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The Significance of the Strong Orthogonality Condition for Geminal Functions in Variational Calculations

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The use of an approximate wave function, for electronic systems, composed of an antisymmetrised product of two electron functions (geminals) has the advantage of maintaining something like the orbital concept while allowing correction of the energy and wave function for the correlation effects between electrons occupying similar regions of space [1]. Two forms have shown the greatest potential: the *configuration interaction geminals* with the expansion

$$G_i(1, 2) = \sum_k C_{ki}\, \varphi_{a(k)}(1)\, \varphi_{b(k)}(2) \tag{1a}$$

where the φ are suitable one-electron basis functions, and the *explicitly correlated geminals* with the expansion

$$G_i(1, 2) = \sum_k C_{ki}\, \varphi_{a(k)}(1)\, \varphi_{b(k)}(2)\, \chi_k(1, 2) \tag{1b}$$

where the φ are as before and χ_k is a function of r_{12}, the interelectronic distance.

If the variational problem based upon an energy expression arising from the use of an antisymmetrised product is to be tractible, it appears necessary to apply restrictions to the geminal functions [5]. By analogy to orbital functions one can apply *complete geminal orthonormality*

$$\langle G_i(1, 2) \mid G_j(1, 2)\rangle = \delta_{ij}\,, \tag{2}$$

the bra-ket notation indicating integration over all available electronic coordinates. A further restriction is the *strong orthogonality* condition

$$\int G_i(1, 2)\, G_j(1, 3)\, d\tau_1 = 0, \qquad i \neq j \tag{3}$$

which also leads to the complete orthogonality condition of Eq. (2).

The purpose of this note is to examine the form of the variational problem to clarify the question as to the origin and necessity of the use of the strong orthogonality constraint. For simplicity, the example of the four-electron case with approximate total wave function

$$\Phi = \mathscr{A}\, [G_1(1, 2)\, G_2(3, 4)] \tag{4}$$

with $\mathscr{A}$ the antisymmetrising operator, will be treated.

Applying the complete orthonormality restriction of Eq. (2) only, one has

$$\langle \Phi \mid \Phi\rangle = 1 - 2\, \langle G_1(1, 2)\, G_2(3,4) \mid G_1(3, 2)\, G_2(1, 4)\rangle\,. \tag{5}$$

The presence of the integral in this expression is unfortunate from the point of view of a manageable formalism. When one attempts to vary the energy expression

$$E = \langle \Phi \mid \mathscr{H} \mid \Phi \rangle / \langle \Phi \mid \Phi \rangle \tag{6}$$

with the denominator given by Eq. (5), and under constraint Eq. (2), a quite formidable expression results. Therefore one finds it practically necessary to reduce the complexity of Eq. (6) by imposing a constraint such that $\langle \Phi \mid \Phi \rangle = 1$, i.e.

$$\langle G_1(1, 2)\, G_2(3, 4) \mid G_1(3, 2)\, G_2(1, 4) \rangle = 0\,. \tag{7}$$

This constraint is, however, equivalent to the strong orthogonality condition. If we define a function

$$F_{ij}(m, n) = \int G_i(k, m)\, G_j(k, n)\, d\tau_k\,, \tag{8}$$

the integral of Eq. (7) becomes

$$\int\!\!\int \mid F_{12}(2, 4) \mid^2 d\tau_2\, d\tau_4 = 0\,. \tag{9}$$

Due to the nature of the integrand, Eq. (9) is only satisfied by

$$F_{12}(2, 4) = \int G_1(1, 2)\, G_2(1, 4)\, d\tau_1 = 0 \tag{10}$$

which defines strong orthogonality. We therefore regard strong orthogonality simply as the condition necessary for the simplification of the formalism arising from the use of the geminal product form in the variational problem starting with Eq. (6).

It is tempting to write the energy expression, taking into account strong orthogonality, and to impose the normalisation constraint by Eq. (2), and the strong orthogonality constraint by Eq. (7), or by the alternant form

$$\langle G_1(1, 2)\, G_2(3, 4) \mid \mathscr{P}_{13} \mid G_1(1, 2)\, G_2(3, 4) \rangle = 0 \tag{11}$$

where $\mathscr{P}_{13}$ is the permutation operator, operating upon electrons 1 and 3. The operator equations derived from the variation of the energy expression, with constraints, are

$$\begin{aligned} \mathscr{F}_1\, G_1 &= \theta_{11}\, G_1 + \theta_{12}\, \mathscr{U}\, G_2 \\ \mathscr{F}_2\, G_2 &= \theta_{22}\, G_2 + \theta_{21}\, \mathscr{U}\, G_1 \end{aligned} \tag{12}$$

where θ_{11}, θ_{22} are Lagrangian multipliers used in conjunction with the normalisation constraints, θ_{12}, θ_{21} are multipliers used with Eq. (11), and $\mathscr{U}$ is an integral operator such that

$$\begin{aligned} \langle G_1(1, 2) \mid \mathscr{U} \mid G_2(1, 2) \rangle &= \langle G_2(1, 2) \mid \mathscr{U} \mid G_1(1, 2) \rangle \\ &= \langle G_1(1, 2)\, G_2(3, 4) \mid \mathscr{P}_{13} \mid G_1(1, 2)\, G_2(3, 4) \rangle\,. \end{aligned} \tag{13}$$

In attempting a further reduction of Eqs. (12) one tries to express the Lagrangian multipliers as integrals involving the operators and geminal functions. Indeed one has

$$\begin{aligned} \theta_{11} &= \langle G_1(1, 2) \mid \mathscr{F}_1 \mid G_1(1, 2) \rangle\,, \\ \theta_{22} &= \langle G_2(1, 2) \mid \mathscr{F}_2 \mid G_2(1, 2) \rangle\,, \end{aligned}$$

but unfortunately

$$\begin{aligned}\langle G_2(1,2) \mid \mathscr{F}_1 \mid G_1(1,2)\rangle &= \theta_{12}\cdot\langle G_2(1,2) \mid \mathscr{U} \mid G_2(1,2)\rangle \\ &= \theta_{12}\,\langle G_2(1,2)\,G_2(3,4) \mid \mathscr{P}_{13} \mid G_1(1,2)\,G_2(3,4)\rangle = 0\,.\end{aligned}$$

The attempt has foundered upon the presence in the expression of Eq. (11) of two statements of strong orthogonality, thus rendering θ_{12} undeterminable.

There remains the method commonly used to ensure strong orthogonality: the choice of two mutually exclusive and orthogonal basis sets for the two distinct geminals [*2, 4, 5*]. Such a choice removes the necessity for employing strong orthogonality as an explicit constraint in a manner analogous to the neglect of orthogonality constraints between orbitals of different symmetry. Such a choice is only feasible for the 'configuration interaction' geminals. No general mutually orthogonal sets exist for the 'explicitly correlated' geminals [*6*]. Consequently, first order corrections for the terms violating the strong orthogonality conditions must be sought, such as Kapuy's 'almost strongly orthogonal' geminals [*3*]. An investigation of this approximation, but in the context of 'configuration interaction' geminals is under way in this laboratory.

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