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OPERATOR EXPANSION: DEFINITION AND MOLECULAR INTEGRAL APPLICATIONS

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RESUM

Es defineix l'expansió general d'operadors com una combinació lineal de projectors i s'exposa la seva aplicació generalitzada al càlcul d'integrals moleculars. Com a exemple numèric, es fa l'aplicació al càlcul d'integrals de repulsió electrònica entre quatre funcions de tipus *s* centrades en punts diferents, i es mostren tant resultats del càlcul com la definició d'escalat respecte a un valor de referència, que facilitarà el procés d'optimització de l'expansió per uns paràmetres arbitraris. Es donen resultats ajustats al valor exacte.

RESUMEN

Se define la expansión general de operadores como combinación lineal de proyectores y se expone la aplicación generalizada al cálculo de integrales moleculares. Un ejemplo numérico se aplica al cálculo de integrales de repulsión electrónica entre cuatro funciones de tipo *s* centradas en puntos diferentes, mostrando tanto resultados de cálculos como la definición de un escalado con respecto a un valor de referencia, que facilitará el proceso de optimización de la expansión para unos parámetros arbitrarios, dando resultados ajustados al valor exacto.

ABSTRACT

A general operator expansion as a linear combination of projectors is defined, and also its generalized application to integral computation. As a numerical example, it has been applied to electron repulsion integral computation between four *s*-type functions centered at different points. Numerical results are shown and a scaling with respect to a reference value is defined, opening an easier way to optimize the expansion for any set of parameters, and giving accurate results with this kind of integrals.

Keywords: Electron Repulsion Integrals, Integral, Gaussian Functions, Operator, Operator Expansion, Repulsion Operator.

INTRODUCTION

At the Institute of Computational Chemistry, our group has been studying the development and applications of some new theories in Quantum Mechanics [1]. In this work, it is proposed a new methodology to obtain an operator expansion as a bilinear combination of projectors. As a particular case, the operator $\hat{r}_{12}^{-1}$ is expanded, and this is applied to the computation of electron repulsion integrals.

OPERATOR EXPANSION

A *Projector*, or *Projection Operator*, can be defined as a Linear Operator $\hat{P}$ in a vector space V such as $\hat{P}^2 = \hat{P}$ [2]. An *Elementary Projector* is a projector build from a normalized vector $|a>$, as

$$\hat{P}_a = |a\rangle\langle a| \tag{1}$$

Any operator $\hat{O}$ can be expanded as a linear combination of elementary projectors:

$$\hat{O} = \sum_{a=1}^{\infty} c_a |a\rangle\langle a| \quad , \tag{2}$$

where the $\{c_a\}$ parameters are coefficients depending on the nature of $\hat{O}$ and $\{|a>\}$. In a more general way, the $\hat{O}$ operator can be expanded as a bilinear form as:

$$\hat{O} = \sum_{p=1}^{\infty}\sum_{q=1}^{\infty} c_{pq} |p\rangle\langle q| , \tag{3}$$

where the elements in the set of vectors $\{|p>\}$ are functions and the expansion coefficients $\{c_{pq}\}$ are collected in the matrix C.
For practical purposes, the expansion is truncated at a finite number of terms:

$$\hat{O} \equiv \sum_{p=1}^{N_p}\sum_{q=1}^{N_q} c_{pq} |p\rangle\langle q| , \tag{4}$$

and thus, the C matrix will become of finite dimension. The $\hat{O}$ operator can be approximated changing the N_p and N_q values, until the expansion is good enough as to obtain numerical results within a desired precision. If the set of vectors $\{|p>\}$ in the expansion (4) forms a complete basis, such an approximation will become an equality.

The expansion of the $\hat{O}$ operator can be applied in any expression where this operator appears; e.g., in the computation of operator matrix elements with respect to the same basis $\{|p>\}$. In this case, the matrix elements have the generic expression:

$$O_{rs} = \langle r|\hat{O}|s\rangle \equiv \langle r| \left(\sum_{p=1}^{N_p}\sum_{q=1}^{N_q} c_{pq} |p\rangle\langle q| \right) |s\rangle = \tag{5}$$

$$= \sum_{p=1}^{N_p}\sum_{q=1}^{N_q} c_{pq} \langle r|p\rangle\langle q|s\rangle$$

or,

$$O_{rs} = \sum_{p=1}^{N_p}\sum_{q=1}^{N_q} c_{pq} S_{rp} S_{qs} \quad , \tag{6}$$

which can be written in matrix form as

$$\boldsymbol{O} = \boldsymbol{S}\ \boldsymbol{C}\ \boldsymbol{S} \tag{7}$$

where the O_{rs} elements are collected in the matrix $\boldsymbol{O}$, $\boldsymbol{C}$ is defined as above and $\boldsymbol{S}$ has as elements the function basis set metric, $S_{rp}=\langle r \mid p\rangle$.
To find the expansion coefficients values, equation (7) has to be solved; so, $\boldsymbol{C}$ matrix is computed as:

$$\boldsymbol{C} = \boldsymbol{S}^{-1}\ \boldsymbol{O}\ \boldsymbol{S}^{-1} \tag{8}$$

and it can be evaluated easily, because $\boldsymbol{S}$ is a definite positive matrix. Then an inverse will always exist. This inverse matrix can be found, for example, by means of Cholesky decomposition algorithm [3].

APPLICATION TO INTEGRAL COMPUTATION

As it has been said before, one of the applications of operator expansion may consist into evaluate integrals where the implied operator appears. The example given in this work is the development of an integral of the kind

$$I = \langle\ \Phi \mid \hat{O} \mid \Phi'\ \rangle \tag{9}$$

where Φ and Φ' are arbitrary functions. In this integral, the expansion can be applied, and an approximate value of the integral can be obtained:

$$I_a = \langle\ \Phi \mid \hat{O} \mid \Phi'\ \rangle = \langle\ \Phi \mid \{ \sum_{p=1}^{N_r} \sum_{q=1}^{N_s} c_{pq} \mid p\ \rangle \langle\ q \mid \} \mid \Phi'\ \rangle = \tag{10}$$

$$= \sum_{p=1}^{N_r} \sum_{q=1}^{N_s} c_{pq} \langle\ \Phi \mid p\ \rangle \langle\ q \mid \Phi'\ \rangle$$

There appear overlap integrals between the operator expansion elements and Φ and Φ' functions. In most cases, an error which measures the degree of fitting between the approximate and the exact value, expressions (10) and (9) respectively, can be defined. In this work the quadratic error is written as the square of the difference between both integrals:

$$\varepsilon^2 = (\ I - I_a\ )^2 \tag{11}$$

An optimization technique can be used to minimize the quadratic error, using as parameters the expansion functions and coefficients of the operator expansion.

ELECTRON REPULSION INTEGRALS

A numerical example is presented here: the application of the $\hat{r}_{12}^{-1}$ operator expansion to the electron repulsion integrals computation between four GTO *s*-type functions $\{\phi_a\}_{a=i,j,k,l}$. As it will be seen, these integrals can be reduced to bielectronic terms like those appearing in equation (9), where Φ and Φ here adopt the form of *s*-type gaussian functions:

$$|\Phi\rangle = e^{-\gamma|r_1-P|^2} \tag{12}$$

and

$$|\Phi'\rangle = e^{-\gamma|r_2-P'|^2} \quad , \tag{13}$$

centered at the points P and P', respectively.
Here, the projectors expanding the electronic repulsion operator are defined as s-type normalized gaussian functions:

$$|p\rangle = \left(\frac{2\alpha_p}{\pi}\right)^{3/4} e^{-\alpha_p r_{12}^2} \tag{14}$$

and the expansion set depends in a parametric form of the exponent set $\{\alpha_p\}$.
Moreover, it must be taken into account that the expansion presented here is from now on defined using $N_p = N_q = N$ in equation (4).
To solve equation (8), it must be considered that the O matrix elements which appear in equation (7) are defined by means of:

$$O_{pq} = \langle p \mid r^{-1} \mid q \rangle = 4\left(\frac{2}{\pi}\right)^{1/2} \frac{(\alpha_p\ \alpha_q)^{3/4}}{(\alpha_p+\alpha_q)} \quad , \tag{15}$$

where $|p\rangle$ and $\langle q|$ are functions from the original basis set. On the other hand, the S matrix elements appearing in (7) are defined as

$$S_{pq} = \langle p \mid q \rangle = \left(\frac{2\ (\alpha_p\ \alpha_q)^{1/2}}{\alpha_p+\alpha_q}\right)^{\frac{3}{2}} \tag{16}$$

and then, every set of projectors can determine, using equation (8), the related coefficient matrix C. To compute the approximate electron repulsion integral, the expansion obtained substitutes the original operator in the corresponding integral.
As the exact integral value is well-known [4], see equation (15), the definition of the quadratic error (11) is applied here to estimate the fitting operator degree. Now, the exact and approximate integral values are given by

$$I = |PP'|^{-1} \frac{\pi^3}{(\gamma\gamma')^{3/2}} erf\left[\left(\frac{\gamma\gamma'}{\gamma+\gamma'}\right)^{1/2} |PP'|\right] \tag{17}$$

and

$$I_a = \left(\frac{(2\pi)^3}{\gamma\gamma'}\right)^{3/2} \sum_{p=1}^{N}\sum_{q=1}^{N} \frac{c_{pq}}{(\alpha_p\alpha_q)^{3/4}} \tag{18}$$

respectively, where α_p and α_p are associate exponents from the set of GTO functions, and γ and γ' are Φ and Φ' function exponents, respectively.
At this stage, an optimization of the quadratic error (11) has to be performed to obtain the optimal operator expansion. The variational parameters in this optimization are the coefficient set $\{c_{pq}\}$ and the set of projector exponents, which are collected in the vector $\boldsymbol{a} = (\underline{\alpha}_1, \underline{\alpha}_2, ..., \underline{\alpha}_N)$.
The optimization process is done following Newton-Raphson method [5], computing analytically the Gradient and Hessian matrix, $\boldsymbol{g}$ and $\boldsymbol{H}$:

$$\boldsymbol{a}^{(i+1)} = \boldsymbol{a}^{(i)} - \boldsymbol{H}^{-1}\, \boldsymbol{g}^T \tag{19}$$

where $\boldsymbol{a}^{(i)}$ and $\boldsymbol{a}^{(i+1)}$ are the values adopted by the exponent vector $\boldsymbol{a}$ in the optimization steps (i) and $(i+1)$ respectively. The $\boldsymbol{g}$ and $\boldsymbol{H}$ matrices are calculated using

$$g_i = \frac{\partial \varepsilon^2}{\partial \alpha_i} = \varepsilon\, \Gamma \left(\frac{c_{ii}}{\alpha_i^{5/2}} + \sigma(i) \right) , \tag{20}$$

where ε is not-squared computed error from equation (11) and Γ and $\sigma(i)$ functions are defined as

$$\Gamma = \frac{3\pi^6}{(\gamma\gamma')^{9/4}} \tag{21}$$

and

$$\sigma(i) = \sum_{k \neq i} \frac{c_{ki}}{\alpha_k^{3/4}} \tag{22}$$

The diagonal $\boldsymbol{H}$ matrix elements have the expression:

$$H_{ii} = \frac{\partial \varepsilon^2}{\partial \alpha_i^2} = \Gamma \left[\frac{12\pi^9}{(\gamma\gamma')^{3/4}}\, \Theta(i)^2 + \varepsilon \left(\frac{-5c_{ii}}{2\alpha_i^{7/2}} - \frac{7\sigma(i)}{4\alpha_i^{11/4}} \right) \right] , \tag{23}$$

where $\underline{\Gamma}$ and $\sigma(i)$ are defined as above, and $\Theta(i)$ is computed using

$$\Theta(i) = \frac{c_{ii}}{\alpha_i^{5/2}} + \frac{\sigma(i)}{\alpha_i^{7/4}} . \tag{24}$$

For non-diagonal terms ($i \neq j$), one has to use

$$H_{ij} = \frac{\partial \varepsilon^2}{\partial \alpha_i \partial \alpha_j} = \Gamma \left[\frac{12\pi^9}{(\gamma\gamma')^{3/4}}\, \Theta(i)\, \Theta(j) - \frac{3\, c_{ij}\, \varepsilon}{4\, (\alpha_i \alpha_j)^{7/4}} \right] \tag{25}$$

The optimization presented here gives enough accurate results even if a small dimension in the expansion is used; in fact, N=2 is good enough for high precision integral computation. When a good expansion is achieved, it can be used for fast

evaluation of electron repulsion multicenter integrals.

SCALING

In practice, when the operator expansion is evaluated and applied in electron repulsion integrals, it is only necessary to compute the optimal coefficient and exponent values in a reference case. That is: when $\gamma=\gamma^{\circ}, \gamma'=\gamma'^{\circ}$ and $|\boldsymbol{PP'}| = |\boldsymbol{PP'}|^{\circ}$. In this reference case, it has been obtained a set of optimal coefficients and exponents, noted as $\{ \alpha_i^{\circ} \}$ and $\{ c_{ij}^{\circ} \}$. When γ, γ' exponents, or $|\boldsymbol{PP'}|$ distance are different from the reference ones, the optimal coefficient and exponent values can be easily computed using the set $\{ \alpha_i^{\circ} \}$, $\{ c_{ij}^{\circ} \}$ and a scale factor, in such a way that

$$\begin{aligned} \alpha_i &= \alpha_i^{\circ} \cdot F \\ c_{ij} &= c_{ij}^{\circ} \cdot \sqrt{F} \end{aligned} \quad ; \forall\, i\,, j \tag{26}$$

The F definition can be found supposing that equation (26) is fulfilled, and evaluating the quotient between the calculated and the reference integral afterwards:

$$\frac{I}{I^{\circ}} = \left(\frac{\gamma^{\circ}\,\gamma'^{\circ}}{\gamma\,\gamma'}\right)^{3/2} \frac{|\boldsymbol{PP'}|^{\circ}}{|\boldsymbol{PP'}|}\; \frac{\mathrm{E}\,(\,\gamma,\,\gamma',\,|\boldsymbol{PP'}|\,)}{\mathrm{E}\,(\,\gamma^{\circ},\,\gamma'^{\circ},\,|\boldsymbol{PP'}|^{\circ})} \quad , \tag{27}$$

where it has been used the function definition:

$$\mathrm{E}\,(\,\alpha,\,\beta,\,|\boldsymbol{A}|\,) = erf\left[\left(\frac{\alpha\beta}{\alpha+\beta}\right)^{1/2}|\boldsymbol{A}|\right] \quad . \tag{28}$$

The same expression for the approximate integrals can be found:

$$\frac{I_a}{I_a^{\circ}} = \left(\frac{\gamma^{\circ}\gamma'^{\circ}}{\gamma\gamma'}\right)^{3/2} F^{-1} \quad , \tag{29}$$

where condition (26) and equation (18) are used. Identifying as equalities $I=I_a$ and $I^{\circ}=I_a^{\circ}$, the scale factor definition is obtained:

$$F = \frac{\mathrm{E}\,(\,\gamma^{\circ},\,\gamma'^{\circ},\,|\boldsymbol{PP'}|^{\circ}\,)}{\mathrm{E}\,(\,\gamma,\,\gamma',\,|\boldsymbol{PP'}|\,)}\; \frac{|\boldsymbol{PP'}|}{|\boldsymbol{PP'}|^{\circ}} \quad . \tag{30}$$

It has been numerically proved that the use of the F factor is accomplished for any dimension in the operator expansion without loss of precision in the integral computations.

RESULTS

The technique previously developed is used as a tool for the four-center electron repulsion integrals computation, when the implied functions are *s*-type functions as in equation (9) . Then, the integral is defined as

$$\left\langle \phi_i(\boldsymbol{r}_1)\ \phi_j^*(\boldsymbol{r}_1) \,\middle|\, \hat{r}_{12}^{-1} \,\middle|\, \phi_k(\boldsymbol{r}_2)\ \phi_l^*(\boldsymbol{r}_2) \right\rangle = \tag{31}$$

$$= \iint \phi_i(\boldsymbol{r}_1)\ \phi_j^*(\boldsymbol{r}_1)\ \hat{r}_{12}^{-1}\ \phi_k(\boldsymbol{r}_2)\ \phi_l^*(\boldsymbol{r}_2)\ d\boldsymbol{r}_1\ d\boldsymbol{r}_2 \quad ,$$

where the expanded operator is $\hat{r}_{12}^{-1}$, and the four $\{ \phi_i, \phi_j, \phi_k, \phi_l \}$ function centers are $\{ \boldsymbol{A}, \boldsymbol{B}, \boldsymbol{C}, \boldsymbol{D} \}$ respectively.

To compute this kind of integrals, it has been used the methodology developed above, where the two functions Φ and Φ' are now *s*-type GTO products. The Gaussian Product Theorem [4] can be applied over the function products depending on the same variable to give another *s*-type gaussian function centered at a point situated on the line joining the two previous centers, and having as exponent the sum of the two previous ones.

As reference set the used values are $\{ \gamma=\gamma'^{\circ} = |\boldsymbol{PP'}|^{0} =1\}$, and its corresponding expansions for N=2 and N=3 are shown in Table 1.

Using a bidimensional expansion, N=2, the obtained results are almost the same than exact computed values, as it is shown in Tables 2, 3 and 4. In Table 2 the exponents are the same as the reference ones, and the four centers appearing in integral (12) are varied. In Table 3, the reference distance $|\boldsymbol{PP'}|$ is maintained constant and the exponents are varied. More examples are given in Table 4.

The obtained error is, for all cases, the same as the machine precision.

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Table 1. Optimized electron repulsion operator expansions for N=2 and N=3 when reference values* are used.

N	a vector	C matrix
2	$\begin{pmatrix} 35.62483411703156 \\ 71.24966823406282 \end{pmatrix}$	$\begin{pmatrix} 48.07664287944661 & -54.21292066838888 \\ -54.21292066838888 & 72.43772070405760 \end{pmatrix}$
3	$\begin{pmatrix} 45.70145504997865 \\ 91.40291009995983 \\ 137.1043651499392 \end{pmatrix}$	$\begin{pmatrix} 157.8142753998670 & -435.5415526261345 & 311.4428844657524 \\ -435.5415526261345 & 1372.300340250810 & -1043.037546040614 \\ 311.4428844657524 & -1043.037546040614 & 827.4261045752368 \end{pmatrix}$

* Reference values are $\gamma'=\gamma'^{\circ} = |\boldsymbol{PP'}|^{\circ} = 1$.

Table 2. Exact and approximate values of four-center electron repulsion integrals

CENTERS	EXPONENTS	INTEGRAL VALUE *Exact* Approximate
A(0,0,0)	1	
B(0,0,0)	1	*3.266126743113372*
C(0,0,1)	1	3.266126743113366
D(0,0,1)	1	
A(0,0,0)	1	
B(0,0,0)	1	*2.496276956156262*
C(0,0,1.5)	1	2.496276956156257
D(0,0,1.5)	1	
A(0,0,0)	1	
B(0,0,0)	1	*1.928827345952527*
C(0,0,2)	1	1.928827345952523
D(0,0,2)	1	
A(0,0,1)	1	
B(0,0,2)	1	*5.10188360077207E-2*
C(0,2,3)	1	5.10188360077206E-2
D(1,0,4)	1	

Table 3. Exact and approximate values of four-center electron repulsion integrals

CENTERS	EXPONENTS	INTEGRAL VALUES *Exact* Approximate
A(0,0,0)	1	
B(0,0,0)	1	*0.2807061700350193*
C(0,0,1)	1	0.2807061700350187
D(0,0,1)	10	
A(0,0,0)	1	
B(0,0,0)	2	*0.3091719339577310*
C(0,0,1)	3	0.3091719339577303
D(0,0,1)	4	
A(0,0,0)	10	
B(0,0,0)	20	*3.2219639431575E-4*
C(0,0,1)	30	3.2219639431575E-4
D(0,0,1)	40	
A(0,0,0)	0.1	
B(0,0,0)	0.1	*1338.227622535886*
C(0,0,1)	0.1	1338.227622535981
D(0,0,1)	0.1	

Table 4. Exact and approximate values of four-center electron repulsion integrals

CENTERS	EXPONENTS	INTEGRAL VALUE *Exact* Approximate
A(0,0,0)	1	
B(0,0,1)	1	*0.684938491456359*
C(0,1,1)	1	0.684938491456357
D(1,1,1)	1.5	
A(0,0,0)	1	
B(0,0,1)	2	*1.530763677257491E-4*
C(1,2,4)	1	1.530763677257489E-4
D(2,1,1)	2	
A(0,0,0)	0.1	
B(2,0,1)	0.1	*305.7822551729557*
C(1,3,5)	0.1	305.7822551729552
D(2,2,1)	0.1	
A(0,0,0)	10	
B(1,1,1)	2	*2.462977733467594E-4*
C(0,0,0)	1	2.462977733467590E-4
D(0.5,0.1,0.1)	10	