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Optimal Double-Configuration Study of the Lowest Excited Π States of H_2

I. Potential Energy Curves and One-Electron Properties

KARL JUG*
Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616
and Department of Chemistry, Saint Louis University, Saint Louis, Missouri 63156

PETER G. LYKOS**
Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616

A. D. MCLEAN
IBM Research Laboratory, San Jose, California 95114

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Various levels of approximation (Hartree-Fock, configuration interaction and double-configuration Hartree-Fock method) are compared for extensive and limited exponent optimization of the atomic orbitals of the wavefunctions. The potential energy curves for the lowest-lying $^1\Pi_u$, $^3\Pi_u$, $^1\Pi_g$, $^3\Pi_g$ states of the hydrogen molecule are presented. The shapes of the curves on the highest level of approximation, i.e. with the optimal double-configuration wavefunction, are basically in agreement with previous, more sophisticated and time-consuming work. The influence of the various approximations is also studied for several one-electron properties: charge distribution of the wavefunction along and perpendicular to the molecular axis, quadrupole moment and core attraction energy distribution. Differences arise to the work of Zemke *et al.* [1], who used a limited exponent optimization with a larger basis set, in the Π_g states where the π orbitals are very diffuse. The differences concern magnitude and location of minima and maxima of potential curves, as well as considerable changes in one-electron properties which depend strongly on the spatial distribution of the orbitals.

Verschiedene Approximationsstufen (Hartree-Fock, Konfigurationenwechselwirkung und Doppelkonfigurationen-Hartree-Fock-Methode) werden für ausgedehnte und begrenzte Exponentenoptimisierung von Atomorbitalen der Wellenfunktionen verglichen. Die Potentialkurven für die niedrigsten $^1\Pi_u$, $^3\Pi_u$, $^1\Pi_g$, $^3\Pi_g$ Zustände des Wasserstoffmoleküls werden angegeben. Die Form der Kurven im Rahmen der besten Näherung, d. h. mit Doppelkonfiguration, stimmen im wesentlichen mit früheren aufwendigeren Rechnungen überein. Der Einfluß der verschiedenen Approximationen wird auch an einigen Einelektroneneigenschaften studiert: Ladungsverteilung der Wellenfunktion längs und senkrecht zur Molekülachse, Quadrupolmoment und Verteilung der Rumpfenergie. Unterschiede erscheinen zur Arbeit von Zemke *et al.* [1], die einen größeren Basissatz mit begrenzter Optimisierung verwandten, bei den Π_g Zuständen, wo die π-Orbitale sehr diffus sind. Die Unterschiede betreffen Größe und Lage der Minima und Maxima der Potentialkurven sowie beträchtliche Änderungen in solchen Einelektroneneigenschaften, die stark von der räumlichen Verteilung der Orbitale abhängen.

Comparaison de différents niveaux d'approximation (Hartree-Fock, interaction de configuration et Hartree-Fock à deux configurations) pour des optimisations étendues et limitées des orbitales atomiques de base. Calcul des courbes d'énergie potentielle pour les plus bas états $^1\Pi_u$, $^3\Pi_u$, $^1\Pi_g$, $^3\Pi_g$ de la molécule d'hydrogène. Pour la fonction d'onde la plus raffinée: H.F. à deux configurations, la forme des courbes est en accord avec les résultats obtenus dans des travaux précédents plus complexes

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* On leave to: Institut für Theoretische Chemie, Universität Stuttgart.

** On leave to: Office of Computing Activities, National Science Foundation, Washington, D.C.

et plus coûteux. On étudie aussi l'influence des diverses approximations sur plusieurs propriétés monoélectroniques: distribution de charge le long de l'axe moléculaire et perpendiculairement à celui-ci, moment quadrupolaire et distribution de l'énergie d'attraction de coeur. On trouve des différences avec le travail de Zemke *et al.* (1), qui utilisent une plus grande base partiellement optimisée, pour les états Π_g où les orbitales π sont très diffuses. Les différences concernent la grandeur et la position des extrema des courbes de potentiel, ainsi que des variations importantes des propriétés monoélectroniques qui dépendent fortement de la distribution spatiale des orbitales.

1. Introduction

The purpose of this paper is to study various levels of approximation in the MO LCAO framework with the example of the lowest-lying $^1\Pi_u$, $^3\Pi_u$, $^1\Pi_g$, $^3\Pi_g$ states of the hydrogen molecule. Different types of wavefunctions were employed. The energies and expectation values of one-electron operators of a single-configuration type wavefunction Φ_{HF} are compared with those of a double-configuration wavefunction of CI type $\Psi_{\mathrm{CI}} = A_{\mathrm{CI}}\Phi_{\mathrm{HF}} + B_{\mathrm{CI}}\Phi_{\mathrm{HF'}}$ and of extended Hartree-Fock type $\Psi_{\mathrm{ODC}} = A_{\mathrm{ODC}}\Phi_{\mathrm{HF}} + B_{\mathrm{ODC}}\Phi_{\mathrm{HF'}}$. In the latter wavefunction the coefficients A and B are also subjected to a self-consistent iteration procedure. The configurations are built up of the proper linear combinations of determinants for each of the four Π states. Φ_{HF} and $\Phi_{\mathrm{HF'}}$ are chosen in such a way that they allow for proper dissociation of the molecular states in excited atomic states. The molecular orbitals used are the lowest σ_g, σ_u, π_u, π_g functions given as linear combinations of a small number of equivalent atomic orbitals on each center.

The present approach was used by Zemke *et al.* [1] to study primarily the $^1\Pi_u$ state, but also some of the characteristic features of the $^3\Pi_u$, $^1\Pi_g$ and $^3\Pi_g$ states. The present work is a generalization and complement of their study. Therefore we shall, in the next sections, be brief about the details of the method and emphasize only the differences arising in the present work. Most of the general features of the method are equal; the emphasis of the work of Zemke *et al.* [1] was on a limited exponent optimization of a medium-sized atomic basis set. Our objective was a full exponent optimization of a smaller basis set. Zemke *et al.* used the following atomic basis on each center $\{1s, 2s, 3s, 2p\sigma, 3d\sigma, 2p\pi, 3p\pi, 3d\pi, 4d\pi, 4f\pi\}$. They optimized the exponents for these 2×10 basis functions for the $^1\Pi_u$ state at $R = 2$ Bohr by minimizing the total energy of this state with a double-configuration function Ψ_{ODC} of extended Hartree-Fock type. They used these exponents for the study of all the other distances from $R = 1.5$ to 10 Bohr of the potential energy curve E_{ODC} of $^1\Pi_u$ and also the $^3\Pi_u$, $^1\Pi_g$ and $^3\Pi_g$ states. We employed a basis $\{1s, 2s, 2p\sigma, 2p\pi, 3d\pi\}$ on each nucleus. We optimized the exponents of the orbitals at a number of distances covering the potential curves from $R = 1.5$ to 10 Bohr. The optimization was performed separately for each of the four states. Details of the optimization can be found elsewhere [2]. For comparison, we have also calculated the properties of the $^3\Pi_u$, $^1\Pi_g$ and $^3\Pi_g$ states with the optimal exponents of the $^1\Pi_u$ states at the same distance.

We find the potential curves characterized properly in magnitude and location of minima and maxima for calculations based on optimized exponents. With comparative calculations with a single-state exponent set, here of the $^1\Pi_u$ state, for all four states we find larger inaccuracies in the magnitude than in the location of the minima. The location of the maxima with a small basis set is a difficult problem. One-electron properties are more uniform for all four states when calculated with a single-state exponent set instead of separate optimization. The $^1\Pi_u$ state exponent set leads to considerable inaccuracies for the Π_g states where diffuse π orbitals are involved. Details of Sections 3 and 4 lead us to the conclusion that exponent optimization of the dominant orbitals is necessary in small basis sets.

2. The Method

We use the Hamiltonian of the hydrogen molecule in the form consisting of kinetic energy $\boldsymbol{T}$ and nuclear attraction $-\frac{1}{r_a}-\frac{1}{r_b}$ of each electron, electronic repulsion $\frac{1}{r_{12}}$ and nuclear repulsion $\frac{1}{R}$

$$\boldsymbol{H}=\boldsymbol{H}_1+\boldsymbol{H}_2+\frac{1}{r_{12}}+\frac{1}{R} \tag{2.1}$$

$$\text{with} \quad \boldsymbol{H}_i=\boldsymbol{T}_i-\frac{1}{r_{ai}}-\frac{1}{r_{bi}} \qquad i=1,2\,.$$

The approximate wavefunction is of double-configuration form

$$\Psi=A\Phi_1+B\Phi_2 \tag{2.2}$$

where Φ_1 and Φ_2 are orthonormal. The total energy of the system is

$$E_{\text{total}}=\frac{1}{A^2+B^2}\{A^2H_A+B^2H_B+2ABH_{AB}\} \tag{2.3}$$

$$\begin{aligned}\text{with} \quad H_A&=\langle\Phi_1|\boldsymbol{H}|\Phi_1\rangle\\ H_B&=\langle\Phi_2|\boldsymbol{H}|\Phi_2\rangle\\ H_{AB}&=\langle\Phi_1|\boldsymbol{H}|\Phi_2\rangle\,.\end{aligned}$$

To obtain a minimal energy with respect to A and B, we have to solve

$$\begin{vmatrix} H_A-E & H_{AB}\\ H_{AB} & H_B-E\end{vmatrix}=0\,. \tag{2.4}$$

We shall use a normalized wavefunction in the following.

Each configuration Φ_i consists of two determinants built up by a sigma MO σ_i and a pi MO π_i

$$^{1,3}\Phi_i=\tfrac{1}{2}\left\{\begin{vmatrix}\sigma_i(1)\,\bar{\pi}_i(1)\\ \sigma_i(2)\,\bar{\pi}_i(2)\end{vmatrix} \begin{matrix}-\\+\end{matrix} \begin{vmatrix}\bar{\sigma}_i(1)\,\pi_i(1)\\ \bar{\sigma}_i(2)\,\pi_i(2)\end{vmatrix}\right\}. \tag{2.5}$$

The minus sign refers to the singlet, the plus sign to the triplet state and the bar to β spin. The MO set $\sigma_1, \sigma_2, \pi_1, \pi_2$ is assumed as orthonormal. With these wavefunctions, H_A, H_B and H_{AB} can be reduced to

$$\begin{aligned} H_A &= H_{\sigma_1} + H_{\pi_1} + J_{\sigma_1\pi_1} \pm K_{\sigma_1\pi_1} \\ H_B &= H_{\sigma_2} + H_{\pi_2} + J_{\sigma_2\pi_2} \pm K_{\sigma_2\pi_2} \\ H_{AB} &= J_{\sigma_1\sigma_2\pi_1\pi_2} \pm K_{\sigma_1\sigma_2\pi_1\pi_2} \,. \end{aligned} \tag{2.6}$$

For convenience, we have dropped the nuclear repulsion.

H_{σ_i} and H_{π_i} are the usual core integrals and J and K the Coulomb and exchange integrals

$$\begin{aligned} J_{\sigma_1\pi_1} &= (\sigma_1\sigma_1 | \pi_1\pi_1)\,, \\ K_{\sigma_1\pi_1} &= (\sigma_1\pi_1 | \pi_1\sigma_1)\,, \\ J_{\sigma_1\sigma_2\pi_1\pi_2} &= (\sigma_1\sigma_2 | \pi_1\pi_2)\,, \\ K_{\sigma_1\sigma_2\pi_1\pi_2} &= (\sigma_1\pi_2 | \pi_1\sigma_2)\,. \end{aligned}$$

If we subject the energy (2.3) to variation with respect to the MO's σ_i and π_i $(i=1,2)$ preserving the orthonormality, we obtain the following set of equations

$$\begin{aligned} A^2(\boldsymbol{H}_1 + \boldsymbol{J}_{\pi_1} \pm \boldsymbol{K}_{\pi_1})\,\sigma_1(1) + AB(\boldsymbol{J}_{\pi_1\pi_2} \pm \boldsymbol{K}_{\pi_1\pi_2})\,\sigma_2(1) &= \lambda_{\sigma_1}\sigma_1(1) \\ B^2(\boldsymbol{H}_2 + \boldsymbol{J}_{\pi_2} \pm \boldsymbol{K}_{\pi_2})\,\sigma_2(1) + AB(\boldsymbol{J}_{\pi_2\pi_1} \pm \boldsymbol{K}_{\pi_2\pi_1})\,\sigma_1(1) &= \lambda_{\sigma_2}\sigma_2(1) \\ A^2(\boldsymbol{H}_1 + \boldsymbol{J}_{\sigma_1} \pm \boldsymbol{K}_{\sigma_1})\,\pi_1(2) + AB(\boldsymbol{J}_{\sigma_1\sigma_2} \pm \boldsymbol{K}_{\sigma_1\sigma_2})\,\pi_2(2) &= \lambda_{\pi_1}\pi_1(2) \\ B^2(\boldsymbol{H}_2 + \boldsymbol{J}_{\sigma_2} \pm \boldsymbol{K}_{\sigma_2})\,\pi_2(2) + AB(\boldsymbol{J}_{\sigma_2\sigma_1} \pm \boldsymbol{K}_{\sigma_2\sigma_1})\,\pi_1(2) &= \lambda_{\pi_2}\pi_2(2)\,. \end{aligned} \tag{2.7}$$

These are the extended Hartree-Fock equations in double-configuration form for this particular two-electron case [3]. The λ's are the Lagrange multipliers. The other multipliers vanish for symmetry reasons: As mentioned in the introduction, we used only one MO of each of the symmetry types $\sigma_g, \sigma_u, \pi_u, \pi_g$. The $\boldsymbol{J}$'s and $\boldsymbol{K}$'s are the usual Coulomb and exchange operators

$$\begin{aligned} \boldsymbol{J}_{\pi_1}\sigma_1(1) &= \left\langle \pi_1(2) \left| \frac{1}{r_{12}} \right| \pi_1(2) \right\rangle \sigma_1(1) \\ \boldsymbol{K}_{\pi_1}\sigma_1(1) &= \left\langle \pi_1(2) \left| \frac{1}{r_{12}} \right| \sigma_1(2) \right\rangle \pi_1(1) \\ \boldsymbol{J}_{\pi_1\pi_2}\sigma_2(1) &= \left\langle \pi_1(2) \left| \frac{1}{r_{12}} \right| \pi_2(2) \right\rangle \sigma_2(1) \\ \boldsymbol{K}_{\pi_1\pi_2}\sigma_2(1) &= \left\langle \pi_1(2) \left| \frac{1}{r_{12}} \right| \sigma_2(2) \right\rangle \pi_2(1) \qquad \text{etc.} \end{aligned}$$

After expansion of the MO's in atomic orbitals Eqs. (2.7) can be written in matrix form

$$\boldsymbol{F}_i\boldsymbol{C}_i = \boldsymbol{S}_i\boldsymbol{C}_i\lambda_i \qquad i = \sigma_1, \sigma_2, \pi_1, \pi_2 \tag{2.8}$$

where the double-configuration self-consistent field Hamiltonians are defined as

$$\begin{aligned} F_{\sigma_1} &= A^2(H_1+Q_{\sigma_1})+A\,B\,W_{\sigma_1}\\ F_{\sigma_2} &= B^2(H_2+Q_{\sigma_2})+A\,B\,W_{\sigma_2}\\ F_{\pi_1} &= A^2(H_1+Q_{\pi_1})+A\,B\,W_{\pi_1}\\ F_{\pi_2} &= B^2(H_2+Q_{\pi_2})+A\,B\,W_{\pi_2}. \end{aligned} \tag{2.9}$$

The repulsion energy matrix Q and coupling energy matrix W are obtained from contraction of supermatrix $\tilde{Q}$. For example

$$\begin{aligned} Q_{\sigma_1} &= D^{\dagger}_{\pi_1\pi_1}\,\tilde{Q}_{\pi_1\pi_1\sigma_1\sigma_1}\,,\\ W_{\sigma_1} &= (P_{\sigma_1\sigma_2}C_{\sigma_2})\,(S_{\sigma_1}C_{\sigma_1})^{\dagger}+(S_{\sigma_1}C_{\sigma_1})\,(P_{\sigma_1\sigma_2}C_{\sigma_2})^{\dagger}\\ \text{with}\quad P_{\sigma_1\sigma_2} &= D^{\dagger}_{\pi_1\pi_2}\,\tilde{Q}_{\pi_1\pi_2\sigma_1\sigma_2}\,,\\ D_{ij} &= C_i C_j^{\dagger} \qquad i,j=\sigma_1,\sigma_2,\pi_1,\pi_2\,,\\ \tilde{Q}_{ijkl} &= J_{ijkl}\pm K_{ijkl}\,. \end{aligned}$$

The J's and K's are the usual electronic repulsion integrals over atomic orbitals i, j, k, l. The formulas for the other cases are similar.

Solutions of the coupled Eqs. (2.8) yield the double-configuration self-consistent field MO's which allow us to calculate the energy and expection values of one-electron operators. The Hartree-Fock case is contained in the formalism with $A=0$ or $B=0$. In the following the energies H_A and H_B are denoted by E_{HF} and $E_{\mathrm{HF'}}$. The configuration interaction energy E_{CI} is then obtained by solving Eq. (2.4). The coupling energy H_{AB}, now denoted by E_{coupling}, has to be calculated separately. The final energy E_{ODC} referring to the MO's which are solutions of the coupled Eqs. (2.8) and (2.9) is obtained after self-consistent iteration of both linear AO coefficients C_i and configuration coefficient A. We employed an iteration procedure which alternately improves C_i and A in single steps.

In the following sections, we have chosen Φ_{HF} consisting of MO's σ_g and π_u for Π_u states and σ_g and π_g for Π_g states, whereas $\Phi_{\mathrm{HF'}}$ consists of σ_u and π_g for Π_u states and σ_u and π_u for Π_g states. The MO's are those belonging to lowest eigenvalue for each symmetry type of operator F of (2.9). The atomic basis set consists of symmetry adapted orbitals: three σ AO's $\{1s, 2s, 2p\sigma\}$ and two π AO's $\{2p\pi, 3d\pi\}$ on each center with equal exponents for equivalent orbitals.

3. Potential Energy Curves

The results of this paper are based on extensive exponent optimization of the symmetry adapted atomic basis set. The final exponents are collected in Table 1. The exponents of the $1s$, $2s$, $2p\sigma$ and $3d\pi$ orbitals were optimized at $R=1.5, 2, 3$, 6 and 10 Bohr. For the other distances the exponents were interpolated linearly. The $2p\pi$-orbital exponents were optimized at all distances listed. All exponents

Table 1. Optimized exponents for three σ-orbital, two π-orbital basis sets of double configuration Π state wave functions of H_2

States $^1\Pi_u\,^3\Pi_u\,^1\Pi_g\,^3\Pi_g$

R	$1s\sigma$				$2s\sigma$				$2p\sigma$				$2p\pi$				$3d\pi$			
1.5	1.09	1.20	1.16	1.02	1.10	1.13	1.11	1.10	1.84	1.75	1.77	1.78	0.453	0.567	0.245	0.245	1.36	1.34	1.05	1.05
1.8	1.10	1.15	1.13	1.07	1.03	1.06	1.04	1.04	1.71	1.62	1.63	1.64	0.446	0.565	0.245	0.245	1.28	1.30	1.00	1.00
1.95	1.11	1.13	—	—	0.99	1.03	—	—	1.65	1.56	—	—	0.443	0.562	—	—	1.24	1.29	—	—
2.0	1.11	1.12	1.11	1.10	0.98	1.02	1.00	1.00	1.63	1.54	1.55	1.56	0.442	0.561	0.245	0.245	1.23	1.28	0.97	0.96
2.2	1.09	1.10	1.09	1.09	0.94	0.99	0.97	0.96	1.57	1.48	1.50	1.51	0.439	0.559	0.244	0.244	1.20	1.25	0.94	0.94
3.0	1.03	1.02	1.01	1.03	0.80	0.90	0.85	0.80	1.34	1.23	1.27	1.28	0.432	0.544	0.239	0.239	1.07	1.13	0.83	0.83
4.0	1.02	1.04	1.02	1.02	0.72	0.91	0.89	0.70	1.23	1.09	1.12	1.21	0.444	0.527	0.455	0.300	0.92	0.96	0.75	0.75
5.0	1.01	1.06	1.03	1.01	0.64	0.93	0.93	0.60	1.12	0.95	0.98	1.15	0.466	0.515	0.520	0.495	0.86	0.88	0.67	0.67
6.0	1.00	1.08	1.04	1.00	0.56	0.95	0.97	0.50	1.01	0.82	0.84	1.09	0.482	0.509	0.510	0.497	0.60	0.60	0.60	0.60
7.0	1.01	1.06	1.04	1.01	0.69	0.95	0.96	0.65	0.98	0.79	0.80	1.04	0.486	0.507	0.508	0.497	0.68	0.66	0.66	0.68
8.0	1.02	1.05	1.04	1.02	0.82	0.95	0.96	0.80	0.95	0.76	0.77	0.99	0.490	0.505	0.506	0.498	0.76	0.71	0.71	0.76
10.0	1.04	1.03	1.03	1.04	1.05	0.95	0.95	1.05	0.90	0.70	0.70	0.90	0.498	0.502	0.502	0.498	0.90	0.85	0.85	0.90

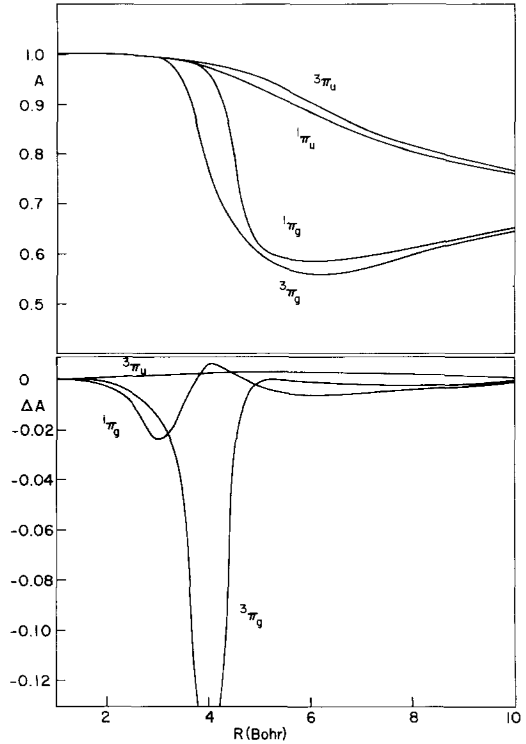

Fig. 1. ODC mixing coefficients A and differences ΔA between $^1\Pi_u$ based and optimal values

were determined by minimizing E_{ODC}, except $^1\Pi_g$ and $^3\Pi_g$ at $R = 1.5$ to 3 Bohr. These exponents were optimized so to minimize E_{HF} rather than E_{ODC}. The reasons for doing so were purely economical. This part of the work involving integrals with such small exponents was finished only recently with a different program, whereas the other part was done two years ago. Our calculations indicate that we can safely assume that configuration interaction is so small for the range $R = 1.5$ to 3 Bohr that not much improvement would result from optimizing E_{ODC}. In principle the values for the $2p\pi$-exponents would slightly increase.

Fig. 1 presents, on the ODC level, optimal coefficients A and differences $\Delta A = A' - A$ between mixing coefficients A' calculated with $^1\Pi_u$ exponents and optimal coefficients A. The results are also that the ODC approximation tries to mix the two configurations more than the CI approximation.

From the potential energy curves in the following tables this will become clearer. If Φ_{HF} is the dominant configuration, A is decreased when going from CI to ODC, otherwise it is increased. For the optimized exponents (Table 1) the configurations of the Π_g states are more strongly mixed than for the non-optimized exponents. The situation is reversed for the $^3\Pi_u$ state.

Tables 2–5 contain the self-consistent field energies E_{HF} and $E_{\mathrm{HF'}}$ of the two configurations Φ_{HF} and $\Phi_{\mathrm{HF'}}$, their configuration interaction energy E_{CI} and the optimum double-configuration energy E_{ODC} and the coupling energy E_{coupling}

Table 2. Potential energy curves and coupling energy for ${}^1\Pi_u$ state of H_2

R	E_{HF}	$E_{\mathrm{HF'}}$	E_{CI}	E_{ODC}	$E_{\mathrm{CI}}^{\mathrm{coupling}}$	$E_{\mathrm{ODC}}^{\mathrm{coupling}}$
1.5	−0.69571	0.02498	−0.69612	−0.69700	−0.00082	−0.00260
1.8	−0.71136	−0.12102	−0.71198	−0.71301	−0.00125	−0.00330
1.95	−0.71249	−0.17596	−0.71326	−0.71433	−0.00155	−0.00369
2.0	−0.71223	−0.19217	−0.71307	−0.71415	−0.00167	−0.00383
2.2	−0.70900	−0.24834	−0.71014	−0.71122	−0.00228	−0.00445
3.0	−0.68040	−0.38819	−0.68378	−0.68447	−0.00668	−0.00809
4.0	−0.64228	−0.46440	−0.65188	−0.65202	−0.01826	−0.01868
5.0	−0.61376	−0.49673	−0.63353	−0.63404	−0.03455	−0.03583
6.0	−0.59494	−0.52087	−0.62097	−0.62701	−0.04133	−0.05193
7.0	−0.58240	−0.52254	−0.62109	−0.62475	−0.05557	−0.06220
8.0	−0.57227	−0.52465	−0.62189	−0.62428	−0.06571	−0.07010
10.0	−0.55476	−0.52626	−0.62379	−0.62448	−0.08084	−0.08212

Table 3. Potential energy curves and coupling energies for ${}^3\Pi_u$ state of H_2

R	E_{HF}	$E_{\mathrm{HF'}}$	E_{CI}	E_{ODC}	$E_{\mathrm{CI}}^{\mathrm{coupling}}$	$E_{\mathrm{ODC}}^{\mathrm{coupling}}$
1.5	−0.71334	0.03694	−0.71383	−0.71426	−0.00098	−0.00185
1.8	−0.73012	−0.09805	−0.73091	−0.73135	−0.00158	−0.00246
1.95	−0.73169	−0.15015	−0.73268	−0.73309	−0.00198	−0.00281
2.0	−0.73156	−0.16590	−0.73263	−0.73303	−0.00213	−0.00294
2.2	−0.72869	−0.22122	−0.73009	−0.73044	−0.00280	−0.00351
3.0	−0.70020	−0.37222	−0.70345	−0.70361	−0.00644	−0.00680
4.0	−0.66119	−0.36585	−0.66829	−0.66847	−0.01371	−0.01421
5.0	−0.63179	−0.50908	−0.64506	−0.64554	−0.02417	−0.02547
6.0	−0.61186	−0.53408	−0.63082	−0.63388	−0.03171	−0.03781
7.0	−0.59760	−0.53971	−0.62643	−0.62886	−0.04327	−0.04825
8.0	−0.58691	−0.54326	−0.62475	−0.62685	−0.05168	−0.05587
10.0	−0.57046	−0.54536	−0.62470	−0.62564	−0.06430	−0.06613

Table 4. Potential energy curves and coupling energies for ${}^1\Pi_g$ state of H_2

R	E_{HF}	$E_{\mathrm{HF'}}$	E_{CI}	E_{ODC}	$E_{\mathrm{CI}}^{\mathrm{coupling}}$	$E_{\mathrm{ODC}}^{\mathrm{coupling}}$
1.5	−0.63663	−0.05059	−0.63671	−0.63671	−0.00017	−0.00017
1.8	−0.65459	−0.18078	−0.65472	−0.65472	−0.00025	−0.00026
2.0	−0.65693	−0.25975	−0.65711	−0.65711	−0.00034	−0.00035
2.2	−0.65513	−0.31647	−0.65536	−0.65536	−0.00046	−0.00047
3.0	−0.63198	−0.46743	−0.63267	−0.63270	−0.00138	−0.00145
4.0	−0.56695	−0.55136	−0.60480	−0.60619	−0.04431	−0.04693
5.0	−0.54497	−0.56928	−0.61136	−0.61802	−0.05158	−0.06290
6.0	−0.54146	−0.57560	−0.61391	−0.62340	−0.05012	−0.06579
7.0	−0.53013	−0.57316	−0.61912	−0.62520	−0.06061	−0.07081
8.0	−0.52685	−0.56765	−0.62155	−0.62563	−0.06869	−0.07562
10.0	−0.52654	−0.55400	−0.62451	−0.62551	−0.08200	−0.08377

Table 5. Potential energy curves and coupling energies for $^3\Pi_g$ state of H_2

R	E_{HF}	$E_{HF'}$	E_{CI}	E_{ODC}	$E_{CI}^{coupling}$	$E_{ODC}^{coupling}$
1.5	−0.63693	−0.05220	−0.63698	−0.63703	−0.00010	−0.00019
1.8	−0.65497	−0.19146	−0.65505	−0.65511	−0.00015	−0.00028
2.0	−0.65739	−0.26142	−0.65750	−0.65757	−0.00020	−0.00036
2.2	−0.65569	−0.31790	−0.65583	−0.65592	−0.00028	−0.00046
3.0	−0.63303	−0.45860	−0.63346	−0.63366	−0.00085	−0.00127
4.0	−0.60143	−0.54674	−0.60558	−0.60634	−0.00775	−0.00931
5.0	−0.56160	−0.58410	−0.60960	−0.61253	−0.03331	−0.03903
6.0	−0.55573	−0.58957	−0.61560	−0.61962	−0.03629	−0.04386
7.0	−0.54934	−0.58753	−0.61942	−0.62247	−0.04384	−0.04975
8.0	−0.54745	−0.58224	−0.62140	−0.62362	−0.05120	−0.05553
100	−0.54629	−0.56944	−0.62366	−0.62444	−0.06375	−0.06528

for all four Π states with the optimal exponents for each state. With respect to the hierarchy of models HF, CI and ODC we observe that most of the correlation energy is in the step from HF to CI and little further energy decrease results from going from CI to ODC level. The difference between CI and ODC energies increases with increasing internuclear distance in the range $R=1.5$ to 10 Bohr, reaching a maximum at $R=6$ Bohr. From calculations not presented here, we can also learn that exponent optimization always improves E_{ODC} but the corresponding E_{HF} might be higher than the E_{HF} of a non-optimized exponent set. This is particularly true when configuration interaction becomes important. For $^3\Pi_u$ and $^3\Pi_g$ this is true for $R \geqq 5$ Bohr, for $^1\Pi_g$ for $R \geqq 4$ Bohr. The Hartree-Fock curves are in general far too high with the ODC optimized basis set and so there is little meaning in considering the difference between E_{ODC} and E_{HF} in our calculations as a good description of the correlation energy. With the (sometimes only little) improvement of E_{ODC} we sacrifice information about E_{HF}. With a larger basis set, even with limited exponent optimization, there seems to be more flexibility in linear combinations to represent *both* self-consistent field states HF and HF′ satisfactorily. This is particularly true for Π_g states, but also for the $^3\Pi_u$ state [4].

The complete set of potential curves for the four Π states is given in Figs. 2–5. The easiest way to describe them is to say that the E_{ODC} curves of $^1\Pi_u$ and $^3\Pi_u$ states calculated with the optimal exponents of Table 1, match almost exactly the results of Browne [5]. For the $^1\Pi_g$ states Browne [6] lists only values at 8 and 10 Bohr. Our values agree with those, too.

For $^1\Pi_u$ our results are inferior to those of Zemke *et al.* [1] for $R<6$ Bohr. For larger distances our results are better because their fixed $2p\pi$ exponent could not converge to the proper limit. The difference between the two curves E_{ODC} and E''_{ODC} is, however, not considerable. Both curves show a minimum at about 1.95 Bohr quite in agreement with the extensive calculation by Kolos and Wolniewicz [7]. At larger distances both E_{ODC} and E''_{ODC} have a hump not visible in the figure. From the virial theorem ratio of potential and kinetic energy this maximum is located in our calculation at about 7.8 Bohr, whereas the more precise calculation by Kolos and Wolniewicz [7] locates it at 9 Bohr.

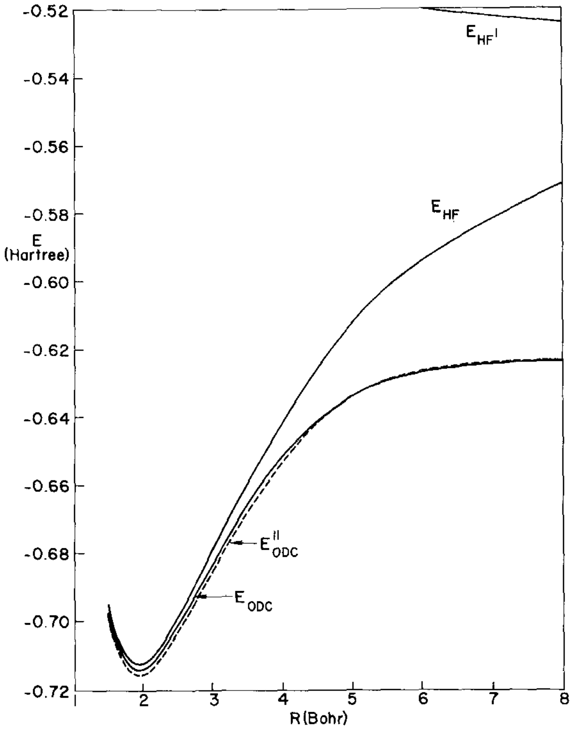

Fig. 2

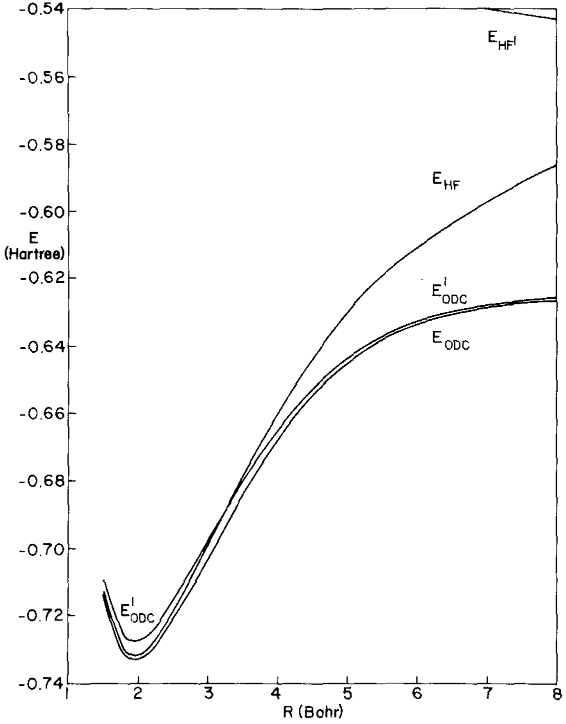

Fig. 3

Fig. 2. Potential energy curves of $^1\Pi_u$ state of H_2; E_{HF} and $E_{HF'}$ Hartree-Fock curves, E_{ODC} present optimal double-configuration curve, E''_{ODC} (dashed) curve of Ref. [1]

Fig. 3. Potential energy curves of $^3\Pi_u$ state of H_2; E_{HF} and $E_{HF'}$ Hartree-Fock curves, E_{ODC} present optimal double-configuration curve, E'_{ODC} curve with $^1\Pi_u$ exponents, E''_{ODC} (not shown because it almost coincides with E_{ODC}) curve of Ref. [1]

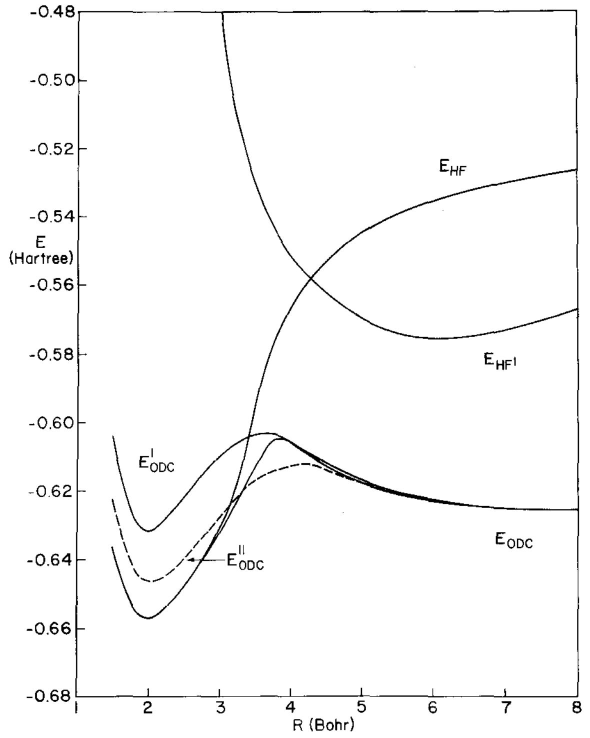

Fig. 4

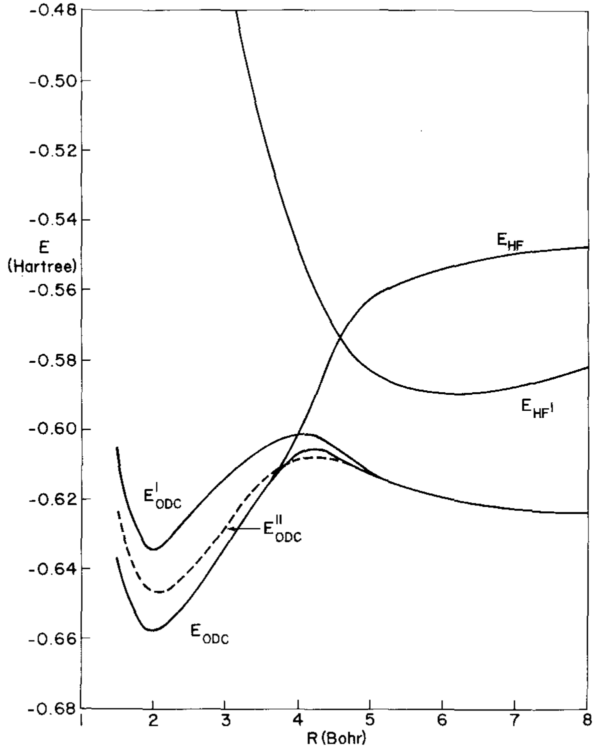

Fig. 5

Fig. 4. Potential energy curves of ${}^1\Pi_g$ state of H_2; E_{HF} and $E_{HF'}$ Hartree-Fock curves, E_{ODC} present optimal double-configuration curve of H_2, E'_{ODC} curve with ${}^1\Pi_u$ exponents, E''_{ODC} curve of Ref. [1]

Fig. 5. Potential energy curves of ${}^3\Pi_g$ state of H_2; E_{HF} and $E_{HF'}$ Hartree-Fock curves, E_{ODC} present optimal double-configuration curve of H_2, E'_{ODC} curve with ${}^1\Pi_u$ exponents, E''_{ODC} curve of Ref. [1]

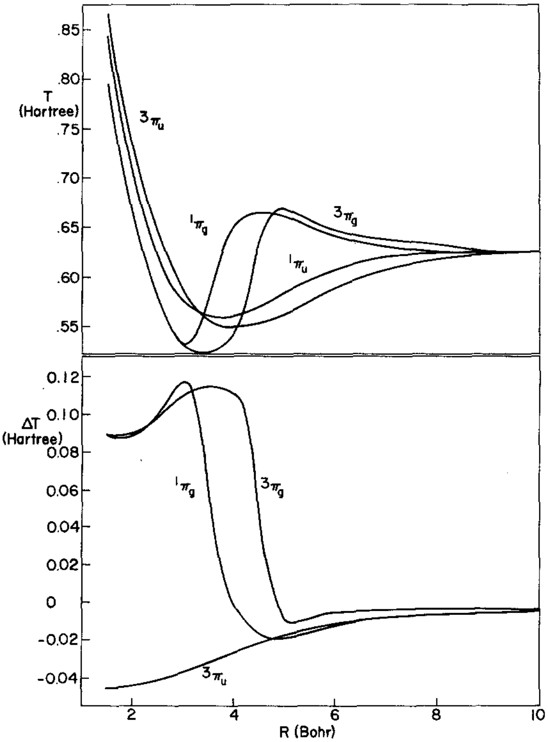

Fig. 6. ODC kinetic energies T and differences ΔT between $^1\Pi_u$ based and optimal values

The $E_{\rm ODC}$ potential curve for $^3\Pi_u$ is slightly lower than Zemke *et al.*'s denoted by $E''_{\rm ODC}$. We prefered not to include it in the figure because it is almost indistinguishable from ours. Both curves have a minimum at $R=1.95$ Bohr and no maximum. The potential curve $E'_{\rm ODC}$ for this state calculated with the exponents of $^1\Pi_u$ is quite inferior to both $E_{\rm ODC}$ and $E''_{\rm ODC}$ but locates the minimum correctly. However, here the virial theorem is not of much help since the internal distribution of kinetic and potential energy is way off the correct ratio for this case.

Most interesting are the Π_g states, where exponent optimization comes to full fruition at small internuclear distances. The fully optimized curve $E_{\rm ODC}$ is lower than Zemke's curve $E''_{\rm ODC}$, which in turn is lower than the curve $E'_{\rm ODC}$, based on the $^1\Pi_u$ optimization. All three curves show minima at about $R=2.00$ Bohr which, for the $^3\Pi_g$ state, is in agreement with the more extensive calculation of Wright and Davidson [8]. For $^3\Pi_g$ there is a maximum between 4 and 5 Bohr which is correctly located on all three levels of approximation $E_{\rm ODC}$, $E'_{\rm ODC}$ and $E''_{\rm ODC}$. Quite interestingly, the larger basis set of Zemke *et al.* is more favorable than the present optimized set at some distances where strong configuration interaction occurs. We attribute this to the flexibility of linear optimization which can decrease the energy of *both* Hartree-Fock curves $E_{\rm HF}$ and $E_{\rm HF'}$, whereas nonlinear parameter optimization seems to favor one curve at the costs of the other.

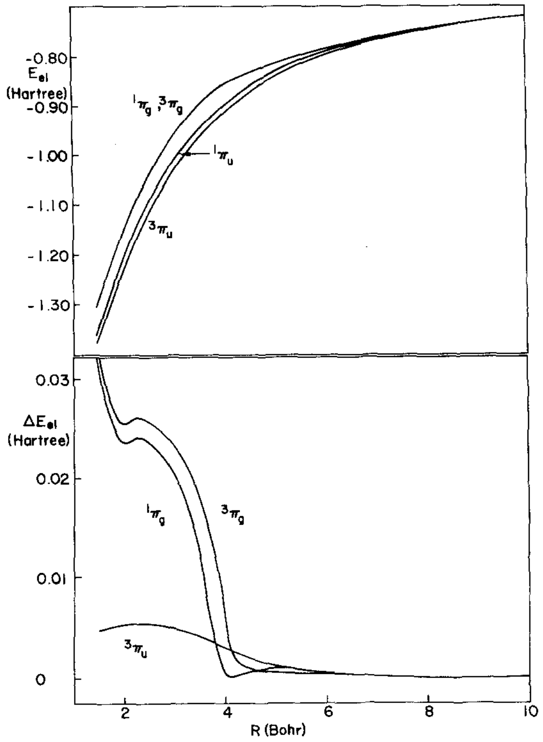

Fig. 7. ODC electronic energies E_{el} and differences ΔE_{el} between $^1\Pi_u$ based and optimal values

For larger distances $R \geqq 6$ Bohr our asymptotic set gains advantage over the unoptimized set by Zemke *et al.*

Similar consquences hold for the $^1\Pi_g$ state, where we locate the maximum at about 3.85 Bohr, whereas Zemke *et al.* located theirs tentatively at about 4.2 Bohr. Since they do not list values referring to the virial theorem, their choice is somewhat arbitrary. The precise location of the maximum has to await further investigation. The features of these curves are well-represented also in the less optimized E'_{ODC} curves although the location of the maxima undergoes a shift to smaller R values.

In the asymptotic limit of the ODC level all four states dissociate to the same atomic states. But $^1\Pi_u$ and $^3\Pi_g$ approach each other more closely and so do $^3\Pi_u$ and $^1\Pi_g$. This is expressed in the energies at 10 Bohr.

Figs. 6–8 contain the ODC energy breakdown and virial theorem for all four Π states with the optimal exponents and differences to $^1\Pi_u$ state based values of these quantities. Further calculations show an increase of kinetic energy when going from the HF level to the ODC levels for $^1\Pi_u$, $^3\Pi_u$ and $^3\Pi_g$ states. For $^1\Pi_g$ there is a surprising decrease of kinetic energy for $R \geqq 7$ Bohr. The increase of kinetic energies is certainly more than compensated by a decrease of potential energy. As far as a comparison of the two levels of exponent optimization is concerned, we can say that exponent optimization increases the kinetic

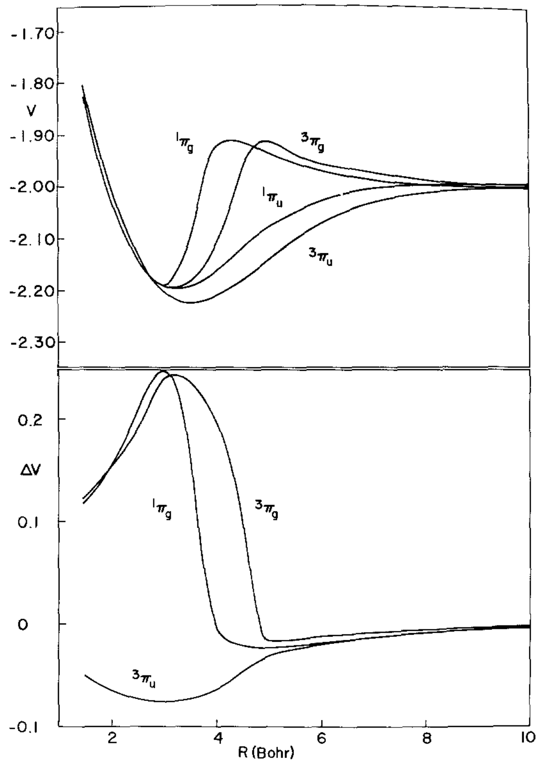

Fig. 8. ODC virial theorem ratios V and differences ΔV between $^1\Pi_u$ based and optimal values

energy of the $^3\Pi_u$ state, but decreases it for internuclear distances smaller than 4 Bohr, for the Π_g states. One might conclude that the wavefunction tries to contract upon exponent optimization for the $^3\Pi_u$ state and expand for the Π_g states. Details can be found in the next section.

4. Properties of One-Electron Operators

The density distribution perpendicular to the molecular axis can be analyzed by studying the expectation values of ϱ^2, the distribution along this axis by studying z_a^2.

Perpendicular to the molecular axis, measured by ϱ^2, there is a slight contraction in the Π_u states, whereas the Π_g states show a contraction for smaller distances and an expansion for larger distances when going from the HF level to the ODC level. Comparison of the four states shows again that $^3\Pi_u$ is more contracted than $^1\Pi_u$ whereas the Π_g are far more expanded (Fig. 9). The distributions of all four states come very close to each other when calculated with the exponents of $^1\Pi_u$.

Comparing the levels of approximation we find that when going from HF to ODC, $\langle z_a^2 \rangle$ increases for the Π_u states and decreases for the Π_g states. Simply speaking, the ODC functions on each atom for the Π_u states try to expand to

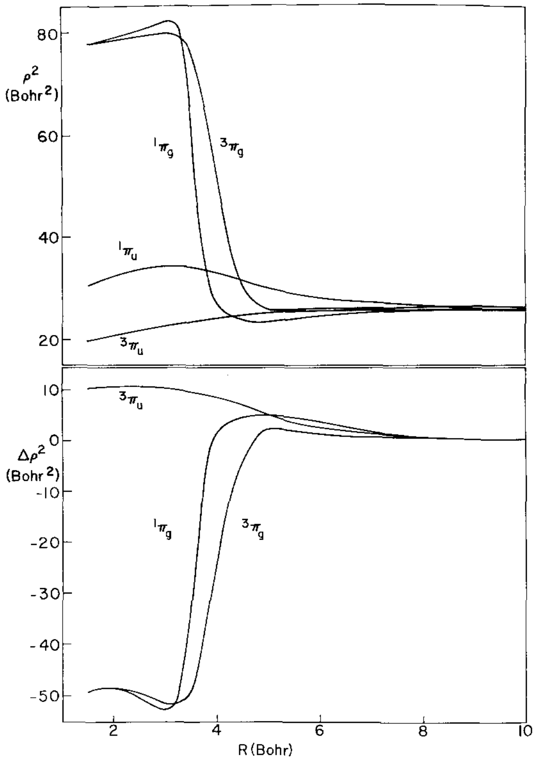

Fig. 9. ODC squares of wavefunction extensions ϱ^2 perpendicular to molecular axis and differences $\Delta\varrho^2$ between $^1\Pi_u$ based and optimal values

gain energy, whereas they try to contract for the Π_g states. This fact can be attributed to the different nodal character of the $\Phi_{\mathrm{HF}'}$ admixture for Π_u and Π_g states. Comparing the extensions of Π_u states with Π_g states calculated with optimal exponents we can say that the Π_g states are more diffuse than the Π_u states and $^3\Pi_u$ is more contracted than the $^1\Pi_u$ state. It is no surprise to find that with the $^1\Pi_u$ optimized exponents the other three try to approach the extensions of $\langle z_a^2\rangle$ of $^1\Pi_u$. For $^3\Pi_u \langle z_a^2\rangle$ increases, whereas for the Π_g states it decreases (Fig. 10). Again we observe that the asymptotic limit shows at 10 Bohr where the ODC values of $\langle z_a^2\rangle$ for $^1\Pi_u$ and $^3\Pi_g$ on one hand and $^3\Pi_u$ and $^1\Pi_g$ on the other hand are very close. This trend can be observed also for the other one-electron properties.

Quantities $\langle\varrho_a^2\rangle$ and $\langle z_a^2\rangle$ allow us to calculate the quadrupole moment $\langle 3z_a^2 - r_a^2\rangle$ with respect to an atomic origin. The calculations show that the Π_u states are more expanded perpendicular to the direction of the molecular axis for small internuclear distances, and in the direction of the molecular axis for large internuclear distances. The Π_g states show a distribution which is always more expanded in the direction of the molecular axis than perpendicular to it.

The major portion of nuclear attraction energy $\left\langle \frac{1}{r_a} \right\rangle$ is due to attraction $\langle \sin^2\theta / r_a\rangle$ perpendicular to the molecular axis than to attraction along the

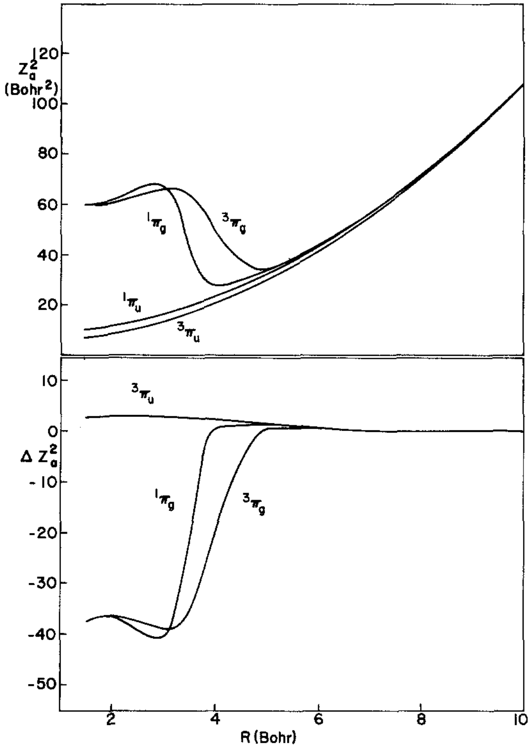

Fig. 10. ODC squares of wavefunction extensions z_a^2 parallel to molecular axis and differences Δz_a^2 between $^1\Pi_u$ based and optimal values

direction of the axis. The ratio $\langle \sin^2 \theta / r_a \rangle / \langle 1/r_a \rangle$ is very similar for all four states, being about 0.6. For comparison, in a spherical distribution this ratio would be 0.666. The expectation values for all four states are coming closer together if they are calculated with the $^1\Pi_u$ optimized exponents.

Tables 6–9 contain the eigenvalues of the double-configuration self-consistent field Hamiltonian F of (2.9). For the Hartree-Fock level, these are the orbital energies of the two MO's of Φ_{HF} and $\Phi_{\mathrm{HF}'}$ calculated separately with $B=0$ or $A=0$. The ordering of the levels is $\lambda_{\sigma_g} < \lambda_{\sigma_u} < \lambda_{\pi_u} < \lambda_{\pi_g}$ except for the Π_g states at 10 Bohr where $\lambda_{\sigma_u} < \lambda_{\sigma_g}$. These levels should approach -0.38 for the σ MO's and -0.003 for the π MO's. There is no indication for these limits at 10 Bohr. The reason is that the electronic interaction is still very strong, i.e. in the order of 0.1 Hartrees; the kinetic energy has already approached the proper limits very closely. The only other remarkable feature is the positive orbital eigenvalue of the MO π_g of $^3\Pi_u$ at 2.2 Bohr with the optimal exponents, which disappears for a $^1\Pi_u$ exponent calculation. The ODC values are the Lagrange multipliers. For small distances, the two multipliers referring to orbitals of configuration Φ_{HF} are close to their corresponding SCF values, whereas the other two have no resemblance to the SCF values. The more mixing occurs between the two configurations Φ_{HF} and $\Phi_{\mathrm{HF}'}$ the more the Lagrange multipliers decrease for the

Table 6. Eigenvalues of ${}^1\Pi_u$ state of H_2

R	σ_g	σ_u	π_u	π_g	
1.5	−1.02222	−0.43665	−0.11454	−0.01860	HF
	−1.02359	−0.00290	−0.11699	−0.00227	ODC
1.8	−0.93406	−0.47430	−0.11230	−0.02505	
	−0.93560	−0.00392	−0.11537	−0.00292	
1.95	−0.89591	−0.48713	−0.11120	−0.02600	
	−0.89750	−0.00455	−0.11461	−0.00330	
2.0	−0.88398	−0.49048	−0.11083	−0.02600	
	−0.88558	−0.00478	−0.11436	−0.00343	
2.2	−0.83939	−0.49993	−0.10942	−0.02490	
	−0.84099	−0.00585	−0.11346	−0.00404	
3.0	−0.70392	−0.50736	−0.10410	−0.02209	
	−0.70391	−0.01381	−0.11093	−0.00793	
4.0	−0.59252	−0.48930	−0.09766	−0.01920	
	−0.58291	−0.04279	−0.11158	−0.01958	
5.0	−0.52220	−0.47062	−0.09069	−0.01959	
	−0.49221	−0.09654	−0.11480	−0.03824	
6.0	−0.47983	−0.47708	−0.08403	−0.03033	
	−0.43009	−0.14979	−0.11701	−0.05573	
7.0	−0.45774	−0.44925	−0.07762	−0.02637	
	−0.38778	−0.19182	−0.11590	−0.06898	
8.0	−0.44396	−0.43427	−0.07024	−0.02614	
	−0.36112	−0.22038	−0.11478	−0.07891	
10.0	−0.42671	−0.41799	−0.05438	−0.02641	
	−0.33111	−0.25657	−0.11336	−0.09315	

Table 7. Eigenvalues of ${}^3\Pi_u$ state of H_2

R	σ_g	σ_u	π_u	π_g	
1.5	−0.98849	−0.42247	−0.13276	−0.00680	HF
	−0.98948	−0.00210	−0.13449	−0.00170	ODC
1.8	−0.90092	−0.44642	−0.13177	−0.00230	
	−0.90208	−0.00300	−0.13403	−0.00229	
1.95	−0.86394	−0.45370	−0.13113	−0.00035	
	−0.86515	−0.00355	−0.13369	−0.00263	
2.0	−0.85239	−0.45592	−0.13089	−0.00009	
	−0.85362	−0.00376	−0.13355	−0.00275	
2.2	−0.80907	−0.46241	−0.12989	0.00182	
	−0.81031	−0.00474	−0.13301	−0.00333	
3.0	−0.68155	−0.48000	−0.12467	−0.00593	
	−0.68196	−0.01147	−0.13020	−0.00677	
4.0	−0.58474	−0.48564	−0.11716	−0.02151	
	−0.57947	−0.03099	−0.12717	−0.01487	
5.0	−0.52749	−0.48025	−0.10891	−0.03264	
	−0.50568	−0.06952	−0.12462	−0.02828	
6.0	−0.49220	−0.48287	−0.10094	−0.04386	
	−0.44518	−0.12015	−0.12010	−0.04424	
7.0	−0.47047	−0.46333	−0.09272	−0.04393	
	−0.39668	−0.16891	−0.11532	−0.05915	
8.0	−0.45706	−0.45163	−0.08488	−0.04516	
	−0.36362	−0.20418	−0.11144	−0.07035	
10.0	−0.44199	−0.43719	−0.07034	−0.04631	
	−0.32668	−0.24583	−0.10678	−0.08487	

Table 8. Eigenvalues of ${}^1\Pi_g$ state of H_2

R	σ_g	σ_u	π_u	π_g	
1.5	−1.13635	−0.49951	−0.09414	−0.05539	HF
	−1.13629	−0.00025	−0.00018	−0.05555	ODC
1.8	−1.04359	−0.52773	−0.09376	−0.05544	
	−1.04344	−0.00041	−0.00028	−0.05569	
2.0	−0.99060	−0.54276	−0.09332	−0.05542	
	−0.99034	−0.00059	−0.00039	−0.05575	
2.2	−0.94358	−0.55509	−0.09270	−0.05541	
	−0.94315	−0.00086	−0.00053	−0.05584	
3.0	−0.79876	−0.58012	−0.08994	−0.05541	
	−0.79615	−0.00384	−0.00181	−0.05663	
4.0	−0.59110	−0.49236	−0.10624	−0.02197	
	−0.38974	−0.25473	−0.09090	−0.05927	
5.0	−0.52912	−0.46234	−0.09248	−0.02147	
	−0.25565	−0.35225	−0.11903	−0.06763	
6.0	−0.49956	−0.45476	−0.08538	−0.03004	
	−0.22853	−0.36530	−0.11989	−0.07187	
7.0	−0.45856	−0.44506	−0.07729	−0.02483	
	−0.22768	−0.36112	−0.11911	−0.07776	
8.0	−0.43739	−0.43710	−0.06940	−0.02441	
	−0.23749	−0.35042	−0.11738	−0.08408	
10.0	−0.41827	−0.42537	−0.05428	−0.02605	
	−0.26029	−0.32995	−0.11452	−0.09476	

Table 9. Eigenvalues of ${}^3\Pi_g$ state of H_2

R	σ_g	σ_u	π_u	π_g	
1.5	−1.13606	−0.50099	−0.09579	−0.05567	HF
	−1.13601	−0.00025	−0.00018	−0.05585	ODC
1.8	−1.04301	−0.52924	−0.09534	−0.05581	
	−1.04289	−0.00040	−0.00027	−0.05608	
2.0	−0.98993	−0.54397	−0.09495	−0.05586	
	−0.98972	−0.00055	−0.00036	−0.05621	
2.2	−0.94258	−0.55624	−0.09425	−0.05596	
	−0.94225	−0.00077	−0.00047	−0.05640	
3.0	−0.79718	−0.58079	−0.09138	−0.05651	
	−0.79535	−0.00299	−0.00142	−0.05761	
4.0	−0.65900	−0.55180	−0.10159	−0.05649	
	−0.62118	−0.04814	−0.01577	−0.06183	
5.0	−0.53888	−0.48251	−0.10747	−0.03852	
	−0.23116	−0.35058	−0.10614	−0.05219	
6.0	−0.50540	−0.47139	−0.09947	−0.04469	
	−0.20069	−0.36807	−0.11008	−0.05680	
7.0	−0.47303	−0.46149	−0.09184	−0.04463	
	−0.20288	−0.36241	−0.10997	−0.06357	
8.0	−0.45573	−0.45341	−0.08415	−0.04558	
	−0.21739	−0.34857	−0.10832	−0.07125	
10.0	−0.43786	−0.44148	−0.06981	−0.04606	
	−0.24691	−0.32383	−0.10555	−0.08417	

configuration Φ_{HF} and increase for the configuration $\Phi_{HF'}$ in absolute value, so that σ_g approaches σ_u and π_u approaches π_g. The asymptotic limits should be -0.25 for σ and -0.06125 for π. Again we observe that the eigenvalues for all four states are close together when all are calculated with ${}^1\Pi_u$ exponents.

Tables 10–13 contain the eigenvectors. For all four states we observe little change in the coefficients of configuration Φ_{HF} when going from the HF level to the ODC level. The changes increase with increasing configuration interaction. They are relatively larger for the less important AO's $2s$, $2p\sigma$ and $3d\pi$ than for the dominant $1s$ and $2p\pi$. The HF′ MO's show decreasing change for the $1s$ and $2p$ with increasing interaction, i.e. they are more stabilized by configuration interaction. There is, at all distances an important change in the coefficients of $2s$, $2p\sigma$ and $3d\pi$ AO's of this configuration $\Phi_{HF'}$. For large distances the coefficients of $1s$ and $2p\pi$ should approach $1/\sqrt{2}$, whereas the other coefficients should vanish. At 10 Bohr this trend becomes apparent. At small distances the most remarkable fact is the great difference in the coefficients of the σ MO's for ${}^1\Pi_g$ and ${}^3\Pi_g$ states which has no counterpart in the energy. It could very well be that the way in which the $1s$, $2s$, $2p\sigma$ exponents for 1.5 Bohr were obtained had an influence on the coefficients. One might conclude that the dependence of the linear coefficients on the exponents is expressed in such a way that the coefficients can take care of a redistribution of the charge so that there is almost no energy change when going from ${}^1\Pi_g$ to ${}^3\Pi_g$. We also emphasize that we did not reoptimize after obtaining the first optimized set of exponents. The discrepancy between ${}^1\Pi_g$ and ${}^3\Pi_g$ coefficients at 1.5 Bohr disappears when results of the Π_g states are based on the ${}^1\Pi_u$ state exponents.

5. Conclusion

The purpose of the present paper was a characterization of the features of the four lowest-lying Π states of the hydrogen molecule. We employed a double-configuration wavefunction and three levels of approximation, namely HF, CI and ODC for energies and one-electron properties. We compared these properties for two sets of exponents: one set based on optimization of the ${}^1\Pi_u$ state and taken also for all the other states and the other set based on optimization of all four states separately.

We found that the potential curves E_{CI} and E_{ODC} are characterized properly with maxima and minima on the CI and ODC level, and also the HF level is represented properly by the E_{HF} and $E_{HF'}$ curves. The emphasis on the accuracy of the HF level is decreased when the accuracy of the ODC level is increased. This can be seen from a comparison of the results for the ${}^3\Pi_u$ and Π_g states with ${}^1\Pi_u$ exponents and optimal exponents. The location of the maxima and minima of the potential curves is also dependent on the exponents. We find minima for Π_u and Π_g states properly at $R=1.95$ and $R=2.00$ with the optimal exponents. The maxima for ${}^1\Pi_u$ at $R=7.8$ Bohr, for ${}^1\Pi_g$ at $R=3.8$ Bohr and ${}^3\Pi_g$ at $R=4.2$ Bohr are less secured. They probably depend on the choice of the basis set.

An analysis of the one-electron properties shows uniformity for the four states when calculated with the same set of exponents, whereas significant differ-

Table 10. Eigenvectors of $^1\Pi_u$ state of H_2

R	σ_g			σ_u			π_u		π_g		
	1*s*	2*s*	2*p*	1*s*	2*s*	2*p*	2*p*	3*d*	2*p*	3*d*	
1.5	0.73563	−0.23537	0.05673	0.92149	0.59895	−0.02590	0.50601	−0.00416	4.0973	0.22399	HF
	0.73514	−0.23455	0.05622	1.02400	0.38657	−0.03350	0.50606	−0.00479	1.0399	−0.46189	ODC
1.8	0.68366	−0.16236	0.06141	0.87386	0.42024	−0.02861	0.50839	−0.00548	3.5594	0.24313	
	0.68318	−0.16144	0.06066	0.92885	0.32705	−0.02231	0.50848	−0.00643	1.0119	−0.45349	
1.95	0.65929	−0.12716	0.06348	0.85195	0.36426	−0.02809	0.50970	−0.00610	3.3437	0.24838	
	0.65885	−0.12620	0.06259	0.88722	0.31000	−0.02002	0.50982	−0.00725	1.0217	−0.44254	
2.0	0.65509	−0.11981	0.06417	0.84817	0.34366	−0.02736	0.51014	−0.00622	3.2710	0.24767	
	0.65466	−0.11883	0.06322	0.87781	0.30114	−0.01886	0.51028	−0.00745	1.0367	−0.43656	
2.2	0.65464	−0.11017	0.06568	0.85530	0.24702	−0.02263	0.51198	−0.00645	2.9821	0.23613	
	0.65424	−0.10912	0.06453	0.86601	0.24078	−0.01459	0.51216	−0.00799	1.1263	−0.40243	
3.0	0.65932	−0.08053	0.06787	0.85276	0.02661	−0.00209	0.52064	−0.00651	2.1238	0.15040	
	0.65925	−0.07928	0.06548	0.83378	0.07490	−0.00150	0.52112	−0.00976	1.4008	−0.20675	
4.0	0.66542	−0.03639	0.05887	0.79156	−0.01557	0.01366	0.53558	−0.00275	1.4514	0.03129	
	0.66595	−0.03513	0.05408	0.77140	0.03097	0.00903	0.53717	−0.01042	1.3765	−0.01945	
5.0	0.68208	−0.01890	0.04377	0.75604	−0.02427	0.02077	0.55352	0.00986	1.1015	−0.03959	
	0.68323	−0.01811	0.03652	0.74199	0.00755	0.01103	0.55802	−0.00840	1.1600	0.01645	
6.0	0.69772	−0.01521	0.02741	0.73590	−0.02280	0.02884	0.55666	0.05821	0.64387	−0.31344	
	0.69829	−0.01451	0.02115	0.72751	−0.00500	0.00993	0.58067	−0.00446	1.0343	0.04262	
7.0	0.70031	−0.00253	0.01532	0.71999	−0.00656	0.02451	0.57755	0.06606	0.81020	−0.13201	
	0.70029	−0.00193	0.01105	0.71153	0.00670	0.00855	0.60140	−0.00437	0.90921	−0.00779	
8.0	0.69414	0.01168	0.00817	0.70410	0.00957	0.01982	−0.60340	0.06386	0.82119	−0.05513	
	0.69326	0.01299	0.00515	0.69660	0.01935	0.00675	0.62102	−0.00316	0.84504	0.00085	
10.0	0.67057	0.04084	0.00379	0.67325	0.03937	0.01074	0.65043	0.03767	0.77303	−0.00905	
	0.66733	0.04452	0.00123	0.66735	0.04607	0.00306	0.65495	−0.00093	0.77417	−0.00052	

Table 11. Eigenvectors of $^3\Pi_u$ state of H_2

R	σ_g			σ_u			π_u		π_g		
	1s	2s	2p	1s	2s	2p	2p	3d	2p	3d	
1.5	0.61854	−0.09745	0.05942	0.77707	0.77644	−0.01791	0.50696	0.01313	3.8216	0.32743	HF
	0.61880	−0.09755	0.05902	0.95421	0.05215	−0.13646	0.50705	0.01246	1.2314	−0.35500	ODC
1.8	0.61709	−0.08332	0.06355	0.78749	0.54458	−0.02079	0.51034	0.01282	3.1278	0.29443	
	0.61756	−0.08358	0.06298	0.95866	0.00034	−0.09517	0.51050	0.01187	1.2578	−0.31273	
1.95	0.61616	−0.07591	0.06523	0.79271	0.45930	−0.01854	0.51214	0.01287	2.8073	0.25658	
	0.61675	−0.07626	0.06456	0.95187	−0.01520	−0.07946	0.51233	0.01176	1.3154	−0.27793	
2.0	0.61855	−0.07675	0.06570	0.79825	0.42932	−0.01751	0.51274	0.01296	2.7215	0.24657	
	0.61920	−0.07714	0.06500	0.95343	−0.02545	−0.07483	0.51294	0.01179	1.3227	−0.26808	
2.2	0.61673	−0.06545	0.06690	0.79929	0.34646	−0.01219	0.51536	0.01327	2.3903	0.20006	
	0.61760	−0.06601	0.06603	0.93716	−0.03130	−0.05710	0.51563	0.01182	1.3688	−0.21945	
3.0	0.63283	−0.05053	0.06901	0.81305	0.12094	0.00899	0.52648	0.01620	1.6077	0.06023	
	0.63531	−0.05236	0.06718	0.89885	−0.08820	−0.01812	0.52717	0.01316	1.3992	−0.06221	
4.0	0.60335	0.03054	0.06129	0.72416	0.10188	0.02196	0.54088	0.02396	1.2066	−0.01808	
	0.60938	0.02572	0.05785	0.77828	−0.00138	0.00261	0.54307	0.01607	1.2402	0.00832	
5.0	0.59207	0.07947	0.04926	0.66740	0.11100	0.02680	0.55679	0.03214	1.0305	−0.03851	
	0.60279	0.07024	0.04386	0.70647	0.04820	0.01020	0.56184	0.01508	1.0797	0.01353	
6.0	0.58870	0.10854	0.03605	0.63576	0.11904	0.03091	0.55849	0.06801	0.72052	−0.23142	
	0.60288	0.09524	0.02985	0.66120	0.08082	0.01221	0.57972	0.01649	0.98468	0.02627	
7.0	0.61436	0.09431	0.02460	0.63626	0.10066	0.02390	0.58057	0.07043	0.81495	−0.10066	
	0.63144	0.07662	0.01873	0.66445	0.06323	0.00946	0.60321	0.00891	0.88864	0.00580	
8.0	0.62963	0.08454	0.01676	0.63767	0.09037	0.01877	0.60388	0.06986	0.81296	−0.04601	
	0.64833	0.06404	0.01163	0.66624	0.05460	0.00724	0.62357	0.00481	0.83460	0.00169	
10.0	0.65261	0.06340	0.00556	0.65151	0.06708	0.00893	0.65018	0.04238	0.77180	−0.00436	
	0.67367	0.03891	0.00279	0.67916	0.03434	0.00275	0.65580	0.00142	0.77251	0.00043	

Table 12. Eigenvectors of $^1\Pi_g$ state of H_2

R	σ_g			σ_u			π_u		π_g		
	$1s$	$2s$	$2p$	$1s$	$2s$	$2p$	$2p$	$3d$	$2p$	$3d$	
1.5	0.66531	−0.15486	0.06159	0.82924	0.70297	−0.02592	0.49892	0.05946	6.3776	0.05858	HF
	0.66525	−0.15477	0.06155	0.85861	0.61339	−0.03792	0.50244	−0.02819	6.3757	0.05812	ODC
1.8	0.65120	−0.12628	0.06742	0.82913	0.46927	−0.03082	0.49908	0.05796	5.3501	0.06252	
	0.65113	−0.12616	0.06735	0.83467	0.46351	−0.02888	0.50300	−0.01570	5.3472	0.06169	
2.0	0.64675	−0.11271	0.07054	0.83589	0.35148	−0.02828	0.49926	0.05723	4.8409	0.06332	
	0.64666	−0.11256	0.07044	0.82666	0.38282	−0.02266	0.50338	−0.00941	4.8367	0.06210	
2.2	0.64702	−0.10355	0.07225	0.84259	0.25803	−0.02236	0.49945	0.05710	4.4299	0.06245	
	0.64692	−0.10336	0.07211	0.82121	0.31361	−0.01626	0.50387	−0.00625	4.4242	0.06068	
3.0	0.66438	−0.09136	0.07670	0.86430	0.01740	0.00010	0.50011	0.06106	3.3092	0.04350	
	0.66424	−0.09097	0.07623	0.83364	0.08310	−0.00037	0.50675	−0.00660	3.2916	0.03716	
4.0	0.64645	−0.02363	0.07924	0.77532	0.01353	0.00617	0.52309	0.04589	1.1294	−0.13740	
	0.64451	−0.01287	0.05793	0.75966	0.04255	0.00954	0.53823	−0.00623	1.2532	−0.06940	
5.0	0.63436	0.02443	0.07404	0.71980	0.03074	0.00603	0.54194	0.06582	0.61233	−0.34944	
	0.63740	0.03418	0.03583	0.70817	0.04859	0.00895	0.57065	−0.01077	0.95518	−0.08590	
6.0	0.64040	0.04169	0.06213	0.69356	0.03761	0.00537	0.54678	0.09398	0.56872	−0.36491	
	0.64320	0.04941	0.02490	0.68432	0.05032	0.00857	0.58765	−0.00432	0.92424	−0.03486	
7.0	0.65295	0.04494	0.04794	0.68354	0.03815	0.00298	0.57140	0.09232	0.75157	−0.18362	
	0.65284	0.05160	0.01705	0.67572	0.04850	0.00667	0.60608	0.00072	0.88035	−0.00544	
8.0	0.66225	0.04410	0.03468	0.67830	0.03892	0.00131	0.59735	0.08831	0.78991	−0.09137	
	0.65906	0.05106	0.01197	0.67141	0.04764	0.00481	0.62463	0.00172	0.83326	0.00017	
10.0	0.68054	0.03066	0.01194	0.68414	0.02837	0.00183	0.64910	0.04860	0.77038	−0.01339	
	0.67436	0.03809	0.00401	0.67813	0.03557	0.00156	0.65586	0.00090	0.77258	0.00087	

Table 13. Eigenvectors of $^3\Pi_g$ state of H_2

R	σ_g			σ_u			π_u		π_g		
	1s	2s	2p	1s	2s	2p	2p	3d	2p	3d	
1.5	0.80812	−0.31896	0.06115	1.00623	0.51229	−0.02620	0.49881	0.06128	6.3608	0.05447	HF
	0.80807	−0.31888	0.06111	1.01924	0.45513	−0.03787	0.44334	−0.57120	6.3582	0.05385	ODC
1.8	0.70128	−0.38548	0.06645	0.89683	0.39252	−0.02825	0.49891	0.06022	5.3257	0.05580	
	0.70123	−0.38530	0.06639	0.89000	0.37822	−0.03892	0.45640	−0.47702	5.3219	0.05478	
2.0	0.65394	−0.12108	0.06979	0.84492	0.34526	−0.02647	0.49881	0.06229	4.8163	0.05515	
	0.65390	−0.12098	0.06970	0.83146	0.34469	−0.03824	0.46401	−0.43406	4.8113	0.05373	
2.2	0.64531	−0.10165	0.07143	0.84216	0.26532	−0.02172	0.49914	0.06040	4.3933	0.05116	
	0.64527	−0.10154	0.07130	0.82602	0.26846	−0.03602	0.47170	−0.38570	4.3870	0.04925	
3.0	0.64371	−0.06725	0.07556	0.84450	0.04902	−0.00101	0.49947	0.06598	3.2500	0.02248	
	0.64383	−0.06716	0.07513	0.83702	0.03444	−0.02111	0.49675	−0.25595	3.2329	0.01654	
4.0	0.64516	−0.01723	0.06798	0.77962	0.01331	0.01101	0.50433	0.06726	2.0455	0.03568	
	0.64795	−0.01920	0.06488	0.79085	−0.02411	0.00325	0.52560	−0.07599	1.9902	0.01037	
5.0	0.65284	0.01430	0.05501	0.73598	0.02457	0.00887	0.54273	0.05295	0.82358	−0.20835	
	0.68676	−0.02040	0.02758	0.74570	−0.00526	0.00668	0.56910	−0.02256	0.95564	−0.10903	
6.0	0.67357	0.01597	0.04333	0.72069	0.01692	0.00842	0.55417	0.07170	0.72799	−0.23195	
	0.70202	−0.01943	0.01496	0.72741	−0.00844	0.00640	0.58714	−0.01225	0.91067	−0.06155	
7.0	0.66767	0.03829	0.03009	0.69902	0.03079	0.00775	0.57968	0.06793	0.83342	−0.08851	
	0.70622	−0.00959	0.00845	0.71197	0.00589	0.00548	0.60449	−0.00427	0.88244	−0.01716	
8.0	0.65784	0.05538	0.02159	0.67924	0.04394	0.00641	0.60670	0.06066	0.82483	−0.03412	
	0.69807	0.00718	0.00483	0.69663	0.01958	0.00425	0.62310	−0.00179	0.83637	−0.00626	
10.0	0.63909	0.07587	0.01128	0.64750	0.06848	0.00440	0.65088	0.03450	0.77380	−0.00334	
	0.66855	0.04314	0.00229	0.66686	0.04661	0.00161	0.65491	−0.00046	0.77405	−0.00141	

ences between the states begin to show when their properties are calculated for each with its own optimal exponents.

There are problems with exponent optimization which are difficult to resolve, in particular, the dependence of the exponents on each other and the dependence of the linear coefficients on the exponents. We find exponent optimization necessary when the MO's are much more diffuse or contracted than either limit for large or small internuclear distances so that a prediction for intermediate distances is not possible. This happens to be the case for the Π_g states at the energy minimum. From our results we conclude that it would be best to optimize the exponents of the dominant orbitals, here $1s$ and $2p\pi$, and add a larger number of further functions which are not optimized but which allow us by linear coefficient optimization to describe the features of potential curves properly.

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Prof. K. Jug
Institut für Theoretische Chemie
Universität Stuttgart
D-7 Stuttgart 1
Relenbergstr. 32
Germany