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Gombás Pseudopotential SCF Calculations for Atoms*

W. H. EUGEN SCHWARZ

Lehrstuhl für Theoretische Chemie der Universität Bonn, Wegeler Straße 12, D-5300 Bonn, Germany

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The "Simplified SCF Method" of Gombás, in which the orbital orthogonality conditions are replaced by statistical pseudopotentials, has been tested for the first time by accurate numerical calculations without any further approximation. Whereas the original version of the method leads to characteristic error trends, a correction factor recently introduced by Gombás into the pseudopotential expression, produces surprisingly good results.

Das sog. „Vereinfachte SCF-Verfahren" von Gombás, bei welchem die Orthogonalitätsbedingungen der Orbitale durch statistische Pseudopotentiale ersetzt werden, wird erstmalig durch saubere numerische Rechnungen getestet. Während die unkorrigierte Version der Methode Resultate mit charakteristischen Fehlern liefert, führt der kürzlich von Gombás abgeleitete Korrekturfaktor im Besetzungsverbotpotential zu überraschend guten Ergebnissen.

La «méthode SCF simplifiée» de Gombás, où les conditions d'orthogonalité des orbitales sont remplacées par des pseudo potentiels statistiques, a été pour la première fois éprouvée avec des calculs numériques précis sans aucune autre approximation. Alors que la version originale de la méthode conduit à des tendances d'erreurs caractéristiques, un facteur de correction récemment introduit par Gombás dans l'expression du pseudo-potential, produit des résultats remarquablement bons.

Introduction

In order to make allowence for the Pauli exclusion principle in Hartree SCF theory, one has to impose the condition on the one-electron orbitals that they have definite numbers of nodal surfaces. In Hartree-Fock theory, in order to get a similar and simple formalism, the orbitals are assumed to be orthogonal. Consequently in both cases the higher orbitals show a pronounced short wavelength oscillatory behaviour near the nuclei. This causes a severe complication in valence-electrons calculations, as it necessitates the use of rather large basis sets (in expansion methods) or rather narrow grids (in numerical methods).

Therefore, Hellmann [1] and Gombás [2] developped the concept of pseudopotentials: no atomic orbital must have inner radial nodes; the kinetic energy associated with these nodes is taken into account instead by a statistical "occupation exclusion" pseudopotential.

In the so-called "Simplified SCF-Method for Atoms" of Gombás [3] one starts with the energy expression

$$E = T_{\mathrm{rad}} + T_{\mathrm{ang}} + V + E_{\mathrm{ex}}\,. \tag{1}$$

V is the potential energy of the atom,

$$V = \sum_{i}^{\mathrm{occ.}} \left\langle i \left| -\frac{Z}{r} \right| i \right\rangle + \sum_{i>j}^{\mathrm{occ.}} \left\langle ij \left| \frac{1}{r_{12}} \right| ij \right\rangle . \tag{2}$$

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* Dedicated to the memory of Professor Paul Gombás.

E_{ex} is the exchange energy correction. The angular kinetic energy is given by

$$T_{\mathrm{ang}} = \sum_i^{\mathrm{occ.}} \left\langle i \left| \frac{l_i(l_i+1)}{2r^2} \right| i \right\rangle \tag{3}$$

and the radial kinetic energy by

$$T_{\mathrm{rad}} = \sum_i^{\mathrm{occ.}} \left\langle i \left| -\frac{\Delta_r}{2} + \bar{G}_i \right| i \right\rangle . \tag{4}$$

Here the pseudopotential $\bar{G}_i$, acting on the electron in the spin-orbital i with radial function $P_{n_i l_i}(r)$ ($\int P^2\,dr = 1$) is given by

$$\bar{G}_i = \frac{\pi^2}{2}(D_i^2 + D_i \cdot P_{n_i l_i}^2) + \frac{1}{8r^2} \tag{5}$$

with

$$D_i = \sum_{n=l_i+1}^{n_i-1} P_{nl_i}^2 . \tag{6}$$

The corresponding SCF-equations [3], obtained by energy variation, differ from the usual Hartree-Fock-Slater equations only by the additional pseudopotential term g_i in the Fock operator,

$$g_i = \frac{\pi^2}{2}(D_i^2 + 2D_i \cdot P_{n_i l_i}^2) + \frac{1}{8r^2} \tag{7}$$

but there are no orthogonality or nodal conditions.

They have been solved by Gombás and coworkers [3, 4]. The results are rather satisfactory. However, several approximations had been made in these calculations, the two most important ones being the following:

1. all orbitals within a shell of principal quantum number n are assumed to be identical (compare, however, Figs. 1 and 2);
2. each orbital is represented by a single (ν, ζ)-optimized STO $r^\nu \cdot \exp(-\zeta r)$ only.

On the other hand, the g-pseudopotential (7) has been used in valence electron calculations without these approximations [5]. There it showed up, that the calculated energies are lower than the experimental ones, or in other words that the pseudopotentials are somewhat too small.

There upon Gombás [6] deduced a correction factor for the D-values (6) in the pseudopotentials (5), (7):

$$D_i^{\mathrm{corr}} = \left[1 + \frac{1}{4}\left(1 + \frac{1}{n_i - l_i - 1}\right)\right] \cdot D_i , \tag{8}$$

which seemed to improve the results [5, 6].

Calculations and Results

The "Simplified SCF Equations" of Gombás have now been solved without any further approximation by numerical integration for a lot of atoms from all over the periodic table. A few results, with and without the correction of Eq. (8)[1],

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[1] The SCF equations with correction (8) show a much better convergence behaviour than the uncorrected ones.

Table 1. SCF calculations on the Kr atom. Orbital parameters ε and orbital expectation values $\langle r^2 \rangle$ and $\langle 1/r \rangle$ in a.u.

		Hartree-Fock HF	Hartree-Fock-Slater HFS	Corrected[a] Gombás CG	Simple[a] Gombás SG
$-\varepsilon$	1*s*	1040	1020	1028	1018
	2*s*	140	132	133	161
	2*p*	126	120	123	115
	3*s*	21.7	18.5	19.6	29.8
	3*p*	16.7	14.0	13.9	16.6
	3*d*	7.7	6.0	6.1	2.7
	4*s*	2.3	1.5	1.7	3.2
	4*p*	1.05	0.60	0.58	0.63
$\langle r^2 \rangle$	1*s*	0.00241	0.00242	0.00241	0.00241
	2*s*	0.0413	0.0416	0.0413	0.0307
	2*p*	0.0320	0.0321	0.0314	0.0321
	3*s*	0.332	0.339	0.325	0.193
	3*p*	0.344	0.349	0.354	0.255
	3*d*	0.371	0.379	0.365	0.492
	4*s*	3.04	2.96	2.64	1.32
	4*p*	4.46	4.60	4.48	3.16
$\langle 1/r \rangle$	1*s*	35.50	35.45	35.50	35.50
	2*s*	7.92	7.88	6.09	7.37
	2*p*	7.89	7.87	7.94	7.87
	3*s*	2.64	2.62	2.05	2.74
	3*p*	2.52	2.51	2.02	2.50
	3*d*	2.28	2.27	2.32	2.09
	4*s*	0.80	0.83	0.73	1.05
	4*p*	0.67	0.68	0.59	0.74

[a] With Dirac-Gáspár exchange potential, see Ref. [7].

Table 2. Gombás SCF results on several atoms. Deviation of total atomic energy *E* and expectation values $\langle r^2 \rangle$ and $\langle 1/r \rangle$ from Hartree-Fock-Slater[a] results in %

Z	Atom	*E*		$\langle r^2 \rangle$		$\langle 1/r \rangle$	
		SG	CG	SG	CG	SG	CG
4	Be	−0.8	−0.00	−20	−1	+0.1	−2
10	Ne	−1.1	+0.00	− 2.5	−0.1	−0.7	−2
12	Mg	−1.2	+0.03	−35	−6	−0.3	−2
18	Ar	−1.9	−0.02	−16	−2	−0.5	−3
20	Ca	−2.1	−0.04	−40	−9	−0.4	−3
26	Fe	−2.4	−0.02	−22	−8	−1.1	−4
36	Kr	−2.7	−0.02	−29	−4	−1.0	−4
54	Xe	−3.4	−0.02	−34	−4	−1.2	−6
86	Rn	−3.9	+0.05	−38	−4	−1.7	−6

[a] With Dirac-Gáspár exchange potential, see Ref. [7].

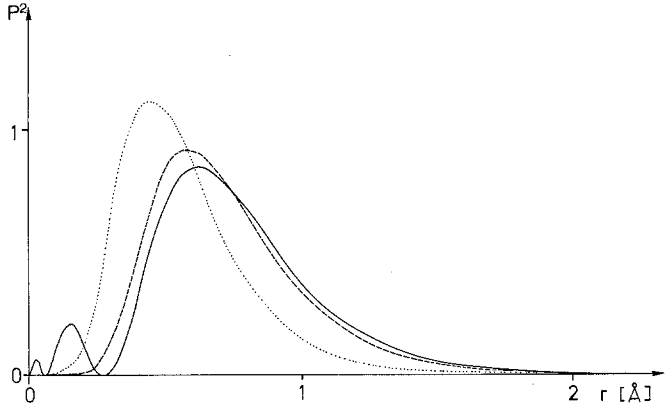

Fig. 1. Radial density $P^2(r)$ of the Ar-3*s*-orbital. ——— HFS results; — — — CG results; ········ SG results

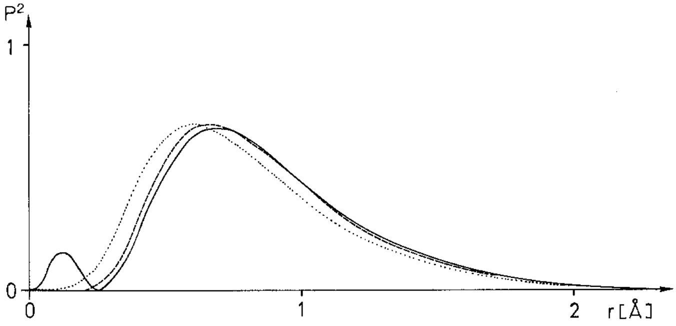

Fig. 2. Radial density $P^2(r)$ of the Ar-3*p*-orbital. ——— HFS results; — — — CG results; ········ SG results

are shown in Tables 1–2 and Figs. 1–2. These results have been obtained with the so-called Kohn-Sham-exchange potential of Dirac and Gáspár [7], and are compared with values from the corresponding version of a Hartree-Fock-Slater (HFS) program [9]. Results obtained with other exchange potentials [7, 8] are very similar to these and are therefore not reproduced here. Results on other atoms than those of the Tables show quite similar trends.

Discussion

In Table 1 orbital parameters and expectation values are given for the Kr atom. The *ε-values* of the corrected Gombás SCF method (CG) compare very nicely with ordinary HFS values, the differences not exceeding a few percent. The simple Gombás version (SG) on the other hand exhibits drastic deviations. *s*-type orbitals (except the lowest one, on which no pseudopotential acts) are much too low, whereas orbitals with $l \geq 2$ come out much too high. As a consequence the 4*s* orbital lies below the 3*d* one. Corresponding inversions of the sequence of the SG orbitals too occur in other atoms, e.g. in Radon

$$\varepsilon_{5s} < \varepsilon_{5p} < \varepsilon_{4f} < \varepsilon_{6s} < \varepsilon_{5d} \quad \text{instead of} \quad \varepsilon_{4f} < \varepsilon_{5s} < \varepsilon_{5p} < \varepsilon_{5d} < \varepsilon_{6s} .$$

That the corrected Gombás orbital parameters, just as the Hartree-Fock-Slater ones, exceed the exact SCF ε-values (especially in the case of the higher orbitals), is not a serious drawback: a) In statistical theories ε corresponds to $\frac{dE}{dN}$ (N = number of electrons), whereas in the usual SCF theory according to Koopmans' theorem $\varepsilon \approx \frac{\Delta E}{\Delta N = 1}$. Slater [11] has shown how to get ionisation potentials from statistical orbital parameters. b) Furthermore the asymptotic behaviour of the orbitals is determined by ε. However the discussion of Handy *et al.* [12] has shown that it is quite questionable wether the long range behaviour of SCF-orbitals is of real physical significance.

The same trends as in the ε-values show up in the $\langle r^2 \rangle$-*values:* HFS and CG values differ by not more than a few percent. In the SG method, however, orbitals with large values of $n - l$, especially the higher s-type ones; are contracted by up to or more than 50%, whereas d (and f) orbitals are too diffuse.

These findings indicate that the simple Gombás pseudopotential (7) is too weak and that the correction factor of Eq. (8), despite its very crude nature [6], is quite sufficient. The pseudopotential – usually of greatest importance to s-type orbitals – in its uncorrected form, is not large enough to prevent the higher s-typ *orbitals* from strongly penetrating into the already occupied regions near the nucleus. This can also be seen from Fig. 1. With p orbitals the situation is similar but less pronounced (see Fig. 2). As a consequence of this contraction of the s and p electrons, the d and f orbitals are then dilated because of the better shielded nucleus. Summarizing the CG method reproduces the main density maxima fairly well, whereas the SG method does not.

The inner density oscillations of the orbitals are by definition not obtained in pseudopotential theory. Therefore expectation values which are strongly dependent on them such as the $\langle 1/r \rangle$-*values* should not directly be compared with normal SCF results. Nevertheless we mention that the differences are not very marked and that the SG values agree somewhat better with the HF or HFS values than the CG results do.

Total atomic expectation values are given in Table 2. The corrected Gombás $\langle r^2 \rangle$ and $\langle 1/r \rangle$ values are in error by only a few percent whereas the simple Gombás $\langle r^2 \rangle$ results are rather useless. But most impressive are the total atomic energy values calculated by Eq. (1). While the simple pseudopotential leads to energies which are definitely too low – especially for heavier atoms, although statistical methods should usually give better results for systems with more electrons – the correction Eq. (8) results in an unexpectedly good agreement with HFS energies for all atoms of the periodic table, far better than 1‰.

Concluding, these results encourage one to use the corrected Gombás statistical pseudopotential in cases where it is impossible to construct the usually preferable semiempirical pseudo- or model-potentials [10].

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Dr. W. H. Eugen Schwarz
Lehrstuhl für Theoretische Chemie
der Universität
D-5300 Bonn, Wegeler Str. 12, Germany