SEMILOCAL AND NONLOCAL SEMIEMPIRICAL MODEL POTENTIALS FOR GROUP IV COMPOUNDS

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Semilocal and nonlocal FSGO model potentials are given for group IV atomic cores, together with a theoretical justification. The parameters were calibrated on experimental molecular data. The model potentials are applied to the molecules CH_4, SiH_4, GeH_4, CH_3SiH_3, CH_3GeH_3 and SiH_3GeH_3. Bond lengths and bond angles are in good agreement with the experimental results.

The FSGO method is a simple *ab initio* method that correlates with chemical concepts such as bonds, lone pairs and inner shells[1]. The many-electron wave function is taken to be a single Slater determinant formed by double occupancy of Gaussian orbitals which can float and vary in size so that the energy is minimized. These orbitals represent the electron pairs of traditional Lewis electron theory[2-4]. Generally a subminimal basis set is used, i.e., each FSGO is occupied by two electrons.

From chemical experience it is well established that valence electrons determine most chemical properties of atoms, molecules and solids. The effect of core electrons is mainly to shield the nuclear charges and to provide an effective field for the valence electrons. Therefore many methods based only on the treatment of valence electrons have been developed. These methods take advantage of pseudopotentials and model potentials, respectively. A necessary first approximation in all calculations to valence-electron-only problems is the 'frozen core approximation'. In solving for the valence wavefunction in this approximation one has to orthogonalize explicitly the valence wavefunction to all core orbitals. This constraint may be removed if one projects out the core states from the valence Hamiltonian. In pseudopotential methods core projection operators are used for this purpose. Model potential methods include a restriction of the functional form of the effective core potential. They contain parameters which are adjusted to fit either theoretically or experimentally determined observables. The pseudopotential and model potential methods are applied to the calculation of various chemical and physical properties. Results of these calculations and the problems to establish the pseudopotential and model potential methods were reviewed in some papers[5-13].

The model potential method has been also applied to FSGO wavefunctions[14-24]. The FSGO model potential methods were used to calculate molecular geometries, energy values and orbital energies. A comparison of FSGO and Hartree–Fock–Roothaan (HFR) wavefunctions and model potentials was carried out[25]. The conclusion is if the description of the core is improved by using a HFR-adjusted model potential the use of FSGO for the valence electron density is not well appropriate and poor results are obtained. Conversely, a FSGO model potential yields satisfactory FSGO valence orbitals, but is not successful in HFR calculations.

THEORETICAL

The many-electron wavefunction is written as

$$\Psi = \mathbf{A}[\varphi_1\alpha, \varphi_1\beta, \ldots, \varphi_\nu\alpha, \varphi_\nu\beta; \Theta_V], \qquad (1)$$

where $\{\varphi_C, C = 1, \ldots, \nu\}$ are the core orbitals, Θ_V is the antisymmetrized valence wavefunction, and $\mathbf{A}$ is a partial antisymmetrizer. If the core-valence orthogonality condition

$$\int \varphi_C(\mathbf{r}_1)\, \Theta_V(\mathbf{r}_1, \ldots, \mathbf{r}_{2\mu})\, \mathrm{d}^3\mathbf{r}_1 = 0 \qquad (2)$$

holds the total electronic energy can be partitioned in core and valence energy. The core energy has the standard form of a closed shell determinantal wavefunction:

$$E_{\text{core}} = 2\sum_C^{\nu} H_{CC} + \sum_C^{\nu}\sum_{C'}^{\nu}(2J_{CC'} - K_{CC'}), \qquad (3)$$

and the valence energy results from the following equation:

$$E_{\text{val}} = 2\sum_V^{\mu} H_{VV} + \sum_V^{\mu}\sum_{V'}^{\mu}(2J_{VV'} - K_{VV'}) + 2\sum_V^{\mu}\sum_C^{\nu}(2J_{VC} - K_{VC}), \qquad (4)$$

where H_{ii} is a matrix element of the one-electron Hamiltonian, J_{ij} and K_{ij} symbolize the Coulomb and exchange integrals, respectively.

Since the FSGO's χ_i are nonorthogonal the energy formulae for E_{core} and E_{val} do not apply. A Loewdin transformation of the χ_i to a set of orthogonal orbitals φ_j,

$$\varphi_j = \sum_i x_i (S^{-1/2})_{ij}, \qquad (5)$$

may be used to derive the desired formulae, where $S^{-1/2}$ is the inverse overlap matrix of the χ_i. This transformation may be carried out separately for the valence and core orbitals, if the overlap integrals between the core and valence orbitals are assumed to be zero.

In the expression of E_{val} a semilocal or nonlocal model potential can be introduced to describe the core-valence interaction. Using a semilocal model potential the following approximation is applied:

$$\sum_C \{2\mathbf{J}_C(\boldsymbol{r}_1) - \mathbf{K}_C(\boldsymbol{r}_1)\} \approx$$

$$\approx \sum_K \{Z'_K |\boldsymbol{r}_1 - \boldsymbol{R}_K|^{-1} + \sum_l^{L\mathrm{max}} V_l(\boldsymbol{r}_1 - \boldsymbol{R}_K) \sum_m \mathbf{P}_{lm}(\nu, \phi; \nu', \phi'; \boldsymbol{R}_K)\} , \qquad (6)$$

where Z_K symbolizes the charge of core electrons, $\boldsymbol{R}_K$ is the position of the core, $\mathbf{J}_C$ and $\mathbf{K}_C$ are the Coulomb and exchange operators, respectively. In the last expression $\mathbf{P}_{lm}$ symbolizes the semilocal projection operator:

$$\mathbf{P}_{lm}\chi_V(\boldsymbol{r}_l) = Y_{lm}(\nu_1\phi; \boldsymbol{R}_K) \int_0^{\pi} \int_0^{2\pi} Y_{lm}(\nu', \phi'; \boldsymbol{R}_K)\, \chi_V(\boldsymbol{r}'_1)\, \mathrm{d}\cos \nu'\, \mathrm{d}\phi' , \qquad (7)$$

where the Y_{lm} are the spherical harmonics and $L_{\max}$ is the highest angular momentum present in the core. $V_l(\boldsymbol{r}_1 - \boldsymbol{R}_K)$ was chosen as:

$$V_l(\boldsymbol{r}_1 - \boldsymbol{R}_K) = A_l \exp\{-\alpha_C(\boldsymbol{r}_1 - \boldsymbol{R}_K)^2\} , \qquad (8)$$

where A_l and α_C are adjustable parameters. If one uses a nonlocal model potential the following approximation can be inserted:

$$\sum_C \{2\mathbf{J}_C(\boldsymbol{r}_1) - \mathbf{K}_C(\boldsymbol{r}_1)\} \approx \sum_K Z_K |\boldsymbol{r}_1 - \boldsymbol{R}_K|^{-1} + \sum_C \mathbf{P}_C(\boldsymbol{r}_1, \boldsymbol{r}'_1) . \qquad (9)$$

$\mathbf{P}_C$ is the nonlocal projection operator which has to be applied as follows:

$$\mathbf{P}_C(\boldsymbol{r}_1, \boldsymbol{r}'_1)\, \chi_V(\boldsymbol{r}_1) = \varphi_C(\boldsymbol{r}_1) \int_0^{\infty} \varphi_C(\boldsymbol{r}'_1)\, \chi_V(\boldsymbol{r}'_1)\, \mathrm{d}^3\boldsymbol{r}'_1 . \qquad (10)$$

Carrying out the Lowdin transformation of the φ_C to nonorthogonal core orbitals χ_K the sum of the projection operators can be rewritten:

$$\sum_C \varphi_C(\boldsymbol{r}_1) \int \varphi_C(\boldsymbol{r}'_1)\, \chi_V(\boldsymbol{r}'_1)\, \mathrm{d}^3\boldsymbol{r}'_1 =$$

$$= \sum_C \sum_k \sum_{k'} (S^{-1/2})_{Ck}\, \chi_k(\boldsymbol{r}_1) \int (S^{-1/2})_{Ck'}\, \chi'_k(\boldsymbol{r}'_1)\, \chi_V(\boldsymbol{r}'_1)\, \mathrm{d}^3\boldsymbol{r}'_1 . \qquad (11)$$

The elements of the inverse overlap matrix remain constant if one applies the frozen core approximation. Therefore the sum of the projection operators has the form

$$\sum_k \sum_{k'} A_{kk'} \chi_k(\boldsymbol{r}_1) \int \chi'_k(\boldsymbol{r}'_1)\, \chi_V(\boldsymbol{r}'_1)\, \mathrm{d}^3\boldsymbol{r}'_1 , \qquad (12)$$

where the $A_{kk'}$ are constants. This expression is reduced using additional approximations. The $A_{kk'}$ was given the value zero if k is different from k'. Further on the χ_k are divided in shells. The orbitals in a shell S get the same parameter A_S. Accordingly the approximate expression is:

$$\sum_S A_S \sum_k \chi_{Sk}(\mathbf{r}_1) \int \chi_{Sk}(\mathbf{r}'_1)\, \chi_V(\mathbf{r}'_1)\, \mathrm{d}^3\mathbf{r}'_1 \,. \tag{13}$$

The nonorthogonal core orbitals χ_{Sk} are FSGO's which are defined as:

$$\chi_{Sk}(\mathbf{r}_1) = \left(\frac{2a_{Sk}}{\pi}\right)^{3/4} \exp\left\{-\alpha_{Sk}(\mathbf{r}_1 - \mathbf{R}_{Sk})^2\right\}, \tag{14}$$

where a_{Sk} and the orbital position $\mathbf{R}_{Sk}$ are used as parameters.

It should be remarked that the introduction of a local model potential is not adequate to the nature of the nonlocal operator $\mathbf{K}_C$.

RESULTS

The most effective core potentials were fitted on experimental or theoretical atomic energy differences. Applying the FSGO method these procedures are not applicable because one cannot calculate the energy of nonoccupied orbitals with it. The introduction of HFR-adjusted potentials in the FSGO formalism did not give satisfactory results. The electron densities of both methods in the region between the cores are very different[25]. Therefore the parameters in our model potentials were calibrated on molecular data according to Nicolas and Durand[26].

The experimental geometries of the molecules ethane, disilane and digermane are the reference data for the parameter A_i in the semilocal and nonlocal model potential. The other parameters correspond to the results obtained earlier[18,27]. In Table I the parameters are presented. In Table II the results of the calculation are compared with the experimental reference data and FSGO results.

The model potentials obtained were applied to the molecules CH_4, SiH_4, GeH_4, CH_3SiH_3, CH_3GeH_3 and SiH_3GeH_3 (Table III). A comparison with experimental and FSGO results is also given.

CONCLUSIONS

Using the semilocal model potential the bond lengths of the reference molecules have a relative error smaller than 3·5% compared with the experimental results. The error in the bond angles is more accurate than 0·7%. They are always smaller than the experimental values. The results in Table III can be summarized as follows. The mean relative errors of bond lengths and bond angles compared with the experimental values amount to 2·6% and 0·7%, respectively. The heavy atom–hydrogen bond lengths of CH_4, SiH_4 and GeH_4 are in better accordance with the experimental values than the FSGO results.

TABLE I

Parameters of the semilocal and nonlocal model potential

Atom	Semilocal model potential		Nonlocal model potential		
	α_C, ref.[18]	A_l	A_j	R_i, ref.[27]	a_i, ref.[27]
C	2·75	9·30	15·90	0·0	9·29988
Si	1·06	9·30	15·90	0·0	57·35734
	1·06	−0·35	3·34	0·01732	3·26732
Ge	1·03	9·30			
	1·03	−0·35			
	1·03	0·25			

TABLE II

Results of reference molecules (all data in atomic units)

Parameters	Model potentials		Experiment[28]	FSGO[18]
	semilocal	nonlocal		
		C_2H_6 (D_{3d})		
$\overline{CC}$	2·833	2·834	2·899	2·836
$\overline{CH}$	2·119	2·122	2·065	2·117
∢HCH	108·3°	108·4°	109·1°	108·2°
E_{val}	−12·80610	−13·00344	—	—
		Si_2H_6 (D_{3d})		
$\overline{SiSi}$	4·450	4·474	4·384	—
$\overline{SiH}$	2·756	2·737	2·797	—
∢HSiH	109·2°	109·1°	109·8°	—
E_{val}	−10·04296	−10·32302	—	—
		Ge_2H_6 (D_{3d})		
$\overline{GeGe}$	4·553	—	4·554	—
$\overline{GeH}$	2·784	—	2·886	—
∢HGeH	109·0°	—	109·8°	—
E_{val}	−9·95557	—	—	—

TABLE III

Results of group IV compounds (all data in atomic units)

Parameters	Model potentials		Experiment[28,29]	FSGO[17,27]
	semilocal	nonlocal		
		CH_4		
$\overline{\mathrm{CH}}$	2·108	2·112	2·07	2·106
E_{val}	−6·89490	−6·98993	—	—
		SiH_4		
$\overline{\mathrm{SiH}}$	2·765	2·737	2·76	2·795
E_{val}	−5·52497	−5·67429	—	—
		GeH_4		
$\overline{\mathrm{GeH}}$	2·791	—	2·89	2·910
E_{val}	−5·48333	—	—	—
		CH_3SiH_3		
$\overline{\mathrm{CSi}}$	3·447	3·451	3·53	—
$\overline{\mathrm{SiH}}$	2·773	2·743	2·81	—
$\overline{\mathrm{CH}}$	2·117	2·115	2·07	—
∢HCH	108·7°	108·9°	107·7°	—
∢HSiH	108·8°	108·7°	108·2°	—
E_{val}	−11·44328	−11·69782	—	—
		CH_3GeH_3		
$\overline{\mathrm{CGe}}$	3·471	—	3·676	—
$\overline{\mathrm{CH}}$	2·146	—	2·047	—
$\overline{\mathrm{GeH}}$	2·799	—	2·899	—
∢HCH	107·2°	—	108·4°	—
∢HGeH	108·3°	—	109·3°	—
E_{val}	−11·39062	—	—	—
		SiH_3GeH_3		
$\overline{\mathrm{SiGe}}$	4·502	—	4·454	—
$\overline{\mathrm{SiH}}$	2·759	—	2·806	—
$\overline{\mathrm{GeH}}$	2·783	—	2·889	—
∢HSiH	109·0°	—	108·2°	—
∢HGeH	109·2°	—	109·3°	—
E_{val}	−9·99914	—	—	—

The results obtained with the nonlocal model potential are similar to the semilocal model potential results. The bond lengths and bond angles of the reference molecules have a relative error which does not exceed 2·7% and −0·6%, respectively. The mean relative errors in CH_4, SiH_4 and CH_3SiH_3 amount to 2·0% (bond lengths) and +0·8% (bond angles).

The application of the nonlocal model potential to Ge-compounds is problematic because the arrangement of the five FSGO's representing the *d*-orbitals of the core may be chosen in different ways.

Our model potentials do not show any indication of instability with respect to a collapse of FSGO's in the model potential center. The errors of the results obtained originate mainly from the subminimal basis set and not from the features of the model potentials used.

REFERENCES

1. Frost A. A.: J. Chem. Phys. *47*, 3707 (1967).
2. Lewis G. N.: J. Am. Chem. Soc. *38*, 762 (1916).
3. Langmuir J.: J. Am. Chem. Soc. *41*, 868 (1916).
4. Lewis G. N.: *Valence and Structure of Atoms*. Chemical Company, New York 1923.
5. Weeks J. D., Hazi A., Rice S. A.: Adv. Chem. Phys. *16*, 283 (1969).
6. Cohen M. L., Heine V.: Solid State Phys. *24*, 37 (1970).
7. Bardsley J. N.: Case Studies Atom. Phys. *4*, 299 (1974).
8. Durand Ph., Barthelat J. C. in: *Localization in Quantum Chemistry* (O. Chalvet, Ed.), Vol. II, p. 91. Reidel, Dordrecht 1976.
9. Kahn L. R., Baybutt P., Truhlar D. G.: J. Chem. Phys. *65*, 3826 (1976).
10. Barthelat J. C., Durand Ph.: Gazz. Chim. Ital. *108*, 225 (1978).
11. Bachelet G. B., Hamann D. R., Schlueter M.: Phys. Rev., B *26*, 4199 (1982).
12. Krauss M., Stevens W. J.: Ann. Rev. Phys. Chem. *35*, 357 (1984).
13. Christiansen Ph. A., Ermler W. C., Pitzer K. S.: Ann. Rev. Phys. Chem. *36*, 407 (1985).
14. Semkov A. M., Suthers R. A., Linnett J. W.: Chem. Phys. Lett. *32*, 116 (1975).
15. Ray R. N., Switalsky J. D.: J. Chem. Phys. *63*, 5053 (1975).
16. Barthelat J. C., Durand Ph.: Chem. Phys. Lett. *40*, 407 (1976).
17. Simons G., Talaty E. R.: J. Chem. Phys. *66*, 2457 (1977).
18. Topiol S., Frost A. A., Moskowitz J. W., Ratner M. A.: J. Chem. Phys. *65*, 4467 (1976); J. Am. Chem. Soc. *99*, 4276 (1977); J. Chem. Soc., Faraday Trans. 2 *74*, 1521 (1978).
19. Topiol S., Frost A. A., Ratner M. A., Moskowitz J. W., Melins C. F.: Theor. Chim. Acta (Berlin) *45*, 177 (1977).
20. Mehandru S. P., Ray N. K.: Chem. Phys. Lett. *54*, 42 (1977).
21. Gaspar R., Gaspar R.: Int. J. Quantum Chem. *15*, 559 (1979).
22. Toman J. J., Frost A. A., Topiol S., Jacobson S., Ratner M. A.: Theor. Chim. Acta (Berlin) *58*, 285 (1981).
23. Gaspar R., Gaspar R.: Int. J. Quantum Chem. *24*, 767 (1983).
24. Gruendler W., Walther P.: Chem. Phys. Lett. *150*, 275 (1988).
25. Ratner M. A., Frost A. A., Topiol S., Sabin J. R.: J. Chem. Soc., Faraday Trans. 2 *74*, 324 (1978).

26. Nicolas G., Durand Ph.: J. Chem. Phys. *72*, 453 (1980).
27. Chu S. Y., Frost A. A.: J. Chem. Phys. *54*, 760 (1970).
28. Sutton L. E.: *Interatomic Distances.* Chem. Soc., Spec. Publ., No. 11 (1958), No. 18 (1965); Cox A. P., Varma R.: J. Chem. Phys. *46*, 2007 (1967).
29. Moccia R.: J. Chem. Phys. *40*, 2164, 2176, 2186 (1964).