Method of explicitly correlated functions

In this method the wave function Ψ (and basis functions Φ_k) depend explicitly on the interelectronic distance $r_{ij} = |\vec{r}_1 - \vec{r}_2|$.

In general the wave function Ψ is expanded in terms of many-electron basis functions Φ_k:

$$\Psi = \sum_k C_k \, \Phi_k$$

The coefficients C_k and the energy of the system are found using the variation method, that is, by diagonalizing the matrix:

$$H_{kl} = \int \Phi_k \hat{H} \Phi_l \, d\tau$$

The basis functions Φ_k are formed by multiplying an orbital product (or the whole Slater determinant) by e function $f(r_{ij})$ called a correlation factor, e.g.,

$$\Phi_k = \psi(\vec{r}_1) \, \psi(\vec{r}_2) \, f(r_{12})$$

The function $f(r_{12})$ much better then the orbital products describes the so-called correlation hole.

Usually $f(r_{12})$ exhibits also the correct cusp at r_{12}=0 while all products of orbitals are analytic (smooth) at r_{12}=0.

Hartree-Fock wave function for helium. No correlation

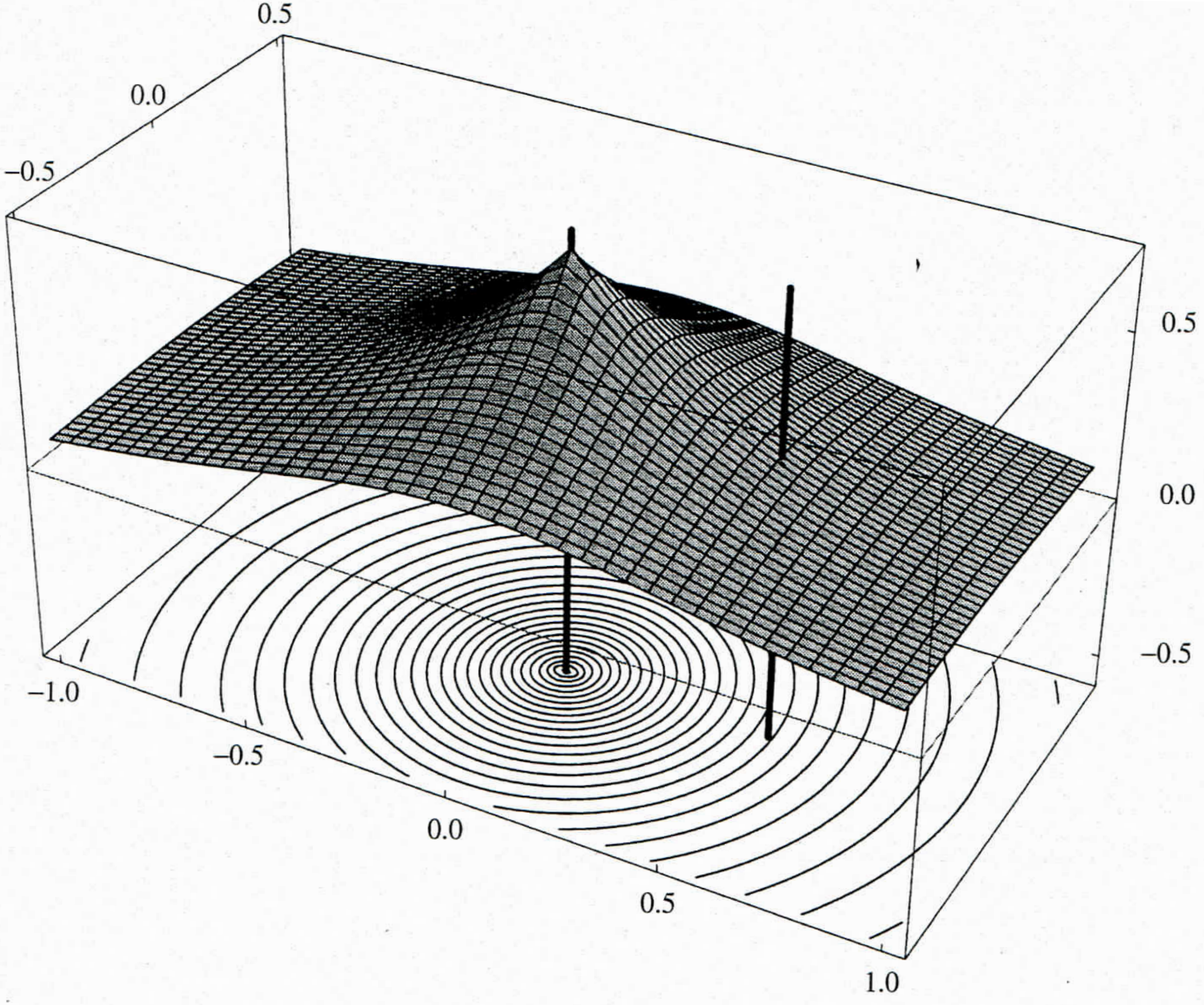

Fig. 7.1. The Hartree–Fock ground-state wave function of the helium atom with one electron fixed at a position $0.5a_0$ away from the nucleus. The wave function is plotted (in atomic units) in a plane that contains the nucleus and the fixed electron, the positions of which are indicated by vertical bars.

Exact wave function for the helium atom.

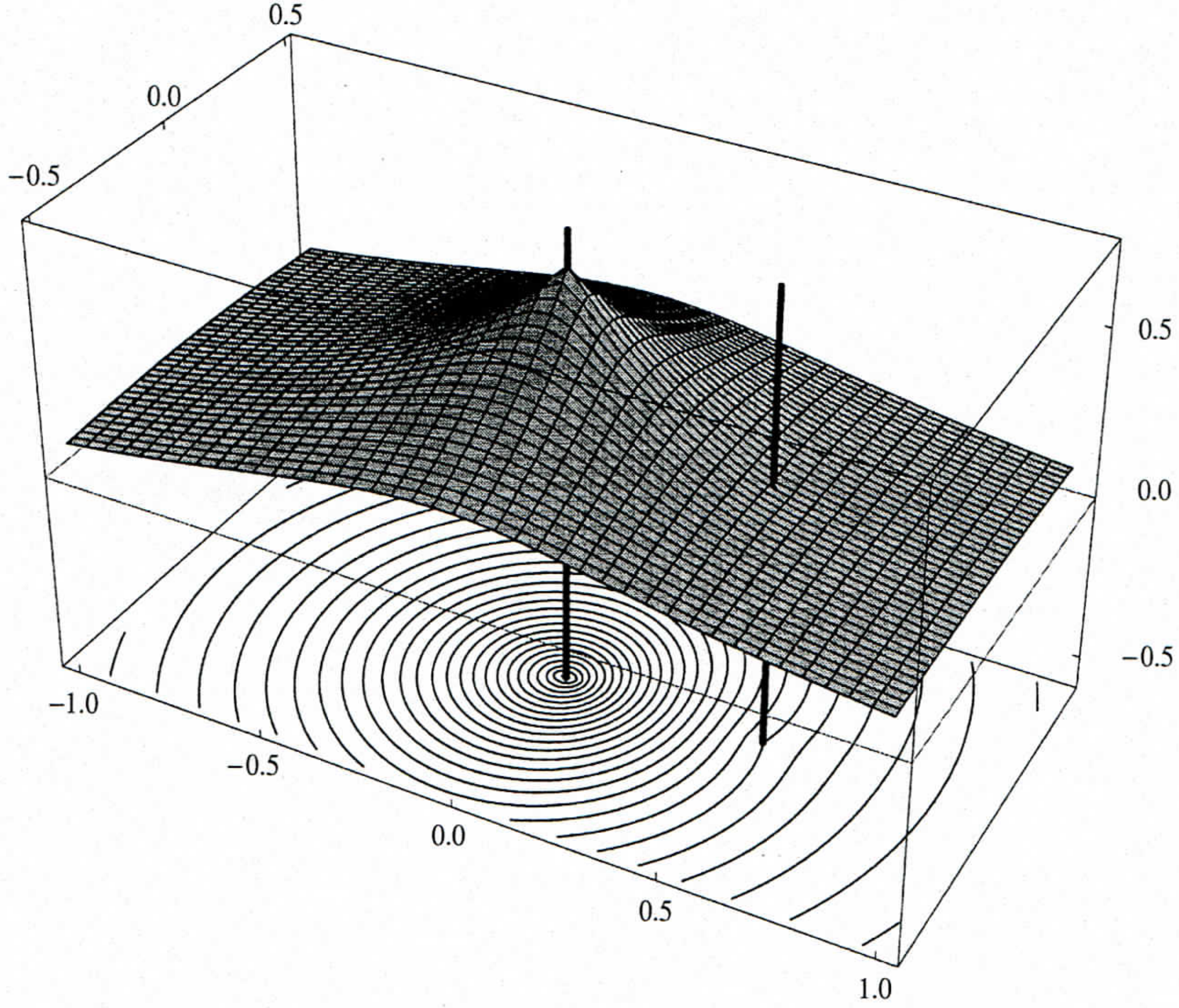

Fig. 7.2. The exact ground-state wave function of the helium atom with one electron fixed at a position $0.5a_0$ away from the nucleus. The wave function is plotted (in atomic units) in a plane that contains the nucleus and the fixed electron, the positions of which are indicated by vertical bars.

Correlation hole for the helium atom.

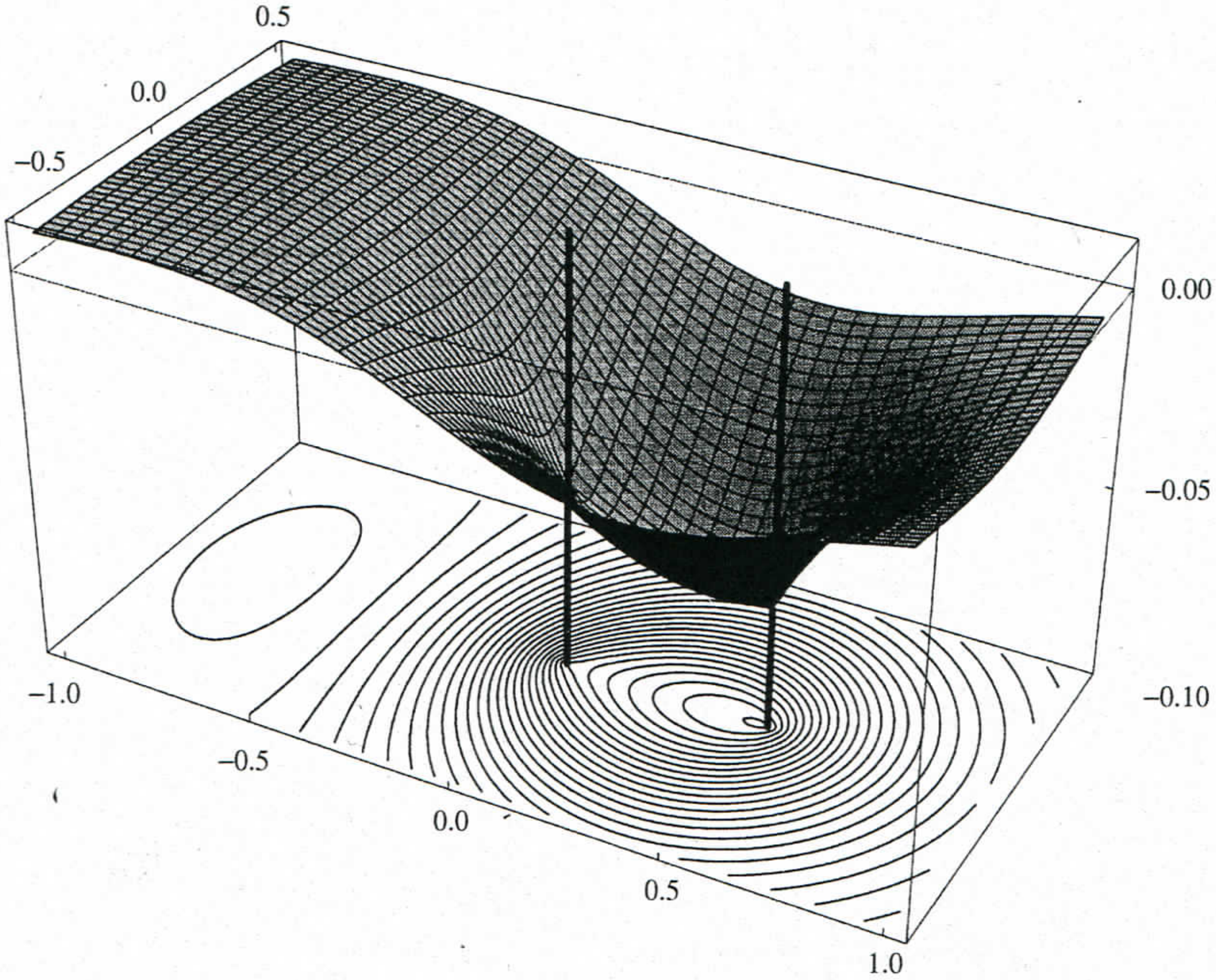

Fig. 7.3. The Coulomb hole in the ground-state helium atom. The plotted function represents the difference between the exact wave function and the Hartree–Fock wave function in a plane that contains the nucleus and the fixed electron, the positions of which are indicated by vertical bars (atomic units).

Interelectronic and nuclear cusps for the helium atom .

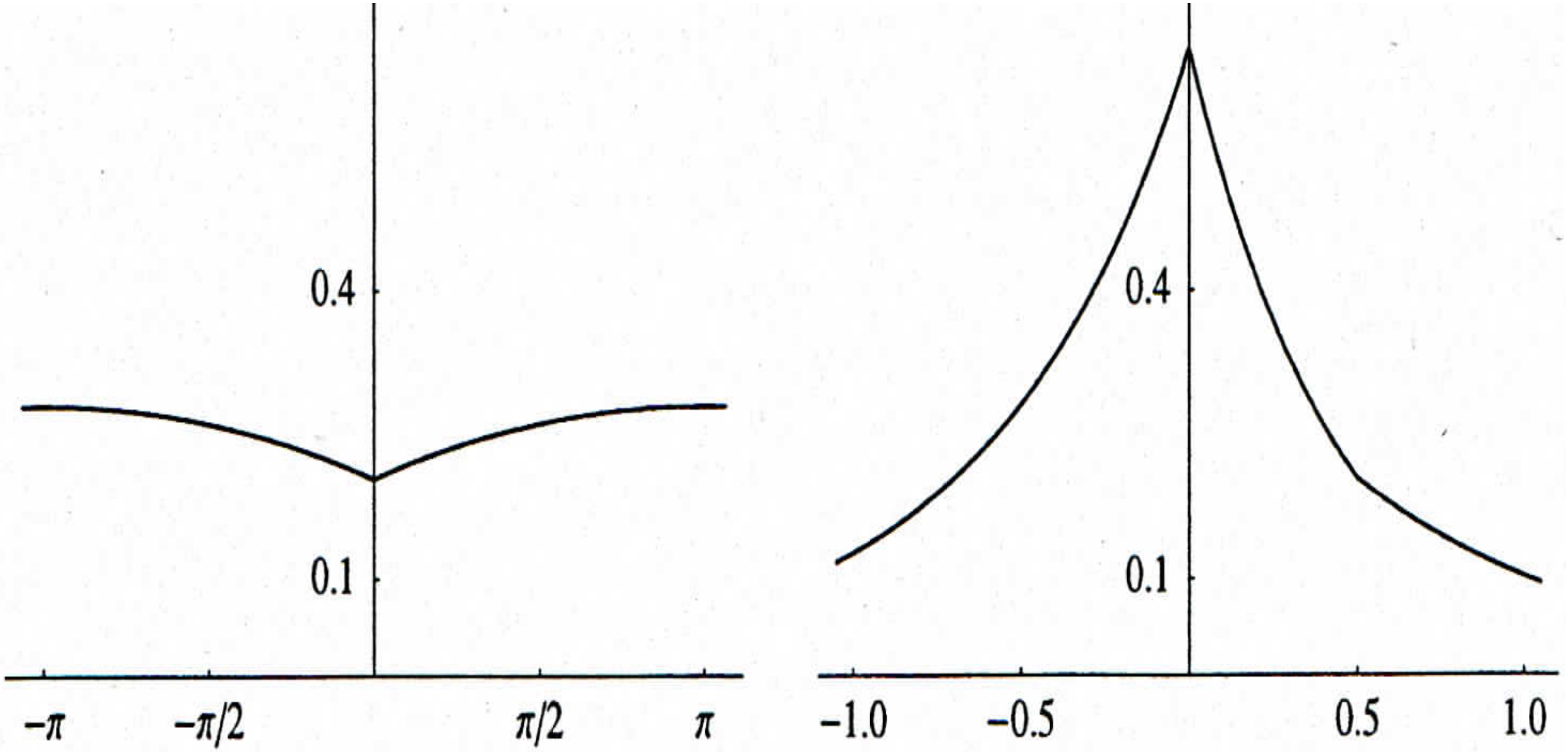

Fig. 7.5. The electronic and nuclear cusps of the ground-state helium atom with one electron fixed at a position $0.5a_0$ from the nucleus (atomic units). On the left, the wave function is plotted on a circle of radius $0.5a_0$ centred at the nucleus; on the right, the wave function is plotted along the axis through the nucleus and the fixed electron.

Expansion of r_{12} (the model of the correlation hole) in terms of products of angular functions through the angular momentum L

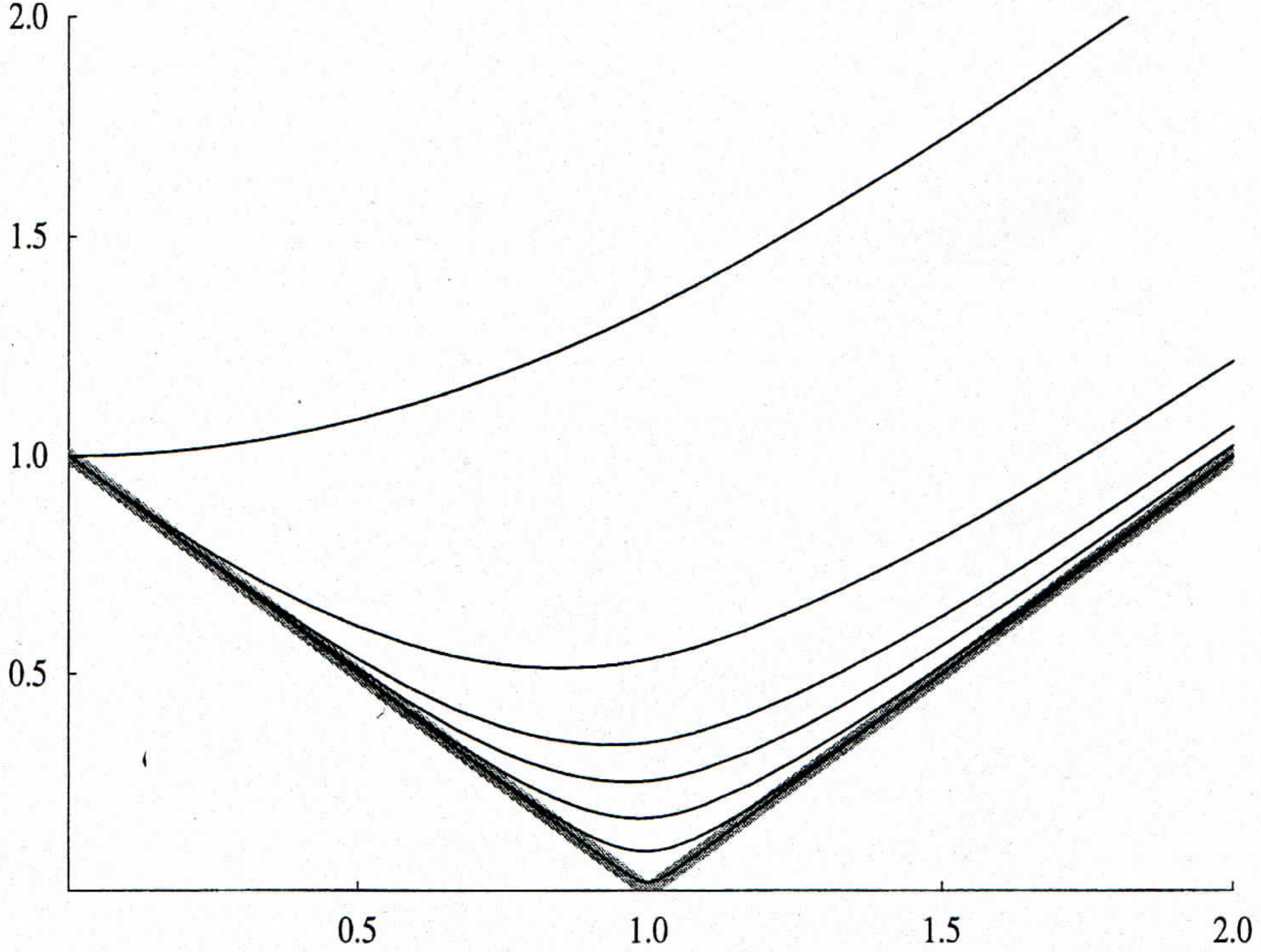

Fig. 7.7. Partial-wave expansions of r_{12} in r_1, r_2 and θ_{12} for $r_2 = 1$ and $\theta_{12} = 0$. The orders of the expansions are $L = 0,1, 2, 3, 5, 10$ and 50. The exact function r_{12} is represented by a thick grey line.

Most important explicitly correlated bases:

Hylleraas Basis (He, Li):

$$\Phi_k = r_1^n r_2^l r_{12}^m \, e^{-\alpha r_1 - \beta r_2}$$

$$\Phi_k = \phi(r_1)\, \phi'(r_2)\, r_{12}^m \qquad \text{that is } f(r_{12}) = r_{12}^m$$

Kołos-Wolniewicz Basis(H_2):

$$\Phi_k = r_{1a}^i r_{2a}^l r_{1b}^{i'} r_{2b}^{l'} r_{12}^n \, e^{-\alpha r_{1a} - \beta r_{2a} - \alpha' r_{1b} - \beta' r_{2b}}$$

$$\Phi_k = \phi(\vec{r}_1)\, \phi'(\vec{r}_2)\, r_{12}^m \qquad \text{that is } f(r_{12}) = r_{12}^m$$

Slater Geminal Basis (He, H_2^+):

$$\Phi_k = e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}}$$

$$\Phi_k = \phi(r_1)\, \phi'(r_2)\, e^{-\gamma r_{12}} \quad \text{that is } f(r_{12}) = e^{-\gamma r_{12}}$$

Gaussian Geminal Basis (Boys)

$$\Phi_k = e^{-\alpha r_{1a}^2 - \beta r_{2a}^2 - \alpha' r_{1b}^2 - \beta' r_{2b}^2 - \gamma r_{12}^2}$$

$$\Phi_k = \phi(\vec{r}_1)\, \phi'(\vec{r}_2)\, e^{-\gamma r_{12}^2} \quad \text{that is } f(r_{12}) = e^{-\gamma r_{12}^2}$$

Gaussian Geminals do not satisfy the cusp condition but, nevertheless, give very good results (also for many-electron systems - e.g., the F12-CCSD method).

Orbital expansion method

The simplest method of allowing for the electron correlation is to include more than one determinant in the expansion of the wave function.

For example, in the case of H_2, the two-configuration wave function

$$\boldsymbol{\Psi = c_1|\psi_1\alpha\ \psi_1\beta| + c_2|\psi_2\alpha\ \psi_2\beta|,}$$

where ψ_1 stands the σ_g and ψ_2 for the σ_u orbital , takes account of the “left-right” correlation end correctly describes the dissociation (the energy is extensive or ,,size-consistent”). Jf

$$\psi_1 = (1s_a + 1s_b)/\sqrt{2} \qquad \text{i} \qquad \psi_2 = (1s_a - 1s_b)/\sqrt{2}$$

then Ψ is a particular case of the wave function of the valence bond method (VB). When the orbitals ψ_1 i ψ_2 are optimized to minimize the energy

$$E = \int \Psi \hat{H} \Psi d\tau$$

one obtains the multiconfiguration SCF method (MC-SCF).

Today we can perform MCSCF calculations optimizing hundreds of orbitals expanding the wave function Ψ in terms of millions determinants (CASSCF).