ANALYTIC EVALUATION OF MULTICENTER INTEGRALS
FOR GAUSSIAN-TYPE ORBITALS

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Abstract

This work contains the evaluation of multicenter integrals with Cartesian Gaussian functions occurring in \( \| \mathcal{H} \psi \| ^2 \). These integrals have to be used if it is necessary to calculate the lower bounds for eigenvalues with the method of the minimization of the variance [1]. Considering the variance \( J(\psi) = \| \mathcal{H} \psi \| ^2 - (\mathcal{H} \psi \psi)^2 \), the integrals from \( (\mathcal{H}^2, \psi) \) are well known in contrast to those for \( \| \mathcal{H} \psi \| ^2 \).

1. Introduction

Almost all calculations of upper bounds for eigenvalues, using the Rayleigh–Ritz variation principle, nowadays are performed with Gaussian functions, because of the difficulties of calculating \((\mathcal{H}^2, \psi)\) for Slater functions. Two methods are dominant: the use of Laplace and Fourier transform [2–4] and recurrence relations [5–8].

In contrast, there are few papers concerning the integrals for \( \| \mathcal{H} \psi \| ^2 \), e.g. the papers by Zimering [9] and Roberts [10]. Starting with Gaussian functions of the type

\[ \chi(\alpha, l, m, n) = x_a^l y_a^m z_a^n e^{-\alpha r_a^2}. \] (1)

\(x_a, y_a\) and \(z_a\) are the components of the vector \(r_a = r - a\) and \(l, m, n\) are integers \(\geq 0\). Four basic integrals are obtained calculating \((\mathcal{H}^2, \psi)\): \(J_1, \ldots, J_4\) according to the nomenclature of Huzinaga et al. [3].

In analogy, \((\mathcal{H}^2, \mathcal{H}^2)\) produces another five types of integrals \(J_5, \ldots, J_9\) (see section 2). For the case \(l = m = n = 0\), these integrals are given in [9, 10]. The general case \(l, m, n \in \mathbb{N}\) can be treated combining the methods of Laplace and Fourier transform.

2. Basic integrals

Looking at the functions \(\psi\) in \(\| \mathcal{H} \psi \| ^2\) in the most general form as a linear combination of products of Gaussian functions, e.g. Slater determinants, then the products of
\begin{align}
\chi_i^j = x_{a_i}^j y_{a_i}^{m_i} z_{a_i}^{n_i} e^{-\alpha_i r_{a_i}^2},
\end{align}

with the centers \( q = a, b, c, \ldots \), can be newly centered with regard to the electrons \( j = 1, 2, 3, \ldots \) [4]. Thus, one obtains linear combinations of Gaussian functions referring to just one center for each electron. With \( H \) as Born–Oppenheimer Hamiltonian, the following basic integrals are then needed for \( \| H \psi \|^2 \):

\begin{align}
J_5 &= (r_{c_1}^{-2} | \chi_1), \\
J_6 &= (\chi_1^1 | r_{12}^{-2} | \chi_2^2), \\
J_7 &= ((r_{c_1} r_{d_1})^{-1} | \chi_1), \\
J_8 &= (\chi_1^1 | (r_{12} r_{c_1})^{-1} | \chi_2^2), \\
J_9 &= (\chi_1^1 | (r_{12} r_{13})^{-1} | \chi_2^2 \chi_3^3),
\end{align}

with

\begin{align}
\chi_1^1 &= x_{a_1}^{l_1} y_{a_1}^{m_1} z_{a_1}^{n_1} e^{-\alpha_1 r_{a_1}^2}, \\
\chi_2^2 &= x_{b_2}^{l_2} y_{b_2}^{m_2} z_{b_2}^{n_2} e^{-\alpha_2 r_{b_2}^2}, \\
\chi_3^3 &= x_{c_3}^{l_3} y_{c_3}^{m_3} z_{c_3}^{n_3} e^{-\alpha_3 r_{c_3}^2}.
\end{align}

For the solution of \( J_5 \) up to \( J_9 \), the following relations are needed [3,9,10]:

\begin{align}
\frac{1}{r} &= \frac{1}{2 \pi^2} \int \frac{dk}{k^2} e^{i k r}, \\
\frac{1}{k} &= \frac{1}{\sqrt{\pi}} \int_0^\infty \frac{d\eta}{\sqrt{\eta}} e^{-\eta k^2} = \frac{2}{\sqrt{\pi}} \int_0^\infty d\eta e^{-\eta^2 k^2}, \\
\frac{1}{r^2} &= \frac{1}{4 \pi} \int \frac{dk}{k} e^{-i k r}, \\
e^{-\delta k^2} &= 2 \delta k^2 \int_0^1 \frac{ds}{s^3} e^{-(\delta/s^2) k^2}.
\end{align}