Analytical Evaluation of Multicenter Integrals needed in Molecular Quantum Mechanical Calculations of some Magnetic Tensors over Slater Type Basis Functions

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Abstract

In the quantum theory of atoms or molecules in magnetic fields of different origin that can be an external homogenous field and that created by the nuclear magnetic moment of a nucleus, some important magnetic tensor appears. The integrals due to magnetic perturbations appeared within coupled Hartree-Fock-Roothaan perturbation Gauge Invariant Atomic Orbitals or in Density Functional Theory (DFT) are analytically evaluated for Slater Type nsnp basis functions. Reduced analytical formulas are obtained using properties of the Levi-Civita tensor of rank 3, properties of rotation matrix and symmetry properties of field-independent atomic orbitals. The condensed formalism is expressed in term of auxiliary functions and integrals. The angular dependence of integrals is also discussed in detail. The multicenter integrals can be monocentric, bicentric or three centric. All monocentric and bicentric integrals with monocentric electron distribution can be calculated rigorously in spherical polar coordinates with the nucleus as origin. Bicentric integrals with bicentric electron distribution were also integrated using elliptic coordinates after an appropriate axis transformation. The three centre integrals with bicentric electron distribution were determined analytically within the London Type approximation. The resulting angular momentum and impulsion integrals whether dipolar or quadrupolar are all computed rigorously in elliptic coordinates.

Keywords: Molecular Magnetic Tensors Integrals, Analytical Multicenter integrals, STOs Basis Functions.

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الحساب التحليلي للتكاملات متعددة المراكز اللازمة للحسابات الميكانيكية الكمومية الجزيئية لبعض التنسورات المغناطيسية باستخدام توابع سلاتر كقاعدة

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الملخص

يظهر في النظرية الكمومية لذرة أو جزيء خاضع لحقول مغناطيسية ذات منشأ مختلف يمكن أن يكون حقلاً خارجياً متجانساً أو حقلاً ناجماً عن العزم المغناطيسي النووي بعض التنسورات المغناطيسية. حسبت التكاملات الناجمة عن الاضطرابات المغناطيسية التي تظهر في نظرية هارتري–فوك–روثان المترابطة أو نظرية تابع الكثافة المستخدمة مدارات ذرية مستقلة العيار تحليلياً باستخدام توابع سلاتر nsnp كقاعدة. تم التوصل إلى علاقات تحليلية مضغوطة بفضل استخدام خصائص تنسور ليفي–سيفيتا من المرتبة الثالثة، خصائص مصفوفة الدوران وعناصر تناظر المدارات الذرية المستقلة عن الحقل المغناطيسي. صِيغتْ أيضاً المعادلات بواسطة توابع وتكاملات وسيطة. دُرست أيضاً التابعية الزاوية للتكاملات بتفصيل كبير. يمكن للتكاملات متعددة المراكز أن تكون أحادية المركز، أو ثنائية المركز أو ثلاثية المركز. حسبت التكاملات أحادية وثنائية المركز ذات التوزع الإلكتروني أحادي المركز جميعها باستخدام الإحداثيات القطبية الكروية التي يقع مركزها على النواة. حسبت التكاملات ثنائية المركز ذات التوزع الإلكتروني ثنائي المركز باستخدام الإحداثيات القطعية بعد إجراء تحويل مناسب لجملة الإحداثيات. بالمقابل حسبت التكاملات ثلاثية المركز وثنائية التوزع الإلكتروني تحليلياً بعد استخدام تقريب لندن، وحسبت تكاملات العزم والاندفاع والتكاملات ثنائية أو رباعية الأقطاب بشكل دقيق باستخدام الإحداثيات القطعية.

كلمات مفتاحية: تكاملات التنسورات المغناطيسية الجزيئية، تكاملات متعددة المراكز، توابع القاعدة من نوع سلاتر.

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I-Introduction

In the quantum mechanical theory of atoms or molecules in magnetic field of different origin that can be an external homogenous field and that created by the nuclear magnetic moment of a nucleus, some important magnetic tensor appears. The theory of second-order magnetic tensors is actually well established in the framework of coupled Hartree-Fock perturbation theory and analytical derivative or in Density Functional Theory (DFT) using field-dependent basis functions called gauge-including atomic orbital (GIAO) :

$$\phi_{s(s)}(\vec{\rho}_r,\vec{B}) = \varphi_{s(s)}(\vec{\rho}_r)\cdot\exp\left[-\frac{i\cdot e}{\hbar\cdot c}\cdot\vec{A}_{s(s)}\cdot\vec{r}\right],\ \vec{\rho}_r = \vec{r} - \vec{d}_{s(s)},\ \vec{A}_{s(s)} = \frac{1}{2}\cdot\left(\vec{B}\wedge\vec{d}_{s(s)}\right)$$

where, respectively, $\vec{r}$ is the position vector of the electron with respect to a fixed frame axes, $\vec{d}_{s(s)}$ is the vector position of nucleus S , $\vec{A}_{s(s)}$ is the potential vector created by the magnetic field $\vec{B}$ at the location of nucleus S and $\varphi_{s(s)}$ is the field independent basis function located at the nucleus S which can be a Slater Type basis function or a Gaussian basis function. At the computational level, the choice of magnetic field-dependent basis functions is important. The integrals due to magnetic perturbations can be calculated, as usually doing in many programs, using Gaussian field-independent basis functions. However, it is known that atomic and molecular orbitals must decay exponentially at long-range distance. They should also possess cusps when two particles approach each other . Therefore, Slater basis functions are the natural choice for a quantum mechanical calculations of zero order properties and this is more true for second order properties. Their use was hindered over the last four decades by integration problems. Consequently, the gauge-including atomic orbital with Slater basis functions were replaced by Gaussian expansions. However, in the field of magnetic properties, the rapid decay and the absent cusps still a problem for obtaining very precise values for the components of theses tensors and their mean values. A very well description of the situation is given by Gaston Berthier in his interview in Paris in 1997: " GTOs are like medicine, you have to

use them as long as they are healing, but once they don't work anymore, you must change them". In this work, we adopt the determination of multicenter integrals involved in magnetic susceptibility and nuclear screening tensors using the Slater Type basis functions. Highly reduced analytical formulas are obtained using properties of the Levi-Civita tensor of rank 3, properties of rotation matrix and symmetry properties of field-independent atomic orbitals. The condensed formalism is expressed in term of auxiliary functions and integrals. The angular dependence of integrals is also discussed in detail. Before presenting the determination of integrals involved in quantum theory of molecular magnetism we examine briefly some properties of the most important field-independent basis functions used in atomic and molecular quantum mechanical calculations at the level of zero order wave functions or higher order properties for justifying our choice of one of the basis functions actually in use.

II-Elliptical coordinates

We use in some molecular quantum mechanical calculations the elliptical coordinates [1,2,3]. We define a fictive diatomic system of coordinate associated with a pair of atoms R and S as shown in the following figure. The electron can occupy the point p.
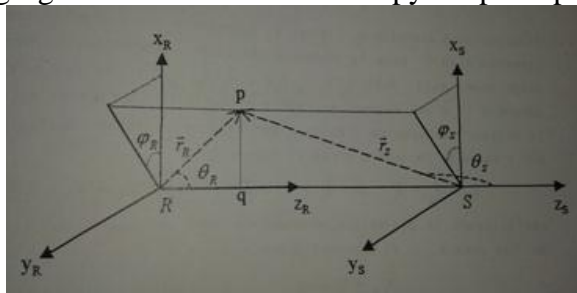
The elliptic coordinates is formed by the three coordinates:

$$\mu \in [1, \infty] \qquad \qquad v \in [-1, +1] \qquad \qquad \varphi \in [0, 2 \cdot \pi]$$

We relit the atomic polar coordinates $(r_R, \theta_R, \varphi_R ; r_S, \theta_S, \varphi_S)$ with elliptic one (μ, v, φ) and some other quantity by the equations :

$$r_R = \frac{d}{2} \cdot (\mu + v) \qquad \qquad \mu = \frac{1}{d} \cdot (r_R + r_S)$$

$$r_S = \frac{d}{2} \cdot (\mu - \nu) \qquad\qquad \nu = \frac{1}{d} \cdot (r_R - r_S)$$

$$\varphi_R = \varphi_S = \varphi \qquad\qquad \varphi = \varphi_R = \varphi_S$$

$$\cos\theta_R = \frac{\mu \cdot \nu + 1}{\mu + \nu} \qquad\qquad \cos\theta_S = \frac{\mu \cdot \nu - 1}{\mu - \nu}$$

$$\sin\theta_R = \frac{1}{\mu + \nu} \cdot \sqrt{(\mu^2 - 1) \cdot (1 - \nu^2)} \qquad \sin\theta_S = \frac{1}{\mu - \nu} \cdot \sqrt{(\mu^2 - 1) \cdot (1 - \nu^2)}$$

$$X_R = X_S = \frac{d}{2} \cdot \cos\varphi \cdot \sqrt{(\mu^2 - 1) \cdot (1 - \nu^2)} \quad Y_R = Y_S = \frac{d}{2} \cdot \sin\varphi \cdot \sqrt{(\mu^2 - 1) \cdot (1 - \nu^2)}$$

$$Z_R = \frac{d}{2} \cdot (\mu \cdot \nu + 1) \qquad\qquad Z_S = \frac{d}{2} \cdot (\mu \cdot \nu - 1)$$

$$d\tau = \frac{d^3}{8} \cdot (\mu^2 - \nu^2) \cdot d\mu \cdot d\nu \cdot d\varphi$$

$$np_{XR}(\vec{r}_R) = N_R \cdot \sin\theta_R \cdot \cos\varphi_R \cdot r_R^{n_R - 1} \cdot e^{-\alpha_R \cdot r_R}$$

$$np_{XR} = N_R \cdot \left(\frac{d}{2}\right)^{n_R - 1} \cdot (\mu + \nu)^{n_R - 2} \cdot \sqrt{(\mu^2 - 1) \cdot (1 - \nu^2)} \cdot \cos\varphi \cdot e^{-\alpha_R \cdot \frac{d}{2} \cdot (\mu + \nu)}$$

III-Slater and Gaussian type Basis Functions: definitions, advantages and disadvantages

Nowadays, Slater Type Orbitals (STO) are used in atomic calculation, especially in highly accurate calculations of atoms, see for example beryllium atom [4], using Hylleraas wave functions and they are used in 2001 in a DFT program: ADF (Amsterdam Density Functional) [5]. The program CADPAC [6] in Cambridge uses techniques like fitting, involving auxiliary Slater type orbitals basis functions to perform Hartree-Fock (HF) and Density Functional Theory (DFT) calculations, a technique that aimed to obtain better Nuclear Magnetic Resonance (NMR) Tensors on the basis involving nuclear cusps. In 1998 a program was written using STO by Steinborn et . al [7,8]. The program SMILES by Fernandez et . al [9,10] appeared in new version

in 2004 for Hartree-Fock and Configuration Interaction (CI) calculations on atoms and molecules. The program STOP by Bouferguen and Hoggan [11] based on single centre strategy [1] appeared in parallel version in 2009. Finally, the program ATMOL of Bunge at . al [12] performs large highly accurate CI calculations on atoms using Slater orbitals. There are actually 90 groups around the world that developing new STO computer programs which are now distributed. This means that much interest is concentrated on generating more efficient calculations algorithms using STO, use of non-integer STO, numerical solution of integrals when using B-functions and in the electron correlation when using Hylleraas wave functions. A basis function is a mathematical description of orbitals of system which is used for approximate theoretical calculations. There are two types of basis functions commonly used in electronic structure calculations and atomic and molecular properties: Staler Type Orbitals (STOs) and Gaussian Type Orbitals (GTOs) which have respectively the functional form:

$$\varphi_{n,lm}(\vec{r},\varsigma) = N \cdot Y_{l,m}(\theta,\varphi) \cdot r^{n-1} \cdot e^{-\varsigma \cdot r}$$

$$\varphi_{n,lm}(\vec{r},\varsigma) = N \cdot Y_{l,m}(\theta,\varphi) \cdot r^{2 \cdot n-2-l} \cdot e^{-\varsigma \cdot r^2}$$

Where N is a normalization constant, ς is a variational parameter, (n,l,m) the quantum numbers, Y_{lm} is the spherical harmonic and r is the distance electron-nucleus.

III-1- Some properties of Slater Type Basis Functions

In 1928 Slater [13] simplified the hydrogen-like wave functions to obtaining orbitals called in the early quantum theory « Hartree-Orbitals » and which we call in modern atomic and molecular physics by « Slater Type Orbitals ». The STOs can be chosen to form a complete basis set and are the most adapted basis functions for atomic and molecular quantum mechanical calculations. Hydrogen-like orbitals have nodes but STOs are node-less and a related problem appears for GTOs. The STOs satisfy Kato's conditions for atomic orbitals: they possess an electronic cusp at nucleus and decay exponentially at long distances for it [14,15]. Furthermore, the STOs

represent well the electron density near the nucleus (cusp) and far from the nucleus (correct asymptotic decay). Thus, the STOs resemble the true orbitals. It is known that if the basis function is not an exact solution of the Schrodinger its convergence is slower. That means that more Slater determinants are required to obtain the same result. Thus Slater orbitals show faster convergence when increasing their number. Another advantage of STOs is the size of the basis. One orbital per electron is of reasonable quality. Furthermore, a multiple-zeta STOs basis functions converge fast to the Hartree-Fock limit. Consequently the number of integrals to be evaluated is dramatically smaller. Finally the STOs give a more intuitive description of the atomic orbitals and of the molecular orbitals formed with them. But the STOs have some disadvantage: the three and four center two-electron integrals appears in electronic structure calculation is extremely difficult to calculate. In fact there is no general analytical solution for them. The existence of analytical solution and for electronic structure integrals is the most effective and fastest way of calculation. Some approximation methods are used involving infinite series or truncated approximations to the Coulomb operator itself. The radial Slater function does not represent the bonding region adequately. So it is necessary to add higher angular momentum functions. It is nevertheless possible to use linear combinations restoring radial nodes. We added that some of the two-center integrals since the times of Roothaan and Rudenberg [16] have been solved for co-axial conformation of atomic coordinate system that is not the molecular frame. Therefore rotations and reflections are necessary. These problems have been solved but it in consequence requires additional calculations.

III-2- Advantage and disadvantage of Gaussian Type Orbitals

In 1954 Boys, Shavitt et al [17, 18] expanded STO into a Gaussian to perform quantum mechanical calculations and theses orbitals are generally used in standard programs like GAUSSIAN, ORCA, CRYSTAL, NWChem. The GTOs are not shaped like analytical orbitals. The GTO have erroneous shape near and far from the nucleus and they have no electronic cusp at the nucleus. One can observe that far from the nucleus the GTO tend to zero much faster than STO. For

these reasons they are not good for the calculations of properties where the density at nucleus has to be well described. Furthermore the radial dependence of GTOs is not well represented and the number of integrals in electronic structure calculation increase dramatically with the dimension of the basis. The major advantage of GTOs is the existence of a product theorem: "the product of two Gaussian functions located on different centers is a new Gaussian function located on a new center". Thus the calculation of multicenter electronic structure integrals was analytically facilitated. The product theorem has been derived by Boys in Cambridge [17]. Concluding, while GTOs can be chosen to form a complete basis set [19], the main defect of GTO expansions is the absence of electron cusp (discontinuous derivative) at nucleus which slows the convergence of the wave function solutions to exact (Hartree-Fock or CI) result.

IV-Integrals of diamagnetic susceptibility and nuclear screening tensors.

It is difficult to overemphasize the importance of magnetic resonance techniques in physics and chemistry. Experimental spectra can usually be successfully interpreted empirically, but more difficult cases require a prediction based on precise electronic structure. In the last 25 years the calculation of magnetic resonance parameters from first quantum mechanical principles become a powerful research tool that can significantly enhance the utility of magnetic resonance techniques when empirical interpretation are insufficient. The quantum mechanical calculation of NMR parameters [20,21] is less straightforward than the calculation of the most other atomic and molecular properties. Understanding the source of these difficulties led to their successful solution. The theory of molecular magnetism is essentially the quantum theory of an atom or molecule in magnetic fields of different origin, namely an external homogeneous field and that created by the magnetic moment of a nucleus. It appears in this theory that second-order properties which are quadratic in the field strength include magnetic susceptibility, nuclear magnetic screening and nuclear spin-spin coupling tensors. The theory of molecular magnetism has a long history which begins by Ramsey Theory [22] and continued to nowadays (Relativistic calculations, Many-Body

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Perturbations Theory, Propagators, and different for Gauges for magnetic fields...). Hameka [23,24] has clarified many of the physical concepts from Ramsey [22] theory paving the way to Ditchfield's fundamental work [25] on Gauge-Independent Atomic Orbitals (GIAOs). From the work of Ditchfield's which developed his theory within a finite perturbation method, along the times a coupled Hartree-Fock-Roothaan perturbations theory using GIAO theory of the diamagnetic susceptibility tensor χ and nuclear screening σ_N theory has been developed in divers forms [25,26]. If we use a field dependent basis functions, the matrix elements of Hamiltonian is :

$$h_{rs} = \left\langle \lambda_{rs} \cdot \theta_{rs} \cdot \varphi_r \left| h^0 - \frac{i \cdot \hbar \cdot e}{m \cdot c} \cdot \left(\vec{A} - \vec{A}_S \right) \cdot \vec{\nabla} + \frac{e^2}{2 \cdot m \cdot c^2} \cdot \left(\vec{A} - \vec{A}_S \right)^2 \right| \varphi_S \right\rangle$$

$$\lambda_{rs} = \exp\left[\frac{i \cdot e}{2 \cdot \hbar \cdot c} \cdot \vec{B} \cdot \left(\vec{d}_r \wedge \vec{d}_s \right) \right] \qquad \theta_{rs} = \exp\left[\frac{i \cdot e}{2 \cdot \hbar \cdot c} \cdot \left(\vec{A}_r - \vec{A}_s \right) \cdot \left(\vec{r}_r \, \vec{r}_s \right) \right]$$

Where λ_{rs} is the London exponential, $\vec{r}_X$ is the electron position vector with respect to atom X, $\vec{d}_X$ is the nucleus position vector in molecular frame, $\vec{A}_X$ is the potential vector on the atom X, and $\vec{B}$ is the magnetic field. . The London approximation [27] yield to $\theta_{rs} \cong 1$. This approximation breaks down the hermiticity of Hamiltonian, but we can re-establish it by making the transformation $h \to \frac{1}{2} \cdot \left(h + h^+ \right)$.

Within the London approximation the following integrals appear in theses magnetic tensors:

$$I^k_{r(R)s(S)} = \left\langle \varphi_r \left| \vec{u}_k \cdot \vec{L}_S \right| \varphi_s \right\rangle - \left\langle \varphi_s \left| \vec{u}_k \cdot \vec{L}_S \right| \varphi_r \right\rangle$$

$$J^k_{r(R)s(S)} = \left\langle \varphi_r \left| \left(\vec{u}_k \wedge \vec{r}_R \right)^2 + \left(\vec{u}_k \wedge \vec{r}_S \right)^2 \right| \varphi_S \right\rangle = \sum_{i \neq k = 1}^{3} \left\langle \varphi_r \left| x^2_{iR} + x^2_{iS} \right| \varphi_s \right\rangle$$

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$$M^k_{r(R)s(S)} = \left\langle \varphi_r \left| \frac{\left(\vec{u}_k \wedge \vec{r}_N\right)\cdot\left(\vec{u}_k \wedge \vec{r}_R\right) + \left(\vec{u}_k \wedge \vec{r}_N\right)\cdot\left(\vec{u}_k \wedge \vec{r}_N\right)\cdot\left(\vec{u}_k \wedge \vec{r}_S\right)}{r_N^3} \right| \varphi_s \right\rangle$$

$$K^k_{r(R)s(S)} = \left\langle \varphi_r \left| \frac{\left(\vec{u}_k \wedge \vec{L}_N\right)}{r_N^3} \right| \varphi_s \right\rangle - \left\langle \varphi_s \left| \frac{\vec{u}_k \wedge \vec{L}_N}{r_N^3} \right| \varphi_r \right\rangle$$

The integrals I^k_{rs} and J^k_{rs} are involved in the tensor χ, K^k_{rs} and M^k_{rs} in the tensor σ_N. In these formulas the index k labels the direction of the magnetic field, $\vec{r}_T$ $(T = R, S, N)$ is the electron position vector in the molecular system with respect to atom T. $\vec{L}_T$ is the angular momentum operator with respect to R, S, N. $\vec{u}_k$ is a unit vector in the molecular frame. $\varphi_{r(R)}$ is a Slater type atomic orbital centered on atom R. For convenience, we adopted the functional form:

$$\varphi_{r(R)}(\vec{r}) = N_r \cdot \chi_r(r) \cdot \Omega_r(\theta, \varphi)$$

In this expression N_r is the normalization constant, χ_r and Ω_r are respectively, the radical and angular functions. Several authors [28-31] have published partial work on integrals obviously defined. These integrals belong to four categories: 1) Monocentric term $S \equiv R$, or $S \equiv R \equiv N$. These integrals are obtained in spherical polar coordinates. Compact forms will be given for arbitrary field direction. 2) Bicentric terms with monocentric charge distributions. Kondo and all [28] have calculated σ_N uniquely at the INDO-STO-2s2p level (Intermediate Neglect Differential Overlap for Slater Type Orbitals) including only first neighbor's interaction. These authors determine the $M^k_{r(R)s(R)}$ and $K^k_{r(R)s(R)}$ $(R \neq N)$ integrals on a diatomic system of coordinates, neglecting all molecular orientation effects. Moreover $K^k_{r(R)s(R)}$ is evaluated numerically and $M^k_{r(R)s(R)}$ analytically in [30]. This work generalizes the method of Kondo in entirely analytical

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form. The integrals $M^k_{r(R)s(R)}$ and $K^k_{r(R)s(R)}$ are given by reduced formulas for general nsnp basis functions which present a great interest for direct use in a Fortran program. 3) Bicentric terms with bicentric charge distribution. Previous work [30] on susceptibilities integrals have been carried out uniquely at the CNDO level (Complete Neglect of Differential Overlap) [3] and for one direction of magnetic field and without arbitrary molecular orientations of axes system. Here, the integrals $I^k_{r(R)s(S)}$ and $J^k_{r(R)s(S)}$ are integrated in elliptical coordinates at the NDDO [3] level (Neglect of Diatomic Differential Overlap), a more advanced level than the CNDO one, and the compact formulas given here are for arbitrary molecular orientation of molecular axes and arbitrary directions of external magnetic field. 4) Bi- and tricentric terms with bi bicentric electron distribution $M^k_{r(R)s(S)}$ and $K^k_{r(R)s(S)}$. These are apparently absent from previous analytical STO's. Here, they are evaluated analytically using a London type approximation relating them $I^k_{r(R)s(S)}$ and $J^k_{r(R)s(S)}$.

V-Analytical forms of monocentric integrals

1-Integrals involved in the susceptibility tensor

Dropping the subscript R the I^k_{rs} integrals are determined by the angular momentum operator on the STO nsnp:

$$\left(\vec{u}_k \cdot \vec{L}\right) \cdot ns(\vec{r}) = 0 \qquad \forall\ i = 1,2,3\ ; \qquad \left(\vec{u}_i \cdot \vec{L}\right) \cdot np_j(\vec{r}) = i \cdot n \cdot \in_{ijk} \cdot np_k(\vec{r})$$

$\in_{ijk}$ is the Levi-Civita 3-tensor [32]. By symmetry of $\langle ns | np_i \rangle$

$$\forall\ k = 1,2,3\ ,\quad I^k_{nsns} = 0 \qquad ,\qquad I^k_{nsnp_t} = 0 \qquad ,\qquad I^k_{np_t ns} = 0 \qquad ,$$

For the integrals I^k_{npnp} :

$$I^k_{np_j np_t} = i \cdot \hbar \cdot \in_{ktl} \cdot \langle np_j | np_l \rangle - i \cdot \hbar \cdot \in_{kjm} \cdot \langle np_t | np_m \rangle$$

This gives by symmetry:

$$I^k_{np_j np_t} = -2 \cdot i \cdot \hbar \cdot \left(1 - \delta_{Jt}\right) \in_{kjt}$$

For J_{rs}^k, using the identity:

$$\left.\begin{array}{l} x = r.\sin\theta.\cos\varphi = r\cdot\omega_1 \\ y = r.\sin\theta.\sin\varphi = r\cdot\omega_2 \\ z = r.\cos\theta \qquad = r\cdot\omega_3 \end{array}\right\} \quad\Leftrightarrow\quad x_k^2 = r^2\cdot\omega_k^2 \quad , \quad \omega_k^2 = \sum_{l=1}^{3}\delta_{kl}\cdot\omega_l^2$$

$r^2 - x_k^2$ gives for any direction of field magnetic field:

$$r^2 - x_k^2 = r^2\cdot\left(1-\omega_k^2\right) = r^2\cdot\left[1-\sum_{l=1}^{3}\delta_{kl}\cdot\omega_l^2\right]$$

J_{rs}^k becomes:

$$J_{rs}^k = 2\cdot N_r\cdot N_s\cdot\left\langle\chi_r\left|r^2\right|\chi_s\right\rangle\cdot\left\langle\Omega_r\left|1-\omega_k^2\right|\Omega_s\right\rangle$$

$$\left\langle\chi_r\left|r^2\right|\chi_s\right\rangle = \int_0^\infty \chi_r\cdot r^2\cdot\chi_s\cdot r^2\cdot dr = \int_0^\infty r^4\cdot\chi_r\cdot\chi_s\,dr$$

$$\left\langle\Omega_r\left|1-\omega_k^2\right|\Omega_s\right\rangle = \left\langle\Omega_r\left|1-\sum_{l=1}^{3}\delta_{kl}\cdot\omega_l^2\right|\Omega_s\right\rangle = \int_0^\pi\int_0^{2\pi}\Omega_r\cdot\left[1-\sum_{l=1}^{3}\delta_{kl}\cdot\omega_l^2\right]\cdot\Omega_s\cdot\sin\theta\cdot d\theta\cdot d\varphi$$

$\left\langle\Omega_r\left|1-\omega_k^2\right|\Omega_s\right\rangle$ also necessary in M_{rs}^k has the values:

$$\left\langle\Omega_{ns}\left|1-\omega_k^2\right|\Omega_{ns}\right\rangle = \frac{8\cdot\pi}{3} \quad , \quad \left\langle\Omega_{ns}\left|1-\omega_k^2\right|\Omega_{np_i}\right\rangle = \left\langle\Omega_{np_i}\left|1-\omega_k^2\right|\Omega_{ns_i}\right\rangle = 0$$

$$\left\langle\Omega_{ns}\left|1-\omega_k^2\right|\Omega_{ns}\right\rangle = \frac{8\cdot\pi}{15}\delta_{ij}\cdot\left(2-\delta_{kj}\right)$$

These relationships give:

$$J_{nsns}^k = \frac{(2n+2)\cdot(2n+1)}{3\cdot\alpha_{ns}^2} \quad ; \quad J_{nsnp_i}^k = J_{np_i ns}^k = 0 \quad \alpha_{ns} = \frac{\varsigma_{ns}}{n\cdot a_0}$$

$$J_{np_i np_j}^k = \delta_{ij}\cdot\left(2-\delta_{kj}\right)\cdot\frac{(2n+2)\cdot(2n+1)}{5\cdot\alpha_{np}^2} \quad ; \quad \alpha_{np} = \frac{\varsigma_{np}}{n\cdot a_0}$$

2- Integrals involved in the nuclear shielding tensors:

The monocentric terms M_{rs}^k:

$$M_{r(N)s(N)}^k = 2\cdot N_r\cdot N_s\cdot\left\langle\chi_r\left|\frac{1}{r}\right|\chi_s\right\rangle\cdot\left\langle\Omega_r\left|1-\omega_k^2\right|\Omega_s\right\rangle$$

This gives:

$$M^k_{nsns} = \frac{4}{3} \cdot \frac{\alpha_{ns}}{n} \qquad , \qquad M^k_{nsnp_i} = M^k_{np_i ns} = 0 \quad , \quad \alpha_{ns} = \frac{\varsigma_{ns}}{n \cdot a_0}$$

$$M^k_{np_i np_j} = \delta_{ij} \cdot \left(2 - \delta_{kj}\right) \cdot \frac{4}{5} \cdot \frac{\alpha_{np}}{n} \qquad , \qquad \alpha_{np} = \frac{\varsigma_{np}}{n \cdot a_0}$$

The integrals K^k_{rs} : it is clear that $K^k_{nsns} = 0 \quad \forall\, k = 1,2,3$

We obtain for nsnp using equation of angular momentum operator:

$$K^k_{nsnp_i} = 2 \cdot i \cdot \hbar \cdot \in_{kji} \cdot N_{ns} \cdot N_{np} \cdot \left\langle \chi_{ns} \left| \frac{1}{r^3} \right| \chi_{np} \right\rangle \cdot \left\langle \Omega_{ns} \middle| \Omega_{np_j} \right\rangle$$

The angular terms being zero $\forall\, j = 1,2,3$ we obtain $K^k_{nsnp_i} = K^k_{np_i ns} = 0$

and for K^k_{npnp} :

$$K^k_{np_i np_j} = 2 \cdot i \cdot \hbar \cdot \in_{kjl} \cdot N^2_{np} \cdot \left\langle \chi_{np_i} \left| \frac{1}{r^3} \right| \chi_{np_i} \right\rangle \cdot \left\langle \Omega_{np_i} \middle| \Omega_{np_l} \right\rangle$$

Also:

$$\left\langle \Omega_{np_i} \middle| \Omega_{np_l} \right\rangle = \frac{4\pi}{3} \cdot \delta_{il} \;\; \Rightarrow \;\; K^k_{np_i np_j} = -i \cdot \hbar \cdot \in_{kij} \cdot \frac{16 \cdot \alpha^3_{np}}{2n \cdot (2n-1) \cdot (2n-2)} \qquad , \qquad \alpha_{np} = \frac{\zeta_{np}}{n \cdot a_0}$$

VI-Coordinate transformation from diatomic to molecular axes

1-Definition of the problem

The molecular integrals $\quad I^k_{r(R)s(S)}, J^k_{r(R)s(S)}; M^k_{r(R)s(S)}, K^k_{r(R)s(S)} \qquad (R \neq N)$

depend on the orientation of the straight line RS or RN with regard to the molecular axes. Direct evaluation of these integrals in the molecular frame is not possible. The problem is avoided by determining the bicentric integrals in parallel axes centered on atoms R and S . These diatomic axes take the RS distance along the z axis. Therefore, elliptic or polar spherical coordinates can be defined enabling analytical evaluation of various bicentric integrals. The actual integral may then be expressed as a function of auxiliary

integrals in the diatomic frame. The molecular integrals may be expanded in combination of fictitious integrals determined in the diatomic frame. The corresponding transformation is just a rotation matrix relating axes on R and S in the diatomic frame to the initial molecular orientation. We define here the rotation matrix.

2-Rotation matrix

Let (R, ijk) the molecular frame (o, ijk) translated to atom R and $(RS, i'j'k')$ the diatomic frame. The vector $\vec{k}'$ follows the RS axis. $\vec{j}'$ is arbitrarily positioned in the (Ri, j) plane. The vector $\vec{i}'$ is perpendicular to $\vec{j}'$ and $\vec{k}'$. In the molecular frame $\vec{k}'$ gives:

$$\vec{k}' = \cos\gamma_x \cdot \vec{i} + \cos\gamma_y \cdot \vec{j} + \cos\gamma_z \cdot \vec{k}$$

The directions cosines are determined as follows. Let $\vec{d}_R(X_{PR}), \vec{d}_S(X_{PS})$, $p = 1,2,3,$ be the position vectors with respect to (o, ijk) and $\vec{d}_S'(X'_{PR})$ be the position vector with respect to (R, ijk). We have for $\vec{d}_S'$ and its orthogonal projection in (R, ijk):

$$\forall i = 1,2,3, \quad \vec{d}_S' = \vec{d}_S - \vec{d}_R \implies X'_{iS} = X_{iS} - X_{iR} \quad , \quad X'_{iS} = R \cdot \cos\gamma_i \quad , \quad R = |\vec{RS}|$$

The γ_i are obtained by use of the last equation:

$$\cos\gamma_i = \frac{X_{iS} - X_{iR}}{R} \quad , \quad R = \left[(X_R - X_S)^2 + (Y_R - Y_S)^2 + ((Z_R - Z_S)^2\right]^{1/2}$$

The vector $\vec{j}'$ decomposed in (R, ijk) gives:

$$\vec{j}' = A_{21} \cdot \vec{i} + A_{22} \cdot \vec{j}$$

The coefficients A_{21} and A_{22} are obtained by orthogonality of $\vec{j}'$:

$$A_{21} = \pm\frac{\cos\gamma_y}{\sin\gamma_z} \quad , \quad A_{22} = \mp\frac{\cos\gamma_x}{\sin\gamma_z}$$

Similarly, $\vec{i}^{\,'}$ in the molecular frame gives:

$$\vec{i}^{\,'} = A_{11} \cdot \vec{i} + A_{12} \cdot \vec{j} + A_{13} \cdot \vec{k}$$

The unknowns A_{3i} ; $i = 1,2,3$; are obtained from:

$$A_{31} = \mp \frac{\cos \gamma_x \cdot \cos \gamma_z}{\sin \gamma_z} \quad , \quad A_{32} = \mp \frac{\cos \gamma_y \cdot \cos \gamma_z}{\sin \gamma_z} \quad , \quad A_{33} = \pm \sin \gamma_z$$

These formulas define four independent determinations. The direct diatomic frame

$$\vec{u}_p^{\,'} \wedge \vec{u}_q^{\,'} = \in_{pqt} \cdot \vec{u}_t^{\,'} \qquad \left(\vec{u}_1^{\,'} \equiv \vec{i}^{\,'} \; , \; \vec{u}_2^{\,'} \equiv \vec{j}^{\,'} \; , \; \vec{u}^{\,'} \equiv \vec{k}^{\,'} \right)$$

Reduce this number to two. One is chosen arbitrarily.

The elements A_{ij} of orthogonal matrix A define a transformation from diatomic to molecular axes with $T = A^+$.

$$
\begin{vmatrix} \vec{i} \\[2mm] \vec{j} \\[2mm] \vec{k} \end{vmatrix}
=
\begin{vmatrix} \dfrac{\cos \gamma_x \cdot \cos \gamma_z}{\sin \gamma_z} & \dfrac{-\cos \gamma_y}{\sin \gamma_z} & \cos \gamma_x \\[4mm] \dfrac{\cos \gamma_y \cdot \cos \gamma_z}{\sin \gamma_z} & \dfrac{+\cos \gamma_x}{\sin \gamma_z} & \cos \gamma_y \\[4mm] -\sin \gamma_z & 0 & \cos \gamma_z \end{vmatrix}
+
\begin{vmatrix} \vec{i}^{\,'} \\[2mm] \vec{j}^{\,'} \\[2mm] \vec{k}^{\,'} \end{vmatrix}
$$

$$\Leftrightarrow \quad \vec{u} = T \cdot \vec{u}^{\,'}$$

Invariance of these vectors for a change of axes shows that the (x, y, z) coordinates transform as unit vectors. The orbitals np_i proportional to x, y and z also behave as unit vectors. The spherically symmetric atomic orbitals ns are invariant. Therefore the last equation can be generalized:

$$v_i = \sum_{j=1}^{4} T_{ij} \cdot v_j^{\,'} \quad \Leftrightarrow \quad v = T \cdot v^{\,'} \quad , \quad v_i = \vec{u}_i \; , \; x_i \; , \; \varphi_i$$

$$\sum_{q=1}^{4} T_{qi} \cdot T_{qj} = \delta_{ij} \quad \Leftrightarrow \quad T \cdot T^{T} = T^{T} \cdot T = I$$

The elements $T_{i4} = \delta_{i4}$ $(i \in [1,4])$ account for the OA ns form vector v including the basis: $v = \begin{pmatrix} np_{x} & np_{y} & np_{z} & ns \end{pmatrix}$.

VII-Exact analytical evaluation of bicentric integrals

1-Integrals for the susceptibility tensor

In the molecular frame the angular momentum operator acting on the $OA's$ gives the I_{rs}^{k} integrals subsequently evaluated in the diatomic axes. The action of angular momentum on orbitals with spherical symmetry implies:

$$I_{ns_{R} ns_{S}}^{n} = 0$$

Using the action of angular momentum operator on basis functions $I_{np_{p} np}^{n}$ becomes:

$$I_{np_{jR} ns_{tS}}^{n} = i \cdot \hbar \cdot \in_{ktl} \cdot \left\langle np_{jR} \middle| np_{1S} \right\rangle - i \cdot \hbar \cdot \in_{kjm} \cdot \left\langle np_{tS} \middle| np_{mR} \right\rangle$$

Expressing this in the diatomic frame:

$$I_{np_{jR} np_{tS}}^{k} = i \cdot \hbar \cdot \in_{ktl} \cdot \left\langle np_{jR} \middle| np_{lS} \right\rangle - i \cdot \hbar \cdot \in_{kjm} \cdot \left\langle np_{tS} \middle| np_{mR} \right\rangle -$$

$$i \cdot \hbar \cdot \in_{kjm} \cdot \sum_{v=1}^{3} \sum_{w=1}^{3} T_{tv} \cdot T_{mw} \cdot \left\langle np_{vS}^{'} \middle| np_{wR}^{'} \right\rangle$$

Eliminating zero integrals and using orthogonality of T:

$$I_{np_{jR} np_{tS}}^{k} = -i \cdot \hbar \cdot \left\{ \begin{matrix} \left[\in_{kjm} \cdot \left(\delta_{tm} - T_{t3} \cdot T_{m3} \right) - \in_{ktl} \cdot \left(\delta_{j1} - T_{j3} \cdot T_{13} \right) \right] \cdot i_{3} + \\ \left[\in_{kjm} \cdot T_{t3} \cdot T_{m3} - \in_{kt1} \cdot T_{j3} \cdot T_{13} \right] \cdot i_{4} \end{matrix} \right\}$$

The same procedure gives:

$$I_{ns_{R} np_{tS}}^{k} = +i \cdot \hbar \cdot \in_{kt1} \cdot T_{13} \cdot i_{1}$$

$$I_{ns_{tR} ns_{S}}^{k} = -i \cdot \hbar \cdot \in_{kt1} \cdot T_{13} \cdot i_{2}$$

$$i_{1} = \left\langle ns_{ZS}^{'} \middle| np_{ZR}^{'} \right\rangle, \quad i_{2} = \left\langle ns_{S}^{'} \middle| np_{ZR}^{'} \right\rangle, \quad i_{3} = \left\langle np_{xR}^{'} \middle| np_{xS}^{'} \right\rangle, \quad i_{4} = \left\langle np_{zR}^{'} \middle| np_{zS}^{'} \right\rangle$$

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Where $k,j,t,m,l=1,2,3.$ similarly J_{rs}^k becomes:

$$J_{rs}^k = \sum_{p=1}^{3}\sum_{q=1}^{3}\sum_{t=1}^{4}\sum_{u=1}^{4}\left(\delta_{pq}-T_{kp}\cdot T_{kq}\right)\cdot T_{rt}\cdot T_{su}\cdot\left\langle\varphi_{t(R)}'\left|x_{pR}'\cdot x_{qR}'+x_{pS}'\cdot x_{qS}'\right|\varphi_{u(S)}'\right\rangle$$

For a (ns,np) basis, using orthogonality of T:

$$I_{ns_R ns_S}^k = \left(1+T_{k3}^2\right)\cdot j_1 + \left(1-T_{k3}^2\right)\cdot j_2$$

$$
\begin{bmatrix}
J_{np_{iR}np_{jS}}^k = \left(\delta_{ij}-T_{i3}\cdot T_{j3}\right)\cdot\left[3\cdot j_8+j_9+T_{k3}^2\cdot\left(j_8-j_9\right)\right]-2\cdot\left[T_{i1}\cdot T_{j1}\cdot T_{k1}^2+T_{i2}\cdot T_{j2}\cdot T_{k2}^2\right]\cdot j_8 \\
+T_{i3}\cdot T_{j3}\cdot\left[j_{10}+j_{11}+T_{k3}^2\cdot\left(j_{10}-j_{11}\right)\right]-2\cdot T_{k1}\cdot T_{k3}\cdot\left(T_{i1}\cdot T_{j2}+T_{i2}\cdot T_{j1}\right)\cdot j_{12}-2\cdot T_{j3}\cdot T_{k3}\cdot \\
\left(\delta_{ik}-T_{i3}\cdot T_{k3}\right)\cdot j_{i13}-2\cdot T_{i3}\cdot T_{k3}\cdot\left(\delta_{ik}-T_{j3}\cdot T_{k3}\right)\cdot j_{13}-2\cdot T_{i3}\cdot T_{k3}\cdot\left(\delta_{jk}-T_{j3}\cdot T_{k3}\right)\cdot j_{14}
\end{bmatrix}
$$

$$J_{ns_R np_{iS}}^k = T_{i3}\cdot\left(1+T_{k3}^2\right)\cdot j_3 - T_{i3}\cdot\left(1+T_{k3}^2\right)\cdot j_4 - 2\cdot T_{k3}\cdot\left(\delta_{ik}-T_{i3}\cdot T_{k3}\right)\cdot j_5$$

$$J_{np_{iR}ns_S}^k = T_{i3}\cdot\left(1+T_{k3}^2\right)\cdot j_6 - T_{i3}\cdot\left(1+T_{k3}^2\right)\cdot j_7 - 2\cdot T_{k3}\cdot\left(\delta_{ik}-T_{i3}\cdot T_{k3}\right)\cdot j_5$$

$$j_p = \left\langle ns_R\left|x_{qR}^2+x_{qS}^2\right|nS_s\right\rangle \qquad\qquad j_p = \left\langle ns_R\left|x_{qR}^2+x_{qS}^2\right|np_{zs}\right\rangle$$

$$j_p = \left\langle np_{ZR}\left|x_{qR}^2+x_{qS}^2\right|nS_s\right\rangle \qquad\qquad j_8 = \left\langle np_{xR}\left|x_{qR}^2+x_{qS}^2\right|np_{xs}\right\rangle$$

$$j_p = \left\langle np_{zR}\left|x_{qR}^2+x_{qS}^2\right|np_{zs}\right\rangle$$

$$j_5 = \left\langle ns_R\left|x_R\cdot z_R+x_s\cdot z_s\right|np_{xs}\right\rangle$$

$$j_{12} = \left\langle np_{xR}\left|x_R\cdot y_R+x_s\cdot y_s\right|np_{ys}\right\rangle$$

$$j_{13} = \left\langle np_{xR}\left|x_R\cdot z_R+x_s\cdot z_s\right|np_{zs}\right\rangle$$

$$j_{14} = \left\langle np_{zR}\left|x_R\cdot z_R+x_s\cdot z_s\right|np_{xs}\right\rangle$$

Substituting $q=1$ gives $j_p=\left(p=1,3,6,8,10\right),$ $q=3$ gives

$$j_p=\left(p=2,4,7,9,11\right).$$

Auxiliary integrals i_p and j_q ; $p \in [1,14]$, in the R and S diatomic frame are computable exactly in elliptic coordinates.

2-Integrals for the nuclear screening tensor

Bicentric integrals with monocentric electron distribution are obtained from general formula by taking $S \equiv R$. The integrals $\left\langle \varphi_{r(R)} \left| \hat{O}_N \right| \varphi_{s(R)} \right\rangle$ become calculated in spherical polar coordinates after translating $\hat{O}_N$ operator to R. The above rotation matrix should be used for directional quantities. Using the matrix equation $v = T \cdot v'$ we expand the integrals M_{rs}^k in the diatomic frame axes:

$$M_{rs}^k = \sum_{p=1}^3 \sum_{q=1}^3 \sum_{t=1}^4 \sum_{u=1}^4 2 \cdot T_{kq} \cdot T_{rt} \cdot T_{su} \cdot \left\langle \varphi_t' \left| \frac{\left(\vec{u}_p' \wedge \vec{r}_R' \right) \cdot \left(\vec{u}_q' \wedge \vec{r}_N' \right)}{r_N^3} \right| \varphi_{u)}' \right\rangle$$

$$\forall i = 1,2,3 \ , \quad \vec{r}_N' = \vec{r}_R' + \vec{R} \qquad \rightarrow \qquad x_{iN}' = x_{iR}' + \delta_{i3} \cdot R$$

$$r_N^3 = \left[r_R^2 + R^2 + 2 \cdot r_R \cdot R \cdot \cos_R \right]^{3/2}$$

The second term in the last equation of M_{rs}^k contains operator of M_{rs}^k integrals.

Within the former expression, this operator can be expanded as follows:

$$\frac{\left(\vec{u}_k \wedge \vec{r}_R \right) \cdot \left(\vec{u}_k \wedge \vec{r}_N \right)}{r_N^3} = \sum_{p=1}^3 \sum_{q=1}^3 T_{kp} \cdot T_{kq} \cdot \frac{\left(\vec{u}_p' \wedge \vec{r}_R' \right) \cdot \left(\vec{u}_q' \wedge \vec{r}_N' \right)}{r_N^3} =$$

$$\sum_{p=1}^3 T_{kp}^2 \cdot \hat{O}\left(R, x_p'\right) - \sum_{q=1}^2 T_{kq} \cdot T_{k3} \cdot \frac{R \cdot x_{qR}'}{r_N^3} - 2 \cdot \sum_{p \langle q} T_{kp} \cdot T_{kq} \cdot \frac{x_{pR}' \cdot x_{qR}'}{r_N^3}$$

$$\hat{O}\left(R, x_p'\right) = \frac{\left(r_R'^2 - x_{pR}'^2 \right) + \left(1 - \delta_{p3} \right) \cdot R \cdot x_{3R}'}{r_N^3}$$

For a (ns, np) basis functions we get:

$$M_{ns_{iR} np_{jR}}^k = 2 \cdot \left[\left(1 - T_{k3}^2 \right) \cdot m_1 + T_{k3}^2 \cdot m_2 \right]$$

$$M^k_{ns_{iR}np_{jR}} = 2 \cdot \left\{ \begin{array}{l} \left(T_{i1} \cdot T_{j1} \cdot T^2_{k1} + T_{i2} \cdot T_{j2} \cdot T^2_{k2} \right) \cdot m_7 + \left(T_{i1} \cdot T_{j1} \cdot T^2_{k2} + T_{i2} \cdot T_{j2} \cdot T^2_{k1} \right) \cdot m_8 + \\[2mm] T_{i3} \cdot T_{j3} \cdot \left(1 - T^2_{k3} \right) \cdot m_9 + T^2_{k3} \cdot \left(\delta_{ij} - T_{i3} \cdot T_{j3} \right) \cdot m_{10} + T_{i3} \cdot T_{j3} \cdot T^2_{k3} \cdot m_{11} - \\[2mm] T_{k3} \cdot \left[T_{j3} \cdot \left(\delta_{ik} - T_{i3} \cdot T_{k3} \right) + T_{i3} \cdot \left(\delta_{ik} - T_{j3} \cdot T_{k3} \right) \right] \cdot \left(m_{12} + 2 \cdot m_{13} \right) - \\[2mm] 2 \cdot T_{k1} \cdot T_{k2} \cdot \left(T_{i1} \cdot T_{j2} + T_{i2} \cdot T_{j1} \right) \cdot m_{14} \end{array} \right\}$$

$$M^k_{ns_{R}np_{jR}} = 2 \cdot \left[T_{j3} \left(1 - T^2_{k3} \right) \cdot m_3 + T_{j3} \cdot T^2_{k3} \cdot m_4 - T_{k3} \cdot \left(\delta_{jk} - T_{j3} \cdot T_{k3} \right) \cdot \left(2 \cdot m_5 + m_6 \right) \right]$$

$$M^k_{ns_{jR}np_{R}} = M^k_{ns_{R}np_{jR}}$$

The monocentric integrals m_i $(i \in [1,14])$ can be evaluated analytically in spherical polar coordinates with the origin on atom R where the AO are centered. As with the M^k_{rs} integrals the K^k_{rs} bicentric terms are expanded in the diatomic frame:

$$K^k_{rs} = \sum_{p=1}^{3} \sum_{t=1}^{3} \sum_{u=1}^{4} T_{kp} \cdot T_{rt} \cdot T_{su} \cdot \left[\left\langle \varphi'_t \left| \frac{\vec{u}'_p \cdot \vec{L}_N}{r^3_N} \right| \varphi'_u \right\rangle - \left\langle \varphi'_u \left| \frac{\vec{u}'_p \cdot \vec{L}_N}{r^3_N} \right| \varphi'_t \right\rangle \right]$$

The center of the operator is translated $\vec{r}_N \rightarrow \vec{r}_R + \vec{R}$; $\overrightarrow{NR}$; and it is expanded in the diatomic frame to give is its molecular frame expression:

$$\vec{u}_k \cdot \vec{L}_N = \vec{u}_k \cdot \left(\vec{r}_N \wedge \vec{p}_N \right) = \vec{u}_k \cdot \left[\left(\vec{r}_R + \vec{R} \right) \wedge \vec{R}_R \right]$$

$$\vec{u}_k \cdot \vec{L}_N = \sum_{i=1}^{3} T_{ki} \cdot \vec{u}'_i \cdot \vec{L}_R + \sum_{i=1}^{3} \in_{i3t} \cdot R \cdot T_{ki} \cdot \vec{u}'_t \cdot \vec{p}'_R$$

$\vec{u}_k \cdot \vec{L}_N$ is the kth component of the angular momentum in the molecular frame. $\vec{u}'_i \cdot \vec{L}_N$ the ith in the diatomic frame. The impulsion of a particle at $\vec{r}$ is given by:

$$\hat{\vec{p}} = -i \cdot \hbar \cdot \frac{\vec{r}}{r} \cdot \frac{\partial}{\partial r} - \frac{1}{r^2} \cdot \sum_{t=1}^{3} \sum_{j=1}^{3} \sum_{k=1}^{3} \in_{tjk} \cdot \vec{u}_t \cdot x_j \cdot \hat{L}_k$$

Replacing the operator $\hat{\vec{p}}$ in $\vec{u}_k \cdot \vec{L}_N$ and using the identity:

$$\sum_{t=1}^{3}\sum_{j=1}^{3}\sum_{k=1}^{3} \in_{i3t} \cdot \in_{tj1} \cdot T_{ki} \cdot x^{'jR} \cdot \hat{L}_{iR} = \sum_{t=1}^{2} T_{kt} \cdot \left(x_{tR}' \cdot \hat{L}_{3R}' - x_{3R}' \cdot \hat{L}_{tR}' \right)$$

$\vec{u}_k \cdot \vec{L}_N$ become:

$$\vec{u}_k \cdot \vec{L}_N = -i \cdot \hbar \cdot \frac{R}{r_R'} \cdot \sum_{i=1}^{2} \in_{i3t} \cdot T_{ki} \cdot x_{tR}' \cdot \frac{\partial}{\partial r_R'} + \left(1 + \frac{R \cdot x_{3R}'}{r_R'^{2}} \right) \cdot \sum_{t=1}^{3} T_{kt} \cdot \hat{L}_{tR}' -$$

$$\frac{R}{r_R'^{2}} \cdot \sum_{t=1}^{3} T_{kt} \cdot x_{tR}' \cdot \hat{L}_{3R}'$$

The radial derivatives are readily carried out and these relations give:

$$K^{k}_{ns_{iR}ns_{jR}} = -i \cdot \hbar \cdot \left\{ \begin{array}{l} \left[T_{i3} \cdot \left(T_{j1} \cdot T_{k2} - T_{j2} \cdot T_{k1} \right) + T_{j3} \cdot \left(T_{i2} \cdot T_{k1} - T_{i1} \cdot T_{k2} \right) \right] \\ \cdot k_7 + 2 \cdot T_{k3} \cdot \left(T_{i1} \cdot T_{j2} - T_{i2} \cdot T_{j1} \right) \cdot k_6 \end{array} \right\}$$

$$K^{k}_{ns_R ns_{iR}} = -i \cdot \hbar \cdot \left(T_{i1} \cdot T_{k2} - T_{i2} \cdot T_{k1} \right) \cdot \left(k_1 + k_2 \right)$$

$$K^{k}_{np_{iR}ns_R} = - K^{k}_{ns_R np_{iR}}$$

Integrals k_i $(i \in [1,7])$ are evaluated analytically as for m_i integrals.

3-Analytical integration for m_i and k_i

m_i and k_i are rigorously integrable in the $\left(R, x_R' y_R' z_R' \right)$ frame in spherical polar coordinates. Let $r_R' \equiv r$, $\theta_R' \equiv \theta$, $\varphi_R' \equiv \varphi$. For a STO basis, m_i or k_i, labeled n_i, become:

$$n_i = \left\langle \varphi_p \left| \hat{O}(\vec{r}) \right| \varphi_q \right\rangle = N_p \cdot N_q \cdot \int_0^\infty \chi_p^* \cdot \left[\int_0^\pi \int_0^{2\pi} \Omega_p^* \cdot \hat{O}(\vec{r}) \cdot \Omega_q \cdot \sin\theta \cdot d\theta \cdot d\varphi \right]$$

$$\cdot \chi_q \cdot r^2 \cdot dr$$

Where $N_i = N_p \cdot N_q \cdot I_{pq}$ and:

$$I_{pq} = \left\langle \chi_p \left| T_{pq}(r) \right| \chi_q \right\rangle = \int_0^\infty \chi_p^* \cdot T_{pq}(r) \cdot \chi_q \cdot r^2 \cdot dr$$

$$T_{pq}(r) = \left\langle \Omega_p \left| \hat{O}(\vec{r}) \right| \Omega_q \right\rangle = \int_0^\infty \int_0^{2\pi} \Omega_p^* \cdot \hat{O}(\vec{r}) \cdot \Omega_q \cdot \sin\theta \cdot d\theta \cdot d\varphi$$

Our procedure for m_i gives:

$$m_1 = \langle ns | \hat{O}(R,x) | ns \rangle = \langle ns | \frac{r^2 \cdot (1 - \sin^2 \theta \cdot \cos^2 \varphi) + r \cdot R \cdot \cos \theta}{\sqrt{(r^2 + R^2 + 2 \cdot r \cdot R \cdot \cos \theta)^3}} | ns \rangle$$

Given the relation $\Omega_{ns} = 1$, the auxiliary integrals T_{nsns} takes the form:

$$T_{nsns} = \langle \Omega_{ns} | \hat{O}(R,x) | \Omega_{ns} \rangle = \int_0^\pi \int_0^{2\pi} \frac{r^2 \cdot (1 - \sin^2 \theta \cdot \cos^2 \varphi) + r \cdot R \cdot \cos \theta}{\sqrt{(r^2 + R^2 + 2 \cdot r \cdot R \cdot \cos \theta)^3}} \cdot \sin \theta \cdot d\theta \cdot d\varphi$$

Or integrating over φ :

$$T_{nsns} = \pi \cdot \left[r^2 \cdot (K_0 + K_2) + 2 \cdot r \cdot R \cdot K_1 \right]$$

$$K_n(r) = \int_{-1}^{+1} \frac{x^n \cdot dx}{\sqrt{(a + b \cdot x)^3}}$$

$$a = r^2 + R^2 \quad , \quad b = 2 \cdot r \cdot R \quad , \quad x = \cos \theta$$

The integrals $K_n(r)$; $n = 0,1,2$; in T_{nsns} give:

$$K_0(r) = \int_{-1}^{+1} \frac{dx}{\sqrt{(a + b \cdot x)^3}} = \frac{-1}{r \cdot R} \left[\frac{1}{r + R} - \frac{1}{|r - R|} \right]$$

$$= \begin{cases} K_0^+(r) = +\dfrac{2}{r \cdot (r^2 - R^2)} & R \prec r \prec \infty \\[3mm] K_0^-(r) = -\dfrac{2}{R \cdot (r^2 - R^2)} & 0 \leq r \prec R \end{cases}$$

$$K_1(r) = \int_{-1}^{+1} \frac{x \cdot dx}{\sqrt{(a + b \cdot x)^3}} = \frac{-1}{r \cdot R} \left[\frac{1}{r + R} - \frac{1}{|r - R|} - \frac{1}{r \cdot R} (r + R - |r - R|) \right]$$

$$= \begin{cases} K_1^+(r) = +\dfrac{2 \cdot R}{r^2 \cdot (r^2 - R^2)} & R \prec r \prec \infty \\[3mm] K_1^-(r) = -\dfrac{2 \cdot r}{R^2 \cdot (r^2 - R^2)} & 0 \leq r \prec R \end{cases}$$

$$K_2(r) = \int_{-1}^{+1} \frac{x \cdot dx}{\sqrt{(a + b \cdot x)^3}} =$$

$$\frac{-1}{r \cdot R} \left[\frac{1}{r + R} - \frac{1}{|r - R|} + \frac{2}{3 \cdot r^3 \cdot R^3} \cdot \left[r \cdot R \cdot (r + R + |r - R|) - (r^2 + R^2) \cdot (r + R - |r - R|) \right] \right]$$

$$= \begin{cases} K_2^+(r) = +\dfrac{2 \cdot (r^2 + 2 \cdot R^2)}{3 \cdot r^3 \cdot (r^2 - R^2)} & R \prec r \prec \infty \\[4mm] K_2^-(r) = -\dfrac{2 \cdot (R^2 + 2 \cdot r^2)}{3 \cdot R^3 \cdot (r^2 - R^2)} & 0 \le r \prec R \end{cases}$$

By replacing K_0, K_1 and K_2 in T_{nsns} we obtain:

$$T_{nsna}^+ = +\frac{8 \cdot \pi}{3 \cdot r} \qquad R \prec r \prec \infty$$

$$T_{nsna}^- = -\frac{4 \cdot \pi \cdot r^2}{3 \cdot R^3} \qquad 0 \le r \prec R$$

As the auxiliary functions $I_{pq}\left(T_{pq} = T_{pq}^+ + T_{pq}^-\right)$, I_{pq} splits up into two integrals:

$$I_{pq} = \int_0^\infty r^{(n_p + n_q)} \cdot e^{-(\alpha_p + \alpha_q)r} \cdot T_{pq}(r) \cdot dr = I_{pq}^- + I_{pq}^+$$

$$I_{pq}^- = \int_0^R r^{(n_p + n_q)} \cdot e^{-(\alpha_p + \alpha_q)r} \cdot I_{pq}^-(r) \cdot dr$$

$$I_{pq}^+ = \int_R^\infty r^{(n_p + n_q)} \cdot e^{-(\alpha_p + \alpha_q)r} \cdot I_{pq}^+(r) \cdot dr$$

When the $I_{pq}^+(r)$ functions are used in I_{pq}, I_{pq}^- and I_{pq}^+ and using Euler's integrals [32]:

$$\int_0^R r^n \cdot e^{-\alpha \cdot r} \cdot dr = \frac{n! - \Gamma(n+1, \rho)}{\alpha^{n+1}}$$

$$\int_R^\infty r^n \cdot e^{-\alpha \cdot r} \cdot dr = \frac{\Gamma(n+1, \rho)}{\alpha^{n+1}}$$

$$\Gamma(n+1, \rho) = \int_\rho^\infty t^n \cdot e^{-t} \cdot dt = n! \cdot e^{-\rho} \cdot \sum_{k=0}^n \frac{\rho^k}{k!}$$

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and stand:

$$\alpha = \alpha_p + \alpha_q \quad , \quad \alpha_p = \frac{Z_p^*}{n_p \cdot a_0} \quad , \quad \alpha_q = \frac{Z_q^*}{n_q \cdot a_0} \quad , \quad \rho = \left(\alpha_p + \alpha_q \right) \cdot R$$

The I_{nsns} becomes:

$$I_{nsns} = \langle \chi_{ns} | T_{nsns} | \chi_{ns} \rangle = \int_0^\infty r^{2n} \cdot e^{-2 \cdot \alpha_{ns} \cdot r} \cdot T_{nsns}(r) \cdot dr =$$

$$\int_0^R r^{2n} \cdot e^{-2 \cdot \alpha_{ns} \cdot r} \cdot T_{nsns}^-(r) \cdot dr + \int_0^R r^{2n} \cdot e^{-2 \cdot \alpha_{ns} \cdot r} \cdot T_{nsns}^+(r) \cdot dr$$

Therefore, posing $\rho = 2 \cdot \alpha_{ns} \cdot R$:

$$m_1 = \frac{2 \cdot \alpha_{ns}}{3 \cdot (2n)!} \frac{1}{\rho^3} \left[-(2n+2)! + \Gamma(2n+3, \rho) + 2 \cdot \rho^3 \cdot \Gamma(2n, \rho) \right]$$

Where $\Gamma(n, \rho)$ is the gamma function. For $1s$ AO, $n = 1$, we get:

$$m_1 = \frac{\alpha_{1s}}{\rho^3} \cdot \left\{ -8 + \left[+8 + 8 \cdot \rho + 4 \cdot \rho^2 + 2 \cdot \rho^3 + \rho^4 \right] \cdot e^{-\rho} \right\}$$

There are four auxiliary integrals $K_n(r)$ required to evaluate K_{rs}^k. We have demonstrated here the procedure of calculation for the most simpler $K_n(r)$, $I_{pq}^\pm(r)$ and m_i integrals concerning the basis functions nsns. For a *nsnp* basis, the calculations are more complex. The integrals m_i and k_i have been calculated over a *nsnp* STO basis, for any integer n, and are expressed using gamma functions in a practical form adapted to a Fortran program.

VIII-Approximate analytical evaluation of integrals in the nuclear screening tensor not retained by NDDO

Taking into account the obvious relation $\vec{r}_N = \vec{d}_A + \vec{r}_A$ $(A = R \ or \ S)$ the integrals M_{rs}^k become:

$$M_{rs}^k = \sum_{i \neq k = 1}^{3} \left[\left\langle \varphi_r \left| \frac{x_{iR}^2 + x_{iS}^2}{r_N^3} \right| \varphi_s \right\rangle + X_{iR} \cdot \left\langle \varphi_r \left| \frac{x_{iR}}{r_N^3} \right| \varphi_s \right\rangle + X_{iS} \cdot \left\langle \varphi_r \left| \frac{x_{iS}}{r_N^3} \right| \varphi_s \right\rangle \right]$$

A London type approximation [27] simplifies their evaluation:

$$\vec{r}_N \cong \frac{1}{2} \cdot \left(\vec{d}_R + \vec{d}_S\right) = \vec{d}_{RS}$$

The M_{rs}^k integrals become:

$$M_{r(R)s(S)}^k = \frac{1}{d_{RS}^3} \cdot \left\{ J_{rs}^k + \sum_{i \neq k=1}^{3} \left[X_{iR} \cdot D_{rs}^{iR} + X_{iS} \cdot D_{rs}^{iS} \right] \right\}$$

$$D_{r(R)s(S)}^{iA} = \left\langle \varphi_{r(R)} \left| x_{iA} \right| \varphi_{s(S)} \right\rangle \quad A = R, S$$

The integrals J_{rs}^k are determined in the above section. The last equation of $M_{r(R)s(S)}^k$ constitute for M_{rs}^k an approximate analytical formula in the molecular frame. The transformation to the diatomic frame of $D_{r(R)s(S)}^{iA}$ is similar to that for $J_{r(R)s(S)}^k$. Finally:

$$D_{r(R)s(S)}^{iA} = \sum_{p=1}^{3}\sum_{t=1}^{4}\sum_{u=1}^{4} T_{ip} \cdot T_{rt} \cdot T_{su} \cdot \left\langle \varphi_{t(R)}' \left| X_{pA}' \right| \varphi_{u(S)}' \right\rangle$$

Orthogonality of T gives the reduced formulas (for $nsnp$ basis):

$$D_{ns_R ns_S}^{iA} = T_{i3} \cdot d_p \qquad \left(A = R \Rightarrow p = 1 \; ; \; A = S \Rightarrow p = 9\right)$$

$$D_{np_{jR} np_{tS}}^{iR} = T_{i3} \cdot T_{j3} \cdot T_{t3} \cdot d_6 +$$

$$\left[T_{i3} \cdot \left(\delta_{j3} - T_{t3} \cdot T_{t3}\right) + T_{j3} \cdot \left(\delta_{i3} - T_{t3} \cdot T_{t3}\right) \cdot d_7 + T_{t3} \cdot \left(\delta_{ij} - T_{i3} \cdot T_{j3}\right) \cdot d_8 \right]$$

$$D_{np_{jR} np_{tS}}^{iS} = T_{i3} \cdot T_{j3} \cdot T_{t3} \cdot d_{12} +$$

$$\left[T_{i3} \cdot \left(\delta_{jt} - T_{j3} \cdot T_{t3}\right) + T_{t3} \cdot \left(\delta_{ij} - T_{i3} \cdot T_{j3}\right) \cdot d_8 + T_{j3} \cdot \left(\delta_{it} - T_{i3} \cdot T_{t3}\right) \cdot d_7 \right]$$

$$D_{ns_R np_{jS}}^{iA} = \left(\delta_{jt} - T_{i3} \cdot T_{j3}\right) \cdot d_2 + T_{i3} \cdot T_{j3} \cdot d_v$$

$$D_{ns_{jR} np_S}^{iA} = \left(\delta_{jt} - T_{i3} \cdot T_{j3}\right) \cdot d_4 + T_{i3} \cdot T_{j3} \cdot d_v \quad \left(A = R \Rightarrow v = 5; A = S \Rightarrow v = 11\right)$$

$$d_p = \left\langle ns_R \left| z_A \right| n_S \right\rangle \quad \left(A = R \Rightarrow p = 1; A = S \Rightarrow p = 9\right)$$

$$d_p = \left\langle ns_R \left| x_{qA} \right| np_{xqS} \right\rangle \quad \left(A = R: q = 1 \Rightarrow p = 2, q = 3; A = S: q = 3 \Rightarrow p = 10\right)$$

$$d_p = \left\langle ns_R \left| x_{qA} \right| np_{xqS} \right\rangle \quad \left(A = R: q = 1 \Rightarrow p = 4, q = 3 \Rightarrow p = 5; A = S: q = 3 \Rightarrow p = 11\right)$$

$$d_p = \left\langle np_{zR} \left| z_A \right| np_{xS} \right\rangle \quad \left(A = R \Rightarrow p = 6 \; ; A = S \Rightarrow p = 12\right)$$

$$d_p = \langle np_{xR} | z_A | np_{xS} \rangle \quad (A = R \Rightarrow p = 7 \; ; A = S \Rightarrow p = 12)$$

The angular moment operators $\vec{L}_N$, $\vec{L}_A$ and the impulsion $\vec{P}_A$, defined respectively with regard to the screened nucleus N and the atom A $(A = R \; or \; S)$ are, owing to the invariance of gradient operator, related by:

$$\vec{u}_k \cdot \vec{L}_N = \vec{u}_k \cdot \vec{L}_A + \sum_{i \neq k=1}^{3} \sum_{q=1}^{3} \in_{ikq} \cdot x_{qA} \cdot \vec{u}_i \cdot \vec{P}_A$$

Substituting the last equation into $K^k_{r(R)s(S)}$ and taking the London type approximation into account we obtain:

$$K^k_{r(R)s(S)} = \frac{1}{d_{RS}^3} \cdot \left\{ I^k_{rs} + \sum_{i \neq k=1}^{3} \sum_{q=1}^{3} \in_{ikq} \cdot \left(X_{qR} + X_{qS} \right) \cdot P^i_{rs} \right\}$$

$$P^i_{r(R)s(S)} = \langle \varphi_{r(R)} | \hat{p}_{iS} | \varphi_{s(S)} \rangle = \langle \varphi_{r(R)} | -i \cdot \hbar \cdot \frac{\partial}{\partial X_{iS}} | \varphi_{s(S)} \rangle$$

It appears that, using our approximation, that bi or tricentric integrals K^k_{rs} can be expressed in terms of bicentric angular momentum $I^k_{r(R)s(S)}$ and impulsion $P^i_{r(R)s(S)}$ integrals. By the action of the derivative operator on a *nsnp* AO basis, we obtain in the molecular system of coordinates:

$$P^i_{r(R)s(S)} = i \cdot \hbar \cdot \langle \varphi_{r(R)} | \alpha_{sS} \cdot r_S^{-1} \cdot x_{iS} - (n_{sS} - 1) \cdot r_S^{-2} \cdot x_{iS} | ns_s \rangle$$

$$P^i_{r(R)np_{jS}} = i \cdot \hbar \cdot \langle \varphi_{r(R)} | \alpha_{pS} \cdot r_S^{-1} \cdot x_{iS} - (np_{sS} - 2) \cdot r_S^{-2} \cdot x_{iS} | ns_{js} \rangle -$$

$$i \cdot \hbar \cdot \delta_{ij} \langle \varphi_{r(R)} | r_S^{-1} | ns_S^P \rangle$$

α_{ps} and n_{ps} are exponent and principal quantum number of the np_{js} AO. α_{sS} and n_{sS} are those of the ns_S AO. The ket $|ns_s^P\rangle$ correspond formally to an *np* AO. These integrals are both bicentric. Their form in the diatomic frame is:

$$P^i_{r(R)np_{jS}} = i \cdot \hbar \cdot \sum_{u=1}^{4} \sum_{v=1}^{3} T_{ru} \cdot T_{iv} \langle \varphi'_{u(R)} | \alpha_{sS} \cdot \frac{x'_{vs}}{r_s} - (n_{sS} - 1) \cdot \frac{x'_{vs}}{r_S^2} | ns'_S \rangle$$

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$$P^i_{r(R)np_{jS}} = i \cdot \hbar \cdot \sum_{u=1}^{4}\sum_{v=1}^{3}\sum_{w=1}^{3} T_{ru} \cdot T_{iv} \cdot T_{jw} \left\langle \varphi'_{u(R)} \middle| \alpha_{sS} \cdot \frac{x'_{vs}}{r_s} - (n_{pS}-2)\cdot \frac{x'_{vs}}{r_S^2} \middle| np'_{wS} \right\rangle$$

$$- i \cdot h \cdot \delta_{ij} \cdot \sum_{u=1}^{4} T_{ru} \cdot \left\langle \varphi'_{u(R)} \middle| \frac{1}{r_S} \middle| ns_S^p \right\rangle$$

Orthogonality of T leads to simplifications:

$$P^i_{ns_R ns_S} = -i \cdot \hbar \cdot \left\{ T_{i3} \cdot [n_{sS}-1] \cdot p_1 - \alpha_{sS} \cdot p_2 \right\}$$

$$P^i_{np_{jR}np_{tS}} = -i \cdot \hbar \cdot \left\{ \begin{array}{c} -\alpha_{pS} \cdot \\ \left\{ \begin{array}{l} [T_{i3} \cdot T_{j3} \cdot T_{t3} \cdot p_{13} + [\delta_{jt} \cdot T_{i3} + T_{t3} \cdot (\delta_{ij} - 2 \cdot T_{i3} \cdot T_{j3})] \\ \cdot p_{1s} + T_{j3} \cdot (\delta_{it} - T_{i3} \cdot T_{t3}) \cdot p_{15} + T_{j3} \cdot (\delta_{it} - T_{i3} \cdot T_{t3}) \cdot p_{17} \end{array} \right\} + \\ (n_{ps}-2) \cdot \left\{ \begin{array}{l} T_{i3} \cdot T_{j3} \cdot T_{t3} \cdot p_{12} + \left[\begin{array}{l} \delta_{jt} \cdot T_{i3} + T_{t3} \cdot \\ (T_{i1} \cdot T_{j1} - T_{i3} \cdot T_{j3}) \end{array} \right] \cdot \\ p_{14} + T_{j3} \cdot (\delta_{it} - T_{i3} \cdot T_{t3}) \cdot p_{16} + \\ T_{i2} \cdot T_{j2} \cdot T_{t3} \cdot p_{18} \end{array} \right\} \\ + \delta_{it} \cdot T_{j3} \cdot p_{19} \end{array} \right\}$$

$$P^i_{ns_R np_{jS}} = -i \cdot \hbar \cdot \left\{ \begin{array}{l} -\alpha_{pS} \cdot [T_{i3} \cdot T_{j3} \cdot p_4 + (\delta_{ij} - T_{i3} \cdot T_{j3}) p_9] + \\ \delta_{ij} \cdot p_7 + (n_{pS}-2) \cdot [T_{i3} \cdot T_{j3} \cdot p_3 + (\delta_{ij} - T_{i3} \cdot T_{j3}) \cdot p_5] \end{array} \right\}$$

$$P^i_{np_{jR}ns_S} = -i \cdot \hbar \cdot \left\{ \begin{array}{l} -\alpha_{sS} \cdot [T_{i3} \cdot T_{j3} \cdot p_4 + (\delta_{ij} - T_{i3} \cdot T_{j3}) p_{11}] + \\ (n_{sS}-1) \cdot [T_{i3} \cdot T_{j3} \cdot p_8 + (\delta_{ij} - T_{i3} \cdot T_{j3}) \cdot p_{10}] \end{array} \right\}$$

$$P_t = \left\langle ns_R \middle| r_S^{-q} \cdot z_S \middle| ns_S \right\rangle \qquad [q=1 \Rightarrow t=2; q=2 \Rightarrow t=1]$$

$$P_t = \left\langle ns_R \middle| r_S^{-p} \cdot x_{qS} \middle| np_{xqS} \right\rangle \qquad \left[\begin{array}{l} p=1 \Rightarrow q=1 \Rightarrow q=3 \Rightarrow t=4; \\ p=2 : q=1 \Rightarrow t=5, q=3 \Rightarrow t=3 \end{array} \right]$$

$$P_t = \left\langle np_{xqR} \middle| r_S^{-p} \cdot x_{qS} \middle| ns_S \right\rangle \qquad \left[\begin{array}{l} p=1 : q=1 \Rightarrow q=3 \Rightarrow t=4; \\ p=2 : q=1 \Rightarrow t=5, q=3 \Rightarrow t=8 \end{array} \right]$$

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$$P_t = \left\langle np_{xrR} \left| r_S^{-p} \cdot x_{qS} \right| np_{xvS} \right\rangle \quad \begin{pmatrix} u = q = v = 3 : p = 1 \Rightarrow t = 13, p = 2 \Rightarrow t = 12 \; ; \\ u = v = 1, q = 3 : p = 1 \Rightarrow t = 15, p = 2 \Rightarrow t = 14; \\ u = 3, q = v = 1 : p = 1 \Rightarrow t = 17, p = 2 \Rightarrow t = 16; \\ u = q = 1, p = 2 \Rightarrow t = 18 \end{pmatrix}$$

$$P_9 = \left\langle np_{zR} \left| r_S^{-1} \right| ns_S^P \right\rangle \qquad P_7 = \left\langle np_R \left| r_S^{-1} \right| ns_S^P \right\rangle$$

The bicentric integrals d_q and p_t ; $t \in [1,19]$; defined in the diatomic frame can be integrals analytically in elliptic coordinates.

IX-Conclusion

At the NDDO level we have given a detailed and rigorous treatment of the integrals involved in the susceptibility and nuclear screening tensors for a GIAO-STO base within the London approximation for arbitrary molecular frames axes and for arbitrary direction of magnetic field. Analytical formulas are established here for a *nsnp* basis and applied to the first three rows of the periodic table. The integrals involved in the nuclear screening tensor (usually zero in NDDO) are also included. Their evaluation involves a London type approximation which allows them to be calculated in elliptic coordinates. Ours analytic and compacts formulas are helpful for a FORTRAN program.

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