Effective Group Potentials. 1. Method

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In the first paper of this series, we will describe a method, called effective group potentials (EGP), aimed at simplifying molecular ab initio calculations for large systems involving bulky ligands as long as these ligands can be supposed to play the role of spectator groups. This method should be applicable to all types of bondings between active and the spectator parts. The different steps used in the definition of the EGP are closely related to those used for atomic effective core potentials (ECP) which are commonly used with great success in ab initio calculations involving heavy atoms.

1. Introduction

There is always a great interest for pushing upward the feasability limits for ab initio calculations. This impulse is responsible for the development of new methods and new programing which have, along with a rapid evolution of computer technology, profoundly extended the possibilities of ab initio methods. For large molecules, it has been recently claimed that calculation times should increase as slowly as $N^{1.3}$,[1] where the basis set size N is related to the number of electrons in the system. Nevertheless, there is still a pressing need for reducing the computational effort by reducing N , either for very large molecular systems or to allow a full exploration, possibly linked to dynamical studies of the potential energy surface. By large molecular systems, we mean polymers and/or biomolecules for which ab initio calculations are still a “tour de force”. By dynamical studies, we mean that the difficult and cumbersome step of a potential energy surface fit might be skipped by on-the-fly calculations of both the total energy and if needed, first and second-order derivatives of the energy with respect to nuclear coordinates.

Many years ago, the chemical evidence of the small influence of core electrons on many molecular properties lead to the theory of effective core potentials (ECP), which has been brought to a very high level of accuracy. The most recent improvements follow.

1. The main weakness of ECPs for transition metal atoms, lanthanides and actinides (i.e., the incorrect reproduction of the small energy differences between the first excited states and the ground state) has been satisfactorily solved.[2,3]

2. It has also been shown that relativistic ECPs which directly include the largest mean scalar relativistic corrections during the parametrization step of the effective potential[4] are the simplest way to study large molecular systems with such heavy atoms. It has been proved in many cases that results are in very good agreement with the more exact but much more computer demanding four component methods corresponding to the Dirac−Fock equation.[5,6]

3. For atoms on the left side of the Mendeleev classification where the number of valence electrons is small, effects involving core polarization and core−valence correlation could not be included in the original ECP approach which is limited by a frozen core approximation but different authors have proposed semiempirical corrections[7,8] which enable extremely precise calculations of ground and excited states to be performed.[8−10]

Successes of ECP are based upon the separability of core and valence orbitals, from both energetic and spatial points of view. Whenever one of these criteria is not fulfilled, applications may run into troubles. For instance in transition metal atoms, with a valence configuration $n\text{d}^p\ (n+1)\text{s}^1$ or $n\text{d}^{p-1}\ (n+1)\text{s}^2$, $n = 3-5$, the nd orbital describing the open d shell is very contracted and is localized in the same region of space as the inner ns and np shells. The large core ECP, for which these inner ns and np shells are included in the core, have been shown to give appreciable differences with respect to all electron calculations.[11]

In view of the great successes of ECP methods, it is tempting to propose another simplification, valid for large molecular systems. In many cases it has been recognized that chemical phenomena are well localized in some active and relatively small part of the molecule. This consideration is the basis for the classification of molecular systems in families whose members only differ by some substituent groups around a central atom or a central group of atoms. Members of the same family must exhibit similar chemical properties but there still exist differences which correspond to different electronic structures of the susbstituent groups. For instance, such notions as “electron rich” or “electron deficient” groups are very useful for rationalizing the substituent influence upon the active center. To reproduce these small variations in ab initio calculations is not an easy task unless we are able to deal with a complete description of the molecular system.

Generally the modeling of large molecules is made by a brute force approach. For instance, a chemical group which is linked to the active site through a single bond is replaced by a single hydrogen atom. In the IMMOM method,[12] this is done for the bonded interactions and the nonbonded interactions between

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atoms of the active site and the modeled part of the system are introduced with a classical molecular mechanics force field. Applications[13,14] have shown that the IMMOM approach really improves the description of the molecule especially if large steric effects are present. In the approach developed by Théry et al.,[15] the linking bond is replaced by an hybrid orbital frozen in a specific situation.

For more complicated situations, we can look for an atom or a small group of atoms which have approximately the same electronic structure as the original one. Recently, some of us[16] have followed the suggestion by Steigerwald and Goddard[17] to replace cyclopentadienyl (Cp) substituent by a Cl atom in theoretical studies of trihydrides complexes of Nb and Ta ($(Cp)_2MH_3$, M = Ta, Nb). A thorough comparison led us to the conclusion that even if the optimized structure of the $M-H_3$ part of the $(Cp)_2M-H_3$ is not strongly affected, charge distributions and energy differences between different minima are not precisely reproduced.

The purpose of this work is to develop a new method called Effective Group Potential method (EGP), closely related to the ECP technique. The main goal of our approach will be the reproduction of subtle electronic differences between different substituents, which will be out of reach for the simple methods mentioned above. Preliminary results were recently published.[18]

2. Effective Potentials for Atomic Cores

To give a clear presentation, we shall first recall the different approaches used for atomic cores. As usual we start from the Hartree−Fock approximation which gives *atomic orbitals* φ_i and *orbital energies* ϵ_i as solutions of the system of equations:

$$F\varphi_i = \epsilon_i\varphi_i \qquad i = 1,n \tag{1}$$

where n is the total number of electrons and the Fock operator F is defined as

$$F = -\frac{1}{2}\Delta - \frac{Z}{R} + \sum_j (2J_j - K_j) \tag{2}$$

and the operators J_j and K_j are

$$J_j\varphi_i(1) = \int dr_2\, \varphi_j^*(2)\, \varphi_j(2)\frac{1}{r_{12}}\varphi_i(1) \tag{3}$$

$$K_j\varphi_i(1) = \int dr_2\, \varphi_j^*(2)\, \varphi_i(2)\frac{1}{r_{12}}\varphi_j(1) \tag{4}$$

We further split the set of orbitals into active n_a and frozen n_f orbitals ($n = n_a + n_f$) and rewrite the Fock operator as

$$F = -\frac{1}{2}\Delta - \frac{Z}{R} + \sum_j^{n_a}(2J_j - K_j) + V_{ad} + W_{ps} \tag{5}$$

where the sum over j runs only over the n_a active electrons and the effective operator W_{ps} is supposed to mimic the interaction between active and frozen electrons. The supplementary operator V_{ad} is adequately defined to facilitate the definition of W_{ps}, and will be explicitly defined in the following sections. Equation 5 is the common starting point for all methods.

2.1. Model Potentials. In the first group of methods,[19] W_{ps} is directly fixed to reproduce the Coulomb J_j and exchange K_j operators corresponding to frozen electrons. Introducing a complete set of orbitals $\{\chi_p\}$, W_{ps} is defined as

$$W_{ps} = O\,[\sum_j^{n_f}(2J_j - K_j) - V_{ad}]O \tag{6}$$

$$O = \sum_{pq}|\chi_p\rangle(S_{pq}^{-1})\langle\chi_q| \tag{7}$$

$$S_{pq} = \langle\chi_p|\chi_q\rangle \tag{8}$$

If we solve eq 1 for the n_a active electrons only, we must add the projection operator onto the occupied atomic orbitals φ_i to the definition of the Fock operator:

$$P = -\sum_j^{n_f} 2|\varphi_i\rangle\epsilon_i\langle\varphi_i| \tag{9}$$

in order to prevent the collapse of the active electron orbitals onto the frozen orbital space. Since it is impossible to use a complete basis set in practical calculations, the potential V_{ad} is chosen to minimize the error due to the use of a finite basis set $\{\chi_p\}$. In many methods, the partial screening of the nuclear charge by the core electrons is taken into account, by defining

$$V_{ad} = -\frac{Z^f}{R} \tag{10}$$

where Z^f is the partial nuclear charge corresponding to the n_f frozen electrons. The screened potential $W_{sc} = -Z^f/R + \sum_{j=1}^{n_f} 2J_j$, spherically symmetric and exponentially decreasing, is easily fitted by a small number of terms. The projection operator O is used only for the exchange part and the effective potential is

$$W_{ps} = W_{sc} + O(\sum_j^{n_f} - K_j)O \tag{11}$$

$$F^{ps} = -\frac{1}{2}\Delta - \frac{Z^a}{R} + \sum_{j=1}^{n_a}(2J_j - K_j) + W_{ps} + P \tag{12}$$

The truncation error due to the incompleteness of the basis set used for defining O is then considerably reduced.

2.2. Shape Consistent and Energy Consistent Potentials. In these methods, W_{ps} is not intrinsically defined by (6) but extrinsically by conditions imposed on the solutions of (5). In the *shape consistent* versions,[20,21] the conditions are

$$F^{ps}\varphi_i^{ps} = \epsilon_i\varphi_i^{ps} \qquad i = 1, n_a \tag{13}$$

ϵ_i is the orbital energy of the corresponding *real valence orbital* φ_i and φ_i^{ps} is a so-called *valence pseudoorbital* which fits φ_i in the valence region. For each symmetry, the lowest *valence pseudoorbital* is nodeless. The specification of the valence pseudoorbital is sufficient to fix the form of W_{ps} completely. In the *energy consistent* version[4], no condition is imposed for the solutions of equation 13 but the latter is solved not only for the ground state but also for a selection of excited states and W_{ps} is determined to reproduce all-electron results for the energy differences between ground and excited states. The corresponding valence pseudoorbitals, solutions of eq 13, are also nodeless and very similar to the orbitals in the shape consistent version. This is probably due to the specific choice of the analytic form of the operator W_{ps}.

3. Extension to Groups of Atoms

If the total Hartree−Fock wave function can be split into two parts, according to the theory of separability of a many electron system developed by McWeeny and Kleiner[22] and Huzinaga:[23]

$$\Psi_{\mathrm{HF}} = NA\ (\Psi_{\mathrm{a}}\Psi_{\mathrm{f}}) \tag{14}$$

an effective group potential (EGP) for the spectator group described by the function Ψ_{f} can be developed in a way similar to the model potential approach. If the spectator group is an atom, the method is exactly equivalent to the atomic core treatment, with the only difference that the summation of (6) runs over all the electrons of the spectator group. For instance, Barandiaran and Seijo[24] have used this approach to produce embedding potentials used in solid-state calculations. If the spectator group is a molecule, the definition of V_{ad} is not straightforward. In a first seminal paper, Mejias et al.[25] have extended the model of EGP to a polycentric spectator group in the case of intermolecular interactions. Sanz and colleagues[26−28] have applied the same model to other chemical groups. The physical effects included are the repulsive energy, through the action of the projection operator P and the electrostatic energy. Since no basis set is used on the spectator group, no charge-transfer effect is possible. Polarization should be included by a semiempirical procedure similar to the one used in ECP calculations.[8] In a more rational way, Day et al.[29] have proposed to express the polarization of the spectator group as a superposition of multiple bond contributions, following the seminal works by Claverie and collaborators.[30] The success of these methods is therefore rather limited to intermolecular systems where a complete separation between active and spectator electrons is justified.

Ohta et al.[31] have proposed an effective fragment potential (EFP) method using localized molecular orbitals in which only two electrons in the lone pair orbital on the nitrogen atom of ammonia are active. When used in a van der Waals complex, like $(NH_3)_2$, the results are in fact in very good agrement with all-electron calculations.

In the same spirit, Peyerimhoff and co-workers[32,33] have developed EFP for molecules like NH_3 or H_2O, where the short-range part of the spectator potential is stored in an intermediate atomic orbital basis set and the longer range of the potential is reproduced via a distributed multipole expansion. The difficulty to fit accurately the short range of the potential, at least for the nonspherical case, is therefore circumvented but the use of matrix elements stored in an intermediate basis set is quite involved. These authors are the first[34] to mention the possibility of using the EFP approach beyond the Hartree−Fock level and they have indeed applied this technique to the study of the solvent shift effects of the $n \rightarrow \pi^*$ transition in CH_2O surrounded by n water molecules, each of these molecules being replaced in the calculation by an EFP.

Colle and Salvetti[35,36] proposed the use of nonlocal representations of the model potential not only for the exchange part but also for the short range of the Coulomb operator, the kernel of which corresponds to localized molecular orbitals on the spectator fragment. Their method has been first applied to a simple case, namely the 1s electrons of the Lithium atom, for which they showed that it is possible to have a completely nonlocal representation of atomic cores (this has also been shown independently by Komiha and collaborators[37]). In a second case, the separability between σ and π electrons in bipyrrole allows an EFP for the σ skeleton to be determined, and the authors demonstrate that the EFP is able to reproduce correctly the transition energies corresponding to the first singlet and the first triplet excitation in the π system. SiH_4 is the third and last example and the fragment corresponds to SiH_3: the EFP is built on the core electrons of Si and the six electrons on the SiH bonds, the active group containing only one SiH bond. The quality of the comparison between exact (i.e., results obtained with all electrons in the active set) and EFP results is good, and shows that EFP might be a useful tool for molecular calculations.

Katsuki[38] has proposed the extension of the model potential approach to the case of a nonspherical and chemically bonded spectator group, like COOH in the CH_3COOH, CH_3CH_2COOH and $CH_3CH_2CH_2COOH$ molecules. He defined four different EGP corresponding to frozen electrons in different sets of MO obtained in an open shell calculation of the COOH radical: (1) the three 1s orbitals on C and O, which corresponds to the usual definition of a model potential for core electrons; (2) the five lowest molecular orbitals; (3) the six lowest molecular orbitals; (4) the nine lowest molecular orbitals.

The performance of these four definitons of W_{ps} has been tested by comparison with all-electron calculations for the $r_{\mathrm{C-C}}$ distance and bond energy corresponding to the link between the terminal CH_3 group and the neighbor C atom. He readily found that the results obtained are in excellent agrement when the frozen electrons correspond to core electrons of C and O atoms, which confirms the validity of ECP approaches. With a larger number of frozen electrons, the quality of the results deteriorates rapidly, and the fourth EGP corresponding to 18 frozen electrons and 6 active ones gives rather unreliable results, at least for CH_3COOH and CH_3CH_2COOH (see Tables III and VI of 38). Applying the same method, he studied the trimer $(NH_3)_3$ by replacing one ammonia by an EGP, and he found that the interaction (distance and energy) between the two other molecules is well reproduced.

In a recent paper, Zhang et al.[39] have developed a "pseudobond approach" which explicitly addresses the problem of the linking atoms in QM/MM methods. Namely, they concentrate on the breaking of a C−C single bond at the limit between QM and MM domains.They propose to replace one of the C(sp^3) by a pseudo C_{ps} with seven electrons, a nuclear charge of seven, the basis set of the fluorine atom and an effective core potential V^{eff}. The analytic form of V^{eff} is chosen identical to the usual forms used for ECP, that is

$$V^{\mathrm{eff}}(r) = V_L^{\mathrm{eff}}(r) + \sum_{l=0}^{L-1} [V_l^{\mathrm{eff}}(r) - V_L^{\mathrm{eff}}(r)] \sum_m |lm\rangle\langle lm| \tag{15}$$

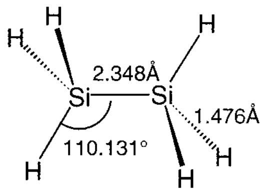
$$V_L^{\mathrm{eff}}(r) = \frac{a_L^* \mathrm{e}^{-b_L^* r^2}}{r} \tag{16}$$

$$V_l^{\mathrm{eff}}(r) - V_L^{\mathrm{eff}}(r) = a_l^* \mathrm{e}^{-b_l^* r^2} \qquad l = 0, 1 ,.., L - 1 \tag{17}$$

L is the maximum l of the basis set. a_i^* and b_i^* are parameters fitted on some characteristics of one of the protoptypes of the C−C single bond like the ethane molecule (lengths of the C−C and C−H bonds, C−C−H angles, Mulliken charges and C−C bond dissociation energy). It has to be pointed out that the specific form chosen for V^{eff} is not grounded on physical facts but it is only aimed to simplify the use of the pseudobond approach in standard ab initio programs. The values of a_i^*, b_i^* clearly depend on the methods used for calculating the characteristics of the ethane molecule. Nevertheless, transferability to other molecules, and very interestingly to highly polar ones, is quite successful (see Table III and IV in 39).

EFPs of spectator groups have also been proposed in order to accurately represent the correct electrostatic and polarization fields of amino acid residues.[40] The EFPs were extracted from

SCHEME 1



separate ab initio calculations on the individual components which are immediate neighbors of the active site of ribonuclease A, a prototype of enzyme catalyst.

This brief review of earlier work on effective group potentials (or any of the different names which have been used in the literature) shows that it is possible to go beyond the usual partition between active and spectator parts which is verified for intermolecular cases. In the present paper, we shall present a different approach which is not derived from the atomic model potential but forms the shape consistent version of effective group potentials. Analogous principle to the EGP methodology has been briefly introduced in ref 41, but neither implementation nor applications have been done.

4. Determination of Effective Group Potential

As stated in the above section, the two criteria (spatial and energetic separations) which are satisfied in the case of the ECP determination cannot be fulfiled for EGP. In general, some of the energies in the active orbitals set are in the same part of the spectrum as the inactive ones. Therefore, we must insist on the *localization criterion*, which is usually verified since the definition of the spectator group is based on spatial separation.

In paper 2 we shall present detailed examples corresponding to different bonding types but in the present outline of the method we take only one example, a single bonded spectator group like SiH_3. In this case, the inactive electrons correspond to the core electrons of Si and the six valence electrons describing the three occupied SiH bonds. There is only one active electron which is responsible for the bonding between SiH_3 and the connected group. However, the definition of the EGP on the isolated silyl radical would lead to severe artifacts since the energy level of the highest singly occupied molecular orbital (SOMO) for SiH_3 is significantly different from the energy level occupied by this active electron when making a covalent bond. Actually, the definition is made following three steps:

1. As a first step, we must choose a *reference* system to fit the parameters of the EGP. In this reference system, the spectator group must have characteristics (type of bonding, ionicity, etc.) close to those which can be expected in the molecular system. A thorough investigation of the *transferability properties* of the EGP (that is its performances when used in various bonding situations) is presented in the accompanying paper. It is also worthwhile to point out that in some cases the definition of the EGP can be achieved independently of any reference system (see for instance the case of Cp^- which will be detailed in a forthcoming paper[42]). The simplest reference system we can think of in this case is the disilane molecule $Si_2\,H_6$ (see Scheme 1). The molecule is represented by two parts; part A contains one silyl group and the Si−Si bond and part B contains the other silyl group. In the molecular EGP representation, part A will be treated exactly and part B replaced by the EGP potential which we will call $Si^{\#}$. In so far as the disilane molecule is used as a test system for our method, it thus seems important to become familiar with a few geometrical and electronic features. Disilane has D_{3d} symmetry, and its electronic ground state is $^1A_{1g}$. The HF optimized geometry is shown on the scheme of the molecule. According to the Mulliken population analysis, Si atoms are depopulated, and H atoms present an anionic character. The center of symmetry implies that the pyramidal SiH_3 fragment remains neutral. Six MOs essentially contribute to the Si−H bonds, while the seventh MO, the HOMO, is strongly Si−Si bonding. The energy of the occupied valence MO, their symmetry, and their contribution to the bonding are reported in Table 1. We first perform Hartree−Fock calculations of the reference system in basis set $\{\chi_q\}$ of dimension n_{ref}, which defines the reference Fock operator F^{ref} and molecular orbitals $\{\phi_i\}$:

TABLE 1: Mulliken Population Analysis and HF Energies (hartree) of the MO of Si_2H_6 in Different Representations[a]

				$SiH_3Si^{\#}$		
D_{3d}	Si_2H_6	C_{3v}	SiH_3R	EGP_1	EGP_2	$SiH_3...H^b$
	Si: 3.538		Si: 3.534	Si: 3.421	Si: 3.535	Si: 3.408
	H: 1.154		H: 1.155	H: 1.199	H: 1.155	H: 1.127
	SiH_3: 7.000		X: 0.999	$Si^{\#}$: 0.982	$Si^{\#}$: 1.000	H: 1.210
σ^+_{SiSi}	−0.40761	σ_{SiSi}	−0.44471	−0.40058	−0.44483	−0.36211
$\pi^-_{SiH_3}$	−0.47722	π_{SiH_3}	−0.49071	−0.44850	−0.49088	−0.52055
$\pi^+_{SiH_3}$	−0.50419					
$\sigma^+_{SiH_3}$	−0.68691	σ_{SiH_3}	−0.73111	−0.69427	−0.73078	−0.73984
$\sigma^-_{SiH_3}$	−0.76633					

[a] Comparison is made for each step of the EGP extraction. Data given in the SiH_3R column correspond to the delocalized MVPOs. The SiH_3R and $SiH_3Si^{\#}$ molecules have the same geometry as for the corresponding atoms of Si_2H_6. [b] The Si...H distance is lengthened to the Si−Si distance in Si_2H_6.

$$F^{ref} = \sum_{i=1}^{n_{ref}} \epsilon_i |\phi_i\rangle\langle\phi_i| \tag{18}$$

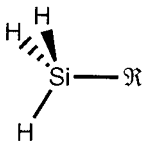
To achieve spatial separation, we localize the molecular orbitals $\{\phi_i\}$, and in this symmetric case, we use a simple rotation transformation (any type of localization methods like Boys[43] or Edmiston and Ruedenberg[44] ones would lead essentially to the same result). In the localized basis set $\{\varphi_i\}$, F^{ref} is

$$F^{ref} = \sum_{i,j=1}^{n_{ref}} \epsilon_{ij} |\varphi_i\rangle\langle\varphi_j| \tag{19}$$

For the occupied orbitals we thus obtain three SiH orbitals localized on the left side, three SiH orbitals localized on the right side and a Si−Si orbital. In the following steps, we will try to build an EGP which reproduces the three localized SiH orbitals on A and the Si−Si orbital as well as possible, which we will call *reference localized orbitals*.

2. In the second step, we define the *truncated basis set* $\{f_p\}$ of dimension n_{tr}, which is composed of the basis set corresponding to the left side A and a smaller set centered on the right side B. There are no theoretically justified arguments for choosing the basis set functions on part B. Since we shall try to reproduce as closely as possible the localized orbitals on A obtained in the first step, a natural choice was made for all the truncated basis sets we have investigated, that is on the same position as the silicon atom of part B. This reduced system is noted R (see Scheme 2). The choice of this truncated set is a very important step for the determination of EGPs since we shall use the same basis set on R in further molecular calculations (this is a strict condition for the applicability of the method).

SCHEME 2



This second step is analogous to the definition of valence pseudoorbitals in the shape consistent version in the ECP determination. We shall call *molecular valence pseudoorbitals* (MVPO, hereafter noted ϕ'_j) the orbitals built in the truncated basis set which are as close as possible to the localized molecular orbitals $\{\varphi_i\}$ of the reference calculation. MVPOs are obtained in three steps: (a) calculate the elements of the S matrix

$$S_{pq} = \sum_{i=1}^{n} \langle f_p|\varphi_i\rangle\langle\varphi_i|f_q\rangle \qquad p, q = 1, n_{\mathrm{tr}} \tag{20}$$

(b) diagonalize S, and (c) select the n_{act} eigenvectors ϕ'_j corresponding to the n_{act} eigenvalues closest to one.

Two criteria will then fix the choice of the basis set on R which is defined iteratively: (a) optimize the exponents and principal quantum numbers of the truncated basis set to obtain overlap between reference active orbitals and MVPOs close to 1 and (b) check the charge distribution which shall be as close as possible to the charge distribution of the reference calculation for part A.

The Gaussian functions on part B are chosen in such a way that the MVPOs expressed in the reduced basis set are as close as possible to the four reference orbitals. As stated before, the definition of the truncated basis set is very important. It is closely related to the nature of the chemical bonding between active and spectator fragments. In the present case of SiH_3 linked by a covalent bond, we have found that one s (exponent 0.17) and one p (exponent 0.16) functions are sufficient for a good reproduction of the reference localized MOs. Their exponent are tuned in order to reproduce the charge transfer between part A and R. Although the Mulliken atomic charges are strongly dependent upon the basis set, due to the arbitrary partitioning scheme, we found that this criterion yields MVPOs in close agreement with the reference localized MOs.

Since the original Fock operator F^{ref} is defined in the reference basis set, we go back to the reference basis set by a projection procedure:

$$|\psi_j\rangle = \sum_{i=1}^{n_{\mathrm{act}}} |\varphi_i\rangle\langle\varphi_i|\phi'_j\rangle \qquad j = 1, n_{\mathrm{act}} \tag{21}$$

and construct the Fock operator corresponding to the truncated system for MVPOs ψ_j:

$$F^{\mathrm{tr}} = \sum_{i,j=1}^{n_{\mathrm{act}}} |\psi_j\rangle\langle\psi_j|F^{\mathrm{ref}}|\psi_i\rangle\langle\psi_i| \tag{22}$$

Diagonalization of the F^{tr} operator yields delocalized MVPOs and their one-electron energies. They are systematically analyzed in order to check that there is no discrepancy between MVPOs and reference MOs. The two lowest delocalized MVPOs have either $\sigma_{\mathrm{SiH_3}}$ or $\pi_{\mathrm{SiH_3}}$ character. Their energies, either −0.73111 or −0.49071 au, are intermediate between $\sigma^{+}_{\mathrm{SiH_3}}$ and $\sigma^{-}_{\mathrm{SiH_3}}$ or $\pi^{+}_{\mathrm{SiH_3}}$ and $\pi^{-}_{\mathrm{SiH_3}}$ MOs of Si_2 H_6, respectively, while the HOMO (−0.44471 au) is 40 mh above the σ_{SiSi} orbital. The good agreement of the Mulliken population and of the MO shapes and energies indicates that the choice of the reduced system and basis set is suitable.

At the end of this iterative process, the MVPOs ϕ'_j will play the same role as the valence pseudoorbitals used in the determination of ECP's in the shape-consistent approach.

3. In the third step, the effective Fock operator F^{eff} is defined as the operator, restricted to the n_{act} active electrons which should reproduce the solutions of the truncated Fock operator F^{tr}. This effective Fock operator F^{eff} is

$$F^{\mathrm{eff}} = h + W_{\mathrm{EGP}} + \sum_{j=1}^{n_{\mathrm{act}}} (2J_{\mathrm{j}} - K_j) \tag{23}$$

h is the core Hamiltonian. It contains the kinetic energy operator, the nuclear attraction operator (eventually taking into account ECPs), and atomic ECPs if needed.

For numerical convenience as detailed in the next paragraph, the EGP operator W_{EGP} is expressed in a nonlocal form:

$$W_{\mathrm{EGP}} = \sum_{\lambda,\mu=1}^{n_{\mathrm{pot}}} c_{\lambda,\mu}|g_\lambda\rangle\langle g_\mu| \tag{24}$$

The EGP nuclei contribution is included in h such that W_{EGP} decreases exponentially. The exponents and locations of the Gaussian functions g_λ and the coefficients $c_{\lambda,\mu}$ are determined to minimize the norm of the difference between F^{tr} and F^{eff}, as proposed by Nicolas and Durand.[45,46]

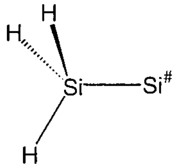
TABLE 2: s, p, and d Parameters Used for the Determination of the Nonlocal Pseudopotentials for Si# EGP$_1$ and Si# EGP$_2$[a]

Si#	Si		H
s and p	s and p	d	s
3.750000	3.750000	0.800000	3.750000
1.875000	1.875000		1.875000
0.937500	0.937500		0.937500
0.468750	0.468750		0.468750
0.234375	0.234375		0.234375
0.110000	0.110000		0.110000

[a] Si# EGP$_1$: the Gaussian functions are located on the pseudo-silicon atom. Si# EGP$_2$: the Gaussian functions are located on all the atoms of the SiH_3R molecule in the optimal geometry of Si_2H_6.

As recalled above, a calculation involving SiH_3 and a one electron pseudo-silicon with a small basis set would yield a poor description of the electronic properties of the SiH_3 fragment and of the Si−Si bonding. The role of W_{EGP} is to fill up the difference between the reference molecule and the truncated system. Various attempts for choosing the EGP (i.e., exponents and locations of g_λ) were made, but we finally adopted two main rules. The first is to keep a local character for the EGP operator in order to ensure its transferability. The second is to define the Gaussian Cartesian functions of W_{EGP} as an even-tempered atomic basis sets, that is by choosing the exponents in geometric progression.[47,48] In the first attempt (EGP$_1$) all basis functions g_λ are located on the Si atom of part B. The set of exponents is defined a priori and not optimized. Thus, the operators may be almost linearly dependent. A canonical orthonormalization with an adequate threshold is needed in order to remove these dependencies.[45] The center of the six s and six p Gaussian functions that define W_{EGP} (Table 2) coincides with the position of the pseudo-silicon atom. As shown in Table 1 (EGP$_1$ column), this EGP does not fit either the Mulliken atomic populations or the delocalized MVPO energies exactly. All the occupied MOs are systematically shifted by approximately 0.04

SCHEME 3



hartree, and the difference between the Mulliken populations is rather small. In a second step,we have attempted to improve the description of MVPOs. We have built another W_{EGP} operator (hereafter called EGP$_2$) developed on many centers. To obtain the best overlap between all the truncated basis functions and the g_λ set, they coincide exactly with the positions of all the atoms of the SiH$_3$ Si$^{\#}$ molecule. Their exponents (6s 6p 1d on Si, 6s on each H, 6s 6p on Si$^{\#}$) are displayed in Table 2. As can be checked in Table 1, the fit is almost perfect. The delocalized MVPO energies are reproduced with an average deviation of 0.003 au. The EGP$_2$ has a tempting behavior, but further investigations are needed before concluding in its favor.

5. Geometry Optimization

5.1. Methodological Details. The main advantage of the nonlocal formulation[37] of W_{EGP} is that the EGP integrals are expressed as products of ordinary overlap integrals of the form:

$$\omega = \langle \chi_{\mathrm{i}} | g_{\mathrm{n}} \rangle \langle g_{\mathrm{m}} | \chi_{\mathrm{j}} \rangle = \langle \chi_{\mathrm{i}} | W_{\mathrm{EGP}}^{\mathrm{nm}} | \chi_{\mathrm{j}} \rangle$$

where $|\chi_{\mathrm{i}}\rangle$ and $|\chi_{\mathrm{j}}\rangle$ are Gaussian-type orbitals centered on atoms I and J, while the Gaussian functions $|g_{\mathrm{n}}\rangle$ and $|g_{\mathrm{m}}\rangle$ may be centered on two different sites N and M, respectively. The EGPs are determined at the Hartree−Fock level of theory. They are intended to simulate HF results. However, the method was checked on some cases at a post-HF level (MP2). Geometry optimizations have been carried out with the Berny method which requires an analytical gradient. We therefore implemented an explicit calculation of the analytical first derivatives into Gaussian98.[49] This is a generalization of the routines written by Klotz[50] to the anisotropic and multicentric cases. The nonzero first derivatives of the integral product ω are the derivatives with respect to the coordinates of atoms I and J and to the centers N and M. The derivatives of the pseudopotential integrals can be written without explicitly calculating the derivatives of the EGP by using the translational invariance of the matrix element:[51,52]

$$\frac{\partial}{\partial R_{\mathrm{N}}} \langle \chi_{\mathrm{i}} | g_{\mathrm{n}} \rangle = \left\langle \chi_{\mathrm{i}} \middle| \frac{\partial g_{\mathrm{n}}}{\partial R_{\mathrm{N}}} \right\rangle = -\left\langle \frac{\partial \chi_{\mathrm{i}}}{\partial R_{\mathrm{I}}} \middle| g_{\mathrm{n}} \right\rangle$$

In the case of the element ω, the contributions to the gradient with respect to coordinates R_{I}, R_{N}, R_{M}, and R_{J} are respectively:

$$\left\langle \frac{\partial \chi_{\mathrm{i}}}{\partial R_{\mathrm{I}}} \middle| W_{\mathrm{EGP}}^{\mathrm{nm}} \middle| \chi_{\mathrm{j}} \right\rangle,\ -\left\langle \frac{\partial \chi_{\mathrm{i}}}{\partial R_{\mathrm{I}}} \middle| W_{\mathrm{EGP}}^{\mathrm{nm}} \middle| \chi_{\mathrm{j}} \right\rangle,\ -\left\langle \chi_{\mathrm{i}} \middle| W_{\mathrm{EGP}}^{\mathrm{nm}} \middle| \frac{\partial \chi_{\mathrm{j}}}{\partial R_{\mathrm{J}}} \right\rangle, \text{ and } \left\langle \chi_{\mathrm{i}} \middle| W_{\mathrm{EGP}}^{\mathrm{nm}} \middle| \frac{\partial \chi_{\mathrm{j}}}{\partial R_{\mathrm{j}}} \right\rangle$$

The generalization to the nth analytical derivatives can be done in an analogous way. However, we have not yet implemented the calculation of the second derivatives. This work is in progress. Nevertheless, force constants and harmonic vibrational frequencies can be determined by single numerical differentiation since the analytical first derivatives are available.

TABLE 3: Geometrical Parameters for the D_{3d} Si$_2$H$_6$ and the C_{3v}SiH$_3$ Si$^{\#}$ Structures (Distances in Angstroms and Angles in Degrees)[a]

		SiH$_3$Si$^{\#}$		
	Si$_2$H$_6$	EGP$_1$	EGP$_2$	SiH$_3$...H
Si−Si[b]	2.348	2.348*	2.348*	2.348*
Si−H	1.476 (3.16)	1.481 (3.07)	1.442 (4.06)	1.462 (3.36)
HSiSi	110.1 (0.75)	112.5 (0.83)	108.4 (2.07)	105.4 (0.61)

[a] Force constants are indicated in parentheses (stretching mode in mdyn·Å^{-1} and bending mode in mdyn·Å·rad^{-2}). [b] Si...H distance in the case of SiH$_3$...H. The asterisk * means that the geometrical parameter is frozen throughout optimization.

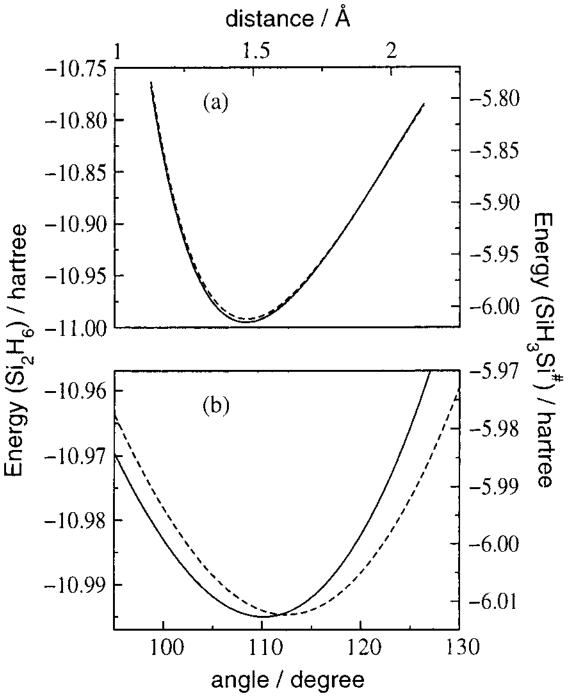


Figure 1. Comparison of the energy (in hartree) of Si$_2$H$_6$ (full lines) and SiH$_3$Si$^{\#}$, EGP$_1$ (dashed lines) according to geometrical deformations: (a) variation of the energy as a function of the SiH distance (angstroms); (b) variation of the energy as a function of the HSiSi angle (degrees). In both cases, C_{3v} symmetry is maintained.

5.2. Test of the Si$^{\#}$ EGPs. Since EGPs reproduce reasonably well the effective MOs, an open question is: is the optimized geometry of the SiH$_3$ molecular group adequately reproduced by the presence of the Si$^{\#}$ EGP? To answer this question, a local optimization was performed, with the Si−Si$^{\#}$ bond length constrained. It yields a geometry very close to the optimal one of Si$_2$H$_6$ (Table 3). The Si−H bond length is 0.005 Å longer with the pseudopotential Si$^{\#}$ EGP$_1$, while the HSiSi angle is 2.4° higher. This result is very promising, and we expect the PES to be comparable in both theoretical treatments. It might be demanding, but a reasonable estimation of the force constants would be interesting. For this purpose, the variation of the energy as a function of various geometrical deformations was computed. Two deformations were considered, in the framework of the C_{3v} symmetry group: the stretching of the Si−H bonds, and the variation of the HSiSi angles. Only one SiH$_3$ molecular fragment was deformed in the case of Si$_2$H$_6$. These data are plotted in Figure 1. It can be seen that the curves are almost superposable in both cases. As could be assumed from the geometry optimization results, the energy curves indicating the angular dependency are slightly out of phase. However, their curvatures are identical. The visual concordance is confirmed by the computation of the force constants, reported in Table 3. Plotting the curves shows the good behavior of the operator beyond the equilibrium position of the active part (see Figure 1).

This one-center Si$^{\#}$ EGP$_1$ has some interesting properties: quite a good reproduction of the molecular orbitals and their energies, an ability to reproduce the potential energy surface without a significant loss in precision. As concerns the second operator (Si$^{\#}$ EGP$_2$), the optimized geometrical parameters are in fair agreement with those of Si_2H_6: the Si−H bond length and the HSiSi angle are 0.034 Å and 1.7° smaller, respectively. The Si$^{\#}$ EGP$_2$ seems to have better properties than the Si$^{\#}$ EGP$_1$, even if the geometry is slightly less precise. Nevertheless, the stretching and bending force constants are not comparable (see Table 3). The error on the bending force constant is 150%. The transferability to other molecules will be a crucial test in order to discriminate among the two EGP's, even if the latter result casts suspicion on the Si$^{\#}$ EGP$_2$. These results have been compared with a SiH_4 model in which one Si−H distance is lengthened to the Si−Si bond length. Indeed, as is done in finite cluster calculations, the saturation of the SiH_3 fragment with an H atom is a solution for avoiding the problem of dangling bonds on surfaces. As can be seen in Tables 1 and 3, the stretched Si−H bond becomes polar, and the agreement of the monoelectronic energy spectrum and of the optimized geometry of SiH_3 with respect to the Si_2H_6 result is not satisfactory. We conclude that this treatment introduces artifacts and that our method is more convenient.

6. Conclusion

In this first paper, we have presented a general methodology to derive effective group potentials in order to simplifiy ab initio calculations, by reducing both the number of active electrons and the size of the basis set. Our approach is general and could be used whatever the connection between active and spectator parts of the molecule would be. The way to derive EGP parameters is very close to the determination of effective core potentials (ECP) in their shape consistent version. The most important step is the definition of modified valence pseudo-orbitals (MVPO), which play the same role as valence pseudo-orbitals in the derivation of ECP. In this step, the choice of a small atomic basis set centered on the spectator group is very determinant for the success of the method. The final form of EGP (expressed as a linear combination of nonlocal projection operators) is simple enough to be easily introduced in any conventional ab initio program, eventually including calculations of gradients and higher order derivatives. The derivation of an EGP for the silyl group has been used as a test example. We have shown that the Si$^{\#}$ EGP$_1$ fairly reproduces electronic populations, molecular orbitals, geometrical parameters, and force constants of the defined active part of disilane. It could be used for describing silicon clusters boundaries in order to avoid the artifacts usually introduced by hydrogenating them. Molecular applications, for silyl and other groups, will be detailed in paper 2, in which the transferabilty and robustness of the EGP method will be tested.

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