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Generalized quantum mechanical two-centre problems. IV. On the accuracy of simple LCAO approximations for H_2^+ states and the Eckart criterion

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If χ denotes an exact solution of the quantum mechanical two centre Coulomb problem, we optimize a normalized LCAO approximation ψ by making the overlap $S=(\chi|\psi)$ a maximum. In this context we study how a weight factor $(r_a r_b)^{-1}$ in the definition of the inner product changes the approximation ψ and the expectation value of electronic energy. Finally we compare the lower bound given by the Eckart criterion with the exact overlap. Results are reported for H_2^+ states $1s\sigma_g$ and $2p\sigma_u$.

Key words: H_2^+—exact overlap of LCAO approximations with exact solutions—Eckart criterion

1. Introduction

Some years ago the author was asked: How large is the coefficient of the LCAO approximation $\psi_+ = |\sigma_g 1s)$ in the expansion of the exact H_2^+ ground state $\chi_+ = |1s\sigma_g)$? The answer to this question depends on how the inner product $(\chi|\psi)$ is defined and on how the effective charge Z in ψ_+ is chosen.

Lately a different but related question arose within an application of the Diatomics-in-Molecules-Method: How well may overlap integrals between exact diatomic orbitals $\chi_\pm$ and linear combinations $\psi_\pm$ of orbitals of the separated atoms be estimated using Eckart's criterion [1]? In this paper we give a survey of the answers to these questions.

Dedicated to Professor Hermann Hartmann on occasion of his 70th birthday on May 4th, 1984

2. Notations and algorithms

Using the notation $|n1\gamma_p; Z_a, Z_b, Q\rangle$ for generalized symmetry-adapted diatomic orbitals introduced in [2] (Eqs. (6) and (7)), we have

$$\chi_+ = |1s\sigma_g; 1, 1, 0\rangle \tag{1}$$

for the H_2^+ ground state and

$$\chi_- = |2p\sigma_u; 1, 1, 0\rangle \tag{2}$$

for the first excited state.

The most simple LCAO-approximations to these states are

$$\psi_+ = |10\sigma_g; Z, 0, 0\rangle = N\{|10\sigma; Z, 0, 0) + |10\sigma; 0, Z, 0)\} \tag{3}$$

and

$$\psi_- = |10\sigma_u; Z', 0, 0\rangle = N'\{|10\sigma; Z', 0, 0) - |10\sigma; 0, Z', 0)\} \tag{4}$$

where Z and Z' are effective charges and N and N' coefficients ensuring normalization.

We generated the orbitals χ_+, χ_-, ψ_+, ψ_- with the procedure GENDO described in [3] and calculated the overlap integrals $S_\pm = (\chi_\pm|\psi_\pm)$ with the procedure MATRIXELEMENT (also mentioned in [3]).

We further defined an altrnative inner product.

$$\tilde{S} = \langle f|g\rangle = \int \frac{f(r)g(r)}{r_a r_b}\, dV = \left(f\left|\frac{1}{r_a r_b}\right|g\right). \tag{5}$$

Here r_a and r_b are the distances from the nuclei A and B respectively. In (5), higher weight is put to the neighborhoods of the centers A and B where the product $r_a r_b$ (contained in the volume element $dV = (R/2) r_a r_b\, d\mu\, d\nu\, d\phi$) vanishes. Evidently (5) is the simplest alternative inner product if all orbitals are defined in prolate spheroidal coordinates μ, ν, ϕ.

We renormalized the four orbitals using this new definition (5) when necessary.

Eckart's criterion [1] states that

$$S^2 \geq \frac{\varepsilon_1 - E_0}{\varepsilon_1 - \varepsilon_0} \quad \text{with } E_0 = (\psi|\underline{h}|\psi). \tag{6}$$

ε_0 and ε_1 are the lowest two eigenvalues of the hamiltonian belonging to states of the same symmetry.

If $E_0 < \varepsilon_1$, we may define a lower bound S_{LB} of S by equating S_{LB}^2 with the right-hand side of (6) and requiring tht S_{LB} be positive.

ε_0 and ε_1 had been tabulated using the procedure HODOPA [4] (states $1s\sigma_g$, $2s\sigma_g$, $3d\sigma_g$; $2p\sigma_u$, $3p\sigma_u$ were needed here because the energy curves $2s\sigma_g$ and $3d\sigma_g$ cross). E_0 was computed using methods described in |3|.

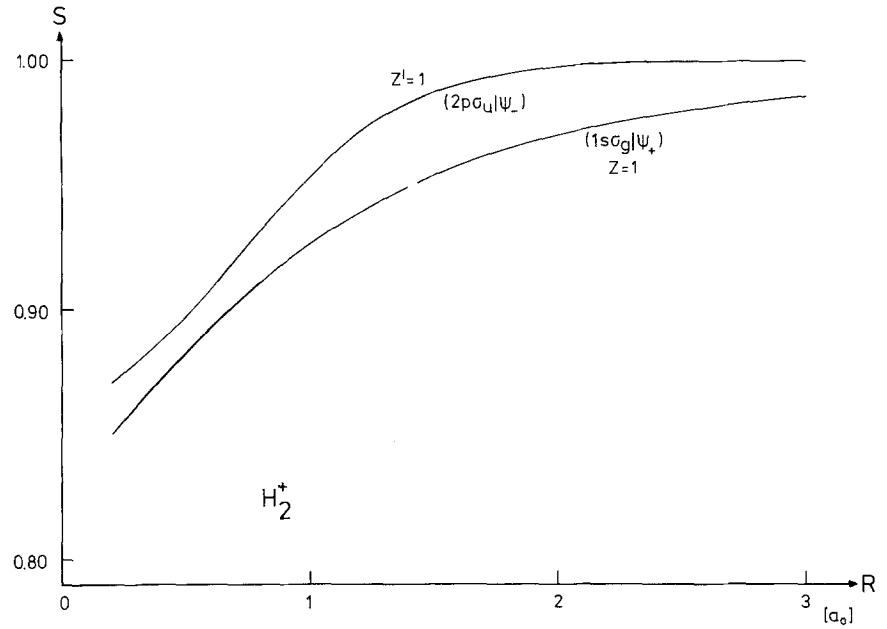

Fig. 1. Overlap S between exact ground (excited) state and corresponding linear combination of hydrogen $1s$ atomic orbitals versus internuclear distance R

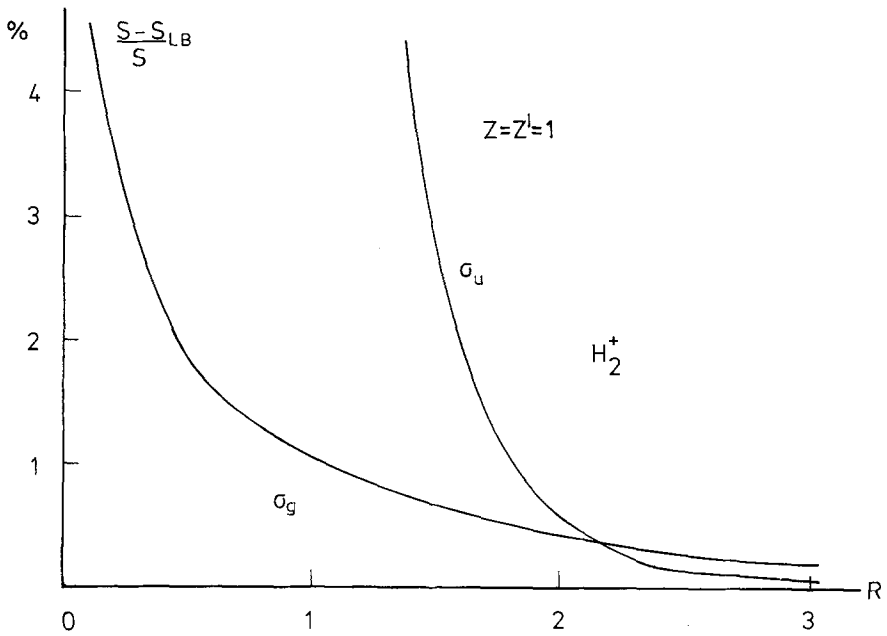

Fig. 2. Relative error of lower bound S_{LB} to overlap versus internuclear distance R

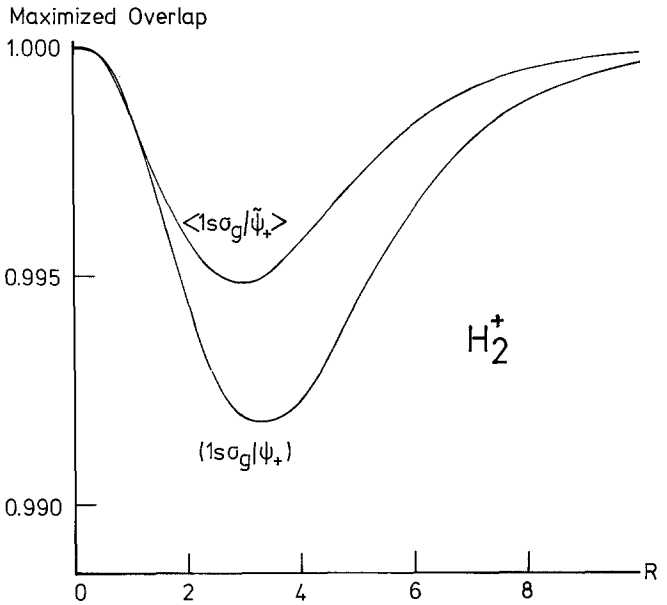

Fig. 3. Maximized overlap $S = (1s\sigma_g|\psi_+)$ and maximized modified overlap $\tilde{S} = \langle 1s\sigma_g|\tilde{\psi}_+\rangle$ for ground state $1s\sigma_g$ versus R. Z has been optimized separately

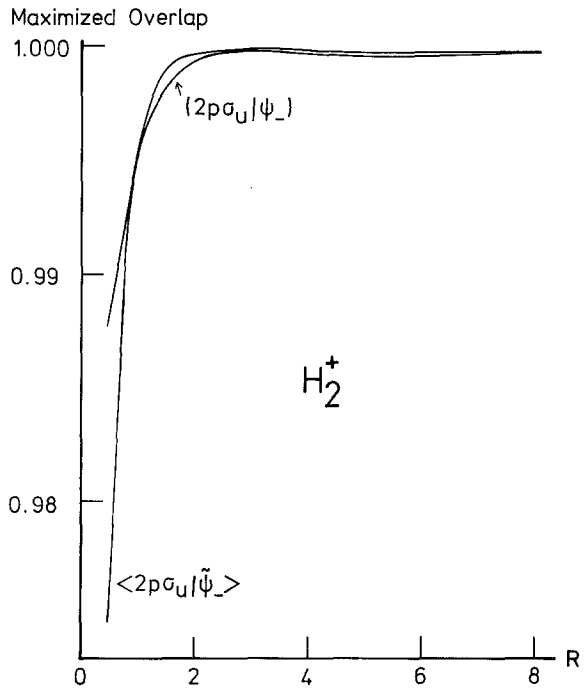

Fig. 4. Maximized overlap $S = (2p\sigma_u|\psi_-)$ and maximized modified overlap $\tilde{S} = \langle 2p\sigma_u|\tilde{\psi}_-\rangle$ for excited state $2p\sigma_u$ versus R. Z' has been optimized separately

3. Results

Three different ways i), ii), iii) of choosing Z and Z' in Eqs. (3) and (4) respectively were applied.

i) Z and Z' were kept fixed to the value 1 (case of separated atoms). The results for S_+ and S_- are exhibited in Fig. 1. In Fig. 2, the relative error $(S - S_{LB})/S$ is plotted against the internuclear distance R. For the state σ_u and for small values of R, the Eckart criterion fails to give a lower bound because E_0 becomes larger than ε_1.

ii) Z in Eq. (3) and Z' in Eq. (4) were separately optimized for each value of the internuclear distance R to make the overlap $S_+ = (1s\sigma_g|\psi_+)$ or $S_- = (2p\sigma_u|\psi_-)$ a maximum.

The results are shown in Figs. 3 and 4.

iii) Finally Z and Z' were optimized to make the modified overlap

$$\tilde{S}_+ = \langle 1s\sigma_g|\psi_+\rangle \quad \text{or} \quad \tilde{S}_- = \langle 2p\sigma_u|\psi_-\rangle$$

(defined according to Eq. (5)) a maximum. The results are also shown in Figs. 3 and 4 respectively.

The two curves in Fig. 3 are very similar. The same result holds for Fig. 4, where the failure of the simple approximation ψ_- for small values of the internuclear distance R is obvious. Atomic p_z orbitals are missing in the LCAO basis.

To conclude this survey we report the values of the electronic energy E_0 and the overlap S with the exact ground state for certain approximations taken at the internuclear distance $R = 2a_0$.

The first column contains the quantity which has been made a maximum or minimum (or which has been kept fixed). The second column contains the optimized value of the effective charge Z. The third column is the corresponding expectation value E_0 of the electronic energy. The last column is the overlap S with the exact ground state.

Table 1

	Z	E_0 (a.u.)	S
1) Case of separated atom	(1.000)	−1.0538	0.9271
2) $S = (1s\sigma_g\|\psi_+)$ Max	1.301	−1.0843	0.9944
3) $\tilde{S} = \langle 1s\sigma_g\|\psi_+\rangle$ Max	1.221	−1.0863	0.9930
4) $(h) = (\psi_+\|h\|\psi_+)$ Min	1.238	−1.0865	0.9936
5) exact solution of $h\chi = \varepsilon\chi$	—	−1.1026	(1.0000)

The approximation 2) which has the highest overlap with the ground state gives a higher energy than the approximation 3) which has been determined using the alternative definition (5) of the inner product. Approximation 3) nearly duplicates the lowest energy approximation 4), the Coulson function [5].

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