Simplified Non-Empirical Unrestricted Hartree-Fock Approximation (SUHF) for the Calculation of Electronic Ground State Properties of Molecules with Closed and Open Valence Shells. II. Diatomic Molecules

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A comparison of numerical Simplified Unrestricted Hartree-Fock (SUHF) results (electronic ground state configurations, total energies, first ionization potentials, atomic charges, atomic spin densities of diatomic molecules) with those of equivalent standard calculations suggests the applicability of the non-empirical but drastically simplified procedure. SUHF may even approach *ab initio* quality obtained with simple (STO-3G) contracted Gaussian basis sets.

Key words: Simplified Unrestricted Hartree-Fock approximation (SUHF); Diatomic molecules; Electronic ground state configurations; Total energies; First ionization potentials; Atomic charges; Atomic spin densities.

1. Introduction

The topic of this paper is a critical examination of some typical results (electronic ground state configurations, total energies, first ionization potentials, atomic charges and spin densities) obtained with the Simplified Unrestricted Hartree-Fock (SUHF) procedure previously described [1]. In its primary form a minimal set of basis functions is considered, preferably atomic orbitals of Slater type (STO) [2]. An equivalent standard Unrestricted Hartree-Fock (UHF) calculation [1] will serve as a measure for the quality of the simplified approach.

Since only one- and two-center integrals over Slater-type atomic orbitals can be evaluated with moderate expense, we begin with the investigation of some selected neutral diatomic molecules with standard interatomic distances R listed in Table 1 (in Å and atomic units (a.u.)). Moreover, diatomic molecules are the smallest chemical objects where the "*neglect of diatomic differential overlap*" approximation (NDDO) [1] causes any effect at all.

In order to qualify numerical deviations of SUHF results from those of the equivalent standard UHF calculation, however, we need an idea of what can be expected at best. Hence, for comparative purposes the standard UHF results were actually obtained using two different but closely related minimal basis sets:

- The Slater-type atomic orbital basis $\{\phi_\mu^{\text{STO}}(\zeta_\mu) \mid \mu = 1, 2, \dots, N_o\}$ defined through an equivalent set of STO-exponents $\{\zeta_\mu \mid \mu = 1, 2, \dots, N_o\}$ [2] and
- a commonly used contracted set of three Gaussian-type orbitals (GTO) per STO [4] with optimized linear coefficients $\{d_{i\mu} \mid i = 1, 2, 3;\ \mu = 1, 2, \dots, N_o\}$ and Gaussian-orbital exponents $\{\alpha_{i\mu} \mid i = 1, 2, 3;\ \mu = 1, 2, \dots, N_o\}$ (STO-3G) [5]:

$$\phi_\mu^{\text{STO-3G}}(\zeta_\mu) = \sum_{i=1}^{3} d_{i\mu}\, \phi_i^{\text{GTO}}(\alpha_{i\mu}), \quad \mu = 1, 2, \dots, N_o. \quad (1)$$

SUHF results were obtained using an atomic STO basis which has been locally orthogonalized by means of Löwdin's symmetrical procedure [1].

For these three types of calculations we introduce the following self-explaining short-hand notations:

UHF (STO), UHF (STO-3G), SUHF (STO).

The minimal basis sets used in this investigations are defined through the usual *Aufbau principle* sequence 1s, 2s, 2p and corresponding sets of Slater orbital exponents summarized in Table 2.

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Table 1. Selected diatomic molecules, total electron numbers N_e, total orbital numbers N_o, interatomic distances R [3], and nuclear repulsion energies $\mathcal{E}_n$ [1].

Molecule	N_e	N_o	R (Å)	R (a.u.)	$\mathcal{E}_n$ (a.u.)
H_2	2	2	0.742	1.402	0.713
LiH	4	3	1.595	3.014	0.995
HF	10	6	0.917	1.733	5.194
LiF	12	7	1.510	2.853	9.462
BeO	12	7	1.331	2.515	12.723
BN	12	10	1.281	2.421	14.458
CO	14	10	1.128	2.132	22.518
N_2	14	10	1.094	2.067	23.702
O_2	16	10	1.207	2.281	28.059
F_2	18	10	1.435	2.712	29.870

Table 2. Minimal basis set Slater orbital exponents [7].

Atom	ζ_{1s}	ζ_{2s}	ζ_{2p}
H	1.20000		
Li	2.69063	0.63961	
Be	3.68478	0.95603	
B	4.67939	1.28808	1.21066
C	5.67263	1.60833	1.56788
N	6.66507	1.92368	1.91703
O	7.65781	2.24588	2.22662
F	8.65007	2.56387	2.54997

According to Koopmans' theorem [4] the absolute value of the highest occupied molecular orbital (HOMO) can be directly identified with the first ionization potential, since electronic correlation and relaxation effects tend to cancel each other.

The virial quotient

$$-\frac{\bar{V}}{\bar{K}} = -\frac{\mathcal{E}_t - \bar{K}}{\bar{K}} \tag{2}$$

can be determined by calculating the kinetic energy expectation value

$$\bar{K} = \sum_{i,j}^{N_o} {}^{\phi}P^t_{ij}\,{}^{\phi}K_{ij}\,. \tag{3}$$

The ${}^{\phi}K_{ij}$ are elements of the ϕ-basis kinetic energy matrix [1]. Whenever the experimental bond length R of Table 1 does not coincide with the corresponding diatomic Born-Oppenheimer potential curve minimum, an exact agreement with the theoretical value of 2.0 will not be found.

Finally, it should be stressed that our main interest is a comparative qualification of the SUHF concept, disregarding any failure of the UHF description itself. It is well known, for instance, that $\mathcal{E}_t(F_2) > 2\mathcal{E}_t(F)$, i.e. the fluorine molecule is predicted not to be stable within the Hartree-Fock picture [8]. In general, one cannot expect the simplified scheme to produce more reliable results than the reference theory does.

2. Computational Details of UHF (STO) and SUHF (STO)

Applying the SUHF approach, we work within a symmetrically (Löwdin-)orthogonalized (λ-)orbital basis throughout [1]. Like in any Pople-Nesbet UHF procedure, both kinds of Fock matrices ${}^{\lambda}\mathbf{F}^{\alpha}$ and ${}^{\lambda}\mathbf{F}^{\beta}$ depend on both kinds of density matrices ${}^{\lambda}\mathbf{P}^{\alpha}$ and ${}^{\lambda}\mathbf{P}^{\beta}$. Consequently, the Pople-Nesbet equations for α and β spin have to be solved iteratively by means of a self-consistent-field procedure (SCF), starting from two *initial guesses* at the two density matrices [1]:

$${}^{\lambda}\mathbf{P}^{\alpha} = \tfrac{1}{2}\,({}^{\lambda}\mathbf{P}^{t} + {}^{\lambda}\mathbf{P}^{s}), \tag{4}$$

$${}^{\lambda}\mathbf{P}^{\beta} = \tfrac{1}{2}\,({}^{\lambda}\mathbf{P}^{t} + {}^{\lambda}\mathbf{P}^{s}). \tag{5}$$

Our SUHF estimate for the initial *total density matrix* ${}^{\lambda}\mathbf{P}^{t}$ is constructed from an initial choice of *atomic charge densities* ${}^{\lambda}\varrho^{t}_{M}$ uniformly distributed on the N_o^M diagonal elements belonging to the atom M under consideration. In general, for a polyatomic molecule built up N_a atoms we then have

$${}^{\lambda}\mathbf{P}^{t} := \frac{{}^{\lambda}\varrho^{t}_{M}}{N_o^M}\cdot\mathbf{1} = \frac{Z_M - {}^{\lambda}q_M}{N_o^M}\cdot\mathbf{1}, \quad M = 1, 2, \ldots, N_a. \tag{6}$$

Z_M is the atomic number of atom M, and ${}^{\lambda}q_M$ is its initial *atomic charge*.

Similarly, the initial *spin density matrix* ${}^{\lambda}\mathbf{P}^{s}$ estimate is lead back to an initial choice of *atomic spin densities* ${}^{\lambda}\varrho^{s}_{M}$:

$${}^{\lambda}\mathbf{P}^{s} := \frac{{}^{\lambda}\varrho^{s}_{M}}{N_o^M}\cdot\mathbf{1}, \quad M = 1, 2, \ldots, N_a. \tag{7}$$

Initial atomic charges ${}^{\lambda}q_M$ and initial atomic spin densities ${}^{\lambda}\varrho^{s}_{M}$ are summarized in Table 3. They fulfil the general conditions

$$\sum_{M}^{N_a} {}^{\lambda}q_M = \sum_{M}^{N_a} Z_M - \underbrace{(N_\alpha + N_\beta)}_{N_e} = Q \tag{8}$$

and

$$\sum_{M}^{N_a} {}^{\lambda}\varrho^{s}_{M} = N_\alpha - N_\beta. \tag{9}$$

N_α and N_β are the numbers of α-spin and β-spin electrons, respectively, and Q is the molecular charge.

Table 3. Initial atomic charges and spin densities (a.u.).

Molecule $A-B$	Initial atomic charges				Initial atomic spin densities			
	$N_\alpha-N_\beta=0$		$N_\alpha-N_\beta=2$		$N_\alpha-N_\beta=0$		$N_\alpha-N_\beta=2$	
	${}^{\lambda}q_A$	${}^{\lambda}q_B$	${}^{\lambda}q_A$	${}^{\lambda}q_B$	${}^{\lambda}\varrho^s_A$	${}^{\lambda}\varrho^s_B$	${}^{\lambda}\varrho^s_A$	${}^{\lambda}\varrho^s_B$
H_2, N_2, O_2, F_2	0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00
LiH, HF, LiF	1.00	−1.00	1.00	−1.00	0.00	0.00	1.00	1.00
BeO, CO	2.00	−2.00	2.00	−2.00	0.00	0.00	1.00	1.00
BN	3.00	−3.00	3.00	−3.00	0.00	0.00	1.00	1.00

Table 4. UHF (STO) results.

Molecule $A-B$	Ground state	Unrestricted ground state configuration	HOMO energy (a.u.)	Total energy $\mathscr{E}_t$ (a.u.)	Virial quotient	Final atomic charges and spin densities* (a.u.)			
					$-\bar{V}/\bar{K}$	${}^{\lambda}q_A$	${}^{\lambda}q_B$	${}^{\lambda}\varrho^s_A$	${}^{\lambda}\varrho^s_B$
H_2	${}^1\Sigma_g^+$	α: $1\sigma_g$ β: $1\sigma_g$	−0.592	−1.128	1.991	0.00	0.00	0.00	0.00
LiH	${}^1\Sigma^+$	α: $1\sigma\ 2\sigma$ β: $1\sigma\ 2\sigma$	−0.290	−7.911	1.972	0.17	−0.17	0.00	0.00
HF	${}^1\Sigma^+$	α: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2$ β: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2$	−0.476	−99.526	1.999	0.15	−0.15	0.00	0.00
LiF	${}^1\Sigma^+$	α: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2\ 4\sigma$ β: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2\ 4\sigma$	−0.203	−106.211	1.985	0.45	−0.45	0.00	0.00
BeO	${}^3\Sigma^-$	α: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2\ 4\sigma\ 5\sigma$ β: $1\sigma\ 2\sigma\ 3\sigma\ 4\sigma\ 5\sigma$	−0.211	−88.902	1.989	0.00	0.00	0.00	2.00
BN	${}^1\Sigma^+$	α: $1\sigma\ 2\sigma\ 3\sigma\ 4\sigma\ 1\pi^2$ β: $1\sigma\ 2\sigma\ 3\sigma\ 4\sigma\ 1\pi^2$	−0.447	−78.714	2.008	−0.05	0.05	0.00	0.00
CO	${}^1\Sigma^+$	α: $1\sigma\ 2\sigma\ 3\sigma\ 4\sigma\ 1\pi^2\ 5\sigma$ β: $1\sigma\ 2\sigma\ 3\sigma\ 4\sigma\ 1\pi^2\ 5\sigma$	−0.504	−112.365	2.009	−0.05	0.05	0.00	0.00
N_2	${}^1\Sigma_g^+$	α: $1\sigma_g\ 1\sigma_u\ 2\sigma_g\ 2\sigma_u\ 1\pi_u^2\ 3\sigma_g$ β: $1\sigma_g\ 1\sigma_u\ 2\sigma_g\ 2\sigma_u\ 1\pi_u^2\ 3\sigma_g$	−0.568	−108.594	2.010	0.00	0.00	0.00	0.00
O_2	${}^3\Sigma_g^-$	α: $1\sigma_u\ 1\sigma_g\ 2\sigma_g\ 2\sigma_u\ 1\pi_u^2\ 3\sigma_g\ 1\pi_g^2$ β: $1\sigma_g\ 1\sigma_u\ 2\sigma_g\ 2\sigma_u\ 3\sigma_g\ 1\pi_u^2$	−0.447	−149.112	2.006	0.00	0.00	1.00	1.00
F_2	${}^1\Sigma_g^+$	α: $1\sigma_u\ 1\sigma_g\ 2\sigma_g\ 2\sigma_u\ 1\pi_u^2\ 3\sigma_g\ 1\pi_g^2$ β: $1\sigma_u\ 1\sigma_g\ 2\sigma_g\ 2\sigma_u\ 1\pi_u^2\ 3\sigma_g\ 1\pi_g^2$	−0.483	−197.869	2.003	0.00	0.00	0.00	0.00

* Löwdin population analysis [12].

Standard UHF procedures, on the other hand, do not work within an orthogonal basis from the beginning. In order to start with equivalent initial guesses, one has to transform both λ-basis density matrices into the original ϕ-basis according to

$$ {}^{\phi}\mathbf{P}^{\alpha} = {}^{\phi}\mathbf{S}^{-\frac{1}{2}}\, {}^{\lambda}\mathbf{P}^{\alpha}\, {}^{\phi}\mathbf{S}^{-\frac{1}{2}}. \tag{10} $$

${}^{\phi}\mathbf{S}$ denotes the ϕ-basis overlap matrix. An equivalent transformation formula holds for beta spin [4].

Only two low multiplicity unrestricted configurations have been selected, defined through the two choices $N_\alpha - N_\beta = 0$ and $N_\alpha - N_\beta = 2$.

In special cases, such as the minimal basis description of H_2, the linear coefficients in C^α and C^β [1] are constant by symmetry [4], i.e. they cannot be varied by means of the SCF procedure. For the BN molecule, SCF convergence [9] of UHF (STO) as well as SUHF (STO) could be achieved only by averaging corresponding density matrices of the last two subsequent iteration steps. Intermediate spatial symmetry breaking in the course of the SCF iteration has always been avoided by allowing equal fractional occupations of degenerate molecular orbitals.

Integral evaluation and orthogonalization procedures have been described in [11].

Results of the reference calculation termed UHF (STO) are summarized in Table 4. All diatomic molecules but O_2 and BeO are predicted to have an

Table 5. UHF (STO-3G) results.

Molecule $A-B$	Ground state	Unrestricted ground state configuration	HOMO energy (a.u.)	Total energy $\mathscr{E}_t$ (a.u.)	Virial quotient	Final atomic charges and spin densities* (a.u.)			
					$-\bar{V}/\bar{K}$	$^{\lambda}q_A$	$^{\lambda}q_B$	$^{\lambda}\varrho_A^s$	$^{\lambda}\varrho_B^s$
H_2	$^1\Sigma_g^+$	α: $1\sigma_g$ β: $1\sigma_g$	−0.588	−1.119	1.990	0.00	0.00	0.00	0.00
LiH	$^1\Sigma^+$	α: $1\sigma\ 2\sigma$ β: $1\sigma\ 2\sigma$	−0.289	−7.816	1.974	0.17	−0.17	0.00	0.00
HF	$^1\Sigma^+$	α: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2$ β: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2$	−0.459	−98.552	2.004	0.19	−0.19	0.00	0.00
LiF	$^3\Sigma^-$	α: $1\sigma\ 2\sigma\ 3\sigma\ 4\sigma\ 1\pi^2\ 5\sigma$ β: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2$	−0.157	−105.236	2.003	−0.01	0.01	0.99	1.01
BeO	$^1\Sigma^+$	α: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2\ 4\sigma$ β: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2\ 4\sigma$	−0.272	−87.884	1.987	0.47	−0.47	0.00	0.00
BN	$^3\Sigma^-$	α: $1\sigma\ 2\sigma\ 3\sigma\ 4\sigma\ 5\sigma\ 1\pi^2$ β: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2$	−0.430	−77.908	2.016	0.17	−0.17	1.44	0.56
CO	$^1\Sigma^+$	α: $1\sigma\ 2\sigma\ 3\sigma\ 4\sigma\ 1\pi^2\ 5\sigma$ β: $1\sigma\ 2\sigma\ 3\sigma\ 4\sigma\ 1\pi^2\ 5\sigma$	−0.495	−111.199	2.014	0.15	−0.15	0.00	0.00
N_2	$^1\Sigma_g^+$	α: $1\sigma_g\ 1\sigma_u\ 2\sigma_g\ 2\sigma_u\ 1\pi_u^2\ 3\sigma_g$ β: $1\sigma_g\ 1\sigma_u\ 2\sigma_g\ 2\sigma_u\ 1\pi_u^2\ 3\sigma_g$	−0.557	−107.468	2.016	0.00	0.00	0.00	0.00
O_2	$^3\Sigma_g^-$	α: $1\sigma_u\ 1\sigma_g\ 2\sigma_g\ 2\sigma_u\ 1\pi_u^2\ 3\sigma_g\ 1\pi_g^2$ β: $1\sigma_u\ 1\sigma_g\ 2\sigma_g\ 2\sigma_u\ 3\sigma_g\ 1\pi_u^2$	−0.419	−147.615	2.011	0.00	0.00	1.00	1.00
F_2	$^1\Sigma_g^+$	α: $1\sigma_u\ 1\sigma_g\ 2\sigma_g\ 2\sigma_u\ 1\pi_u^2\ 3\sigma_g\ 1\pi_g^2$ β: $1\sigma_u\ 1\sigma_g\ 2\sigma_g\ 2\sigma_u\ 1\pi_u^2\ 3\sigma_g\ 1\pi_g^2$	−0.459	−195.938	2.008	0.00	0.00	0.00	0.00

* Mulliken population analysis [1].

electronic closed-shell singlet ground state identical to that of *Restricted Hartree-Fock* theory (RHF) [13].

3. UHF (STO-3G) Results [14]

Unrestricted ground state configurations of LiF, BeO, and BN are predicted to have a qualitatively different nature as those of UHF (STO). Besides these three significantly different predictions only the β electron orbital energy sequence $1\sigma_g\ 1\sigma_u$ of the O_2 triplet ground state is interchanged.

HOMO energies of UHF (STO-3G) are always higher (up to about 0.027 a.u. for comparable ground states) than the corresponding UHF (STO) values. Consequenly, all first Koopmans ionization potentials are too low.

Total energies are probably the primary quantities available from non-empirical *ab initio* calculations. Compared to UHF (STO) they are always higher as well (up to about 1.9 a.u. for comparable ground states), due to the short contraction length of the STO-3G expansion (1).

Virial quotients coincide quite closely (with maximal absolute deviations of about 0.005 for comparable states).

Atomic charges and spin densities were available only by means of Mulliken's instead of Löwdin's population analysis [1, 14]. Thus, there is no way of a direct comparison. It can be easily verified, however, that indeed all molecular ground states with $N_\alpha = N_\beta$ in their experimental equilibrium bond length of Table 1 are closed shells showing no spin density localizations.

4. SUHF (STO) Results

Unrestricted ground state configurations: Some different orbital sequences occur (for the $^1\Sigma^+$ states of BN and CO, for $^1\Sigma_g^+$ of N_2, and for $^3\Sigma_g^-$ of O_2). Nevertheless, there is only one qualitative disagreement concerning the nature of the BeO ground state. In fact, the observed BeO ground state is a singlet [3], in accordance with the prediction of SUHF (STO).

HOMO energies are not uniformly higher or lower than corresponding reference values as in the UHF (STO-3G) case. Absolute values of comparable ground states maximally differ from another by about 0.24 atomic units ($^3\Sigma_g^-$ of O_2).

Total energies differ from their UHF (STO) counterpart at most by 2.7 a.u. for N_2 and at least by

Table 6. SUHF (STO) results.

Molecule $A-B$	Ground state	Unrestricted ground state configuration	HOMO energy (a.u.)	Total energy $\mathscr{E}_t$ (a.u.)	Virial quotient	Final atomic charges and spin densities* (a.u.)			
					$-\bar{V}/\bar{K}$	${}^{\lambda}q_A$	${}^{\lambda}q_B$	${}^{\lambda}\varrho^s_A$	${}^{\lambda}\varrho^s_B$
H_2	${}^1\Sigma_g^+$	α: $1\sigma_g$ β: $1\sigma_g$	−0.623	−1.188	2.044	0.00	0.00	0.00	0.00
LiH	${}^1\Sigma^+$	α: $1\sigma\ 2\sigma$ β: $1\sigma\ 2\sigma$	−0.333	−7.946	1.986	0.07	−0.07	0.00	0.00
HF	${}^1\Sigma^+$	α: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2$ β: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2$	−0.524	−100.360	2.046	−0.03	0.03	0.00	0.00
LiF	${}^1\Sigma^+$	α: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2\ 4\sigma$ β: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2\ 4\sigma$	−0.187	−106.289	1.993	0.58	−0.58	0.00	0.00
BeO	${}^1\Sigma^+$	α: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2\ 4\sigma$ β: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2\ 4\sigma$	−0.065	−88.849	1.995	1.00	−1.00	0.00	0.00
BN	${}^1\Sigma^+$	α: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2\ 4\sigma$ β: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2\ 4\sigma$	−0.498	−80.863	2.121	−0.35	0.35	0.00	0.00
CO	${}^1\Sigma^+$	α: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2\ 4\sigma\ 5\sigma$ β: $1\sigma\ 2\sigma\ 3\sigma\ 1\pi^2\ 4\sigma\ 5\sigma$	−0.392	−114.892	2.105	−0.47	0.47	0.00	0.00
N_2	${}^1\Sigma_g^+$	α: $1\sigma_u\ 1\sigma_g\ 2\sigma_g\ 1\pi_u^2\ 2\sigma_u\ 3\sigma_g$ β: $1\sigma_u\ 1\sigma_g\ 2\sigma_g\ 1\pi_u^2\ 2\sigma_u\ 3\sigma_g$	−0.498	−111.266	2.096	0.00	0.00	0.00	0.00
O_2	${}^3\Sigma_g^-$	α: $1\sigma_u\ 1\sigma_g\ 2\sigma_g\ 1\pi_u^2\ 2\sigma_u\ 3\sigma_g\ 1\pi_g^2$ β: $1\sigma_u\ 1\sigma_g\ 2\sigma_g\ 2\sigma_u\ 1\pi_u^2\ 3\sigma_g$	−0.209	−150.630	2.049	0.00	0.00	1.00	1.00
F_2	${}^1\Sigma_g^+$	α: $1\sigma_u\ 1\sigma_g\ 2\sigma_g\ 2\sigma_u\ 1\pi_u^2\ 3\sigma_g\ 1\pi_g^2$ β: $1\sigma_u\ 1\sigma_g\ 2\sigma_g\ 2\sigma_u\ 1\pi_u^2\ 3\sigma_g\ 1\pi_g^2$	−0.386	−198.534	2.016	0.00	0.00	0.00	0.00

* Löwdin population analysis [1].

0.03 a.u. for LiH and by 0.08 a.u. for LiF. In all comparable cases, SUHF (STO) ground state energies are lower than their reference equivalent. The observed differences are considerable, so that SUHF (STO) total energies often remain under the *Hartree-Fock limit* [4] of the full theory and even under the exact theoretical value (of −1.174448 a.u. for H_2, for instance [15]). Their absolute values (not their sign!), however, are definitely comparable to also considerable absolute differences between corresponding STO and STO-3G variants of the complete (i.e. not simplified) UHF calculation. For LiH and LiF, SUHF (STO) even leads to quite similar total energies.

Virial quotients coincide only with maximal absolute deviations of about 0.1 for comparable states. Nevertheless, they are not completely incompatible with the theoretical 2.0 value.

Atomic charges and spin densities indicate, that SUHF (STO) ground states of heteronuclear diatomic molecules often are predicted to be more polarized than their UHF (STO) equivalents. The charge distribution of HF, for example, does not agree with our common chemical intuition. Furthermore, the spin densities of Table 6 again shows us that all ground states with $N_\alpha = N_\beta$ are pure singlets, equivalent to the restricted configurations of RHF theory [13].

5. Conclusion

As far as our selected diatomic examples with standard bond lengths are concerned, SUHF (STO) at least leads to qualitatively correct predictions.

Differences between the results of two equally rigorous UHF calculations with different minimal basis set choices (STO and STO-3G) suggest that SUHF may even approach *ab initio* STO-3G quality.

In a similar study, Duke and Collins [16] emphasized the poor agreement of an “*ab initio* NDDO” approach with the corresponding full molecular orbital method. However, in our aspect the agreement of full *ab initio* results obtained with two different but comparable minimal basis sets of Slater and Slater-simulating (e.g. STO-3G) type, respectively, is also poor. From this point of view, the total rejection of a non-empirical but drastically simplified NDDO approximation appears to be precipitant. Further investigations are in progress.

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[5] A change from any Slater-orbital exponent ζ'_μ to another exponent ζ_μ only requires a scaling of the corresponding Gaussian-orbital exponents $\alpha'_{i\mu}$ to get the new $\alpha_{i\mu}$ according to

$$\alpha_{i\mu} = \alpha'_{i\mu} \left(\frac{\zeta_\mu}{\zeta'_\mu} \right)^2 \qquad i = 1, 2, 3; \quad \mu = 1, 2, \ldots, N_o .$$

The linear contraction coefficients $\{d_{i\mu} | i = 1, 2, 3; \mu = 1, 2, \ldots, N_o\}$ remain unaffected under such scaling [4]. Optimized $\alpha'_{i\mu}$ values corresponding to unity Slater exponents ($\zeta'_\mu = 1.0$) are available from Stewart [6].

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[13] In vicinity of their equilibrium bond length diatomic closed-shell state energies of UHF and RHF generally are expected to be the same [1, 4].

[14] UHF (STO-3G) results were obtained using the following program system: M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, and J. A. Pople, Gaussian 90, Revision H. Gaussian Inc., Pittsburgh, Pennsylvania 1990.

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