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Pseudopotential Calculations Using the FSGO Method: Application to First-Row Hydrides

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Various pseudopotential schemes are examined in floating spherical Gaussian orbital (FSGO) calculations on the first row hydrides to help determine which pseudopotential scheme, if any, would be most useful in the FSGO method.

Key words: Floating spherical Gaussian orbital method – First row hydrides

1. Introduction

The use of pseudopotentials in a floating spherical Gaussian orbital (FSGO) [1] framework has been the subject of some recent investigations [2–5]. It is not clear however whether pseudopotentials designed primarily with an eye towards performing Hartree-Fock type calculations are directly compatible with FSGO calculations. Those factors which make a pseudopotential "good" in a Hartree-Fock calculation may have unfavorable effects when used in an FSGO framework. Thus for example, a well structured pseudopotential, designed to give an accurate description of the effects of the core orbitals, may give very poor results in an FSGO calculation. This is because of the limited flexibility of the FSGO's. By definition an FSGO cannot change its shape to adjust to the structure of the pseudopotential. Instead, the FSGO must change its size and/or position to adjust itself to a given field, which in turn results in a shift of the nuclear coordinates. A slight amount of structure in a pseudopotential may therefore cause a grossly exaggerated change in the molecular geometry.

To help gain a better understanding as to which, if any, pseudopotentials can safely be used in an FSGO scheme, as well as the features which would render such a pseudopotential "useful" in an FSGO sense, we present in the present communication FSGO calculations employing a series of the more widely used pseudopotentials for the first row hydrides. Included also are the methane results presented in an earlier paper [5].

Sect. 2 contains a brief description of the pseudopotentials used in this work, with the results presented in Sect. 3.

2. Description of the Pseudopotentials Used

The purpose of the pseudopotential molecular orbital Hartree-Fock scheme is to allow one to work within the framework of the valence orbitals only. This is accomplished through the use of a one-electron pseudo-Hamiltonian given by

$$H^{\mathrm{PS}} = -\tfrac{1}{2}\nabla^2 - \frac{n_v}{r} + V_{\mathrm{coul}}^{\mathrm{VAL}} + V_{\mathrm{exch}}^{\mathrm{VAL}} + V^{\mathrm{PSEUD}} \tag{1}$$

where n_v is the number of valence electrons, $V_{\mathrm{coul}}^{\mathrm{VAL}}$ and $V_{\mathrm{exch}}^{\mathrm{VAL}}$ are the appropriate Coulomb and exchange operators respectively due to the valence shell, and V^{PSEUD} denotes the potential which must replace the effects of the core orbitals on the valence orbitals.

The pseudopotentials used here can be broken into two categories: the core projection and the angular momentum projection pseudopotentials. The core projection pseudopotentials are given by

$$V^{\mathrm{PSEUD}} = V(r) + \sum_c B_c |\varphi_c\rangle\langle\varphi_c| \tag{2}$$

where $V(r)$ is a local, spherically symmetric term containing some parameters, B_c is a parameter and the φ_c are the ground state core orbitals of the atom to which V^{PSEUD} belongs. In the Coffey *et al.* [6] pseudopotential

$$V(r) = -\frac{n_c}{r} \mathrm{e}^{-\alpha r} \tag{3}$$

where n_c is the number of core electrons and α is a parameter adjusted to give optimum agreement with calculated valence energies. The parameter B_c is $(\varepsilon_v - \varepsilon_c)$ the difference between the orbital energy of a given core orbital and the valence orbital energy of the valence orbital with the same symmetry, and the φ_c are the single zeta Slater orbitals (from which the orbital energies were taken). For the purpose of the present work, where Gaussian orbitals will be used, we follow the recommendation of Coffey *et al.* and expand $V(r)$ in terms of six Gaussians, as well as expanding the Slater orbitals into three Gaussians each.

The Bonifacic-Huzinaga [7] pseudopotential defines

$$V(r) = \sum_{i=1}^{n_a} \frac{A_i}{r} \mathrm{e}^{-\alpha_i r^2} \tag{4}$$

For the first row atoms $n_a = 2$, while A_i and α_i, as well as B_c in (2), are adjustable parameters determined from atomic calculation, and the φ_c are given by an 11-s Gaussian expansion of the 1s orbital [7].

The second class of pseudopotentials comprises the angular momentum projection operator pseudopotentials, which are given by

$$V^{\mathrm{PSEUD}}=\sum_{l=0}^{\infty}\sum_{m=-l}^{l} V_l(r)|Y_{lm}\rangle\langle Y_{lm}| \tag{5}$$

where the Y_{lm} are the spherical harmonics, used to separate the different angular momentum components on the atom on which the pseudopotential is defined, and $V_l(r)$ is in general a different radial potential for each angular momentum component. In the Simons [8] pseudopotential $V_l(r)$ is given by

$$V_l(r)=\begin{cases}\dfrac{C_l'}{r^2} & l\leq l_{\mathrm{MAX}}\\[2ex] 0 & l>l_{\mathrm{MAX}}\end{cases} \tag{6}$$

where C_l' is an adjustable parameter (adjusted so that the single-valence-electron atoms or ions have orbital energies equal to the experimental ionization potentials) and l_{MAX} is the highest orbital angular momentum value in the ground state of the atom. For the Schwartz *et al.* [4, 9] pseudopotential we have

$$V_l(r)=\begin{cases}\dfrac{C_l'}{r}\mathrm{e}^{-\alpha r^2} & l\leq l_{\mathrm{MAX}}\\[2ex] \dfrac{C_{l\mathrm{MAX}}'}{r}\mathrm{e}^{-\alpha r^2} & l>l_{\mathrm{MAX}}\end{cases} \tag{7}$$

where C_l' is analogous to C_l and where α now serves as an additional parameter for each atom. For this work all higher C_l' are set at this highest l value (Refs. [10, 11]). At this point we mention that for the purpose of simplifying FSGO calculations Semkow *et al.* [3] and Ray Switalski [4] have replaced the projection operator terms by a single spherical term with C_{AV}, (or C'_{AV}) given by

$$C_{AV}, (\text{or } C'_{AV})=\frac{\sum\limits_l C_l\,(\text{or } C_l')M_l}{\sum\limits_l M_l} \tag{8}$$

where M_l is the number of valence orbitals in the atom of l symmetry incorporated into $V(r)$. As pointed out in Refs. [2, 5], this averaging is not justified.

For the Topiol *et al.* [10, 11] pseudopotentials one has

$$V_l(r)=\sum_i \frac{D_{i,l}\exp(-\zeta_{i,l}r^2)}{r^{m_{i,l}}} \tag{9}$$

where the $D_{i,l}$, $\zeta_{i,l}$ and $m_{i,l}$ are adjustable parameters and l goes from zero to at least 1 higher than the highest l value in the core being replaced (e.g. $l_{\mathrm{MAX}}\geq 1$ for Li through Ne) and all higher V_l are set equal to the V_{LMAX}.

Table 1. Valence only FSGO pseudopotential energies at the minimum-energy geometry in each case (energy in Hartrees)[a]

Molecule	LiH	BeH_2	BH_3	CH_4	NH_3	H_2O	HF
Pseudopotential							
Coffey *et al.*	−0.64308	−1.96359	−4.06135	−6.97338	—[b]	—[b]	—[b]
Bonifacic-Huzinaga	−0.61376	−1.88101	−3.87754	−6.76378	—[b]	—[b]	—[b]
Simons	−0.64745	−1.86494	−3.78639	−6.78104	−9.53744	−13.8837[c]	−20.07483
Simons (C_{AV})	−0.5575[d]	−1.9422[d]	−3.5665[d]	−6.5242[d]	−13.4106[d]	−18.1571[d]	−23.3783[d]
Schwartz-Switalski	—[e]	—[e]	−3.91681	−6.73685	−9.66164	−13.87048	−19.71939
Schwartz-Switalski (C'_{AV})	−0.591[f]	−1.786[f]	−3.933[f]	−6.9267[f]	−11.131[f]	−16.054[f]	−22.779[f]
Topiol *et al.*	−0.59822	−1.78565	−3.30945	6.11999	−9.04242	−13.23374	−19.21193

[a] Values reported are from this work unless otherwise indicated.

[b] The lone pairs collapsed onto the pseudopotential center in these calculations.

[c] Barthelat, J. C., Durand, Ph.: Chem. Phys. Letters **40**, 407 (1976).

[e] Only C'_0 is given Ref. [4] for Li and Be, so these potentials are identical to those using C'_{AV}.

[f] Ref. [4].

3. Results and Discussion

Table 1 gives the total (valence) energies for the final optimized geometries in these first row hydride calculations. These total energies are not directly comparable since the energies found in these calculations depend on the form of the potential as well as the values of the parameters, which can be adjusted to give as low an energy as desired. They do, however, allow one to monitor the calculations to spot check for any possible collapsing onto the core. Thus, for example for the NH_3 calculations, both of the core projection type pseudopotentials did not prevent lone-pair orbitals from collapsing into the core. This is because the non-local core projection term ($|\varphi_c\rangle\langle\varphi_c|$) is basis-set dependent. An FSGO orbital basis has sufficient flexibility to penetrate such a pseudopotential, thus leading to the observed collapse. Such collapse was not observed in the hydrides of Be, B, C or Li. For the first three of these, FSGO constrains the bonding orbitals to be equivalent; thus their collapse would be prevented by bond pair-bond pair repulsion, independent of the pseudopotential. For LiH, the H^+ attraction may help to prevent collapse. At any rate, the parameters as given in Refs. [6, 7] do lead to lone-pair collapse.

Before beginning the discussion of the resulting geometries, we point out that all of the pseudopotentials used here are based on either experimental or more accurate *ab initio* calculations. The FSGO method itself depends on a consistent treatment of a crude model, in which certain errors due to the rough (subminimal) valence description are compensated for by a consistent treatment of all orbitals. One would then hope that when pseudopotentials are used in conjunction with the FSGO scheme, one would maintain this consistency, thus obtaining the all-electron FSGO or improved results. Poor results may be an indication of an incompatibility between the FSGO setup and the particular pseudopotential in question.

For the angular momentum projection operator potentials, the Simons potential, as suggested by Barthelat and Durand [2], seems to give the best agreement with full FSGO calculation (Tables 2 and 3). In both the Simons and the Schwartz and Switalski potentials, the results tend to deteriorate when one uses C_{AV} in place of the

Table 2. Equilibrium FSGO bond distances (in a.u.)[a]

Molecule	LiH	BeH_2	BH_3	CH_4	NH_3	H_2O	HF
Source							
FSGO	3.23	2.67	2.35	2.11	1.91	1.67	1.48
Experiment[g]	3.02	(2.54)	(2.3)	2.07	1.91	1.81	1.73
Coffey *et al.*	3.06	2.59	2.32	2.09	—[b]	—[b]	—[b]
Bonifacic-Huzinaga	3.38	2.73	2.43	2.18	—[b]	—[b]	—[b]
Simons	2.94	2.63	2.34	2.06	1.91	1.66[c]	1.47
Simons (C_{AV})	3.33[d]	2.39[d]	2.46[d]	2.12[d]	2.98[d]	3.0[d]	3.09[d]
Schwartz-Switalski	—[e]	—[e]	2.36	2.15	1.92	1.68	1.49
Schwartz-Switalsi (C'_{AV})	3.63[f]	3.02[f]	2.42[f]	2.13[f]	1.84[f]	1.63[f]	1.46[f]
Topiol *et al.*	3.66	3.02	3.01	2.50	2.12	1.91	1.65

[a–f] See footnotes a–f to Table 1.

[g] Ref. [12].

C_l (consistent with the discussion above, and Refs. [2, 5]). The bond distances from the Simons potential tend to be shorter than the all-electron FSGO results. Since the all-electron FSGO bond lengths are too long on the left of the periodic table, the use of the Simons potential improves these results. On the other hand, towards the right side of the periodic table, where the all-electron FSGO results tend to be too short [1], the use of the Simons potential gives slightly poorer results.

The Schwartz and Switalski potentials tend to give results which exaggerate the FSGO errors. Thus, to the left of the periodic table, where the all-electron FSGO bond lengths are already too long, the use of the Schwartz and Switalski potential makes them longer (and analogously to the right of the table).

The Topiol *et al.* pseudopotentials tend to give bond distances that are too long (except for HF). It is suggested that the more structured nature of this potential makes it difficult for the FSGO scheme to adjust itself to the potential.

Table 3. Bond angles[a] (in degrees)

Molecule	NH_3	H_2O
Source		
FSGO	87.6	88.4
Experiment	106.6	104.5
Simons	87.5	87.4[b]
Simons (C_{AV})	120[c]	180[c]
Schwartz and Switalski	88.9	88.6
Schwartz and Switalski (C'_{AV})	83.9[d]	85.3[d]
Topiol *et al.*	92.9	92.7

[a] Values reported are from this work unless otherwise indicated.
[b] Barthelat, J. C., Durand, Ph.: Chem. Phys. **40**, 407 (1976).
[c] Ref. [3].
[d] Ref. [4].

4. Conclusion

It appears that the core-projection type pseudopotentials cannot safely be used in an FSGO calculation. Of the angular momentum projection pseudopotentials tested here, the Simons potential appears to be the best, perhaps because of its limited flexibility (little structure in the $V_l(r)$) and the semiempirical fit to ionization potentials. One should point out, however, that because of the functional form (C/r^2), these potentials die off rather slowly. Because of this, one should test for possible long range effects which may interfere with the calculations on larger molecular systems. The generally poor results of these calculations suggest that a pseudopotential more compatible with the FSGO scheme is required; work on this is continuing.

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