We have since learned to use the expression full CI in the case where the one-electron basis is finite (Löwdin made a sarcastic comment about our use of the word complete in the complete active space (CAS) concept at a Sanibel Conference in 1980). He computes the matrix elements between the Slater determinants without assuming orthogonality between the MOs. These are the famous Löwdin matrix elements, which generalized the Slater formulae to the nonorthogonal case.

The method of CI is outlined in all detail. Of course, he was not the first person to do this. Small CI calculations had been performed in the 1930s and he himself refers to the work of Boys and others and notes "that have overcome the numerical, difficulties by aid of electronic computers," but for me it was the first time I saw the CI method outlined in a systematic and detailed fashion. He also states that "one can solve secular equations of comparatively high orders by means of the modern electronic computers and one can expect a steady development of the methods of programming, etc." One might recall that at this time such a view of the future was not uncontroversial. He finally points out that there is a need for a simple physical interpretation of the complicated CI wave function. The tool are the natural orbitals (NOs).

2.2 The natural spin orbitals

The orbitals that diagonalize the first-order reduced density matrix are the natural spin orbitals χ:

$$\gamma(x_1'|x_1) = \sum_k \chi_k^*(x_1')\chi_k(x_1)\eta_k \ , \tag{4}$$

where η_k is the occupation number of natural spin orbital k with the property

$$0 \leq \eta_k \leq 1; \quad \sum_k \eta_k = N \ . \tag{5}$$

He notices that the relation $\gamma^2 = \gamma$ (all occupation numbers are 1 or 0) is a sufficient condition for the possibility to reduce the wave function to a single Slater determinant. However, if this is not the case, but only a finite number of the occupation numbers are essentially different from zero, the wave function can be expressed as a sum of comparatively few terms and this would provide a simple solution to the CI convergence problem. Today we know that this was an overoptimistic view, but in this statement lies the basic idea behind multiconfigurational self-consistent-field (MCSCF) theory and in particular CASSCF.

The importance of the NO concept has been exactly these two things: analysis of correlation effects and the inspiration to develop methods to determine the most important NOs, MCSCF theory.

2.3 Extended Hartree–Fock

Actually Löwdin goes quite a long way to develop the MCSCF formalism. He defines a full CI on a limited one-electron basis set and points out that since the expansion is no longer complete, it is now important not only to determine the CI coefficients but also the MOs in order to obtain a solution "which is as accurate as possible." When the number of spin orbitals, M equals the number of electrons, N, this becomes the ordinary Hartree–Fock equations, but when $M > N$ we obtain what he calls the extended Hartree-Fock equations. Twenty-five years later it became known as the CASSCF method. He writes the condition for optimum orbitals in the form

$$\sum_l \hat{F}_{kl}\psi_l = \sum_l \epsilon_{kl}\psi_l \ , \tag{6}$$

where

$$\hat{F}_{kl} = \hat{h}\gamma(k|l) + \sum_{m,n} \int \psi_m^*(2)\frac{1}{r_{12}}\psi_n(2)\mathrm{d}x_2\Gamma(ln|km) \ , \tag{7}$$

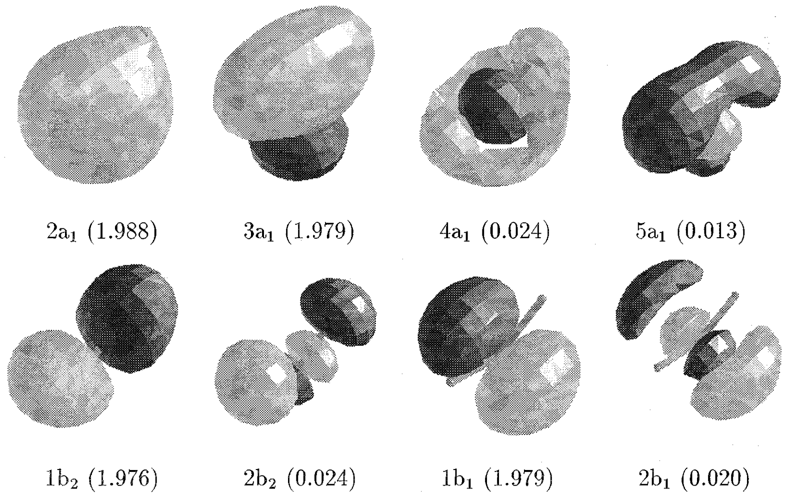
and ϵ_{kl} are the Lagrangian multipliers, which form an Hermitian matrix. Integrating, the condition for optimal orbitals becomes equivalent to the condition that the matrix

$$F_{kl} = \sum_m h_{km}\gamma(m|l) + \sum_{m,n,o}(mn|ok)\Gamma(on|lm) \tag{8}$$

is Hermitian. This is nothing but what was later to become the extended Brillouin condition and the matrix above is what we today call the MCSCF Fock matrix. May be it should be emphasized that Löwdin did these formal derivations, but he did not suggest any effective procedures which could be used to obtain the CI coefficients and the MCSCF orbitals. This was left to the "programmers" of the next generation.

2.4 NOs for H_2O

As an illustration of the interpretative power of the NOs, we show here the eight most important orbitals for the water molecule. Löwdin was correct in assuming that only a rather small number of orbitals will have appreciable occupation numbers. He was less right in presuming that this would lead to a quickly converging CI expansion. Today we know that the contrary is true



$2a_1$ (1.988) $3a_1$ (1.979) $4a_1$ (0.024) $5a_1$ (0.013)

$1b_2$ (1.976) $2b_2$ (0.024) $1b_1$ (1.979) $2b_1$ (0.020)

Fig. 1. Eight natural orbitals for the water molecule. They were obtained from a complete active spare self-consistent-field calculation using a basis set of the size (O4*s*3*p*2*d*/H3*s*2*p*)

and that the reason for the slow convergence is the two-electron cusp, which is not easily described in an MO framework.

Typically, for a closed-shell molecule at equilibrium geometry there will be a set of NOs with occupation numbers close to 2 and a second set (usually valence in character) of about the same size with occupation numbers in the range 0.01–0.05. The rest of the NOs will have slowly decreasing occupation numbers without much structure.

The MOs with occupation numbers above 0.01 will describe clearly defined correlation effects: horizontal (along a bond), radial (sometimes called in-out), and angular. The strongly occupied NOs will of course resemble closely the Hartree–Fock orbitals. All this is nicely illustrated for the water molecule in Fig. 1.

We can see the four strongly occupied valence orbitals $2a_1, 3a_1, 1b_2$, and $1b_1$ and notice that their occupation numbers vary in the range 1.97–1.99. For each of these orbitals there is a correlating orbital with an occupation number that lies in the range 0.01–0.03. This pairing seems to be a rather general feature of closed-shell molecules. The correlation orbital will describe horizontal correlation for bonding orbitals ($4a_1$ and $2b_2$) and radial correlation for nonbonded electrons ($5a_1$ and $2b_1$). The latter will be composed of extra valence basis functions. Still, they have occupation numbers in the same range as the correlating orbital we can construct from valence orbitals. If larger calculations are performed, the additional NOs will have occupation numbers well below 0.01. The occupation numbers of the strongly occupied orbitals will decrease somewhat, but those of the correlating orbitals shown in Fig. 1 will not change much. It is a general experience that occupation numbers of NOs are very stable against variation in the correlation treatment, changes of basis set, etc.

3 Final remarks

I have talked mostly about the contents of the first of the series of three articles. There is no doubt that it is the most important part. The second article studies the ordinary Hartree–Fock approximation. There is not much new in this treatment but Löwdin concludes that many systems cannot be treated by a single Slater determinant, in particular not for the open-shell case, since they are not eigenfunctions of the spin. In the third article he starts out to tackle this problem. He introduces spin projection operators and discusses the possibility of using different orbitals for different spins. The alternant orbital method would emerge, which was to be used with some success by other members of the Uppsala quantum chemistry group. Löwdin was, however, a little bit overoptimistic about the possibility to treat correlation effects by the use of different orbitals for different spins. The latter developments of theories for electron correlation was to take other routes. The work on open-shell Hartree–Fock theory was a prelude to the later developments of open-shell Hartree–Fock theory in the late 1950s.

Quantum chemistry has had many actors. Per-Olov Löwdin was one of the dominating leaders in the late 1950s and the 1960s. Many were educated at his summer schools. In a way he set the stage for much of the development that was to come during the period 1960–80, when most of the computational strategies were developed. His 1955 article is certainly one of the foundation stones of modern computational quantum chemistry.

Acknowledgements. It should now be clear to the reader that the articles reviewed have had a considerable impact on the scientific career of the present author. I would therefore like to take this opportunity to express my gratitude to Per-Olov Löwdin for having written the articles that became such an inspiration for my own work in quantum chemistry. I am sure that I am not the only quantum chemist of my generation that has been strongly influenced by this work.