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

IV. Application to the ground state of the Hydrogen molecule in a one-center expansion

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The wave function of the ground state of the H_2 molecule is calculated directly in its natural expansion form, the approximate natural orbitals (NO) being expressed as linear combinations of Slater type functions centered at the midpoint of the molecule. One obtains as total energy (in the equilibrium distance) -1.168 a.u. (exact -1.174 a.u.) which seems to be the best one-center result for H_2 known so far; 96% of the binding energy is accounted for. The accuracy of this approach is limited due to the rather slow convergency of the one-center expansion of the orbitals. The Hartree-Fock energy calculated with the same basis (-1.129 a.u.) is about as much in error with respect to the exact HF energy (-1.136 a.u.) as the energy of the NO expansion with respect to the experimental one.

Die Wellenfunktion für den Grundzustand des H_2-Moleküls wird direkt in der Form ihrer natürlichen Entwicklung berechnet, wobei die natürlichen Orbitale (NO) angenähert werden als Linearkombinationen von Slater-Funktionen, die um den Schwerpunkt des Moleküls definiert sind. Die Energie des Zustands im Gleichgewichtsabstand ergibt sich zu $-1{,}168$ a. u. (exakt $-1{,}174$ a. u.), was anscheinend der beste bisher bekannte Wert für eine Einzentrenentwicklung des H_2 ist; 96% der Bindungsenergie werden erfaßt. Die Genauigkeit der Rechnung wird eingeschränkt durch die langsame Konvergenz der Einzentrenentwicklung der Orbitale. Die Hartree-Fock-Energie, berechnet mit der gleichen Basis ($-1{,}129$ a. u.), unterscheidet sich von der „exakten" Hartree-Fock-Energie ($-1{,}136$ a. u.) um etwa den gleichen Betrag wie diejenige der NO-Entwicklung von der experimentellen Energie.

La fonction d'onde de l'état fondamental de la molecule H_2 est calculée directement dans son developpement naturel, les orbitales naturelles (NO) approchées étant représentées comme combinaisons linéaires des fonctions de Slater définies par rapport au centre de la molecule. On obtient $-1{,}168$ a.u. pour l'energie totale à la distance de l'equilibre (la valeur exacte vaut $-1{,}174$ a.u.) et on tient compte de 96% de l'energie de liaison. Cette valeur est probablement la meilleure obtenue jusqu'ici dans le cadre d'un developpement monocentrique. La precision de ce calcul est limitée due à la convergence lente du developpement monocentrique. L'écart de l'energie Hartree-Fock calculée dans la même base ($-1{,}129$ a.u.) par rapport à la valeur exacte ($-1{,}136$ a.u.) vaut à 0,001 a.u. près celui de l'energie du developpement naturel par rapport à l'energie experimentale.

1. Introduction

Since the first quantum mechanical treatment of the H_2-molecule by HEITLER and LONDON [*14*] a surprisingly large number of alternative approaches to the same problem have been proposed (for bibliographies see [*3, 25*]). The aim of only a few of these approaches was to get better wave functions than known before, most of them were formally rather simple and were introduced to justify more or less new physical pictures of chemical binding.

A final point was put to these attempts by H. Shull [*26*], who showed that all the wave functions which had been proposed so far could be discussed and interpreted from one general point of view, namely in terms of their natural expansions [*15*, *24*]. A pertinent result of this analysis was that wave functions which looked very different and which suggested quite different physical pictures were shown to belong to the same type of limited natural expansions.

A spinfree two electron function for a singlet ground state in its natural expansion has the form:

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

Different types of H_2-molecule wave-functions differ by the number of terms after which one truncates the expansion (1) and by the accuracy by which the NOs χ_i are approximated. MO functions contain one term, VB funktions two terms (the second one accounting for "left-right" correlation) etc. In a MO-SCF function χ_1 is very well approximated [*7*, *8*, *26*]. The expansion (1) was first shown by Lennard-Jones et al. [*15*, *23*] to be possible and useful before it had been proposed in a different context by Löwdin and Shull [*24*] as "natural expansion".

It is somewhat unsatisfactory to start from a given numerical wave function and analyse it afterwards in terms of natural orbitals rather than to perform calculation and interpretation in one step by introducing the concept of natural orbitals at the very beginning.

This is, in fact possible. Integro-differential equations which allow one to calculate the natural orbitals (NO) for two electron functions have been derived by one of the present authors in paper I of this series [*20*] (here referred to as I) and applied successfully to two-electron atoms in papers II [*21*] and III [*1*].

Rather good approximations to the NOs can be obtained by resolving the following rather simple set of integro-differential equations (after specifiying a set of one electron basis functions) in matrix form

$$(H + J^1)\chi_1 = \lambda_{11}\chi_1 \tag{2}$$

$$Q_i\,[n_i\,(H + K^i) + K^1]\,Q_i\,\chi_i = \lambda_{ii}\,\chi_i \tag{3}$$

$$n_k = \frac{(1k \mid k1)}{E_1 - E_k} \tag{4}$$

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

As to the meaning of the notations and the iterative procedure for the solution of the system the reader is referred to the earlier paper of this series, especially I and III. Eq. (2) is the Hartree-Fock equation for the system. The correlation potential, the role of which has been discussed in detail in III is ignored here which amounts to ignoring the small difference between the strongly occupied NO χ_1 and the Hartree-Fock orbital φ_{HF}. This kind of procedure has been justified in III.

This work is preliminary in sofar as we did not choose the most appropriate set of one-electron functions — in terms of which the NOs are expanded — but rather a set which facilitates the computational problem, i.e. a set of Slater type orbitals localized at the midpoint of the molecule.

2. Pilot calculations on H_2^+

In order to test the accuracy of the one-center expansion method we started with some calculations of the ground state of the H_2^+-ion with this same expansion. The results (for the equilibrium distance $R = 2.0$ a.u.) are collected in Tab. 1.

After we had finished these calculations the slightly better results by Joy and Handler [*16*] were published. Their best energy values are given for comparison. Our best one-center energy for H_2^+ is 0.2% off the total electronic energy, which means that the error of the binding energy is about 2%. The convergence of one-center expansions of H_2^+ has been discussed by Joy and Handler [*16, 17*]. There is evidence that the s-limit, i.e. the best energy obtained with s-functions only is -1.018502 a.u. (see also Hauk and Parr [*12*]), whereas the $(s + d)$-limit is near to -1.083676 a.u. [*16, 17*].

Table 1. *One-center calculations for the* H_2^+ *ground state* ($R = 2.0$ *a.u.*)

number of basis functions	type of basis functions (α-values in parenthesis)	electronic energy	error of the energy %
10	$1s$ (1.); $2s$ (1.); $1s$ (2.); $2s$ (2.); $3d$ (2.); $4d$ (3.); $5d$ (4.); $5g$ (4.); $6g$ (5.); $7g$ (5.)	−1.0905	1.
18	$1s$ (0.5, 1., 2., 3.); $2s$ (0.5, 1., 2., 3.); $3s$ (3.); $3d$ (2.); $4d$ (3.); $5d$ (4.); $5g$ (4.); $6g$ (5.); $7g$ (6.); $7i$ (6.); $8i$ (7.); $9i$ (8.)	−1.0984	0.4
21	$1s$ (1.12); $2s$ (1.56); $3s$ (2.94); $4s$ (3.70); $4s$ (4.0); $5s$ (4.78); $3d$ (2.); $4d$ (3.); $5d$ (4.); $5g$ (4.); $6g$ (5.); $7g$ (6.); $7i$ (6.); $8i$ (7.); $9i$ (8.); $9k$ (8.); $10k$ (9.); $11m$ (10.); $12m$ (11.); $13o$ (12.); $14o$ (13.)	−1.1005	0.2
12	s, d, i orbitals; among others functions like $73d$ (34.); $33i$ (32.)	−1.0999	0.3
14	four s, four d, two i, k and m-orbitals	−1.1012	0.15
exact [*2*]		−1.1026	

The first three rows are from this work, the other two from Joy and Handler [*16*].

The eventually rather slow convergence of the one-center expansion (the energy contributions of terms with large l probably go like l^{-4} [*16*]) depends on the behaviour of the wave function at the Coulomb singularities. Recently it has been proposed to improve one-center wave functions in small regions of space [*5*].

3. One-center SCF-MO calculation of the H_2 ground state

The SCF-MO calculation using a one-center basis is straight-forward. That the results are disappointing (see Tab. 2) compared to those for H_2^+ is essentially due to the fact that we were obliged to work with a smaller basis set. One can guess by extrapolation that with a basis of about 20 one-center Slater type orbitals an

Table 2. *One-center Hartree-Fock calculations for* H_2 *(*$R = 1.4$ *a.u.)*

number of basis functions	type of basis functions (α-values in parenthesis)	electronic energy (+ nuclear repulsion)	error of the energy %
10	$1s$ (1.2); $2s$ (1.4); $3s$ (2.8); $4s$ (4.3); $3d$ (2.8); $4d$ (4.3); $5d$ (5.7); $5g$ (5.7); $6g$ (7.1); $8i$ (10.0)	−1.1289	0.3
exact [8]		−1.1336	

HF energy − 1.132 a.u. should be obtained. (Since the computational effort goes about proportional to the 5th power of the dimension, calculations with a more extended set were not feasible on the IBM 7040 16 K computer available to us.) A similar result may be obtained with the same size of the basis, but by careful optimization of this basis; which is, however, computer-time consuming.

4. Calculation of the natural orbitals and the natural expansion coefficients

Since the ground state of H_2 is totally symmetric, the natural orbitals are adapted to the symmetry group $D_{\infty h}$; they can therefore be classified by three quantum numbers n, λ, p where λ is the angular quantum number, $p(= g$, or $u)$ the parity with respect to inversion at the center and n labels NOs of the same symmetry species. The natural expansion reads then

$$\psi(1, 2) = \sum_{n=1}^{\infty} \left\{ \sum_{p=g,u} c_{n0p}\, \chi_{n0p}(1)\, \chi_{n0p}(2) + \frac{1}{\sqrt{2}} \sum_{\lambda=1}^{\infty} c_{n\lambda p}{}^{*} \right. $$
$$\left. [\chi_{n\lambda p}(1)\, \chi^{*}_{n\lambda p}(2) + \chi^{*}_{n\lambda p}(1)\, \chi_{n\lambda p}(2)] \right\} . \tag{6}$$

Each orbital is expanded in terms of the basis set

$$\chi_{n\lambda p}(r, \vartheta, \varphi) = \sum_{l=\lambda}^{\infty} f_{n\lambda pl}(r)\, Y_l^{\lambda}(\vartheta, \varphi) \tag{7}$$
$$f_{n\lambda pl}(r) = \sum_k d^{(k)}_{n\lambda pl}\, R_{k\alpha}(r);\; R_{k\alpha}(r) = N\, r^{k-1}\, e^{-\alpha r}$$

For the σ_g-type NOs χ_{n0g} we used 10 basis orbitals $R_{k\alpha}(r)\, Y_l^0(\vartheta, \varphi)$, $l = 0, 2, 4, 6$ for σ_u – and π_u – NOs 7 and for π_g – and δ_g – NOs 6 basis orbitals. Natural orbitals of type δ_u, φ_g and those with higher angular quantum number were ignored after their contributions had been estimated to be negligeable.

Table 3. *Type of basis orbitals* $R_{k\alpha}(r)\, Y_l^0(\vartheta, \varphi)$ *used in the* NO-*calculations*

Nr.	1	2	3	4	5	6	7	8	9	10
k	1	2	3	4	3	4	5	5	6	8
l	0	0	0	0	2	2	2	4	4	6
α	1,2	1,4	2,8	4,3	2,8	4,3	5,7	5,7	7,1	10,0
							π_g, σ_g			
					σ_g					
k	2	3	4	4	5	6	6			
l	1	1	1	3	3	3	5			
α	1,4	2,8	4,3	4,3	5,7	7,1	7,1			
				σ_u, π_u						

The basis functions together with their orbital exponents α are listed in Tab. 3. The parameters k and α have been chosen such that the $R_{k\alpha}(r)$ $(k > 1)$ have their maximum at $r = 0{,}7$ a.u., i.e. at the position of the nuclei. It was not attempted to optimize the k and α values by repeated calculations.

The coefficients $c_{n\lambda p}$ in the expansion (6) and the total energy of our NO-calculation (for the equilibrium distance) are collected in Tab. 4 together with similar results obtained indirectly [*7*, *11*] (i.e. starting from wave functions which had been computed previously by a conventional method). The error in the total energy is 0.5%, in the binding energy about 4% for our calculation. One sees, however, that the error in the total energy is about the same as the error in the SCF energy. The difference between the total energy and the Hartree-Fock energy obtained in this one-center basis is 0.039 a.u. which is to be compared with the corresponding difference between the exact values (the correlation energy) 0.040 a.u. This result suggests that our method is capable of accounting for electron correlation in a satisfactory way and that its defects reside essentially in the unadequate SCF value.

Table 4. *Total energies for the* H_2 *ground state and coefficients of the natural expansion*

	This work calculated directly	calculated indirectly (from given wave functions)		
		[*11*]	[*7*]	[*11*]
	One-center expansions		Two-center expansions	
$-E$	1.167506	1.16141	1.173044	1.173128
σ_g 1	−.99145	−.99068	−.99106	−.99088
2	.05263	.06094	.05481	.05506
3	.00927	.01496	.00997	.01035
4	.00581	.00825	.00655	.00736
5	.00252	.00330		.00287
6	.00145	.00143		
σ_u 1	.09752	.09934	.09947	.10796
2	.00824	.01027	.00975	.00943
3	.00218	.00228		.00250
4	.00193			
π_u 1	.06514	.06672	.06604	.06590
2	.00786	.00961	.00662	.00951
3	.00288			.00269
4	.00131			
π_g 1	.01145		.00838	.01263
2	.00310			.00330
3	.00107			
δ_g 1	.00924		.00688	.00932
2	.00255			.00219
3	.00100			

Nevertheless our result ($E = -1.1675$ a.u.) seems to be the best result obtained so far by one center calculation of the H_2 molecule. (The second best being the one by HAGSTRÖM and SHULL [*10*] [$E = -1.1614$ a.u.], followed by BISHOP's [*4*] [$E = -1.1605$ a.u.), see also [*18*]).

Table 5. *Energies of truncated* NO *expansions*

		NOs calculated directly This work		NOs calculated indirectly [7]	
n	a)	$-E$	$[\Delta E]$	$-E$	$[\Delta E]$
1	σ_g	1.128847		1.133467	
			.017888		.018630
2	σ_u	1.146735		1.152097	
			.010981		.010844
3	π_u	1.157716		1.162941	
			.006601		.007028
4	σ_g	1.164317		1.169969	
			.000709		.000850
5	π_g	1.165026		1.170719	
10	–	1.166975		1.173044	
20	–	1.167506		–	

n number of natural configurations in the expansion.
ΔE energy improvement.
a symmetry species of the last added NO.

That the higher NOs are not too badly approximated may also be concluded by comparing their coefficients with those obtained indirectly by HAGSTRÖM and SHULL [*11*].

Tab. 5 finally gives the energies of truncated natural expansions together with the corresponding values obtained indirectly by DAVIDSON and JONES [*7*]. The latter author's values are better than ours because they involve expansions in term of two-center orbitals. The improvements of the energy by adding subsequently one more term of the natural expansion are however very similar in both cases. Depending on the desired precision one may decide how many natural terms one wants to take into account. With two terms on accounts for "left-right" correlation (cf. [*8*]), the next important terms involve "in-out"-angular correlation etc.

5. Conclusions

It is possible to calculate the wave function of the Hydrogen molecule directly in its natural form and so combine calculation and interpretation from the very beginning.

A one-center expansion is possible, but not very convenient if one wants high accuracy, because the large dimension of the basis set necessary in this case is difficult to handle.

The error of 0.5% in the total energy or 4% in the binding energy obtained here comes from the fact that we were forced to perform the Hartree-Fock calculations with a basis of 10 funtcions only. Electron correlation seems to be accounted for correctly, however.

It seems worthwhile to repeat these calculations with a better convergent set of one-electron functions, especially in view of the application of our method to other molecular systems. We have started calculations with two-center orbitals and with Gaussians. Finally, H_2 is not the most favourable case for a one-center expansion. We believe that for systems like CH_4 the direct one-center calculation of natural orbitals in the geminal product approximation [*22*]—should give more satisfactory results.

The problem of calculating directly natural orbitals is closely connected to the one to minize the energy with respect to a linear combination of Slater determinants [*20, 13, 19, 27, 28*] i.e. to the problem of calculating "optimum multiconfiguration wave functions" by a self-consistent field procedure [*9*]. The method outlined in this series of papers is actually a solution of this problem for two-electron problems — and can be generalized to many-electron systems [*22*]. More recent approaches to calculate many-configuration wave functions [*6*] follow actually similar lines.

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