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# Effective potentials for spectator groups in molecular systems I. Potential curves and binding energies

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**Summary.** A method for representing inactive groups, i.e. spectator groups, in a molecular system by an effective potential is presented. The matrix elements for the spectator's short-range Hartree–Fock potential is stored in an intermediate AO basis, from which it can be transferred into the user basis for the active part of the molecular system. The longer-range of the potential is transferred via a (distributed) multipole expansion. The method is illustrated for the $NH_3 \cdot X$ ($X = NH_3$, $H_2O$, HF) complexes: binding energies could be reproduced to within 5% by employing the effective $NH_3$ potential (whereby the lone pair was included in the active system), the entire $NH_3 \cdot HF$ potential curve with a depth of 50 kJ/mol is reproduced within 2 kJ/mol if various intermediate basis sets are chosen. Technical details are discussed; the effective potential can directly be introduced in CI calculations.

**Key words:** Spectator groups – Effective potential – Molecular systems

## 1 Introduction

In many chemical reactions or other processes of importance in larger molecular systems a certain locally well-defined part of the system is not directly involved in the process under consideration and thus plays only the role of a "spectator group". Examples are methyl or larger groups in organic molecules, large portions of molecules involved in hydrogen-bonding or considerable parts of metal-ligand complexes. The spectator description indicates that this part of the molecule exhibits its influence on the process under consideration only by its electrostatic potential, but does not change its own character by polarization or relaxation. Hence such a definition suggests the idea to replace the spectator groups by an effective potential, thereby reducing the computational expenditure in the description of the system considerably. Effective potentials are in wide use for the representation of inner shells of electrons (for example see [1, 2, 3]); such potentials are spherically symmetrical around the nucleus and thus relatively easy to describe. Potentials of spectator groups generally do not have such properties but are anisotropic, a feature which complicates their description considerably. There have been various attempts so far in the literature for a simple description of spectator groups. For example the effective potentials derived by Huzinaga and coworkers [4–7] to simulate Hartree–Fock potentials have been successfully employed for the theoretical description of spherical ions in a crystal field. Ohta and coworkers [8] have approximated the Coulomb potential of the spectator by a fit in a basis of analytical functions, whereas the nonlocal exchange potential of the spectator is simulated by projection operators containing adjustable parameters. Those projection operators are also needed to prevent a reoccupation of the already doubly occupied orbitals of the spectator. Jortner et al. [9] have developed a pseudopotential for $H_2O$ consisting of local Coulomb, polarization, exclusion, and exchange contributions used to simulate the interaction of the water–molecule with an electron.

In the present work we present an alternative way for the representation of such spectator group potentials. Our goal is to represent the effective potentials in form of a matrix in an intermediate atomic orbital basis. This approach has the advantage that difficulties which arise in the fitting procedure for non-spherical potentials are circumvented (for this reason our approach is different from the effective potentials for spherical ions described in Refs. [4–6] which include an analytical fit of the Coulomb-potential). The nonlocal exchange potential together with the Coulomb-potential is represented by the matrix in the intermediate basis in our method whereas Ohta et al. have to treat the exchange potential separately because this potential is not representable as a fit in a basis of local functions. By the term intermediate AO basis we want to indicate, that the effective potential is stored in an intermediate basis, but that it has to be transferred before application in a certain molecule into the AO-basis of the total system under consideration, the "user basis". This final user basis requires in certain instances that some AO functions of the spectator be directly included, in particular if a certain portion of the spectator cannot be considered entirely inactive in the process (i.e. if some polarization is induced in the spectator by the process). This flexibility accounts for the reality, namely that spectator groups do not remain entirely inactive if processes occur in neighbouring parts of the system.

In order to transfer the effective potential from its storage in the intermediate basis into an arbitrary user basis, this intermediate basis must certainly be very flexible. Thus there is the practical question about the size of the intermediate basis, whereby its size should be easily manageable in actual calculations. We will therefore investigate in the present work, whether a single intermediate basis is adequate for the transfer of the entire anisotropic spectator potential or whether several intermediate basis sets are to be preferred for certain areas of space. There is the further question, whether the long-range part of the potential is transformed best in the intermediate basis or whether a multipole expansion is more effective for the description of the long-range portion of the potential. And finally, there is the question to which extent such effective spectator potentials can be employed in computations which account for electron correlation, i.e. in standard CI-type calculations. The present paper will present the results of such a study. In particular the study will show how the hydrogen-bonded complexes $NH_3 \cdot X$ ($X = HF, H_2O, NH_3$) can be described with an effective $NH_3$ potential, maintaining thereby the direct treatment of an active part, i.e. the lone pair of $NH_3$, in order to allow for a certain amount of polarization of the $NH_3$ molecule by the approaching Partner X. In particular we will compare the $NH_3 \cdot HF$ potential curve with an all-electron calculation.

The question, whether the spectator potential is not only adequate for the description of the complexes, but also for evaluating other properties, will be the subject of a following paper.

## 2 Theory

### 2.1 Construction of the effective potential for spectator groups

A typical example for the interaction of spectator groups with the other part of the molecule is indicated in Fig. (1). The spectator involves the $NH_3$ group with the exception of the nitrogen lone-pair, which together with the partner X, forms the so-called active part of the molecule. The lone-pair is included in the active region to allow for a certain degree of polarization of $NH_3$ due to the bonding of partner X. In addition to the electrons an equivalent number of nuclear charges is also attributed to the spectator. This number can be either the total nuclear charge of the spectator or its charge can be distributed between the spectator and the electrons. In the present example $NH_3 \cdot X$ there are five nuclear charges which belong to the genuine spectator and two charges which must be incorporated into the active part. In analogy to conventional atomic pseudo-potentials the five charges compensate the "inner electrons" and the two positive charges compensate the valence electrons, i.e. in this case the $NH_3$ lone-pairs.

The spectator is described by a closed-shell determinant:

$$\Psi_{sp} = |\varphi_1(1)\alpha\varphi_1(2)\beta\varphi_2(3)\alpha\varphi_2(4)\beta \cdots \varphi_{N_{sp}}(N-1)\alpha\varphi_{N_{sp}}(N)\beta| \tag{1}$$

$N$: number of electrons of the spectator

$N_{sp}$: number of orbitals of the spectator

This closed-shell Ansatz for its wavefunction is consistent with the conception of an inactive spectator in a reaction process, which in most cases will possess only doubly filled electron shells. The orbitals $\varphi_i$ in this determinant are considered to be localized orbitals (LMO) in all our considerations. They can be viewed as core orbitals, bonding electron pairs or lone pairs, just as they are conceived in qualitative chemical terms. Computationally the LMO are obtained by a unitary transformation of the canonical Hartree–Fock MO's, where the coefficients of the transformation matrix are determined such that the LMO's are preferentially localized in a small region of space. In the present work the LMO are generated by the simple Boys localization procedure [10] applied to the SCF solution for the isolated spectator group; in some instances it might also be adequate to obtain the LMO by a transformation of the solution of the entire molecule.

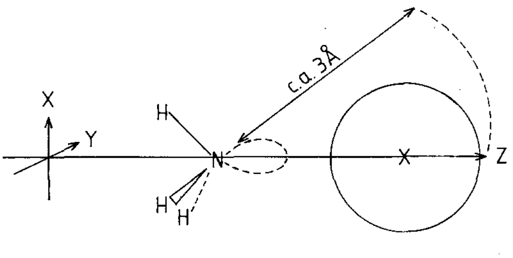

**Fig. 1.** Illustration of the method with the complexes $NH_3 \cdot X$ as an example. The active part of the system consists of the lone pair (drawn in dashed lines) and of the binding partner X. By the circle those AO's of the intermediate basis set are symbolized which facilitate the transfer of the $NH_3$ potential to partner X. Outside of an area with a radius of about 3.0 Å the potential is transferred by a multipole expansion

The Hamiltonian for the total system including the effective potential and the active part of the molecule can be written as:

$$\hat{H}'_{ep} = \sum_{i=1}^{n} t_i + \sum_{i=1}^{n} g_i^{ac} + \sum_{i<j}^{n} \frac{1}{r_{ij}} + V_{NN}^{ac}$$
$$+ \sum_{i=1}^{n} \left[ g_i^{sp} + \sum_{\alpha=1}^{N_{sp}} (2\hat{J}_\alpha^i - \hat{K}_\alpha^i) + \sum_{\alpha=1}^{N_{sp}} \varepsilon_\alpha |\varphi_\alpha(i)\rangle \langle \varphi_\alpha(i)| \right]$$

Details of the derivation [11] as well as examples for the use in effective core potentials can be found in the literature [2, 3, 12]. The first three terms refer to the $n$-electrons of the active part of the molecule representing the kinetic energy operator $t$, the potential of the nuclei in the active part and the operator for the electron–electron interaction. The fourth term is the repulsion of the nuclear charges of the molecular-active region. The contribution of the effective potential of the spectator contains two terms:

$$g_i^{sp} + \sum_{\alpha=1}^{N_{sp}} (2\hat{J}_\alpha^i - \hat{K}_\alpha^i) =: V_{sp}$$

$$\sum_{\alpha=1}^{N_{sp}} \varepsilon_\alpha |\varphi_\alpha(i)\rangle \langle \varphi_\alpha(i)| =: LS_{sp}$$

in the standard notation for the coulomb $\hat{J}_\alpha$ and exchange $\hat{K}_\alpha$ operators of the spectator.

$$\hat{J}_\alpha^1 f(1) = \int dv_2 \, \varphi_\alpha(2) \varphi_\alpha(2) \frac{1}{r_{12}} f(1)$$

$$\hat{K}_\alpha^1 f(1) = \int dv_2 \, \varphi_\alpha(2) \varphi_\alpha(1) \frac{1}{r_{12}} f(2)$$

$$\varphi_\alpha \text{ MO of spectator}$$

The term $V_{sp}$ is the Hartree–Fock potential of the spectator corresponding to the closed-shell determinant of Eq. (1). The second term $LS_{sp}$ is the level-shift operator, i.e. a sum of projection operators on the orbitals $\varphi_\alpha$ multiplied by a level-shift parameter $\varepsilon_\alpha$ to be choosen freely. The operator $LS_{sp}$ has the function of keeping the wavefunction of the active part $\psi_{ac}$ orthogonal to the spectator orbitals $\varphi_\alpha$ as exactly as possible, since the orbitals $\varphi_\alpha$ are already doubly occupied in the $\psi_{sp}$ wavefunction.

In the ideal case of canonical closed-shell spectator orbitals the level-shift operator just shifts the spectator orbitals $\varphi_\alpha$ to higher energies by an amount $\varepsilon_\alpha$ without changing the closed-shell orbitals of the active part at all. The open-shell orbitals of the active part are not independent of the $\varepsilon_\alpha$ parameters even in this ideal case since the open-shell Fock operator and the closed shell Fock operator of the RHF (restricted Hartree–Fock) method differ. The optimal $\varepsilon_\alpha$ parameters for the determination of the open-shell orbitals of the active part are the orbital energies multiplied by minus two, as was pointed out by Höjer and Chung [13]. In this article they clarified the function of the level-shift operator as a part of the effective potential in case of inner-shell electrons. In our method the spectator orbitals generally are localized orbitals rather than canonical orbitals; for this reason all the orbitals of the active part depend on the $\varepsilon_\alpha$ values, and only the closed-shell orbitals of the active part reach exact orthogonality to the spectator in the limiting case of $\varepsilon_\alpha \rightarrow \infty$.

The level-shift operator $LS_{sp}$ is only an exact projection operator if the AO basis employed for the calculation of the entire system making use of the description of the spectator in form of an effective potential is able to fully represent all $\varphi_0$. This is generally not the case (i.e. the AO's on the spectator which contribute to the $\varphi_\alpha$ are generally not present anymore in the user basis) and thus the results are not entirely independent of the level-shift parameters; adequate values for the $\varepsilon_\alpha$ have therefore to be determined empirically by test calculations. It has generally been found in the construction of effective potentials that there is a large range of $\varepsilon_\alpha$ values in which the results depend very little on the size of these parameters. If the $\varepsilon_\alpha$ become too small the energy of the total molecule (active part plus spectator, see Sect. 2.2) collapses to a value below the eigenvalue of the non-relativistic Hamiltonian because the Pauli principle is violated and the wavefunction $\psi_{ac}$ loses its orthogonality to the orbitals of the spectator. This problem has been discussed from various aspects in the literature [11].

Since the terms $V_{sp}$ and $LS_{sp}$ modelling the spectator's effective potential are one-electron terms (Eq. (2)), their implementation in existing molecular code is straightforward: the matrix of the effective potential can simply be added to the $T$ and $V$ integrals computed for the active part of the molecule, provided the effective potential is evaluated in the AO basis employed for this calculation (user basis). The computational advantage of a scheme in which spectator groups are treated as effective potentials is obvious: a reduction in the size of the AO basis set and in the number of electrons that have to be treated explicitly in the SCF calculation and furthermore, an appreciable reduction in the size of the ensuing configuration interaction (CI) procedure.

The problem is the actual representation of the effective potential $V_{sp}$ and $LS_{sp}$ of Eq. (2), which has to be stored in a form independent of its later application. For this reason it is represented in this work in a matrix based on a so-called *intermediate* AO basis (IB) $|i\rangle$, $|j\rangle$ according to Eq. (2);

$$O^I_{i,j} = \left\langle i \left| g^{sp} + \sum_{\alpha=1}^{N_{sp}} (2\hat{J}_\alpha - \hat{K}_\alpha) + \sum_{\alpha=1}^{N_{sp}} \varepsilon_\alpha \right| \varphi_\alpha \right\rangle \langle \varphi_\alpha | j \rangle \tag{2}$$

from this AO basis it can then be transferred into the so-called *user basis* (UB), used for the calculation of the entire system to be treated.

The intermediate AO basis consists of the entire AO basis of the isolated spectator plus a large number of additional basis functions in the area in which the bonding partner X is to be expected. In order to generate the electronic Hartree–Fock potential in the IB, the computation of the density matrix of the spectator and the computation of all integrals involving the two electron operator $1/r_{12}$ over all AO's of the IB is necessary. In order to generate the level shift operators and the nuclear potential terms only one-electron integrals in the IB have to be evaluated.

The transfer of the effective potential represented in the IB (Eq. (2)) into the UB $|l\rangle$, $|m\rangle$ is achieved according to Eq. (3):

$$O^A_{l,m} = \left\langle l \sum_{i=1}^{N_{IB}} \middle| i \right\rangle \left\langle i \left| g^{sp} + \sum_{\alpha=1}^{N_{sp}} (2\hat{J}_\alpha - \hat{K}_\alpha) + \sum_{\alpha=1}^{N_{sp}} \varepsilon_\alpha \right| \varphi_\alpha \right\rangle \left\langle \varphi_\alpha \sum_{j=1}^{N_{IB}} \middle| j \right\rangle \langle j | m \rangle \tag{3}$$

or in matrix representation:

$$\mathbf{O}^A = \mathbf{T}(\mathbf{S}^I)^{-1}\mathbf{O}^I(\mathbf{S}^I)^{-1}\mathbf{T}^\dagger \tag{4}$$

$\mathbf{O}^A$: effective potential in the user basis

$(\mathbf{S}^I)^{-1}$: inverse overlap matrix in the intermediate basis

$\mathbf{T}$: overlap matrix between the user basis and the intermediate basis

$\mathbf{O}^I$: effective potential in the intermediate basis

where the intermediate basis has the function of an inserted incomplete unit operator. The occurrence of the inverse overlap matrix $(\mathbf{S}^I)^{-1}$ results from the non-orthogonality of the cartesian Gaussian functions which make up the intermediate as well as the user basis.

If the spectator group has a different spatial orientation in the final molecule that in the situation from which the effective potential has been extracted, the cartesian components of the potential matrix in the IB within the same shell (i.e. $p_x$, $p_y$, $p_z$) are reflected in the $xy$ plane if necessary, and then rotated before the transfer into the UB is made. In this manner any spatial orientation of the spectator relative to the active part of the system can be accounted for, i.e. a final coordinate system $x$, $y$, $z$ can be defined.

The quality of the IB requires some further comments. The transfer of the effective potential into the UB according to Eq. (3) can be looked upon as computing a weighted average of the matrix elements $\langle i|\hat{O}|j\rangle$ in which the weighting factors are the expansion coefficients $\langle a|i\rangle$ or $\langle a|j\rangle$. In order to obtain reliable values for the matrix elements, all AO's of the UB should be expandable in linear combinations of the IB with the coefficients $\langle a|i\rangle$. In order to guarantee this, the IB should be adequate for the representation of the orbitals of the UB in all areas in which the partner X is expected to occur, indicated by a circle in Fig. (1). If the number of AO's in the IB is way above 100, numerical stability problems may occur in the inversion of the overlap matrix (Eq. (4)) because of the non-orthogonality of the AO's. A possibility to avoid this dilemma would be the usage of various IB's defined with respect to different origins in space. A further possibility to limit the space in which the IB must transfer the potential is the use of a multipole-expansion for the transfer of the effective potential in the long-range region of the spectator, also indicated in Fig. 1.

In case that the relative positioning between spectator and active part of the molecule is changed in a study, as necessary in the computation of potential energy surfaces, the accuracy of the transfer process for the effective potential must be especially high. This aspect will be taken up in Sect. 2.2.

### *2.2 Transfer of the spectators effective potential to the active part of the molecule*

As already outlined in the last section, the effective potential stored in the IB has to be transferred into the UB before it can be added to the elements of the Fock matrix for the system under consideration. The transfer of the $LS_{sp}$ term of Eq. (2) does not cause any difficulties. For the exact transfer the IB has simply to include the AO's of the spectator in which the orbitals $\varphi_\alpha$ are expanded. In order to achieve exact transfer of the second term, $V_{sp}$ of Eq. (2), the exact unit operator, i.e. in practice an arbitrary large intermediate AO basis $|i\rangle\langle i|$ would have to be inserted in Eq. (3). The accuracy in the transfer of $V_{sp}$ from the IB to a matrix element $O_{l,m}^{A}$ in the UB decreases with the angular quantum numbers of $|l\rangle$, $|m\rangle$, i.e. the effective potential can be transferred best to $s$ functions and with greater difficulties or smaller accuracy to $f$ functions, for example (higher spherical harmonics have not been included in the present work). In essence, with an increasing number of nodal planes in the AO of the UB it becomes more difficult to expand this AO with sufficient accuracy in terms of the IB. Furthermore, it is also obvious that the transfer to diffuse orbitals is better than to compact AO's, for the same reasoning, and it is also easier to diagonal terms than to off-diagonal elements.

The accuracy with which an AO of the UB can be expanded as a linear combination of AO's of the IB can be seen from its norm:

$$N_l = \left( \left\langle l \sum_{i=1}^{N_{IB}} \middle| i \right\rangle \langle i | l \rangle \right)^{1/2} \tag{5}$$

If $|i\rangle$ approaches a complete basis the positive definite quantity $N_l$ tends toward unity.

Satisfactory accuracy in the transfer of the potential can be expected if the $N_l$ for the AO's of the UB are in the order of 0.98 or larger. This requires a very flexible IB; of course $N_l = 1$ can be obtained in the trivial case that the UB is a genuine subset of the IB, but such a choice does not allow the generality in the effective potential representation which is sought here.

Experience has shown that the accuracy attempted above cannot be obtained if only a single IB is chosen. The best procedure seems to be the usage of several IB's (at different origins) combined with a multipole expansion to transfer the long range part of the potential. For the latter the general method by Stone [14, 15] is chosen. It is a distributed multipole expansion, i.e. the charge density of the spectator is divided into various parts and each part is described by a separate expansion around a different origin. The highest moment included is the quadrupole moment; the origins are the nuclear centers and the middle of the bonds. The matrix element $\langle l|V_{sp}|m\rangle$ is then approximated by the multipole potential of the spectator.

The general procedure is shown as follows: for each individual matrix element $\langle l|V_{sp}|m\rangle$ the product of the norms:

$$NP_{l,m} = \left( \left\langle l \sum_{i=1}^{N_{IB}} \middle| i \right\rangle \langle i | l \rangle \left\langle m \sum_{j=1}^{N_{IB}} \middle| j \right\rangle \langle j | m \rangle \right)^{1/2} \tag{6}$$

is evaluated. This expression describes the products of the norms $N_l$ and $N_m$ (Eq. (6)) of the AO's $|l\rangle$ and $|m\rangle$ projected into the IB. The IB for which $NP_{l,m}$ is closest to 1.0 is then chosen for the transfer of $V_{sp}$. In case that none of the IB yields a norm product which is larger than a given threshold, the multipole expansion is chosen for the transfer of the potential. Outside of a certain radius (Fig. 1) the multipole expansion is selected automatically, since in the outer area the norm product is small because of the small numbers of AO's available from the IB in that area.

A further increase in the accuracy of the $V_{sp}$ transfer can be obtained if all matrix elements, to which $V_{sp}$ is transferred via the IB, are divided by their norm product. In this manner the physically non realistic decrease in the magnitude of the matrix element could be corrected, which occurs as a result of the reduction in the norm of the AO's of the UB to values below 1.0 affected by the insertion of the IB.

## 3 Use of the effective spectator potentials for the complexes $NH_3 \cdot X$

The procedures outlined above are tested for the spectator $NH_3$ bound to various partners $X = NH_3$, $H_2O$ and HF, *the polarity of which is widely different.* By the different choice of the partners the flexibility of the spectator potential and its representation can be studied. All computations are carried out at the SCF level; results of CI calculations employing spectator potentials will be treated in a subsequent paper.

### 3.1 Technical details of the calculation

Most computations are performed at the equlibrium structure of the components given in Fig. (2). The geometries are taken from Refs. [16–18] optimized in SCF calculations. They are slightly modified for the present purpose in order to have identical inner coordinates for the $NH_3$ and in order to have a linear arrangement of the nuclei N–H–X (X = N, O or F).

For $NH_3 \cdot H_2O$ and $NH_3 \cdot HF$ experimentally determined geometries are also known [19], [20]; apart from very minor changes in the inner coordinates they are the same as those in Fig. (2). The $NH_3 \cdot NH_3$ complex has been found to prefer the linear arrangement (Fig. 2) according to SCF calculations, but a cyclic asymmetric structure is found to be the lowest energy according to coupled-pair-functional CPF calculations [16]. Since the energy difference between the two structures is extremely small (ca. 1 kJ/mol), one cannot determine with certainty which of the two is the most stable. Recent measurements by double-resonance infrared spectroscopy [21] show that the $NH_3$ dimer oscillates with high frequency between different structures. Hence $NH_3 \cdot NH_3$ seems to be a very floppy molecule to which a definite structure cannot be assigned.

The AO basis sets employed for the calculations are the (8*s*, 5*p*) basis sets [22] [(9*s*, 5*p*) for *N* [23]] of Huzinaga in the (4*s*, 2*p*) contraction (Ref. [22] for O/F and

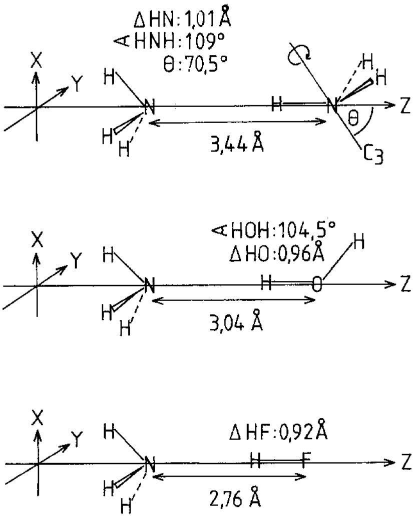

**Fig. 2.** Equilibrium geometries employed for the complexes $NH_3 \cdot X$

**Table 1.** Basis sets for $NH_3 \cdot X$

| | | |
|---|---|---|
| basis N: | Huzinaga | $(9s/5p) \rightarrow (4s/2p)$<br>contraction: 6111/41<br>$\alpha(d) = 0.864$ |
| basis O: | Huzinaga | $(8s/4p) \rightarrow (4s/2p)$<br>contraction: 5111/31<br>$\alpha(d) = 1.2$ |
| basis F: | Huzinaga | $(8s/4p) \rightarrow (4s/2p)$<br>contraction: 5111/31<br>$\alpha(d) = 1.4$ |
| basis H: | Huzinaga | $(4s) \rightarrow (2s)$<br>contraction: 31<br>scaled with $\eta^2 = 2.0$ |

Ref. [24] for N) with one *d*-function as indicated in Table 1. The hydrogen basis is a (4*s*) expansion contracted to 2*s*, scaled by $\eta^2 = 2.0$. Hence the basis can be described as being of double-zeta quality plus polarization functions on the heavier atoms (N, O, F).

### *3.2 Relaxation effects in the spectator $NH_3$*

The dissociation energies of the $NH_3 \cdot X$ systems are computed as the difference of the molecular energy at equilibrium and a supermolecule calculation at a distance of 100 bohr. Before the effective $NH_3$ spectator potential is generated, it is important to determine whether the entire system $NH_3$ or possibly only a portion thereof can be treated as a spectator. For this reason conventional SCF calculations are made as a reference point and the $NH_3$ system is treated in three variations of the so-called 'frozen-orbital' SCF calculations. In such calculations the coefficients of some localized molecular orbitals (LMO) of $NH_3$ are held fixed ("frozen") and are not subject to the SCF optimization procedure for the remaining orbitals in the molecule. The three variants are:

a) the LMO's of the donor $NH_3$ are those of the $NH_3 \cdot X$ equilibrium structure

b) the LMO's of the donor $NH_3$ are those of the dissociated $NH_3 \cdot X$ state, i.e. as in the isolated $NH_3$ fragment

c) as (b), but the LMO's for the lone pair are subject to optimization

The results of Table 2 show clearly, that variant (a) yields a dissociation energy which is much too high, variant (b) a result which is unrealistically low. Variant (c) gives a value for the dissociation energy which is close to that of the SCF calculations. As a result it is obvious that the lone pair in $NH_3$ cannot be treated as spectator but must be incorporated into the active part of the molecule. The relaxation in $NH_3$ occurs to more than 80% in its lone pair. Similar observations have been made by [8]. All other LMO, namely the three N–H bonds and the 1*s* core can be considered as spectators in the $NH_3 \cdot X$ process.

**Table 2.** Dissociation energies (in kJ/mol) of the $NH_3 \cdot X$ complexes obtained from various calculations

| $NH_3 \cdot HF$ | $NH_3 \cdot H_2O$ | $NH_3 \cdot NH_3$ | Type of calculation |
|---|---|---|---|
| 68.3 | 30.2 | 13.7 | all LMO's of $NH_3$, generated at the equilibrium of the compound, are held fixed ("frozen") |
| 36.2 | 20.2 | 9.5 | all LMO's of $NH_3$, generated for the $NH_3$ fragment, are held fixed ("frozen") |
| 48.1 | 24.9 | 11.0 | lone-pair LMO can relax, only NH-bonds and 1*s* are frozen (generated for the free $NH_3$) |
| 51.7 | 26.3 | 11.3 | standard SCF, all orbitals optimized |
| 53.1 | 27.6 | | Ref. [16] SCF-calc. |
| | | 15.0(3.0) | Ref. [25] experimental |

### 3.3 *Influence of the level shift*

The results of the previous section suggest that the three LMO's representing the N–H bonds and the 1*s* core of $NH_3$ can be considered as the spectator part; the corresponding nuclear charges are 5.0 at the nitrogen center and 1.0 at each of the hydrogen nuclei. The effective spectator potential is generated at the geometry of the isolated $NH_3$.

Two different UB are tested, which have to describe the active part of the $NH_3 \cdot X$ system, i.e. the fragment as well as the nitrogen lone pair. In the first, the full basis of the nitrogen atom was included in addition to the basis for the X fragment; in the second the two most compact *s* functions on nitrogen (generally representing the 1*s* electrons) are also deleted so that in essence 2*s*, 2*p* and a polarization *d* function are available in the UB for the nitrogen lone pair description. In the first the level shifts are different for the 1*s* orbital (a fixed value of 500.0 Hartree is chosen) and the LMO of the NH bonds (which are varied), in the second the level shifts are the same for N–H bonds and 1*s* core for a given calculation. Calculations are again carried out for the $NH_3 \cdot X$ system at equilibrium and for the dissociated conformation (100.0 a.u. separation). The IB in this case consists for the sake of simplicity of the $NH_3$ basis plus the X basis, always taken at the equilibrium nuclear geometry. This choice guarantees the exact transfer of the effective potential at the equilibrium geometry (the UB is a genuine subset of the IB); for the separated fragments the partner X lies far away from the area in which the IB acts, so that a transfer of the potential to the AO's of X is not possible, but the spectator potential on X is zero anyway at such distances, so that at this geometry there is also no error introduced in the transfer of the potential.

The calculated energies for the bound complexes and the separated fragments are displayed in Table 3 for various values of the level shift. It is seen that the computed value for the dissociation energy increases slightly in the first UB variant (calculation a) for all three compounds when $\varepsilon$ decreases from 500.0 to 5.0. For smaller values of the level shift we observe variational collapse. For $\varepsilon = 5.0$ the energies are almost the same as those obtained in an all-electron calculation in which the LMO expansion coefficients for all orbitals with the exception of the lone pair are kept fixed at their values of the isolated $NH_3$ (Table 2). Hence the optimal level-shift value seems to lie around $\varepsilon = 5.0$, and there is a wide range in which the results depend very little on $\varepsilon$. The level shift for the 1*s* orbital was chosen as

**Table 3.** Influence of the level shift parameter $\varepsilon$. Dissociation energies (in kJ/mol) obtained for the various $NH_3 \cdot X$ compounds by employing different level shifts $\varepsilon$ (in a.u.) in the effective $NH_3$ potential

| $NH_3 \cdot HF$ | $NH_3 \cdot H_2O$ | $NH_3 \cdot NH_3$ | $\varepsilon$[a.u.] |
|---|---|---|---|
| a) 45.2 | 23.9 | 10.5 | 500.0 |
| 45.4 | 24.2 | 10.5 | 50.0 |
| 48.1 | 25.5 | 11.0 | 5.0 |
| 23.9 | 12.1 | 4.5 | 2.0 |
| b) 54.3 | 28.4 | 12.6 | 500.0 |
| 54.9 | 28.6 | 12.9 | 50.0 |
| 57.2 | 30.2 | 13.4 | 5.0 |
| 55.7 | 29.7 | 13.4 | 2.0 |
| 76.1 | 42.5 | 20.5 | 1.0 |

In calculation a) the user basis for the active part of the system includes all nitrogen AO's; for the 1*s* orbital of N $\varepsilon$ is always 500.0. In calculation b) only valence AO's of nitrogen are included in the user basis.

$\varepsilon = 500.0$, and this high value is adequate since the UB in this variant still includes all functions required for the 1*s* expansion. In employing the effective potential these compact nitrogen functions make it possible that all MO's in the active region can in principle form orthogonality nodes to the 1*s* nitrogen shell. By increasing $\varepsilon$, all these MO's approach the exact orthogonality to the 1*s*, and the 1*s* level shift will not make up any (unphysical) contribution to the total energy nor will it deform the MO's of the active molecular part.

The second UB (calculation b in Table 3) yields somewhat higher values for the dissociation energy than the reference SCF calculation with frozen LMO's. These values are possibly a consequence of a small deformation of the nitrogen lone pair due to the level shift operator for the 1*s* orbital. Since in this UB variant the two most compact *s*-functions (representing the 1*s* shell) are not included, which are important for the description of the orthogonality nodes of the MO's relative to the 1*s* shell, it is conceivable that the 1*s* level shift operator is not sufficiently accurate.

### *3.4 Optimizing the transfer of the effective spectator potential into the user basis*

In order to allow a good transfer of the spectator potential into the user basis, the AO's of the user basis have to be expandable to high accuracy as linear combinations of functions in the intermediary basis (see Sect. 2.2). High accuracy means in this case that the product of norms (Eq. (6)) is in the order of at least 0.98. A very flexible transfer is required for potential surface calculations, i.e. the situation in which the influence of the effective potential changes with elongation of bond length. This situation requires very high accuracy for the representation of the spectator potential in the UB, not only for one geometric arrangement but over the entire range of geometrical variables.

The sensitivity of the effective potential can be illustrated by the following considerations:

The total energy can be divided into the energy of the spectator, the energy of the active part and the interaction energy between spectator and active part (the separation of the total energy can be done as it is outlined here provided the wavefunctions of spectator $\psi_{sp}$ and active part $\psi_{ac}$ are orthogonal). The energy of the spectator is the expectation value of the closed-shell determinant $\psi_{sp}$ of Eq. (1), note that in the nuclear terms only the charges attributed to the spectator occur. The energy of the active part is given by $\langle \psi_{ac} | \hat{H}_{ac} | \psi_{ac} \rangle$, whereby $\hat{H}_{ac}$ is the operator for the isolated active part, i.e. the operator $H'_{ep}$ (Eq. (2)) of the entire system (Eq. (2)) without the terms for the effective spectator potential. The interaction energy between spectator and active part has two components, i.e. the interactions of the spectator with the electrons of the active part and the interaction with the nuclear charges. The first term is the expectation value $\langle \psi_{ac} | V_{sp} + LS_{sp} | \psi_{ac} \rangle$.[1] Together with the total energy of the active part it yields $\langle \psi_{ac} | H'_{ep} | \psi_{ac} \rangle$, i.e. the result of an energy calculation employing the effective potential. The second part of the spectator-active part interaction can be evaluated directly as $\langle \psi_{sp} | g_{ac} | \psi_{sp} \rangle$, in which $g_{ac}$ stands for the nuclear charges in the active part. This term depends on the geometric arrangement of the active part relative to the spectator, and has to be computed at each point of the energy hypersurface in addition to the energy expectation value $\langle \psi_{ac} | H'_{ep} | \psi_{ac} \rangle$. The first component of the interaction between active part and spectator $\langle \psi_{ac} | V_{sp} + LS_{sp} | \psi_{ac} \rangle$ is subject to errors due to the transfer of the effective potential via the intermediate basis, whereas the second component can be computed exactly. Both components are of the magnitude of several atomic units and they almost cancel each other. As a consequence, the relative errors in the interaction energy are much larger than in the term $\langle \psi_{ac} | V_{sp} + LS_{sp} | \psi_{ac} \rangle$ itself. Unfortunately the interaction energy is the contribution to the total energy with the largest variations when potential surfaces with changes in distance or relative orientation between the active part and the spectator are to be calculated.

As a test of the procedures outlined in Sect. 2.2 for the accurate transfer of the effective potential to the partner X, potential energy curves for the dissociation of $NH_3 \cdot HF$ are calculated. Potential curves which are computed using several intermediate basis sets in combination with a multipole expansion are compared with a reference curve with exact transfer of the effective potential. All localized orbitals (LMO) of $NH_3$ except the lone pair and the 1*s* of nitrogen are included in the effective potential for $NH_3$ (see Sect. 3.2). On the basis of the results from Sect. 3.3 values of 5.0 a.u. for the N–H bonds are taken for the level shift parameter $\varepsilon_\alpha$. The 1*s* orbital of nitrogen is not included in the effective potential as described in Sect. 2, but it is represented by a pseudopotential according to the method of Durand and Barthelat [1] instead; the 1*s* orbital of fluorine is also replaced by such a pseudopotential (parameters, see Table 4). Owing to the employment of the Durand–Barthelat pseudopotentials the orbitals of the active part (i.e. the lone pair of nitrogen and the valence MO's of HF) do not have to form orthogonality nodes to the 1*s* core. For this reason the two most compact *s* functions in the AO basis

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[1] The level shift operator $LS_{sp}$ can yield a small contribution to the energy $\langle \psi_{ac} | V_{sp} + LS_{sp} | \psi_{ac} \rangle$ since it is not an exact projection operator if some AO's of the spectator group are neglected in the user basis (see Sect. 3.3). This energy contribution has been found to be small and nearly independent of the binding partner X

**Table 4.** ECP-parameters for the description of the 1*s*-core according to the method of Durand and Barthelat [26]

$$\text{ECP: } \sum_{l=0}^{2}\left(\sum_{i=1}^{N_l} c_{i,l} r^{n_{i,l}} e^{\alpha_{i,l} r^2}\right)|l\rangle\langle l|$$

| | | Nitrogen | | | Fluorine | | |
|---|---|---|---|---|---|---|---|
| l | i | $n_{i,l}$ | $\alpha_{i,l}$ | $c_{i,l}$ | $n_{i,l}$ | $\alpha_{i,l}$ | $c_{i,l}$ |
| 0 | 1 | − 2 | 0.77911 | 1.09851 | − 2 | 1.26132 | 1.12060 |
| 0 | 2 | 2 | 0.77911 | − 0.33854 | 2 | 1.26132 | − 0.98560 |
| 1 | 1 | − 1 | 4.76414 | − 0.43676 | − 1 | 8.17605 | − 0.44625 |

sets of N and F can be deleted in the user basis (UB) (AO basis of nitrogen and of HF) without facing problems similar to those described in Sect. 3.3 with the second UB.[2] This saving has the great advantage that the very difficult transfer of the effective potential to compact AO's of the partner X (i.e. the HF molecule) is circumvented (see Sect. 2.2).

All intermediate basis sets consist of a (5*s*, 3*p*, 1*d*) AO-basis at the nitrogen atom (see Points 2. and 3. in Table 6) plus a (1*s*, 1*p*, 4*d*, 4*f*) one-center expansion at some point on the *z* axis in variable distance from the nucleus of nitrogen (see Point 1. in Table 6 and Fig. 1). The one-center expansion of the first IB lies at the approximate location of the hydrogen nucleus of HF at its equilibrium distance (see Fig. 2). Each succeeding IB differs from the preceding one by a shift of the origin of the one-center expansion away from $NH_3$; the magnitude of this shift is 0.264 Å for the first five IB's and 0.528 Å shift for the following IB's. This combined use of several IB's guarantees that a one center expansion for the exact transfer of the effective potential to partner X is at disposal everywhere in the area which is accessible for partner X. At larger distances from the spectator $NH_3$ the exact transfer of the potential is facilitated by a multipole expansion instead. The accuracy of the multipole expansion can be judged from the fact that the multipole potentials of $NH_3$ and of $NH_3$ without lone pair deviate less than one percent from the corresponding exact Hartree–Fock potentials at the location of the oxygen atom in the complex $NH_3 \cdot H_2O$. In calculations with five IB's plus multipole expansion the average error in the transfer of the $NH_3$ Hartree–Fock potential can be reduced to less than $10^{-4}$ Hartree for one matrix element in the user basis (UB). The transfer of the potential to AO's of nitrogen, where it has its largest absolute values, is exact since the AO's of the UB at the nitrogen atom (see Table 5) form a genuine subset of all IB's (see Table 6).

In Table 7 the deviation of potential curves for $NH_3 \cdot HF$ computed with a different number of IB's from the reference curve is displayed; a different number of IB's means that the chain of consecutive one-center expansions terminates at different distances from $NH_3$ on the *z* axis. The reference curve is calculated with exact transfer of the effective potential since at each point of the reaction path the full basis of the complex $NH_3 \cdot HF$ with the corresponding N–F distance is used as

---

[2] The remaining AO's of N and F respectively see Table 5 are modified with respect to the valence AO's of N and F respectively from Table 1 since special valence AO basis sets are to be used in conjunction with the Durand Barthelat pseudopotentials in order to obtain nodeless valence orbitals

**Table 5.** Valence AO-basis for N and F to be used in conjunction with the 1*s* ECP-parameters

| | Nitrogen exponent | coeff. | Fluorine exponent | coeff. |
|---|---|---|---|---|
| 1*s* | 86.2442 | – 0.007458 | 161.502 | – 0.007179 |
| | 11.026 | – 0.047907 | 20.8143 | – 0.046459 |
| | 0.643562 | 0.554216 | 1.17289 | 0.542086 |
| 2*s* | 0.2133 | 1.0 | 0.368772 | 1.0 |
| 1*p* | 11.821 | 0.043362 | 20.2556 | 0.048639 |
| | 2.75664 | 0.227848 | 4.71088 | 0.246670 |
| | 0.768047 | 0.509199 | 1.29071 | 0.508251 |
| 2*p* | 0.1654 | 1.0 | 0.336485 | 1.0 |
| 1*d* | 0.864 | 1.0 | 1.4 | 1.0 |

- The valence AO-basis sets are taken from [26]
- The exponents of the *d*-functions and the 2*s*/2*p* functions of nitrogen were taken from all-electron basis sets of Table 1 (see Sect. 3.1)

**Table 6.** Intermediate basis sets for the transfer of the Hartree–Fock potential of $NH_3$ without lone pair to the partner X

1. one-center expansion at the possible locations of partner X (for the position of the origins of the expansion see Sect. 3.4)

| AO type* | exponents | | | |
|---|---|---|---|---|
| *s* | 0.9 | | | |
| *p* | 0.9 | | | |
| *d* | 1.728 | 0.0864 | 0.432 | 0.216 |
| *f* | 2.56 | 1.28 | 0.64 | 0.32 |

2. the complete all-electron basis of $NH_3$ at the location of $NH_3$
3. compact *s*- and *p*-functions for nitrogen from Table 1 at the nitrogen location of the donor $NH_3$

* more diffuse *s*- and *p*-functions are not necessary since they are already included as linear combinations of the cartesian components of the *d*- and *f*-functions, respectively

the intermediate basis set. The threshold for the product of norms $NP_{l,m}$ is given at the head of each column in Table 7; if none of the IB's yields a $NP_{l,m}$ which is larger than the threshold for a certain matrix element $l, m$ in the UB, then the potential is transfered via multipole expansion to this matrix element $l, m$ (see Sect. 2.2).

It is obvious from Table 7 that the deviations from the reference energies decrease steadily with increasing number of intermediate basis sets. For five IB's the observed errors can still be considered small in comparison to the binding energy of 50 kJ/mol. This finding is also clear from the inspection of the potential curve computed with five IB's relative to the reference curve shown in Fig. 3. The chain of five IB's ends at a distance of 3.0 Å from the nitrogen atom. This distance is somewhat larger than the radius beyond which the multipole expansion is

**Table 7.** Deviations in kJ/mol from the reference potential curve for the dissociation of $NH_3 \cdot HF$

Comparison of the SCF calculation in which the exact transfer of the effective potential is made with those, in which the effective potential is transferred using *n* intermediate basis sets (IB)*

| ΔN-F (Å) | 7 I.B. TN = 0.95 | 5 I.B. TN = 0.97 | 4 I.B. TN = 0.95 | 4 I.B. TN = 0.98 | 1 I.B. 0.95 |
|---|---|---|---|---|---|
| 2.5 | 1.8 | 1.1 | 1.8 | 1.8 | 31.8 |
| 2.8 | 1.3 | 0.8 | 2.6 | 3.4 | 46.2 |
| 3.3 | 0.8 | 1.8 | 4.5 | 3.9 | 13.1 |
| 3.8 | 0.8 | 2.4 | 5.0 | 2.6 | 4.7 |
| 5.4 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| 10.7 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 53.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

TN: selection threshold for the product of norms (see Sect. 3.4)

* All potential curves with *n* intermediate basis sets lie below the reference curve at all distances N–F

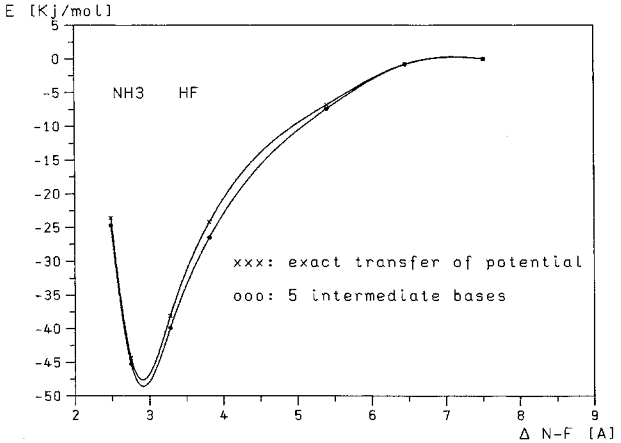

**Fig. 3.** Potential energy curves for the dissociaiton of $NH_3 \cdot HF$, obtained from SCF calculations employing an effective potential for $NH_3$. The curve *xxx* is obtained for the exact transfer of the effective potential into the user basis while the curve *ooo* results from employing five intermediate bases plus multipole expansion for the long-range part and renormalization

sufficiently accurate (see Sect. 2.2). A certain overlap is necessary, however, in order to achieve accurate potential transfer to matrix elements between AO's on different atoms as well. This is the case because *both* AO's of a matrix element have to be expanded accurately in the IB if the potential is to be transferred via the IB whereas only the *location of the product* of the two AO's is of importance for the transfer of the potential via the multipole expansion.

The size of the threshold for the product of norms $NP_{l,m}$ also has some influence on the magnitude of errors. An optimal choice for $NP_{l,m}$ is achieved when the average errors for the transfer of the potential using the intermediate basis are of the same size as the average errors for the transfer of the potential using the multipole expansion at the radius of the sphere in which the intermediate basis sets are effective. In order to guarantee the proper transfer of the potential in the general case it is necessary to have an adequate density of IB functions in the segment of space between the spectator and the possible locations of binding partner X. The computational effort implied by this requirement is non-negligible but we think that the method is practical also in the general case for the following reasons:

- More economic arrangements and structures of the IB's than those applied in this study can be found to achieve a further reduction of the required computational effort.

- The dissociation of hydrogen bonded systems like $NH_3 \cdot X$ is a very difficult testing case since the interaction energy is small and because the inaccuracies in the transfer of the spectator potential have only an influence on the energy of the bound system but have no effect on the computed energy of the dissociated system at all. Very recent results in our laboratory for the isomerization of *para*-dimethylbenzene to its dewar-form employing effective potentials for the methyl-groups indicate that reliable results can be obtained using moderate intermediate basis sets if the inaccuracies in the potential have roughly the same effect on the initial state and the final state of the process considered and if the energy difference to be calculated is not too small.

## 4 Conclusions

The aim of the present study was to develop an effective potential to simplify the description of spectator groups in molecular systems treated by *ab initio* calculations. The main problem arises because such effective potentials are generally very anisotropic in space and therefore do not allow a representation by simple functions. In the present work the effective potential of a spectator was represented in form of a matrix in a large intermediate basis set. It was found that in the system $NH_3 \cdot X$, with $X = NH_3$, $H_2O$, HF the N–H bonds and the 1*s* electron can indeed be treated as an effective potential and that only the nitrogen lone pair is important in the description of the bonding properties. Binding energies could be reproduced to within 5% by employing the effective potential. The influence of the magnitude of the level shift is also found not to be critical.

Problems arise in the determination of potential curves because on one hand the intermediate basis set has to be flexible enough to allow an accurate expansion of the AO's of the user basis, and on the other hand it cannot exceed a certain size because it must be still manageable in calculations. Sample calculations of the potential curve for the $NH_3 \cdot HF$ dissociation show that it is necessary to use a number of intermediate basis sets with different origins to achieve a sufficiently accurate transfer of the potential. It is also necessary to use a multipole expansion for the transfer of the long range components of the $NH_3$ potential to AO's at larger distances from $NH_3$, but this can easily be achieved. Employing the intermediate basis at five origins the $NH_3 \cdot HF$ potential curve can be reproduced to within 2 kJ/mol, whereby the total depths of the well is in the order of 50 kJ/mol.

If computations on systems in a fixed geometry with several spectators are to be performed (i.e. complexes with several ligands or molecules with several substituents), it is also possible to circumvent the problem of the transfer of the potential. For each spectator the AO basis of the active part of the system plus the AO basis of the spectator is taken as intermediate basis set in this case. This procedure guarantees an exact transfer of the effective potential and the full two-electron file for the complete system has never to be evaluated. Such a strategy requires, however, the generation of the effective potential anew for each spectator in each application.

The indication is that the used spectator potentials might be quite efficient for large and bulky groups; in such cases the reduction in computational effort due to the reduced number of electrons in the system employing effective potentials would be sizeable and the representation of the effective potential in an intermediate basis as -well as the transfer into the user basis is not expected to require much more computational expenditure as for small spectator groups.

The present approach can be immediately taken over to configuration interaction calculations. This aspect will be studied in the consecutive paper, in particular to see to what extent the spectator potential is able to characterize other properties besides energies.

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## References

1. Durand P, Barthelat JC (1975) Theor Chim Acta 38:283
2. Sakai Y, Huzinaga S (1982) J Chem Phys 76:2537
3. Petterson LGM, Wahlgren U, Gropen O (1987) J Chem Phys 86:2176
4. Barandarián Z, Seijo J (1988) J Chem Phys 89:5739
5. Seijo L, Barandarián Z (1989) J Chem Phys 91:7011
6. Seijo L, Barandarián Z, Huzinaga S, Klobukowski M (1987) J Chem Phys 86:2132
7. Seijo L, Barandarián Z (1991) J Chem Phys 94:8158
8. Ohta K, Yoshioka Y, Morukuma K, Kitaura K (1983) Chem Phys Lett 101:12
9. Barnett RN, Landmann U, Dhar S, Kestner NR, Jortner J, Nitzan A (1989) J Chem Phys 91:7797
10. Foster JM, Boys SF (1960) Rev Mod Phys 32:300
11. Szasz L (1985) Pseudopotential theory of atoms and molecules. Wiley, NY
12. Bonifacić V, Huzinaga S (1974) 60:2779
13. Höjer G, Chung J (1978) Int J Quantum Chem 14:623
14. Stone AJ (1981) Chem Phys Lett 83:233
15. Stone AJ, Alderton M (1985) Mol Phys 56:1047
16. Sagarik KP, Ahlrichs R, Brode S (1986) 57:1247
17. Del Bene JE (1988) J Phys Chem 92:2874
18. Caroll MT (1988) Mol Phys 63:387
19. Hurst GJB, Fowler PW, Stone AJ, Buckingham AD (1986) Int J Quantum Chem 29:1223
20. Herbind P, Dyke FR (1985) 83:3768
21. Havenith M, Linnartz H, Zwart E, Kips A, ter Meulen JJ, Meerts WL (1992) submitted
22. Poirier R, Kari R, Csizmadia IG (1985) Handbook of gaussian basis sets. Elsevier, NY
23. Huzinaga S (1965) J Chem Phys 42:1293
24. Dunning Jr. TH (1970) 53:2823
25. Haar L, Gallagher S (1978) J Chem Phys Ref Data 7:635
26. Pacchioni GF, Fantucci P, Giunchi G, Barthelat JC (1980) Gazz Chim Ital 110:183