

## Regular article

# A new method for modelling spectator chemical groups in ab initio calculations: effective group potentials

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**Abstract.** A new method for an increased numerical efficiency of ab initio calculations is proposed. It is based on the assumption that in most cases chemical properties of functional groups in molecules are mainly controlled by a few electrons. This statement allows one to distinguish between two classes of nuclei and electrons: active and inactive ones. The effective group potential (EGP) method presupposes that the effect of inactive electrons in a functional chemical group can be described by a pseudopotential, in the same way that core electrons are replaced by effective core potentials in atoms. It is shown that EGPs are able to predict chemical and structural features of the active part of a molecule and at a fraction of the ordinary computational cost. The preliminary results reported here concern the determination of EGPs for ammonia, the methyl radical and the cyclopentadienyl ligand, which represent different types of bonding.

**Key words:** Ab initio – Effective group potentials

## 1 Introduction

The present method is based upon the spatial separability of functional groups in molecules. Although this is a weaker criterion of separability than the separation of core and valence electrons in atoms, it is assumed that this property is justified, since the chemical groups under consideration behave as spectator groups. For example, the donor property of ammonia can be mainly described solely by its lone pair, while the bonding properties of the methyl radical depend on its unpaired electron in an orbital oriented along the direction of coordination. We consider these functional groups like theoretical synthons (in close analogy with the term used in experimental synthesis chemistry) and it can be postulated that they could be described by a fictitious system bearing an

effective group potential (EGP). Keeping the  $\text{NH}_3$  case in mind, the four nuclei and eight valence electrons of this chemical group are reduced to a fictitious system, noted  $\text{N}^f$ , build with a pseudo nitrogen atom (nuclear charge  $Z^f = 2$ ) bearing two valence active electrons in a hybrid *sp* atomic orbital (AO) which mimics the lone pair. Of course, this yields a poor description of the bonding of  $\text{N}^f$  with a Lewis acid. Thus, one understands the necessity to add an effective potential in order to restore the effect of the whole  $\text{NH}_3$  group. In the following, a pseudo atom bearing a group pseudopotential is labelled  $\text{N}^\#$  (Fig. 1).

The derivation of the EGP for  $\text{NH}_3$  as a Lewis base will illustrate the principal features of our technique. The results obtained with the  $\text{NH}_3$ ,  $\text{CH}_3$  and  $\text{C}_5\text{H}_5$  chemical groups will illustrate the potential and usefulness of our method.

## 2 Computational details

Ab initio calculations were carried out with the Gaussian 98 series of programs [1], in which the calculation of the integrals and the first and second derivatives of the EGP were implemented. The valence basis set used was of double-zeta-polarised quality for phosphorus, nitrogen, aluminium, tellurium and hydrogens linked to a metal atom, double zeta for carbon and hydrogen of  $\text{C}_5\text{H}_5$  and  $\text{NH}_3$  and triple-zeta-polarised quality for tantalum and iridium. Durand and Barthelat [2] effective core potentials were used systematically, except for the iridium atom [3]. All the calculations were performed at the Hartree–Fock (HF) level. During geometry optimisation, the chemical group replaced by an EGP was held fixed at the value of the reference calculation. All the geometrical parameters kept frozen during the optimisation process are indicated by a star in the tables.

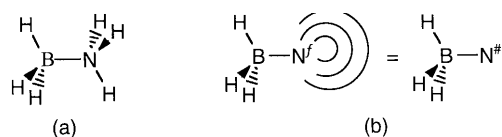
## 3 Methodological aspects

### 3.1 An example of a Lewis base in donor–acceptor bond type: $\text{NH}_3$

The  $\text{BH}_3\text{NH}_3$  molecule illustrates the need for including a potential in the Hamiltonian so far as the  $\text{NH}_3$  functional group is replaced by a reduced system. The first column of Fig. 2 shows the energy and the shape of the seven occupied valence molecular orbitals (MO) of

$\text{BH}_3\text{NH}_3$  and the charge transfer between the Lewis acid and base. In that case, the fragment considered inactive, i.e. the  $\text{NH}_3$  fragment, is reduced to a fictitious system  $\text{N}^f$  which brings two electrons into the  $s$  and  $p$  AOs. Note that the effect of the nitrogen core electrons is not suppressed, since the N atomic pseudopotential is taken into account. The second column of Fig. 2 shows the molecular spectrum and the charge transfer obtained from a calculation on the fictitious system  $\text{BH}_3\text{N}^f$ . Obviously the comparison is very bad.  $\text{N}^f$  alone is unable to reproduce the molecular spectrum of the rest of the molecule, i.e., the three B—H bonds and the B— $\text{N}^f$  bond. The atomic charge transfer is also unrealistic.

The bad behaviour of the  $\text{N}^f$  reduced system must be corrected, and this should be the role of the EGP. Formally, if one defines  $F_1$  and  $F_2$  as the Fock operators of



**Fig. 1.** **a** Lewis acid-base complex (14 valence electrons). **b** Fictitious molecule with a pseudo  $\text{N}^f$  atom of nitrogen bearing a group potential (eight valence electrons)

	$\text{BH}_3\text{NH}_3$	$\text{BH}_3\text{N}^f$	$\text{BH}_3\text{N}^\#$
	energy	energy	energy
$\pi_{\text{BH}_3}$	-0.41191	-0.43884	-0.42990
$\pi_{\text{NH}_3}$	-0.41191	-0.43884	-0.42990
$\sigma_{\text{B}_N}, \sigma_{\text{BH}_3}$	-0.50503	-0.38505	-0.53579
$\sigma_{\text{B}_N}, \sigma_{\text{NH}_3}$	-0.70336	-0.69450	-0.69816
$\pi_{\text{NH}_3}$	-0.72548		
$\pi_{\text{BH}_3}$	-0.72548		
$\sigma_{\text{N}^f}$	-1.24772		
CT	0.30	1.01	0.25

**Fig. 2.** Molecular orbital shapes and energies and charge transfer (CT) for  $\text{BH}_3\text{NH}_3$ ,  $\text{BH}_3\text{N}^f$  and  $\text{BH}_3\text{N}^\#$  (see text for details)

the reference and reduced systems, respectively, the operator which should be added to  $F_2$  is the exact EGP operator:  $F_{\text{EGP}} = F_1 - F_2$ ; however, this  $F_{\text{EGP}}$  operator is molecule-dependent, has a complex expression and is obviously not transferable to other systems. It is thus necessary to find a quantity which represents the difference between the reference system and the fictitious system and to extract a pseudopotential due to that quantity. From a practical point of view, the Fock operators  $F_1$  and  $F_2$  are expressed in a basis of pseudo MOs. In the case of  $\text{BH}_3\text{NH}_3$ , the four pseudo MOs ( $|\phi\rangle$ ) correspond to the highest four occupied HF MOs ( $|\phi\rangle$ ), developed in a reduced basis set defined with the atomic functions of  $\text{BH}_3$  and specific functions on the  $\text{N}^f$  fragment. As a matter of fact, the exponents of the  $s$  and  $p$  functions of the  $\text{N}^f$  atom are optimised in order to maximise the overlap between  $|\phi\rangle$  and  $|\phi\rangle$ . In the pseudo MO basis set the previous expression for  $F_{\text{EGP}}$  becomes  $F_{\text{EGP}} = F_1 - F_2$ , but  $F_{\text{EGP}}$  is not straightforwardly transferable. In order to ensure the transferability of the EGP operator, we define a one-electron nonlocal operator [4]:

$$W_{\text{EGP}} = \sum_n \sum_m \alpha_{nm} |g_n\rangle \langle g_m|$$

where the  $|g_n\rangle$  form a basis set of Gaussian functions with a priori defined even-tempered exponents.

The  $\alpha_{nm}$  coefficients are determined with a least-square-fit procedure [5] in order to minimise the difference between  $F_{\text{EGP}}$  and the matrix representation of  $W_{\text{EGP}}$ :

$$\|F_{\text{EGP}} - W_{\text{EGP}}\|^2 \text{ min}$$

The adapted basis set on  $\text{N}^f$  and the exponents of the  $|g_m\rangle$  functions are given in the Appendix.

The third column of Fig. 2 shows the results obtained for  $\text{BH}_3\text{N}^\#$ . Clearly, the EGP is able to fill the difference between the fictitious system and the reference one. The valence MO spectrum and the charge transfer of the active part are well reproduced. A step further is to check the influence of the  $\text{N}^\#$  EGP on the geometrical parameters describing the active  $\text{BH}_3$  part (distances, angles and force constants). The results in Table 1 show that the performance of the  $\text{N}^\#$  EGP is very good in this area.

Although the  $W_{\text{EGP}}$  operator is formally transferable to various molecular systems, the crucial point is its chemical transferability. Clearly, the EGP strategy should be stopped at this point. This implies deriving a new EGP for each chemical surrounding and reduces considerably the usefulness of our approach. We tried to

**Table 1.** Geometrical parameters for  $\text{BH}_3\text{NH}_3$  and  $\text{BH}_3\text{N}^\#$  structures (distances in angstroms and angles in degrees, the stretching and bending force constants, noted  $k_{\text{BH}}$  and  $k_{\text{NBH}}$ , respectively, are expressed in  $\text{mdyn } \text{\AA}^{-1}$  and in  $\text{mdyn } \text{\AA} \text{ rd}^{-2}$ )

	$R_{\text{BN}}$	$R_{\text{BH}}$	$\theta_{\text{NBH}}$	$k_{\text{BH}}$	$k_{\text{NBH}}$
$\text{BH}_3\text{NH}_3$	1.700	1.219	104.0	3.63	0.92
$\text{BH}_3\text{N}^\#$	1.700*	1.222	103.5	3.58	0.87

test the chemical transferability of the  $N^\#$  EGP, i.e. testing geometrical parameters and force constants for  $XH_3NH_3$  adducts, with  $X = Al$  and  $Tl$ . In this case, the  $NH_3$  fragment is bound to an atom belonging to the same column of the periodic table of the elements. It can be stated that the geometry and force constants of  $XH_3N^\#$  compare very well with the  $XH_3NH_3$  reference values (Table 2). The  $N^\#$  EGP seems to be a transferable group potential able to reproduce the variation of geometrical parameters for various elements of group IIIA.

### 3.2 An example of an alkyl group: $CH_3$

The method was also checked on a basic functional group involved in a covalent bond. The same technique was used to determine an EGP for the methyl group, noted  $C^\#$ . The parameterisation of the operator was achieved on the ethane molecule. In this case the reduction of the system leads to a fictitious system,  $C^f$ , bringing one unpaired electron into a single  $p$  orbital. Tests of transferability were performed on  $CH_3SiH_3$  and *trans*-butene.

The Mulliken population analysis and the HF energy of the MO for  $C_2H_6$  and  $CH_3C^\#$  are reported in Table 3. In this case the comparison is less obvious due to the fact that the replacement of one  $CH_3$  fragment by an EGP will remove the possibility of bonding and antibonding and thus there is no one-to-one correspondence between orbitals. While in the reduced system one should still identify the  $\sigma_{C-C}$  MO, the energies of the  $\pi_{CH_3}$  and  $\sigma_{CH_3}$  should be averaged values of the  $\pi_{CH_3}$  and  $\sigma_{CH_3}$  reference MO energies, respectively. It can be seen that the

**Table 2.** Geometrical parameters for the  $XH_3NH_3$  and  $XH_3N^\#$  structures ( $X = Al, Tl$ ) and force constants (units: same convention as Table 1)

	$X$	$R_{XN}$	$R_{XH}$	$\theta_{NXH}$	$k_{XH}$	$k_{NXH}$
$XH_3NH_3$	Al	2.090	1.606	99.4	2.15	0.61
	Tl	2.622	1.735	95.0	1.87	0.46
$XH_3N^\#$	Al	2.090*	1.606	98.5	2.17	0.60
	Tl	2.622*	1.734	94.1	1.89	0.44

**Table 3.** Mulliken population analysis and Hartree-Fock energy (hartree) of the molecular orbitals for  $C_2H_6$  and for  $CH_3C^\#$

$C_2H_6$	$CH_3C^\#$
C: 4.28	C: 4.20
H: 0.91	H: 0.92
$CH_3$ : 7.00	$C^\#$ : 1.04
$\pi_{CH_3}$	$\pi_{CH_3}$
$\sigma_{C-C}$	$\sigma_{C-C^\#}$
$\pi_{CH_3}$	$\pi_{CH_3}$
$\sigma_{CH_3}$	$\sigma_{CH_3}$
$\sigma_{CH_3}$	

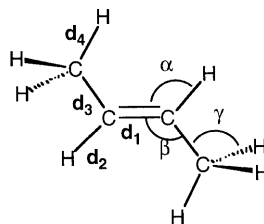
agreement is fairly good. Geometrical parameters (bond lengths and angle values) for  $C_2H_6$ ,  $CH_3C^\#$ ,  $SiH_3CH_3$  and  $SiH_3C^\#$  are given in Table 4. As in the  $NH_3$  case, the geometrical parameters of the part of the molecule considered as active are influenced in the same way with the EGP as the real  $CH_3$  fragment. Furthermore, transferability to another atom of the same column is very satisfactory.

Let us concentrate now on the case of the *trans*-butene molecule. A schematic representation is given Fig. 3. The  $C^\#$  was also tested in the case of this alkylated unsaturated hydrocarbon, which represents a more severe test of transferability. Preliminary results are presented in Table 5 and are compared with reference calculations. Geometrical optimisations were performed using one and two  $C^\#$  instead of a  $CH_3$  group.

It can be seen in the second column of Table 5, where only one  $CH_3$  fragment has been replaced and where a large number of parameters are available for comparison, that the results are excellent. Even in the case where two fragments are removed good overall agreement is observed. The mean relative errors on the bond lengths are 0.18 and 0.45% with one and two  $C^\#$  EGP, respectively. The  $C^\#$  EGP which was determined from ethane is thus sufficiently flexible to be used in different contexts. This can give confidence in the transferability of that EGP.

**Table 4.** Geometrical parameters for the  $XH_3CH_3$  and  $XH_3C^\#$  structures ( $X = C, Si$ ) (units: same convention as Table 1)

	$X$	$R_{XH}$	$\theta_{HXC}$
$XH_3CH_3$	C	1.093	111.3
	Si	1.477	110.7
$XH_3C^\#$	C	1.101	112.6
	Si	1.487	112.4



**Fig. 3.** Geometrical description of the  $C_4H_8$  molecule

**Table 5.** Geometrical parameters of the *trans*-butene molecule (units: same convention as Table 1)

	$C_4H_8$	$C^\#CH = CHCH_3$	$C^\#CH = CHC^\#$
$d_1$	1.332	1.339	1.348
$d_2$	1.088	1.088	1.089
$d_3$	1.519	1.518	1.519*
$d_4$	1.092	1.092	—
$\alpha$	126.10	125.4	125.4
$\beta$	117.9	116.8	115.8
$\gamma$	111.3	111.2	—

### 3.3 An example of a metal ligand: $C_5H_5$

$\pi$ -Cyclopentadienyl (Cp) complexes offer great structural and spectroscopic diversity, due, in particular, to the fluxional behaviour of the Cp–metal interaction [6]. This molecular frame is of great importance in coordination chemistry. For example, it is involved in transition-metal trihydrides having unusual NMR properties due to quantum mechanical hydrogen exchange [7]. However, the large number of electrons and nuclei involved in the ligand does not allow routine theoretical calculations on such complexes [8]. An application of the EGP technique to this case is thus attractive. The Cp EGP ( $Cp^\#$ ) was extracted from a  $CpTaH_4$  complex as a reference molecule. The fictitious system is made of five pseudo carbon atoms, each bearing one electron in a  $p$  orbital. This reduction keeps the  $\pi$  system and preserves the main bonding features of the real Cp ligand in  $\pi$ -Cp complexes. The potential is a multicentre one, i.e. it is expanded on the five pseudo carbon atoms. The optimum geometrical parameters obtained with the  $Cp^\#$  operator are compared with the reference calculation in Table 6.

Good agreement is clearly observed. Ta–H distances and angle values were determined with acceptable precision. Note that transferability to the  $CpNbH_4$  complex is under investigation at various levels of calculations. The preliminary results are very encouraging. We show here the ability of the  $Cp^\#$  potential to behave properly in the  $[(C_5H_5)Ir(PH_3)H_3]^+$  transition-metal complex (see schematic description in Fig. 5). This case, while providing fair results, opens some questions about the reduction of the  $\pi$ -Cp complex to a  $\pi$ -system only.

The iridium atom is not isoelectronic with tantalum and this complex has appreciably different geometry than the  $CpTaH_4$  complex. It is thus a stringent test of transferability, although the hapticity is the same ( $\eta^5$ ). Geometry optimisations using  $Cp^\#$  were made on the

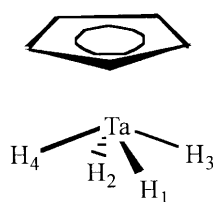


Fig. 4.  $CpTaH_4$  molecule

Table 6. Geometrical parameters for the  $CpTaH_4$  and  $Cp^\#TaH_4$  molecules.  $X$  designates the centre of mass of the cyclopentadienyl group (units: same convention as Table 1)

	$CpTaH_4$	$Cp^\#TaH_4$
$XTa$	2.130	2.130*
$TaH_1$	1.775	1.796
$TaH_2$	1.791	1.800
$TaH_{3-4}$	1.780	1.793
$H_1TaX$	112.3	113.7
$H_2TaX$	116.4	114.9
$H_{3-4}TaX$	114.4	114.3
$H_{3-4}TaH_1$	77.1	79.8
$H_{3-4}TaXH_1$	85.5	89.2

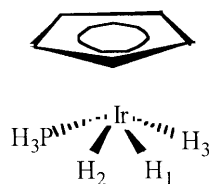


Fig. 5.  $[(C_5H_5)Ir(PH_3)H_3]^+$  molecule

$Cp^\#Ir(PH_3)H_3$  and  $CpIr(PH_3)H_3$  complexes. The comparison between the two geometries is reported in Table 7. Very good agreement is observed for bond lengths, while some angle parameters are somewhat less satisfactory. In fact, the  $Cp^\#$  potential tends to favour a pseudoeclosed conformation, with the H–Ir– $X$  ( $X$  designates the centre of mass of Cp) angle too small, whereas the conformation of the real complex is clearly a staggered one. It is well known that the barrier of rotation between the two conformations is usually small. We have been confronted with the fluxionality of the  $\pi$ -Cp complexes from the beginning of this study. For instance, the bending force constant of one of  $HTaH$  angle was found to be  $9 \cdot 10^{-5}$  mdyne  $\text{\AA} \text{ rad}^{-2}$ . This very small value shows that the potential-energy surface is very flat with respect to angular variation. Moreover, we checked in the  $CpTaH_4$  case that the modification of some parameters in the calculation, such as the atomic pseudopotential and/or the basis set on Ta, yields variations in the angles of the order of 4–5°. Thus, the slight discrepancy between  $Cp^\#Ir(PH_3)H_3$  and  $CpIr(PH_3)H_3$  should not be analysed as disappointing behaviour of the  $Cp^\#$  EGP; however, it seems from a careful analysis of the structural data that the shape of the  $\pi$ -Cp complexes is influenced by a subtle balance of steric effects [6]. Further investigations are in progress to test the necessity to add steric contributions to the present formulation.

## 4 Conclusion

We have presented here a new method to perform accurate but not-time-consuming calculations on large molecules. The crucial idea is that such molecules can be

Table 7. Geometrical parameters for  $[CpIr(PH_3)H_3]^+$  and  $[Cp^\#Ir(PH_3)H_3]^+$  minimum structures.  $X$  labels the centre of mass of the cyclopentadienyl group (units: same convention as Table 1)

	$[(C_5H_5)Ir(PH_3)H_3]^+$	$[(Cp^\#)Ir(PH_3)H_3]^+$
$IrH_1$	1.565	1.571
$IrH_2$	1.570	1.580
$IrH_3$	1.573	1.576
$IrP$	2.394	2.406
$H_1IrH_2$	61.1	67.1
$H_1IrH_3$	59.6	67.7
$H_1IrX$	128.6	119.8
$H_2IrX$	121.3	119.2
$H_3IrX$	121.8	116.3
$PIrX$	129.4	125.6
$H_2IrXH_1$	76.2	78.9
$H_2IrXH_3$	255.5	258.0
$H_2XIrP$	150.8	157.1

divided into active and inactive parts and that the whole inactive part can be replaced by a pseudopotential acting on the other part. This means the replacement of several nuclei and many electrons by a pseudopotential (EGP) and a few electrons; however, such a strategy will be useful if one can show that, once extracted on a reference molecule, this EGP is transferable to other types of active groups. Thus, we performed three different studies representing three types of chemical bonding: a donor–acceptor bond, a covalent bond and a metal–ligand bond. In all cases we showed that compared to a reference molecule, the replacement of one of its parts by an EGP could reproduce, at chemical precision, all geometrical properties and the form of the orbitals.

Furthermore, and this is the more encouraging point, this EGP was shown to be transferable. This means that once extracted on a molecule the EGPs can be used in others situations, often bonded to atoms of the same column but also as in the case of  $\text{CpIr}(\text{PH}_3)\text{H}_3$  to quite another type of bond.

A lot of work remains to be done in order to include missing effects, such as steric effects, or to see if excited states are also preserved by the EGP, but the usefulness of such an approach can be appreciated already. Large molecules which, because of computational limitations, are often modelled in quite a drastic way could be studied in a reasonable time with a minimum loss of precision.<sup>1</sup>

## Appendix

**Table A1.** Basis set for  $N^f$ ,  $C^f$  and  $\text{Cp}^f$ .  $n$  is the number of electrons on the fictitious system  $s(l=0)$ ,  $p(l=1)$ , parameters used for the determination of the nonlocal operator. The Gaussian functions are located on the corresponding pseudo atom. The  $\text{Cp}^\#$  is expanded on five pseudo carbons

Chemical group	Pseudo atom	$n$	$l$	Exponents	Coefficients	EGP	$l=0$	$l=1$
$\text{NH}_3$	$N^f$	2	0	1.1098781	1	$N^\#$	7.0	3.5
				0.2882241	1		3.5	1.75
				0.0500062	1		1.75	1.167
							1.167	0.778
							0.778	0.5185
		0.5185	0.2000					
$\text{CH}_3$	$C^f$	1	1	0.304718	1	$C^\#$	7.0	1.5
							3.5	0.75
							1.75	0.375
							1.167	0.250
							0.778	0.17
							0.5185	0.11
							0.3460	0.07
							0.23	
0.154								
0.1								
$\text{C}_5\text{H}_5$	$\text{Cp}^f$	5	1	0.368	1	$\text{Cp}^\#$		3.00
								1.5
								0.750
								0.350

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<sup>1</sup>For instance, one step of geometry optimisation lasts 330 s for  $\text{CpIr}(\text{PH}_3)\text{H}_3$  and 70 s for  $\text{Cp}^\#\text{Ir}(\text{PH}_3)\text{H}_3$