

Two-Dimensional Fully Numerical Solutions of Molecular Schrödinger Equations. II. Solution of the Poisson Equation and Results for Singlet States of H_2 and HeH^+

LEIF LAAKSONEN, PEKKA PYYKKÖ, AND DAGE SUNDHOLM

Department of Physical Chemistry, Åbo Akademi, 20500 Åbo (Turku), Finland

Abstract

Two-dimensional fully numerical solutions of the Hartree-Fock problem are reported for the singlet ground states of H^- , He, H_2 , and HeH^+ . The H_2 energy at $R = 1.4$ a.u. is -1.13362957 a.u.

1. Introduction

The principles of a two-dimensional (2D) relaxation solution of molecular Schrödinger equations are explained in Paper I of the present series [1]. As a further test on the method, we now extend the treatment to singlet states of two-electron molecules. In this case the exchange potential vanishes. The interelectronic Coulomb potential V_e can be solved using the same relaxation subroutines, now applied on the Poisson equation

$$\nabla^2 V_e = -4\pi\rho_e, \quad (1)$$

where $\rho_e = \psi^2$ is the electron density.

We actually find that, for the academic model problem of the H_2 Hartree-Fock limit, the present method seems to be slightly more accurate than the previous ones [2,3]. As another test we considered the asymmetric HeH^+ [4]. The atomic systems H^- [5] and He [6], treated in 2D, provide further tests.

The earlier seminumerical 2D molecular calculations by McCullough et al. [7] were summarized in Paper I.

2. Method

A. Treatment of the Poisson Equation

The expressions for ∇^2 in the transformed elliptic coordinates (q, η, ϕ) or (t, η, ϕ) are given in Paper I. In order to obtain suitable boundary conditions, the functions

$$Y_{\text{atom}} = r_1 V_e \quad (2)$$

or

$$Y_{\text{mol}} = r V_e \quad (3)$$

were introduced, r being the distance from the molecular center. Then the boundary conditions become

$$\lim_{q \rightarrow 1, \eta \rightarrow 1} Y_{\text{atom}}(q, \eta) = 0, \quad (4)$$

$$\lim_{q \rightarrow 0} Y(q, \eta) = z, \quad (5)$$

where z is the number of electrons, giving rise to the potential. What resulted, however, was that even with $n_q > 250$, our last $Y(q, \eta)$ were too far from 1 for the numerical derivation formulas to work smoothly.

We also experimented with the combination of the variable q and a non-Coulombic potential

$$Z(q, \eta) = V_e(q, \eta) - z/r. \quad (6)$$

Although

$$\lim_{q \rightarrow 0} Z = 0, \quad (7)$$

bad accuracy for the derivatives $\partial^2 Z / \partial q^2$ was again obtained, due to the large steps Δr per Δq near $q = 0$.

The best results were obtained using the variables (t, η) in conjunction with Y . In

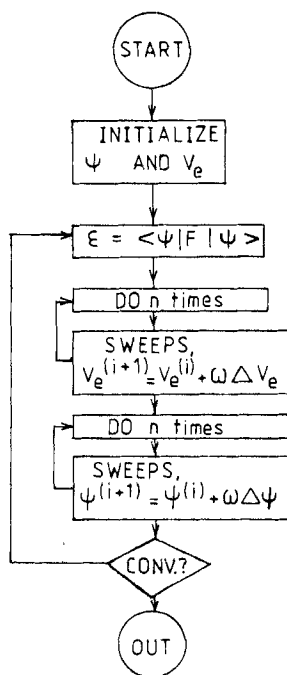


Figure 1. Flow scheme for solving the Hartree-Fock equations.

this case the boundary conditions near practical infinity were obtained from the multipole series

$$V_e = \sum_{l=0}^{l_{\max}} Q_l r^{-l-1} P_l(\cos\theta), \quad (8)$$

with the multipole moments

$$Q_l = \langle \psi | P_l(\cos\theta) r^l | \psi \rangle \quad (9)$$

evaluated from the z -electron wave function. We found it satisfactory to use this procedure for the two last values of l , with $l_{\max} = 4$.

B. Iterative Procedure

An overview of the two-electron program is given in Figure 1. The potential V_e is initialized with a superposition of two Thomas-Fermi potentials. The number of sweeps n was typically 10. The same overrelaxation procedure as for ψ [Eq. (25) of Paper I] was used for V_e , with the same value of ω , typically 1.85.

3. Results

Some results, obtained for H^- and He using five-point formulas in Case a and seven-point formulas in case b, are given in Table I. Further results for H_2 at $R = 1.4$ a.u. and HeH^+ at $R = 1.455$ a.u. using seven-point formulas, are given in Table II.

TABLE I. Hartree-Fock results in a.u. for the H^- and He ground states.

System	Property	Value	Reference
H^-	E_T	-0.4879294	Present work ^a
		-0.487929726	Present work ^b
		-0.487929734372	Roothaan and Soukoup [5]
	ϵ	-0.04622228	Present work ^a
		-0.046222452	Present work ^b
		-0.046222445628	Roothaan and Soukoup [5]
He	$\langle r^2 \rangle$	9.41110666	Present work ^b
	E_T	-2.8617	McCullough [7]
		-2.8616795	Present work ^a
		-2.86167997	Present work ^b
		-2.861679995624	Roothaan and Soukoup [5]
		-2.861679995612	Szalewicz and Monkhorst [6]
		-2.8616799956122	Gázquez and Silverstone [8]
	ϵ	-0.9179552	Present work ^a
		-0.91795554	Present work ^b
		-0.917955562859	Roothaan and Soukoup [5]
	$\langle r^2 \rangle$	1.18482848	Present work ^b
		1.184828	Froese Fischer [9]

^a Variable q .

^b Variable l . "Bond length" $R = 1.4$ a.u.

TABLE II. Hartree-Fock results (in a.u.) for the ground states of H_2 at $R = 1.4$ a.u. and HeH^+ at $R = 1.455$ a.u.

System	Property	Value	Reference
H_2	E_T	-1.1336	McCullough [7]
		-1.1336315	Present work ^a
		-1.133629	Cade and Wahl [3] ^d
		-1.133630	Kołos and Roothaan [2] ^d
		-1.13362957	Present work ^b
	ϵ	-0.59465	Cade and Roothaan [3]
		-0.59465857	Present work ^b
	Q_2^q	0.24322	Berns and Wormer [10] ^d
		0.26483	Berns and Wormer [10] ^c
		0.243289	Present work ^a
		0.2434	Kołos and Roothaan [2] ^d
		0.2579	Kołos and Roothaan [2] ^c
		0.2432888	Present work ^b
		0.2946	Ramsey [11] (expt.)
	$\langle r^2 \rangle$	2.573930	Present work ^a
		2.5736	Kołos [2]
		2.573930	Present work ^b
		2.593	Ramsey [11] (expt.)
	Q_4^q	0.15	Sharma and Kern [12]
		0.090721	Present work ^b
		0.0988	Karl et al. [13] ^c
HeH^+	E_T	-2.9330	McCullough [7]
		-2.933126	Peyerimhoff [4]
		-2.933072	Bartlett and Brändas [14]
		-2.93310325	Present work ^b
	ϵ	-1.6374	McCullough [7]
		-1.6375	Peyerimhoff [4]
	$\langle z \rangle = Q_1^{e,f}$	-1.63745062	Present work ^b
		-0.4945	McCullough [7]
		-0.49445996	Present work ^b
		0.3737269	Present work ^b
	$Q_3^{e,f}$	-0.2315246	Present work ^b
	$Q_4^{e,f}$	0.1739662	Present work ^b
	$\langle r^2 \rangle$	1.3408323	Present work ^b

^a Variable q .^b Variable t .^c CI.^d HF.^e Contribution per electron.^f From molecular midpoint.

4. Conclusions

We have demonstrated that a fully numerical relaxation solution of the Hartree-Fock (HF) problem for the singlet states of the simplest two-electron systems can challenge the numerical accuracy of earlier approaches. The HF energy of H_2 at R

= 1.4 a.u. is calculated to be -1.13362957 a.u. Quadrupole and hexadecapole moments are also reported.

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