Exponent Optimization for Π States of H_2

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The total energy of the lowest $^1\Pi_u$, $^3\Pi_u$, $^1\Pi_g$, $^3\Pi_g$ states of H_2 was minimized in an extended Hartree-Fock procedure employing a double configuration wavefunction. The exponents of the basis functions $1s$, $2s$, $2p\sigma$, $2p\pi$, $3d\pi$ were optimized separately for all four states at various internuclear distances. The results show that the exponents are strongly state and distance dependent. They cannot be generally represented by atomic or equilibrium values. The details of the optimization process are presented.

Die Gesamtenergie der niedrigsten $^1\Pi_u$, $^3\Pi_u$, $^1\Pi_g$, $^3\Pi_g$ Zustände des H_2 wurde in einem erweiterten Hartree-Fock Verfahren mit einer Doppelkonfiguration minimisiert. Die Exponenten der Basis-funktionen $1s$, $2s$, $2p\sigma$, $2p\pi$, $3d\pi$ wurden unabhängig für alle vier Zustände bei verschiedenen Kern-abständen optimisiert. Die Ergebnisse zeigen eine starke Zustands- und Abstandsabhängigkeit der Exponenten. Diese können nicht allgemein durch atomare oder Gleichgewichtswerte dargestellt werden. Die Einzelheiten des Optimisierungsverfahrens werden angegeben.

Minimisation de l'énergie totale des plus bas états $^1\Pi_u$, $^3\Pi_u$, $^1\Pi_g$, $^3\Pi_g$ de H_2 dans un procédé Hartree-Fock à deux configurations. Les exposants des fonctions de la base: $1s$, $2s$, $2p\sigma$, $2p\pi$, $3d\pi$ ont été optimisés séparément pour les quatre états pour différentes distances internucléaires. Les résultats montrent que les exposants dépendent fortement de l'état et de la distance. Ils ne peuvent pas être généralement représentés par des valeurs atomiques et des valeurs d'équilibre. Description des détails du processus d'optimisation.

1. Introduction

The purpose of the present series of papers was to study the consequences of exponent optimization in limited basis sets in the MO LCAO framework. We chose the lowest excited Π states of H_2 because this seemed to be the simplest case where such a comparative study would be interesting and feasible. In this paper we are concerned with the optimization process and the dependence of exponents on state and internuclear distance. Two subsequent papers give results for potential curves and one-electron properties [1] and $\sigma - \pi$ separation [2]. Our results suggest that in small basis sets exponent optimization of at least the dominant basis orbitals is necessary for each particular state and distance. Since

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we find the exponents strongly state and distance dependent, it seems to be impossible to represent them by atomic or single equilibrium values.

We used double-configuration wavefunctions of the type

$$\varPsi = A\varPhi_{\mathrm{HF}} + B\varPhi_{\mathrm{HF'}}\,. \tag{1}$$

For the $\varPi_u$ states $\varPhi_{\mathrm{HF}} = (\sigma_g\pi_u)$, $\varPhi_{\mathrm{HF'}} = (\sigma_u\pi_g)$ and for the $\varPi_g$ states $\varPhi_{\mathrm{HF}} = (\sigma_g\pi_g)$, $\varPhi_{\mathrm{HF'}} = (\sigma_u\pi_u)$ were chosen. The terms in parentheses are the proper linear combinations of two determinants to define configurations of open-shell singlet and triplet states. The determinants are built up of MO's σ_g, σ_u, π_u, π_g. These MO's, below denoted by ψ, are given as linear combinations of atomic orbitals χ_μ with exponents ζ_μ

$$\psi_i = \sum_\mu C_{i\mu}\chi_\mu(\zeta_\mu)\,. \tag{2}$$

We used the following basis set of three σ AO's and two π AO's on each nucleus: $1s, 2s, 2p\sigma, 2p\pi, 3d\pi$. We then built up symmetry AO's where equivalent orbitals on each center were assigned the same exponents. The total energy of the double-configuration (1)

$$\begin{aligned} E_{\mathrm{ODC}} = {} & A^2\langle\varPhi_{\mathrm{HF}}|H|\varPhi_{\mathrm{HF}}\rangle + B^2\langle\varPhi_{\mathrm{HF'}}|H|\varPhi_{\mathrm{HF'}}\rangle \\ & + 2AB\langle\varPhi_{\mathrm{HF}}|H|\varPhi_{\mathrm{HF'}}\rangle \end{aligned} \tag{3}$$

was minimized with respect to coefficients C_μ and A and exponents ζ_μ in a multi-configuration SCF procedure for various internuclear distances in the range of $R = 1.5$ to 10 Bohr. Details of the method can be found elsewhere [1, 3]. In this paper, we are primarily concerned with some qualitative and quantitative consequences of the exponent optimization problem.

2. Optimization Process

The optimization was performed in the following way. We started with the exponents of the subset $\{1s, 2s, 2p\sigma, 2p\pi, 3d\pi\}$ of the larger set $\{1s, 2s, 3s, 2p\sigma, 3d\sigma, 2p\pi, 3p\pi, 3d\pi, 4d\pi, 4f\pi\}$ of Zemke et al. [3] for $R = 2$ Bohr. First we optimized the exponent of the $1s$ AO by keeping the exponents of all the other orbitals fixed. By trial and error attempts, we searched for three exponent values for which the corresponding total energy contained a minimum. The optimal exponent was obtained by fitting a parabola through the three initial exponents. To make sure that the final exponent yields indeed a lower energy than any of the three initial values, the total energy was again calculated with all other exponents unchanged. Then, in sequence, the $2s$-, $2p\sigma$-, $2p\pi$- and $3d\pi$-exponents were optimized in the same way. No reoptimization of the exponents was attempted because of the expensive and time-consuming procedure. This means we relied on the assumption that each exponent optimization is independent of the others. This seems reasonable except perhaps for $1s$- and $2s$-orbitals. However, our goal was not high accuracy, rather it was to recognize the general problems of exponent optimization. In this spirit, most of the calculation was done in single precision except for a few cases where double-precision seemed to be necessary.

Table 1 contains the energy dependence and virial theorem of such an optimization for the $^1\varPi_u$ state at $R = 2$ Bohr. It is obvious that the $2p\pi$-orbital

Table 1. Exponent optimization for $^1\Pi_u$ state at 2 Bohr

$1s\sigma$	$2s\sigma$	$2p\sigma$	$2p\pi$	$3d\pi$	E_{ODC}	$\langle V\rangle/\langle T\rangle$
1.09	1.10	1.47	0.453	1.0	−0.713301	−2.0021
0.99					−0.712618	−1.9964
1.19					−0.713030	−1.9998
1.11	1.10				−0.713305	−2.0021
	1.20				−0.712039	−2.0049
	1.00				−0.713843	−2.0097
	0.90				−0.713640	−2.0257
	0.98	1.47			−0.713861	−2.0123
		1.37			−0.713549	−2.0151
		1.57			−0.714005	−2.0097
		1.67			−0.714008	−2.0073
		1.77			−0.713892	−2.0052
		1.63	0.453		−0.714022	−2.0083
			0.35		−0.709494	−2.0615
			0.6		−0.701948	−1.9048
			0.445	1.0	−0.714078	−2.0131
				1.1	−0.714131	−2.0128
				1.3	−0.714143	−2.0122
				1.45	−0.714101	−2.0118
			0.42	1.00	−0.713822	−2.0274
			0.442	1.23	−0.714152	−2.0142
1.09	1.10	1.47	0.453	1.0	−0.715675	Ref. [3]
	plus additional orbitals					
					−0.71859	experimental

plays the dominant role and changes in the $2p\pi$-orbital exponents cause significant changes in the total energy. Gradually less important are $1s$-, $2s$-, $2p\sigma$-orbital exponents, whereas the $3d\pi$-orbitals do not significantly influence the total energy upon exponent variation. From the virial theorem ratio $\langle V\rangle/\langle T\rangle$ in Table 1 we can also conclude that the location of the minimum of the potential curve is shifted to values $R > 2$ Bohr with increasing $\zeta_{2p\pi}$. This indicates a necessity for exponent optimization of the $2p\pi$-orbital exponent in the range of R values about the equilibrium distance.

We then proceeded to calculate points of the potential energy curves of all the four Π states at $R = 1.5, 1.8, 2.2, 3, 4, 5, 6, 7, 8, 10$ Bohr. With the above results of relative significance of the orbital exponents in mind, we optimized the $2p\pi$-exponents for all these distances, whereas the exponents of $1s$-, $2s$-, $2p\sigma$- and $3d\pi$-orbitals were optimized only at $R = 1.5, 3, 6, 10$ Bohr and interpolated for the other distances. We took the optimal set of one distance as the starting set for a neighbor distance. Some of the particular features of general interest are discussed.

The energy of the $^1\Pi_g$ state at 4 Bohr shows a rather flat minimum with respect to $2p\pi$-exponent variation. However, there is a significant dependence of $\langle V\rangle/\langle T\rangle$ on this exponent. Due to strong configuration interaction, the energy curve features a maximum in the range of internuclear distances $3.5 \leqq R \leqq 4.5$ Bohr. The location of this maximum depends significantly on exponent optimization. Similar conclusions hold for the $^3\Pi_g$ state. However, the $2p\pi$-exponents of $^1\Pi_g$

Table 2. Analysis of $^1\Pi_g$ and $^3\Pi_g$ state energies at 4 Bohr

	$^1\Pi_g$			$^3\Pi_g$		
	A	B	C	A	B	C
$\zeta_{2p\pi}$	0.444	0.455	0.236	0.444	0.300	0.254
E_{HF}	-0.56811	-0.56695	-0.60075	-0.58126	-0.60146	-0.60273
E_{CI}	-0.60514	-0.60480	-0.60348	-0.59976	-0.60561	-0.60499
E_{ODC}	-0.60586	-0.60619	-0.60364	-0.60132	-0.60636	-0.60554
$\langle V\rangle/\langle T\rangle$	-1.9277	-1.9263	-2.1856	-1.9131	-2.1167	-2.1686

A all exponents optimized for $^1\Pi_u$ state.
B $\zeta_{2p\pi}$ optimized for E_{ODC} for Π_g state.
C $\zeta_{2p\pi}$ optimized for E_{HF} for Π_g state.

and $^3\Pi_g$ at 4 Bohr differ from each other considerably and so does the location of the maxima. Since the location of the maxima seems to be of interest, we have also investigated the following point of view: Consider the energy of a single configuration Φ_{HF} as reference energy and optimize the $2p\pi$-exponent in order to obtain a minimum of the SCF energy of this configuration. With this exponent, proceed to the multi-configuration SCF procedure. The results for $^1\Pi_g$ and $^3\Pi_g$ states are in Table 2. It is clear from this table that the flat minimum of the E_{ODC} curve of $^1\Pi_g$ with respect to $\zeta_{2p\pi}$ does not imply a flat minimum of the E_{HF} curve. Quite the opposite is true, namely there is an important dependence of the latter energy on the choice of the $2p\pi$-exponent. For the $^1\Pi_g$ state this fact is more expressed since the optimal exponents $\zeta_{2p\pi}(ODC) = 0.455$ for ODC optimization and $\zeta_{2p\pi}(HF) = 0.236$ and for SCF optimization differ much more than for the $^3\Pi_g$ state. Comparing $\langle V\rangle/\langle T\rangle$ for E_{ODC} calculated with either ODC or SCF optimized $2p\pi$-exponents, we obtain a different internuclear distance R for the energy maximum in each case.

At 6 Bohr the Π_g states show another peculiarity. The $3d\pi$-orbital exponent was tentatively determined as 0.6 on the ODC level. We observed a distortion of the HF curve when this value was employed. The ODC energy curve was smooth. We checked this point and found that the distortion of the HF curve disappears for ζ values of about 0.65 to 0.7. This shows again that the SCF optimization follows a path different from ODC optimization.

For 10 Bohr a particular problem arises because of the asymptotic limits. All four Π states dissociate to hydrogen atom states $(1s, 2p)$ with $\zeta_{1s} = 1.00$ and $\zeta_{2p\pi} = 0.5$. The other orbitals are eliminated, *i.e.* their linear coefficients in the MO's decrease to zero. This requires a high degree of accuracy in the integrals if the optimal exponents of $2s$-, $2p\sigma$-, and $3d\pi$-orbitals are desired, since they contribute very little to the total energy. It is hard to predict to which limits these orbitals converge or even whether this is a meaningful question to ask.

3. Optimal Exponents

We have collected the results of our exponent optimization in Figs. 1–5. Here we have smoothed out the effect of interpolation for the exponents. The dashed part of Fig. 1 seems to be an artifact. The exponents should increase
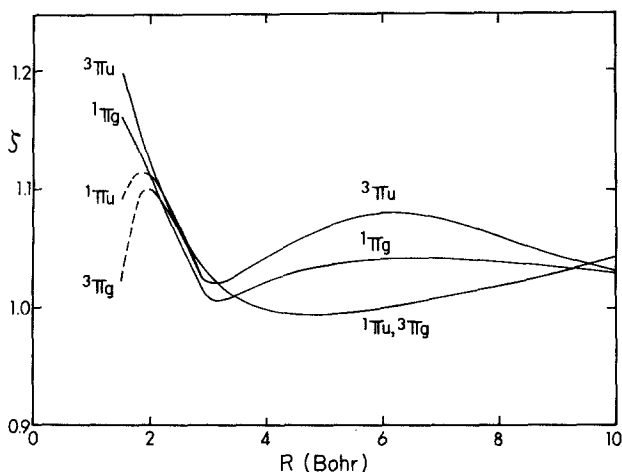
Fig. 1. Optimal 1s-orbital exponents ζ for Π states of H_2 in dependence of internuclear distance R
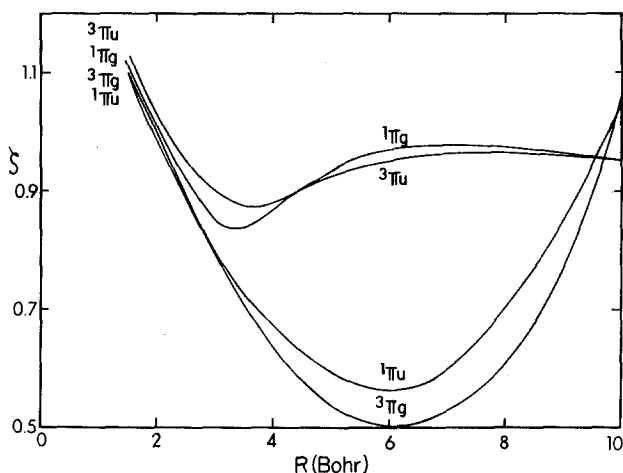

Fig. 2. Optimal 2s- orbital exponents ζ for Π states of H_2 in dependence of internuclear distance R

toward the united atom limit with decreasing internuclear distance. The curves for the $3d\pi$-orbitals are probably less accurate than for the orhers, because their energy contribution was very difficult to trace. The figures show clearly a high dependence of the optimal exponents on the internuclear distance. There is no way to make a good guess how they behave, except for the dominant orbitals at small and large R. There is a little *a priori* knowledge how significantly an orbital contributes to the total energy or another physical quantity at a particular distance. Some exponents would have to be optimized to four figures to guarantee six significant figures in the energy. There was no attempt made to achieve this goal, rather we were interested in the general features of nonlinear parameter optimization. There are indications that small sets of orbitals even
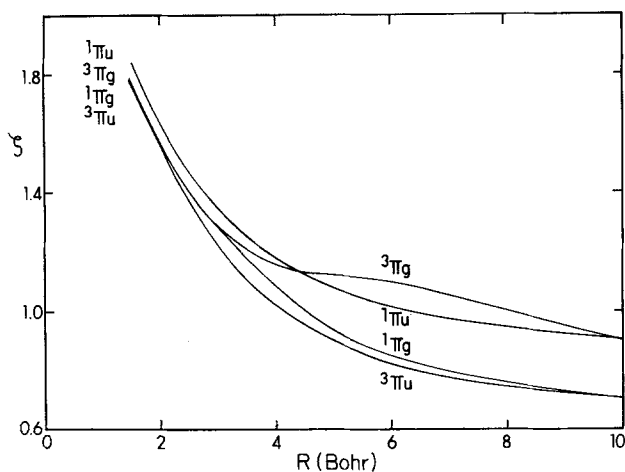
Fig. 3. Optimal $2p\sigma$-orbital exponents ζ for Π states of H_2 in dependence of internuclear distance R
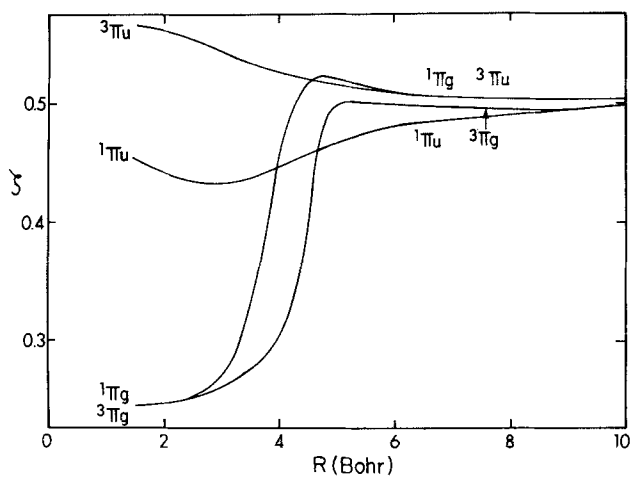
Fig. 4. Optimal $2p\pi$-orbital exponents ζ for Π states of H_2 in dependence of internuclear distance R
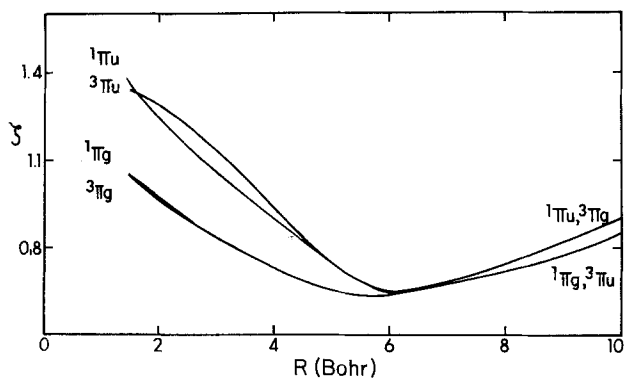
Fig. 5. Optimal $3d\pi$-orbital exponents ζ for Π states of H_2 in dependence of internuclear distance R

with optimized exponents are not necessarily superior to medium-sized sets with little optimization [3]. Perhaps the best compromise would be to optimize the exponents of a minimal basis set over the whole range of internuclear distances and then add a number of orbitals so that the larger set can take care of the features of potential curves by linear parameter optimization only.

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