Theoret. chim. Acta (Berl.) 5, 289—304 (1966)

On the Solution of the Quantum Mechanical Two-Electron Problem by Direct Calculation of the Natural Orbitals

III. Refined Treatment of the Helium-Atom and the Helium-like Ions

R. Ahlrichs, W. Kutzelnigg and W. A. Bingel

Lehrstuhl für Theoretische Chemie der Universität Göttingen

Received April 19, 1966

Natural orbitals (NO) and natural expansion coefficients for the ground states of the He atoms and some isoelectronic ions are calculated directly as numerical self-consistent solutions of integro-differential equations derived previously. These new applications differ from previous ones insofar as larger and more flexible sets as one-electron functions are used and as certain simplifications are no longer made. The wave functions and energies obtained here compete with the best configuration interaction results known so far and are obtained in an easier and more straightforward way. Plots of the NO's show clearly that different NO's of the same state are localized in the same region of space. Special attention is given to the problem of the convergency of the natural expansion and to the role of the correlation potential, which is defined as the difference between the effective one-electron Hamiltonians for the 1st (strongly occupied) NO and the Hartree-Fock (HF) orbital respectively. If one takes this correlation potential into account using an iterative procedure one can obtain better approximations to the first NO than the HF-orbitals are. If one is only interested in the energy it is — except for the H^--ion — irrelevant whether or not one ignores the difference between the 1st NO and the HF-orbital.

Natürliche Orbitale (NO) und Koeffizienten der natürlichen Entwicklung für den Grundzustand des He-Atoms und einiger isoelektronischer Ionen werden direkt berechnet als numerische, selbstkonsistente Lösungen von früher abgeleiteten Integro-Differentialgleichungen. Diese neuen Rechnungen unterscheiden sich von früheren zum gleichen Problem dadurch, daß größere und flexiblere Basissätze von Einelektronenfunktionen verwendet werden und daß gewisse Vereinfachungen der Gleichungssysteme nicht mehr gemacht werden. Die hier erhaltenen Wellenfunktionen und Energien können mit den besten bisher bekannten Ergebnissen von Konfigurationswechselwirkungs-Ansätzen wetteifern, sie sind dabei in einer einfacheren und systematischeren Weise zu erhalten. Graphische Darstellungen der Radialfaktoren der NO zeigen deutlich, daß verschiedene NO's zum gleichen Zustand im gleichen räumlichen Bereich lokalisiert sind. Besondere Beachtung finden das Problem der Konvergenz der natürlichen Entwicklung sowie die Rolle des Korrelationspotentials, das als Differenz zwischen den effektiven Einelektronen-Hamilton-Operatoren für das erste (stark besetzte) NO und für das Hartree-Fock (HF-) Orbital definiert ist. Trägt man diesem Korrelationspotential in einer iterativen Weise Rechnung, so gelingt es, eine bessere Näherung für das erste NO zu erhalten als sie das entsprechende HF-Orbital darstellt. Sofern man sich nur für die Energie interessiert, so ist es — außer für das H^--Ion — unwesentlich, ob man die Verschiedenheit zwischen erstem NO und HF-Orbital berücksichtigt oder nicht.

Les orbitales naturelles (NO) et les coéfficients du devéloppement naturel des états fondamentaux de l'atome He et de quelques ions isoéléctroniques sont calculés directement comme solutions numériques self-consistantes d'un system, derivé antérieurement, d'équations integro-differentielles. Ces calculs nouveaux different des précédents par le fait qu'on se sert maintenant de bases plus larges et plus flexibles de fonctions monoéléctroniques. En plus certaines simplifications ne sont plus faites. Les fonctions d'onde et les énergies obtenues ici sont comparables aux meilleurs resultats de calculs d'interaction de configurations connus jusqu'ici. Elles sont pourtant obtenues d'une facon plus simple et plus systématique. Les dessins des facteurs radiaux des NO demontrent que les NO appartenant au même état sont localisés dans la même région de l'espace. On s'intéresse en particulier au problème de la convergence du devéloppment naturel et au potentiel de corrélation qui est défini comme la difference des operateurs effectifs monoéléctronique pour la première NO (la NO fortement occupée) et pour l'orbitale Hartree-Fock (HF). Si l'on tient compte de ce potentiel de corrélation par un procédé iteratif on réussit à obtenir des meilleures approximations pour la première NO que celle fournie par l'orbitale HF. Pourvu qu'on ne s'intéresse qu'à l'énergie, il est — sauf pour l'ion H^- — sans importance si l'on utilize l'orbitale HF ou une meilleure approximation pour la première NO.

1. Introduction

In the first paper of this series [*11*], here referred to as I, integro-differential equations have been derived which allow one to calculate the natural orbitals of a two-electron-system without prior knowledge of the total wave function. They have to be treated separately for (i) closed-shell type ground states, (ii) excited singlet states of a symmetry species different from that of the ground state, and (iii) lowest triplet states. The equations valid for ground states have been applied numerically to the He isoelectronic series in the second paper of this series [*12*], here referred to as II. Certain simplifications of the rather involved equations were necessary to make a numerical solution possible.

With the approximate natural orbitals thus obtained configuration interaction calculations were performed which, by virtue of the properties of natural orbitals, led to secular equations of quite small dimensions. The wave functions and energies thus obtained fulfil the variation principle, i.e. energies are upper bounds to the true ones and the goodness of the energy is a measure of the goodness of the wave function.

Since our previous calculations had to be done on the rather small IBM 1620 computer, it seemed worthwhile to repeat and refine them using the IBM 7040 available in Göttingen.

The refinements consisted in using larger and more flexible basis sets in terms of which the natural orbitals are expanded, and in relaxing some of the simplifications introduced previously.

Special attention was given to the following point: The "strongly occupied" natural orbitals — which are known to be almost identical with the Hartree-Fock orbitals [*18*] (at least for the two-electron systems considered here) should be computed from an effective one-electron equation which differs from the usual Hartree-Fock equations in the appearance of a (non-local) correlation potential. The latter depends on the "weakly occupied" natural orbitals, an iterative procedure hence recommends itself. In II we had ignored the correlation potential and with it the difference between Hartree-Fock orbitals and the "strongly occupied" natural orbitals.

The specification "refined" in this title should not be understood in the sense that we wanted to compete with other highly accurate treatments of the Helium-atom [*9, 22, 28*]. These calculations on the Helium ground state are not an end in itself, but they should be regarded as one step further towards a better understanding of more complicated systems.

2. The computational scheme

The following sets of equations derived in part I are used to calculate the approximate NO's

$$(H + J^1 + C)\,\chi_1 = \lambda_{11}\,\chi_1 \tag{1}$$

$$Q_i\,[n_i\,(H + K^i) + K^1]\,Q_i\,\chi_i = \lambda_{ii}\,\chi_i\,; \qquad i \neq 1 \tag{2}$$

$$n_k = \frac{(1k \mid k1)}{E_1 - E_k}\;. \tag{3}$$

Here χ_1 is the "strongly occupied" (spinfree) natural orbital, χ_i a "weakly occupied" one, Q_i the projection operator projecting onto the subspace complementary to the one spanned by the first $(i - 1)$ natural orbitals. H is the one-electron part of the Hamilton-operator, J^i and K^i are coulomb and exchange operators produced from an electron pair in orbital χ_i. $(1k \mid k1)$ is an exchange integral involving orbitals χ_1 and χ_k. C is the "correlation potential", which will be discussed in section 4. For the detailed definitions of these quantities the reader is referred to I.

The equations are solved algebraically, each NO being regarded as a linear combination of given orthonormal one-electron functions. We start from Slater-type-orbitals with appropriately chosen orbital exponents and construct orthonormal orbitals out of them by a symmetrical orthonormalisation procedure. Those orbitals corresponding to an eigenvalue of the overlap matrix less a given threshold value (in general $\leq 10^{-5}$) are omitted, in order to avoid difficulties due to approximate linear dependencies [*21*]. The basis integrals and the Hartree-Fock calculations are performed in double precision arithmetic.

Contrary to what had been done in II the (small) operators K^i in (2) are no longer neglected.

In the first "*macro*-iteration" cycle the correlation potential C is ignored. The solution of (1) and (2) necessitate "*micro*-iteration" cycles; especially for the solution of (2) one starts by putting $n_i = 0$; having got a first approximation χ_i one computes n_i from (3) and so forth. Self-consistency is reached, in general after 3 or 4 iterations.

The coefficients c_i in the natural expansion of the spinfree wave function

$$\psi(1, 2) = \sum_i c_i\,\chi_i(1)\,\chi_i(2) \tag{4}$$

are obtained finally from the secular equation

$$2c_i\,H_{ii} + \sum_k c_k\,(ik \mid ki) = \mu\,c_i\,. \tag{5}$$

The lowest value for μ is then an upper bound to the total energy of the ground state.

3. Discussion of the results

We limit ourselves in this section to a discussion of the results obtained with one single macro-iteration cycle.

Tab. 1 gives the best total energy for the Helium ground state obtained in this scheme together with the coefficients of the natural expansion eq. (4) of the corresponding wave function. Like in II the a_i $[= (2l + 1)^{\frac{1}{2}} \cdot c_i]$ are coefficients of

Table 1. *Energy and natural expansion coefficients a_i for the best calculation of the* He *ground state*

		$-E$	2,90322		
1*s*	−.99622	3*d*	0.01219	5*g*	0.00194
2*s*	0.06003	4*d*	0.00330	6*g*	0.00076
3*s*	0.00681	5*d*	0.00104		
4*s*	0.00144	6*d*	0.00033	6*h*	0.00098
				7*h*	0.00025
2*p*	0.06005	4*f*	0.00426		
3*p*	0.00956	5*f*	0.00143	7*i*	0.00050
4*p*	0.00232	6*f*	0.00047		
5*p*	0.00070				

a NO-configuration, rather than of a simple NO-product. (The expansion coefficients of the NO's in terms of the basis Slater-type-orbitals are not tabulated, but can be furnished on request.) The energy obtained here is identical with, or even slightly better than the best configuration interaction result known so far [*33*]. Our scheme is, however, simpler and more straightforward than the conven-

Table 2. *Energies (compared to values from the literature) and natural expansion coefficients for the ground state of* He *and the* He-*like ions*

Z	1	2	3	4	6
$-E$ (exact) [*22, 25, 28*]	0.52775	2.90372	7.27991	13.65557	32.40625
$-E$ (best CI) [*33*]	0.52751	2.90320	7.27924	13.65481	32.40540
$-E$ (this work)	0.52679	2.90317	7.27911	13.65464	32.40501
$-E$ (previous NO) [*12*]	0.5245	2.9021	7.2777	13.6532	32.4034
$-E_{\text{rad}}$ [*5*]	0.51449	2.87902	7.25249	13.62686	32.37629
$-E_{\text{rad}}$ (this work)	0.51131	2.87878	7.25231	13.62669	32.37631
$-E_{\text{HF}}$ [*24*]	0.48793	2.86168	7.23641	13.61330	32.36119
$-a_i$ 1*s*	−.97562	−.99622	−.99848	−.99918	−.99965
2*s*	0.18603	0.06001	0.03582	0.02553	0.01620
3*s*	0.01423	0.00684	0.00435	0.00321	0.00208
4*s*	0.00312	0.00126	0.00104	0.00077	0.00049
2*p*	0.11250	0.06008	0.04003	0.02993	0.01988
3*p*	0.01509	0.00956	0.00654	0.00436	0.00328
4*p*	0.00383	0.00231	0.00149	0.00115	0.00076
5*p*	0.00089	0.00069	0.00028	0.00031	0.00012
3*d*	0.01894	0.01222	0.00857	0.00656	0.00442
4*d*	0.00507	0.00328	0.00228	0.00174	0.00115
5*d*	0.00169	0.00104	0.00070	0.00048	0.00032
6*d*	0.00068	0.00033	0.00015	0.00010	
4*f*	0.00640	0.00428	0.00305	0.00235	0.00154
5*f*	0.00228	0.00144	0.00101	0.00076	0.00044
6*f*	0.00090	0.00047	0.00022	0.00018	
5*g*	0.00291	0.00196	0.00134	0.00104	0.00061
6*g*	0.00122	0.00077	0.00046	0.00023	0.00015

tional CI method, especially since the crucial question which configuration to choose does not arise here. The particular choice of the basis of Slater-type-orbitals (in particular the orbital exponents) is not crucial at all, so that for a series of calculations of the Helium-like-ions just one basis set was guessed for each system and no refinement by variation of the basis set was tried.

These results are collected in Tab. 2. As to He the essential difference between the results in Tab. 1 and Tab. 2 is the omission of natural orbitals with $l > 4$ in the latter. Again the results in Tab. 2 are very close to the best CI results known so far. Note that we obtained these energy values by a final CI calculation involving only 17 configurations, whereas a conventional CI calculation using the same one-electron basis would involve 88 configurations. It is interesting to compare the "radial limits" obtained in this scheme with the very accurate ones by Davis [*5*]. The agreement between the two sets increases with increasing nuclear charge — as one would expect. (The higher Z the more does the first order density matrix approach idempotency and the more rapid ought to be the CI expansion). This result *seems* to be in contradiction with the diminishing accuracy of the total energy for increasing Z, as also has been observed in conventional CI calculations [*33*].

Table 3. *Contributions of the* NO-*configurations to correlation energy of the ground states of* He *and* He-*like ions*

Z	1	2	3	4	6
$2s$	.02037	.01534	.01445	.01408	.01376
$3s$	.00083	.00088	.00088	.00088	.00087
$4s$	.00010	.00010	.00009	.00009	.00010
$2p$	.01408	.01945	.02093	.02162	.02229
$3p$	.00113	.00179	.00195	.00203	.00210
$4p$	.00019	.00027	.00029	.00030	.00030
$3d$	.00126	.00215	.00245	.00260	.00275
$4d$	.00026	.00042	.00047	.00050	.00050
$5d$	.00006	.00010	.00010	.00011	.00010
$4f$	.00028	.00050	.00058	.00062	.00066
$5f$	.00009	.00014	.00016	.00016	.00015
$5g$	.00009	.00017	.00019	.00021	.00021
$-E_{\mathrm{corr}}$[a]	.03886	.04149	.04270	.04334	.04381
$-E_{\mathrm{corr}}$[b]	.03982	.04210	.0435	.0443	.0451
[c]	97.7	98.6	98.2	97.7	97.2

[a] Sum of the contributions.
[b] Exact values.
[c] Percentage of the exact correlation energy accounted for.

One understands this discrepancy better if one considers the contributions of the different NO-configurations to the correlation energy in Tab. 3. The definition of these contributions is the same as in II.

$$\Delta E_i = (2l+1)\frac{c_i}{c_1}(1i \mid i1) = \sqrt{2l+1}\,\frac{a_i}{a_1}(1i \mid i1)\,. \tag{6}$$

One sees that energy contributions of NO-configurations with large l increase with increasing Z, and so does the error due to truncation of the expansion at a fixed value of l.

The remaining error of 1 to 3% in the correlation energy (1, 2% for the best He-calculation) is probably due to neglect of NO's with $l \geq 5$. Addition of just a few l-values would, however, not improve the energy in an appreciable way as one can see by extrapolation. This observation agrees with those of other authors [*25, 33*] and comes probably [*16, 27*] from the fact that the wave-function for the He ground state has a correlation cusp, as a consequence of which the wave-function should have the following form for small r_{12}:

$$\psi(r_1, r_2, r_{12}) = \psi_0(r_1, r_2)\,(1 + \tfrac{1}{2}\,r_{12}) + \dots \tag{7}$$

Any CI-wave-function can, of course, be transformed to a Legendre expansion:

$$\psi(r_1, r_2, \vartheta_{12}) = \psi_0\,(r_1, r_2) + \sum_{k=1}^{\infty} \psi_k\,(r_1, r_2)\,P_k\,(\cos\vartheta_{12}) \tag{8}$$

or alternatively to

$$\psi(r_1, r_2, r_{12}) = \psi_0\,(r_1, r_2) + \sum_{k=1}^{\infty} \tilde{\psi}_k\,(r_1, r_2)\,r_{12}^{2k} \tag{9}$$

since $\cos\vartheta_{12} = \dfrac{r_{12}^2 - r_1^2 - r_2^2}{2r_1r_2}$ and $P_k\,(\cos\vartheta_{12})$ is a polynomical in $\cos\vartheta_{12}$ and hence also in r_{12}^2.

An expansion of ψ in terms of even powers of r_{12} multiplied by appropriate functions of r_1 and r_2 is convergent in the sense of the mean square approximation, it cannot be uniformly convergent [*16*]. It is evident, that the rather important term linear in r_{12} will need a very big number of even powers in r_{12} (or polynomicals in $\cos\vartheta_{12}$) to be well approximated in the mean.

$$\begin{aligned} r_{12} = \frac{r_{12}^2}{r_{12}} &= (r_1^2 + r_2^2 + 2r_1\,r_2\cos\vartheta_{12}) \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}}\,P_k\,(\cos\vartheta_{12}) \\ &= r_{12}^2 \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}}\,P_k\left(\frac{r_{12}^2 - r_1^2 - r_2^2}{2r_1\,r_2}\right). \end{aligned} \tag{10}$$

Although the cusp itself (i.e. the discontinuity of the first derivative of ψ with respect to r_{12} at $r_{12} = 0$) has no direct influence on the energy [*6*], it is nevertheless responsible for the eventually slow convergency of the CI expansion [*10, 27*]. A very similar problem occurs, if one wants to expand the wave function of H_2^+ in terms of Slater-type-orbitals centered at the midpoint [*1, 7, 8*]. Again orbitals with very high l give non-neglegible contributions and the expansion is slowly convergent. This seems to be a very general result occuring whenever one wants to approximate a function with a cusp as a linear combination of functions whose first derivatives are continuous everywhere. It has been made plausible for these two types of expansions that the energy contributions from orbitals with high l should be proportional to l^{-4} [*8, 27*] or $(l + \frac{1}{2})^{-4}$ [*16*]. We have therefore collected in Tab. 4 the energy contributions $E(l)$ of NO's with given l together with $E(l) \cdot (l + \frac{1}{2})^{-4}$ which ought to be constant for constant Z. It should be noted that our

Table 4. *Contributions to the energy $E(l)$ of NO's with a given l, together with* $(l+\frac{1}{2})^4 E(l)$

$Z \rightarrow$	1	2	3	4	6
$E(1)$	.01540	.02151	.02317	.02395	.02469
$(\frac{3}{2})^4 E(1)$	.07796	.10889	.11730	.12125	.12499
$E(2)$	.00158	.00267	.00302	.00321	.00335
$(\frac{5}{2})^4 E(2)$	.06172	.10430	.11797	.12539	.13086
$E(3)$	.00037	.00064	.00074	.00078	.00081
$(\frac{7}{2})^4 E(3)$	.05552	.09604	.11105	.11705	.12155
$E(4)$	.00009	.00017	.00019	.00021	.00021
$(\frac{9}{2})^4 E(4)$	.03691	.06971	.07791	.08611	.08611

$E(4)$, i.e. the contribution of g-type NO's, is probably too small, since we used only 2 g-type basis functions.

The eventually slow convergency of the NO-expansion (like that of any CI-expansion) should not obscure the fact that in order to get very good rather than extremely precise energies one needs very few configurations. This can be seen from Tab. 5, where the energy values calculated by configuration interaction with 1, 2, ... 6 natural configurations are tabulated, together with the corresponding values taken from DAVIDSON [*4*], who used approximative NO's obtained indirectly from a Kinoshita-type wave function.

With 4 configurations one obtains more than 90% and with 6 configurations more than 95% of the correlation energy. This is of practical importance for more complicated systems. The big advantage of the present scheme is, that it can rather easily be generalized to systems with more than two electrons, whereas those methods involving direct r_{12}-dependence of the wave function, which are superior for 2-electron systems will probably resist generalisation to big systems for quite some time. Although an accuracy of about 0.0005 a.u. (~ 0.01 eV ~ 100 cm^{-1} ~ 0.3 kcal) may seem disappointing for Helium — for which more accurate calculations are available — one should not forget that the most reliable values for the Be-ground-state [*32*, *33*] — as obtained from calculations satisfying the variation principles — are about 0.005 a.u. in error which is nearly 10 times as much.

Table 5. He-*ground state energies calculated with minimum numbers of* NO-*configurations*

n	$-E^a$	$-E^b$	l	v
1	2.861653	2.86168	0	
2	2.882049	2.88223	1	48.8
3	2.897434	2.89764	0	85.5
4	2.899243	2.89948	2	92.5
5	2.900903	2.90098	1	93.5
6	2.901697	2.90170	0	95.2

n: Number of configurations.

l: Angular momentum quantum number of the last added NO

v: Percentage of the exact correlation energy taken into account.

[a] Values from DAVIDSON [*4*].

[b] This work.

The radial factors of the approximate NO's of the Helium ground state are plotted in Fig. 1. Although, as has been stated in I, the accuracy of these NO's should decrease with decreasing contribution to the energy expectation value and hence roughly with their occupation number, these plots are quite illustrative.

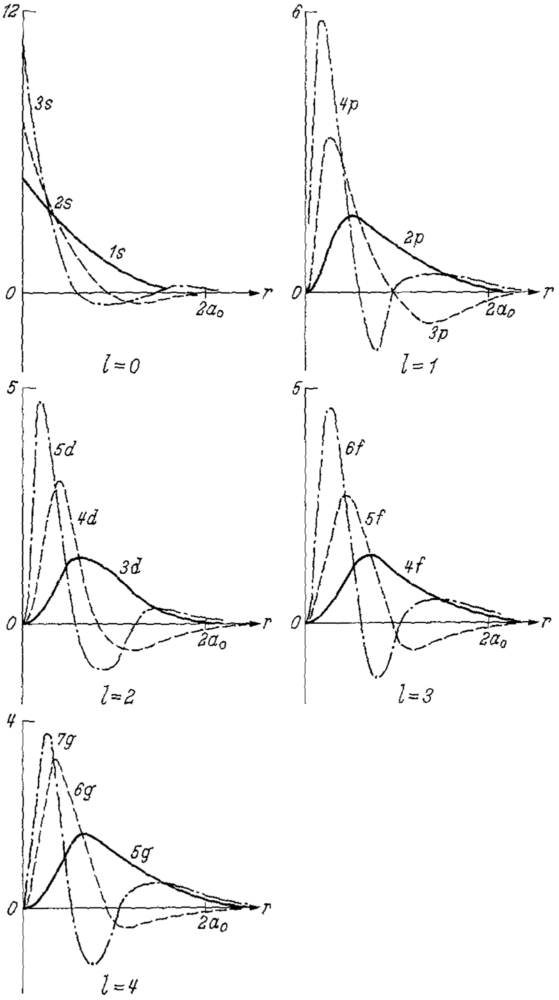

Fig. 1 Radial factors $f_{nl}(r)$ of the most important NO's of the He-ground state.

Table 6. *Expectation values of one-electron operators r^{μ} with respect to different NO-configurations (For He)*

μ	−1	1	2	3	μ	−1	1	2	3
1s	1.687	0.927	1.185	1.940	3d	1.152	0.998	1.130	1.440
2s	1.912	1.253	2.387	5.425	4d	1.604	0.888	1.080	1.590
3s	2.690	1.059	2.009	4.926	5d	2.030	0.836	1.030	1.560
4s	3.090	1.330	3.020	8.530	6d	3.160	0.619	0.706	1.15
2p	1.220	1.006	1.205	1.680	3f	1.14	0.974	1.05	1.24
3p	1.700	0.967	1.360	2.350	4f	1.55	0.870	0.990	1.38
4p	2.283	0.840	1.160	2.080	6f	2.03	0.770	0.880	1.29
5p	4.210	0.659	0.931	1.770					
					5g	1.13	0.962	1.00	1.13
					6g	1.70	0.746	0.708	0.809

They show that the NO's are all localized in the same region of space. The $2p, 3d, 4f$ and $5g$-orbitals have almost the same radial factor except for the different behaviour near $r = 0$. From Fig. 1 one can understand why the ideas of BOYS [*2, 3*], of TAYLOR and PARR [*31*] and others [*19, 20*] to choose the "virtual" orbitals for a configuration interaction such that the radial factors have maximum overlap with the $1s$-orbital were rather successful.

The fact that the NO's are localized in the same region of space can also be deduced from the expectation values of one-electron operators r^μ calculated with respect to the different natural configurations (Tab. 6).

4. The role of the correlation potential

If one minimizes the energy expectation value with respect to a wave function of the form (4) one obtains integro-differential equations for the natural orbitals. If in these equations one neglects the correlation potential C — which amounts to replacing eq. (1) by a simple Hartree-Fock equation — one can give a new interpretation to this simplified scheme in the following way. One then actually minimizes the energy expectation value with respect to a function of the form:

$$\Phi(1, 2) = c_1 \varphi_1(1) \varphi_1(2) + \omega(1, 2) \tag{11}$$

where

$$\omega(1, 2) = \sum_{i>1} c_i \chi_i(1) \chi_i^*(2); \qquad (\chi_i, \chi_j) = \delta_{ij}; \qquad (\varphi_1, \chi_i) = 0 \tag{12}$$

and φ_1 is the Hartree-Fock-orbital of the system.

If $\omega(1, 2)$ were completely flexible except for (simple) orthogonality to $\varphi_1(1) \varphi_1(2)$, this ansatz (11) would be completely general. The expansion (12) of ω with its orthogonality conditions is still general, provided that c_i and χ_i can be varied freely and independently — and that $\omega(1, 2)$ is strongly orthogonal to $\varphi_1(1) \varphi_1(2)$, i.e. that

$$\int \varphi_1^*(1) \varphi_1^*(2) \omega(1, 2) d\tau_1 = 0 . \tag{13}$$

Whereas simple orthogonality of ω to $\varphi_1(1) \varphi_1(2)$ does not mean a loss of generality, strong orthogonality means a restriction.

If on the other hand we treat this problem formally by (Rayleigh-Schrödinger) perturbation theory, we then find that the 1st order correction to $\varphi_1(1) \varphi_1(2)$, i.e. the 1st order approximation $\omega^1(1, 2)$ to $\omega(1, 2)$ is strongly orthogonal [*34*] to $\varphi_1(1) \varphi_1(2)$. Since $c_1 \varphi_1(1) \varphi_1(2) + \omega^1(1, 2)$ determines the energy through 3rd order, non-strongly-orthogonal terms in $\omega(1, 2)$ will effect the energy only to 4th and higher order.

If we replace the Hartree-Fock-orbital φ_1 by the strongly occupied natural orbital χ_1, then the ansatz (11), which is now identical to (4) is rigorous even with a strongly orthogonal ω of the form (12). The best energy obtained with the general ansatz (4) will differ only by terms of 4th and higher order from that obtained with the slightly less general ansatz (11), (12) — provided of course that the basis in one-electron Hilbert space is the same.

From this one must conclude, that one cannot expect an appreciable improvement in the energy if one takes the correlation potential into account by "macro-iterating" the systems (1), (2), (5) until self-consistency is reached.

Anyway the change in energy so obtained will be small compared to the error due to truncation of the expansion after a fixed l-value.

One also understands why the energy values at the end of the first macroiteration cycle are so close to the best CI-results by WEISS [*27*].

Only for H^-, where the coefficient c_1 deviates more from unity than in the other systems and where the perturbation parameter $1/Z$ has its highest value may one expect an appreciable difference between φ_1 and χ_1 and a possible improvement in the energy.

The correct solution of (1) has, however, some principal interest:

(i) It has been stated [*13*, *15*], that the first natural configuration rather than the Hartree-Fock-function is the best one-determinant approximation to the true wave function — both in the sense of the "best density" and the "best overlap" criterion. It is therefore desirable that the "best approximation" could be calculated directly in a rather simple way and that it could be compared with the Hartree-Fock-function.

(ii) It is expected that the first natural configuration gives — on the whole — better approximations to the expectation values of one-electron operators than the Hartree-Fock-function. Using DAVIDSON's [*4*] indirectly calculated first NO as an approximation to the true one some of these expectation values have been calculated previously [*15*]; they compare favorably with those obtained with the Hartree-Fock-orbitals. These results ought to be checked on natural orbitals optained in an independent way.

(iii) The first natural orbital is in this particular case identical to the solution of the "exact self-consistent field" equations [*10*, *17*] or to BRUECKNER's self-consistent-field equations [*19*].

(iv) The differences between strongly occupied orbitals and Hartree-Fock-orbitals — which are small for closed-shell states [*14*, *18*] (and only for those) — are closely connected to the occurence of singly excited configurations with respect to the Hartree-Fock function in the true function, or — equivalently — to the occurence of "one-particle clusters". SINANOGLU [*29*] believed so strongly in the irrelevance of these contributions, that he even proposed a method to "purify" approximate wave functions from "one-particle clusters", which it may contain "by chance".

(v) It may be possible for some applications to approximate the true (non-local) correlation potential by some simplified potential, like WIGNER's [*35*] statistical one or by a potential which is proportional to the Coulomb potential [*12*]. On this basis it should then be possible to justify semiempirical schemes in a more consistent way. The solutions of eq. (1) with an approximate rather than the true correlation potential merit therefore some attention. Results by BERTHIER and SUREAU [*30*], show that a Wigner type correlation potential is not satisfactory in this sense, essentially because it does not give the correct Z-dependence of the correlation energy.

The natural orbitals χ_i are solutions of the system of coupled integro-differential equations [*11*].

$$F^i \chi_i = \sum_k \lambda_{ik} \chi_k \tag{14}$$

$$F^i = c_i^2 H + c_i \sum_k c_k K^k . \tag{15}$$

One can reduce this system of coupled equations to pseudo-eigenvalue equations by "absorbing" the off-diagonal Lagrange-multipliers on the left-hand side using a procedure which is an extension of that proposed by Roothaan [23] for a special case of systems of the form (14).

Suppose that we have (in an iterative manner) obtained those χ_i which satisfy the system, then we obtain, keeping in mind that the λ_{ik} form a hermitean matrix:

$$\lambda_{ik} = \lambda_{ki}^* = (\chi_k, F^i\chi_i) = (\chi_i, F^k\chi_k)^* = (\chi_k, F^k\chi_i) \tag{16}$$

$$\lambda_{ik} = (\chi_k, G^{ik}\chi_i); \qquad G^{ik} = a_{ik}F^i + b_{ik}F^k; \qquad a_{ik} + b_{ik} = 1 \,. \tag{17}$$

The a_{ik} and b_{ik} can be chosen arbitrarily, provided that each pair sums up to unity.

Let $O_i = |\chi_i\rangle\langle\chi_i|$ be the projection operator which projects out the χ_i-component of any wave function and $P_i = 1 - O_i$ the complementary projection operator. We then define new hermitean operators

$$M^i = \sum_{k\,(\neq i)} \{O_k\, G^{ik} + G^{ik}\, O_k\} \,. \tag{18}$$

One sees easily that

$$\begin{aligned}(\chi_k, M^i\chi_i) = (\chi_i, M^k\chi_k) = (\chi_k, G^{ik}\chi_i) &= \lambda_{ik}\,(1 - \delta_{ik})\\ (\chi_k, [F^i - M^i]\,\chi_i) &= \lambda_{ii}\,\delta_{ik}\end{aligned} \tag{19}$$

if χ_i are the orbitals which one has used to construct the P_i and F^i. The operator $\tilde{F}^i = F^i - M^i$ is diagonalized by the χ_i, the χ_i are consequently eigenfunctions of the $\tilde{F}^i$ with eigenvalues λ_{ii}.

Can one use this system to obtain the χ_i in an iterative way by solving pseudo-eigenvalue equations? In order to understand what this question means let us suppose that we had put $a_{ik} = 1$; $b_{ik} = 0$.

Then we would have obtained

$$\begin{aligned} G^{ik} &= F^i\\ M^i &= P_i\, F^i + F^i\, P_i\\ \tilde{F}^i &= F^i - M^i = O_i\, F^i + F^i\, P_i \end{aligned} \tag{20}$$

and we see immediately that the χ_i which we have used to construct the P_i will automatically be eigenfunctions of $\tilde{F}^i$! It is therefore impossible to improve the guess for the χ_i by computing the eigenfunctions of $\tilde{F}^i$.

The situation is, however, different if we put $a_{ik} \neq 1$; $b_{ik} \neq 0$. Eq. (16) will then be satisfied only if the χ_i are the self-consistent ones. Before self-consistency is reached, $(\chi_k, F^i\chi_i)$ will be somewhat different from $(\chi_i, F^i\chi_k)$; and the F^i of the n-th iteration will not be diagonalized by the χ_i of the $(n-1)^{\text{st}}$ iteration. Self-consistency is reached as soon as the two matrix-elements become equal. Whether the procedure converges and whether it converges towards the correct solution is hard to decide a priori, but in practice is does.

Knowing the role of the a_{ik} and b_{ik} we may now choose them in the most convenient way. In this particular case we have

$$G^{ik} = a_{ik}\,(c_i^2\, H + c_i \sum_j c_j K^j) + b_{ik}\,(c_k^2\, H + c_k \sum_j c_j\, K^j) \,. \tag{21}$$

If we choose

$$a_{ik} = \frac{c_k}{c_k - c_i} \qquad b_{ik} = \frac{-c_i}{c_k - c_i}$$

we get

$$\begin{aligned} G^{ik} &= \frac{c_i^2 c_k - c_i c_k^2}{c_k - c_i} H = -c_i c_k H \\ M^i &= -c_i T_i H - c_i H T_i; \qquad T_i \equiv \sum_{k(\neq i)} c_k O_k \qquad (22) \\ \widetilde{F}^i &= c_1^2 H + c_i \sum_k c_k K^k + c_i T_i H + c_i H T_i . \end{aligned}$$

The correlation potential C for the first NO is defined essentially as the difference between F_1 and the Hartree-Fock-operator

$$F_{\mathrm{HF}} = H + K^1$$

$$F_1 = c_1^2 (F_{\mathrm{HF}} + C) = c_1^2 H + c_1^2 K^1 + c_1 \sum_{k \neq 1} c_k K^k + c_1 T_1 H + c_1 H T_1 \qquad (23)$$

$$C = \frac{1}{c_1} \left(\sum_{k(\neq 1)} c_k K^k + T_1 H + H T_1 \right) = \frac{1}{c_1} \sum_{k(\neq)1} c_k (K^k + O_k H + H O_k) .$$

The first sum is the "exchange part" of the correlation potential, the two other terms the "orthogonality part". Weakly occupied orbitals χ_k with an angular quantum number different from that of χ_1 only contribute to the exchange part.

From the considerations of this chapter it is evident that the part of the correlation potential which comes from *s*-type (weakly occupied) NO's is by far the most important one. Calculations in which we took into account the contributions to C of NO with $l \neq 0$ only, showed in fact that they left the H.F. orbital and the total energy practically unchanged. This is why in what follows we used the *s*-part of the correlation potential rather than the complete one. If, with this slightly simplified correlation potential, one limits oneself to a calculation involving *s*-type NO's only, then one may interpret this scheme as an attempt to calculate the "radial limit" of the energy by a natural expansion method. The results of a pure *s*-calculation can be seen from Tab. 7. The difference between the *s*-energy obtained by our scheme and what is supposed to be the *s*-limit is considerably reduced if one takes the correlation potential into account which amounts to using better approximations to the first NO than the H.F. orbital is. The improvement is rather striking for H^- and it falls off rapidly with increasing Z. Self-consistency is reached for He after three macro-iterations, whereas for H^- 4 to 5 (depending on the basis set) are necessary. One macro-iteration cycle consisted of one calculation of all the NO's and subsequent CI calculation. If in the natural expansion one replaces the H.F. orbital by a better approximation to the first natural orbital, then the expansion coefficient of the first natural configuration is slightly reduced whereas the coefficients of the other NO configurations increases somewhat. This can be seen in Tab. 7 too.

Although the energy obtained with a natural expansion involving only *s*-orbitals is considerably improved if one takes the correlation potential into account, the improvement is much less pronounced as to the energy obtained with the natural expansion not limited to $l = 0$. For He the energy remains even constant within the limits of errors. Only the relative contributions of orbitals with different

Table 7. *Energies and expansion coefficients from calculations involving the correlation potential*

Macro-iteration	$-E$(CI with $l = 0$ only)	$-E$(CI, $l = 0$ and $l \neq 0$)	$-E(1s)$	$c(1s)$	$c(2s)$
H$^-$					
1	.51132	.52679	.48792	.97873	−.20443
2	.51348		.48639	.97334	−.22863
3	.51386		.48548	.97099	−.23840
4	.51397	.52706	.48492	.96972	−.24349
(best values)	.51449 [*5*]	.52775 [*22*]			
He					
1	2.87877	2.90317	2.86168	.997994	−.06285
2	2.87891		2.86156	.997944	−.06362
3	2.87892	2.90318	2.86155	.997941	−.06368
(best values)	2.87902 [*5*]	2.90372 [*22*]			

l are shifted. If one uses the H.F. orbital instead of the first NO one obtains a too small s-contribution to the correlation energy, whereas the contributions with $l \neq 0$ are somewhat too big and compensate partially the defeciency of the s-contribution. Only for the H$^-$ ion the total energy is improved, although not to the same extent as the s-energy (see Tab. 7). The remaining error in the total correlation energy is reduced from 2.3% to 1.7%.

The difference between the approximate first NO and the H.F. orbital is shown graphically on Fig. 2. The 1st NO is slightly higher and steeper near the nucleus. The curvature $\frac{\partial^2 \psi}{\partial r^2}$ is bigger and so is consequently the kinetic energy (which latter by virtue of the virial theorem is for the H.F. orbital as much in error as the expectation value of H). Some expectation values for one electron in

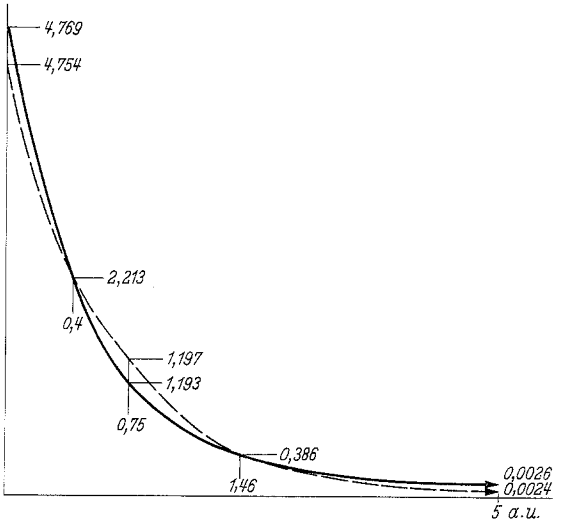

Fig. 2 Radial factors of the Hartree-Fock orbital (- - -) and the approximate first natural orbital (——) for the He-ground state. (The difference being too small to be detected on correct scale, is exaggerated. The indicated numbers are, however, correct).

the H.F. orbital and in the first NO respectively are given in Tab. 8. For comparison the corresponding values calculated [*15*] with Davidson's [*4*] first NO of the He ground state are added. The agreement between our and Davidson's 1st NO is not excellent. The corresponding expectation values differ from those calculated with the H.F. orbital however in the same direction. The difference between the two types of NO concerns essentially the expectation values of high powers of r, i.e. the behaviour in regions of space far from the nucleus on which any energy criterion is not very sensitive. One should note further that in Davidson's paper [*4*] some numerical instabilities occur due to almost linear dependence of the basis. Whether it is possible to calculate in independant approaches reproducible NO's is still an open question.

Table 8. *Expectation values for one-electron operators (and the Hamiltonian) for one-determinant wave functions compared to the exact ones*

Operator	Exact [*22*]	HF	1st NO from [*4*]	our NO
H⁻				
H	−.52775	−.48794		−.48492
$-\Delta_1$	.52775	.48794		.50040
$(r_1)^{-1}$	$(<$ .68818)	.68582	—	.68173
r_1	$(>$ 2.5436)	2.4993		2.7426
r_1^2	$(>$ 9.5068	9.3273		12.150
r_1^3	$(>$ 45.95)	47.396		75.674
$\delta(r_1)$	.1645	.1543		.1632
He				
H	−2.90372	−2.86168	−2.86165	−2.86155
$-\Delta_1$	2.90372	2.86168	2.8716	2.8632
$(r_1)^{-1}$	1.6883	1.6873	1.6899	1.6869
r_1	.9295	.92727	.9273	.9317
r_1^2	1.1935	1.1848	1.1866	1.2013
r_1^3	$(>$ 1.9621)	1.9406	1.9483	1.9920
$\delta(r_1)$	1.8104	1.7980	1.8094	1.8096

(The values in parenthis are estimated from the 6th order wave functions by Scherr and Knight [*26*]).

It is rather astonishing how close the expectation value of $\delta(r)$ (which is proportional to the electron density at the nucleus) calculated with the first natural configuration is to the exact value.

For H⁻ there are neither Davidson values nor sufficient exact ones available. The 6th order expectation values of powers of r as taken from Scherr and Knight [*25*] are probably not very close to the true ones, since the contributions of the first 6 orders in the $1/Z$ expansion have the same order of magnitude and the following orders are supposed to behave similarly.

It should be mentioned that the "orthogonality part" of the correlation potential is as important as the "exchange part". Calculations in which the further was neglected led to self-consistency, but yielded worse energy than one obtained without the correlation potential.

5. Calculation of the natural orbitals as solutions of one single pseudo-eigenvalue equation

It has been shown in chapter 4 that the coupled pseudo-linear-system of integro-differential eq. (14) can be transformed into a non-coupled system of pseudo-eigenvalue equations. It is even possible to combine these such that they yield one single pseudo-eigenvalue equation, in other words, so that all the natural orbitals are solutions of one and the same effective one-particle operator. This operator is

$$F_{\mathrm{NO}} = \sum_i \{c_i^2\, HO_i + c_i^2\, O_i H + c_i\, O_i \sum_k c_k K^k + c_i \sum_k c_k K^k\, O_i + \\ + c T_i\, HO_i + c_i\, O_i\, HT_i\} \,. \tag{24}$$

It is hermitean and one sees that

$$\begin{aligned} (\chi_i, F_{\mathrm{NO}}\, \chi_i) &= 2(\chi_i, F^i\, \chi_i)\,, \\ (\chi_i, F_{\mathrm{NO}}\, \chi_k) &= (\chi_i\, F^i\, \chi_k) + (\chi_i\, F^k\, \chi_k) + c_k\, (\chi_i\, T_k\, H\, \chi_k) + c_i\, (\chi_i\, HT_i\, \chi_k)\,, \\ &= (\chi_i\, F^i\, \chi_k) + (\chi_i\, F^k\, \chi_k) + 2c_i\, c_k\, (\chi_i\, H\, \chi_k)\,. \end{aligned} \tag{25}$$

The operator will be diagonal if

$$(\chi_i\, F_i\, \chi_k) + (\chi_i\, F_k\, \chi_k) + 2c_i\, c_k\, (\chi_i\, H\, \chi_k) = 0\,. \tag{26}$$

This is evidently the case for the correct NO's because they satisfy (16) and (22)

We did not as yet attempt to calculate the NO's from this effective one particle operator, because we think that the method we actually use is simpler and accurate enough, but it seems rather tempting nevertheless to use this new scheme. One might start by putting $c_1 = 1$, $c_i = 0$, $i \neq 1$ then calculate the NO's of the first iteration, which are equal to the Hartree-Fock and virtual Hartree-Fock orbitals, do a CI calculation (5) with them, insert the c_i in the operator (24), calculate new χ_i and so forth.

Acknowledgement. The work reported here was sponsored in part by the „Deutsche Forschungsgemeinschaft". Discussions on the topics of this paper with Dr. G. Berthier, Dr. G. del Re and Prof. R. McWeeny were made possible through a NATO contract for research and collaboration.

Bibliography

[1] Ahlrichs, R., W. Kutzelnigg, and W. A. Bingel: Theoret. chim. Acta (In press).
[2] Boys, S. F.: Proc. Roy. Soc. (London) **A 201**, 125 (1950); **217**, 136, 235 (1953).
[3] — Rev. mod. Physics **32**, 296 (1960).
[4] Davidson, E. R.: J. chem. Physics **39**, 875 (1963).
[5] Davis, H. L.: J. chem. Physics **39**, 1827 (1963).
[6] Gilbert, T. L.: Rev. mod. Physics **35**, 491 (1963).
[7] Hagström, S., and H. Shull: J. chem. Physics **30**, 1314 (1959).
[8] Joy, H. W., and G. S. Handler: J. chem. Physics **42**, 3047 (1965).
[9] Kinoshita, T.: Physic. Rev. **105**, 1490 (1957).
[10] Kromhout, R. A.: Physic. Rev. **107**, 215 (1957).
[11] Kutzelnigg, W.: Theoret. chim. Acta (Berl.) **1**, 327 (1963).
[12] — Theoret. chim. Acta (Berl.) **1**, 343 (1963).
[13] —, and V. H. Smith jr.: J. chem. Physics **41**, 896 (1964).
[14] — — J. chem. Physics **42**, 2795 (1965).
[15] — — Technical report 130, July 15. 1964, Quantum Chemistry Group, Uppsala, Sweden.
[16] Lakin, W.: J. chem. Physics **43**, 2954 (1965).
[17] Löwdin, P. O.: J. math. Physics **3**, 1171 (1962).

[18] Nazaroff, G. V., and J. O. Hirschfelder: J. chem. Physics **30**, 617 (1959).
[19] Nesbet, R. K.: Adv. chem. Physics **9**, 321 (1965).
[20] —, and R. E. Watson: Physic. Rev. **110**, 1073 (1958).
[21] Nordling, J. O., and J. S. Faulkner: J. mol. Spectry. **12**, 171 (1964).
[22] Pekeris, C. L.: Physic. Rev. **112**, 1649 (1958); **115**, 1216 (1959).
[23] Roothaan, C. C. J.: Rev. mod. Physics **32**, 179 (1960).
[24] —, L. M. Sachs, and A. W. Weiss: Rev. mod. Physics **32**, 186 (1960).
[25] Scherr, C. W., and R. E. Knight: J. chem. Physics **40**, 1777 (1964).
[26] — — J. chem. Physics **40**, 3034 (1964).
[27] Schwartz, C.: Physic. Rev. **126**, 1015 (1962).
[28] — Physic. Rev. **128**, 1146 (1962).
[29] Sinanoğlu, O.: Rev. mod. Physics **35**, 517 (1963).
[30] Sureau, A.: C. r. acad. Sci. **260**, 1348 (1965).
[31] Taylor, G. R., and R. G. Parr: Proc. Nat. Acad. Sci. (US) **38**, 154 (1952).
[32] Watson, E. R.: Physic. Rev. **119**, 170 (1960).
[33] Weiss, A. W.: Physic. Rev. **122**, 1826 (1961).
[34] —, and J. B. Martin: Physic. Rev. **132**, 2118 (1963).
[35] Wigner, E. P.: Physic. Rev. **46**, 1002 (1934).

Dr. Werner Kutzelnigg
Lehrstuhl f. Theoretische Chemie
Universität Göttingen
3400 Göttingen, Bürgerstr. 50a