

A new approach to Kołos-Wolniewicz wave functions

Tomasz Kubacki, Jacek Komasa

Quantum Chemistry Group, Department of Chemistry,
A. Mickiewicz University, ul. Grunwaldzka 6, 60-780 Poznań

Abstract

The Kołos-Wolniewicz (KW) wave functions are well known in quantum chemistry. In this work we study a possibility of generalization of KW functions towards greater flexibility and compactness. We report on a new approach to evaluation of integrals which allows numerical integration to be avoided. Some preliminary results illustrating an acceleration in energy convergence are reported.

Introduction

Nowadays quantum chemistry enables extremely accurate prediction of energy and other properties of small atomic and molecular systems. Such accurate results can serve as reference values for other less sophisticated theoretical models or for verification of experimental output. Wave functions employed in such precise calculations are designed to properly describe correlation of the movement of electrons. Such functions often contain an explicit interelectron distance variable r_{12} and are called explicitly correlated wave functions. Among them the two-electron James-Coolidge (JC) and Kołos-Wolniewicz wave functions are the most famous as they supplied benchmark results for many decades [1].

In 1933 James and Coolidge [2] applied their wave function to hydrogen molecule. Their ansatz can be written as

$$\Psi(1,2) = \sum_{i=1}^K c_i (\psi_i(1,2) + \psi_i(2,1)) \quad (1)$$

with basis functions expressed in elliptic coordinates

$$\psi_i(1,2) = e^{-\alpha(\xi_1 + \xi_2)} \xi_1^{m_i} \xi_2^{n_i} \eta_1^{k_i} \eta_2^{l_i} \left(\frac{2r_{12}}{R} \right)^{\mu_i} \quad (2)$$

In equation (2) ξ_i , η_i are the coordinates of the i -th electron, r_{12} and R are interelectron and internuclear distance, respectively. The basis functions differ from each other by a set of integer powers k_i , l_i , m_i , n_i , and μ_i whereas the exponential parameter α is common to all the basis functions. Using thirteen such basis functions ($K=13$) James and Coolidge achieved energy accurate to within 1 millihartree. In 1960s Kołos and Wolniewicz [3] modified the JC function (2) adding a term which accounts for a proper asymptotic behavior of the function

$$\psi_i(1,2) = e^{-\alpha\xi_1 - \bar{\alpha}\xi_2} \xi_1^{m_i} \xi_2^{n_i} \eta_1^{k_i} \eta_2^{l_i} \left(\frac{2r_{12}}{R} \right)^{\mu_i} \left(e^{\beta\eta_1 + \bar{\beta}\eta_2} + (-1)^{k_i + l_i + s} e^{-\beta\eta_1 - \bar{\beta}\eta_2} \right) \quad (3)$$

where s determines *gerade* or *ungerade* symmetry of the state. Simultaneously, they increased the number of exponential parameters of the wave function to four:

$$\alpha, \bar{\alpha}, \beta \text{ and } \bar{\beta} \quad (4)$$

In the new approach described here we increase the flexibility of the wave function by assigning each basis function ψ_i its own set of four parameters:

$$\alpha_i, \bar{\alpha}_i, \beta_i \text{ and } \bar{\beta}_i. \quad (5)$$

In such a multiple basis the total number of the nonlinear parameters to be determined variationally increases to $4K$, where K is the number of the basis functions. Additionally, we relax the limitation on the integer powers k_i and l_i and we let them become real nonnegative numbers which fulfill the following condition

$$\forall_{i,j \in \{1,2,\dots,K\}} (k_i + l_j = 0 \vee k_i + l_j \geq 1). \quad (6)$$

In this extended approach the powers k_i and l_i can be optimized together with parameters (5) and the total number of variational parameters increases to $6K$.

The wave functions described above are employed as trial functions in variational method of solving the electronic Schrödinger equation $\hat{H}\Psi = E\Psi$ with the clamped nuclei Hamiltonian

$$\hat{H} = -\frac{\Delta_1}{2} - \frac{\Delta_2}{2} - \frac{1}{r_{a1}} - \frac{1}{r_{b1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b2}} - \frac{1}{r_{12}} + \frac{1}{R}. \quad (7)$$

During the optimization of the wave function the energy is computed many thousands of times. It is therefore crucial that the evaluation of matrix elements is as fast as possible. In the past, some of the integrals composing the matrix elements were evaluated numerically. In our approach all the needed integrals are expressed in terms of elementary or special functions or in terms of series with a controlled convergence. The most important of them are described shortly below.

Elementary integrals

The overlap and Hamiltonian matrix elements can be written down in terms of several types of basic integrals. The first type involves the Legendre's second type function $Q_n(x)$ [4] and can be evaluated using an iterative formula

$$\int_1^{\infty} e^{-ax} x^k Q_n(x) dx = \frac{(2n-1) \int_1^{\infty} e^{-ax} x^{k+1} Q_{n-1}(x) dx - (n-1) \int_1^{\infty} e^{-ax} x^k Q_{n-2}(x) dx}{n}. \quad (8)$$

The elementary integrals appearing on the right hand side of Eq. (8) read

$$\int_1^{\infty} e^{-ax} x^k Q_0(x) dx = \frac{1}{2} \left(\int_1^{\infty} e^{-ax} x^k \ln(x+1) dx - \int_1^{\infty} e^{-ax} x^k \ln(x-1) dx \right), \quad (9)$$

$$\int_1^{\infty} e^{-ax} x^k \ln(x-1) dx = \frac{e^{-a}}{a} \left(\sum_{i=1}^k \frac{k!}{(k-i)! a^i} \left(1 + \frac{1}{2} + \dots + \frac{1}{i} \right) - (\gamma + \ln a) \sum_{i=0}^k \frac{k!}{(k-i)! a^i} \right), \quad (10)$$

$$\int_1^{\infty} e^{-ax} x^k \ln(x+1) dx = \frac{e^{-a} \ln 2 + k \int_1^{\infty} e^{-ax} x^{k-1} \ln(x+1) dx + \int_1^{\infty} e^{-ax} \frac{x^k}{x+1} dx}{a}, \quad (11)$$

$$\int_1^{\infty} e^{-ax} \frac{x^{k+1}}{x+1} dx = \int_1^{\infty} e^{-ax} x^k dx - \int_1^{\infty} e^{-ax} \frac{x^k}{x+1} dx, \quad (12)$$

$$\int_1^{\infty} \frac{e^{-ax}}{x+1} dx = -e^a Ei(-2a), \quad (13)$$

where γ is the Euler's constant and Ei is the exponential-integral function [5] defined as

$$Ei(x) = - \int_{-x}^{\infty} \frac{e^{-t}}{t} dt, \quad x > 0. \quad (14)$$

In equation (8) there is a difference of similar values, which may be a source of numerical precision loss. To eliminate these potential errors we applied multiple precision modules by D. H. Bailey [6] and R. Brent [7].

Another way of solving integral (8) leads through an integral representation of the Legendre function

$$Q_n(x) = \frac{1}{2^{n+1}} \int_{-1}^1 \frac{(1-t^2)^n}{(x-t)^{n+1}} dt. \quad (15)$$

The integrals appearing then can be expressed by means of a converging series

$$\int_{-1}^1 e^{-ax} x^i Ei(-a(1-x)) dx = (\gamma + \ln a) \int_{-1}^1 e^{-ax} x^i dx + \int_{-1}^1 e^{-ax} x^i \ln(1-x) dx + \sum_{k=1}^{\infty} (-1)^k \frac{a^k}{kk!} \int_{-1}^1 e^{-ax} x^i (1-x)^k dx \quad (16)$$

In this case no multiple precision routines are needed but computation time slightly increases.

In the old implementation of the KW method the following two-dimensional integral, containing the Legendre's first type function $P_n(y)$

$$\int_1^{\infty} Q_n(x) \left\{ e^{-ax} x^i \int_1^x e^{-by} P_n(y) y^j dy + e^{-bx} x^j \int_1^x e^{-ay} P_n(y) y^i dy \right\} dx \quad (17)$$

was evaluated by means of numerical quadratures. We have found that it can be evaluated analytically in terms of Eq. (8).

Second type of elementary integrals are given in Eqs. (18) and (19)

$$\int_{-1}^1 e^{ax} x^{2k} \sqrt{1-x^2} dx = \frac{\sqrt{\pi}}{2} \frac{{}_1F_2\left(k + \frac{1}{2}; \frac{1}{2}, k+2; \frac{a^2}{4}\right) \Gamma\left(k + \frac{1}{2}\right)}{\Gamma(k+2)}, \quad (18)$$

$$\int_{-1}^1 e^{ax} x^{2k+1} \sqrt{1-x^2} dx = \sqrt{\pi} \frac{{}_1F_2\left(k + \frac{3}{2}; \frac{3}{2}, 3+k; \frac{a^2}{4}\right) \Gamma\left(k + \frac{5}{2}\right) a}{(2k+3)\Gamma(k+3)}, \quad (19)$$

where ${}_1F_2(a; b, c; x)$ is the hypergeometric function [4,5] and $\Gamma(x)$ is the Euler's Gamma function [4,5]. In the case of real powers of η_i , subject to condition (6), a generalization of the integrals (18) and (19) is needed. Although it introduces complex valued matrix elements, no serious obstacles in evaluating them has been found.

Another type of the basic integrals, displayed in Eqs. (20)-(23), can be computed using the Bessel functions [4,5]

$$\int_1^{\infty} e^{-ax} \sqrt{x^2-1} dx = \frac{BesselK_1(a)}{a}, \quad (20)$$

$$\int_1^{\infty} e^{-ax} x \sqrt{x^2-1} dx = \frac{BesselK_2(a)}{a}. \quad (21)$$

Integration by parts gives

$$\int_1^{\infty} e^{-ax} x^2 \sqrt{x^2-1} dx = \frac{BesselK_1(a)}{a} + 3 \frac{BesselK_2(a)}{a^2} \quad (22)$$

and leads to the following recursive formula:

$$\int_1^{\infty} e^{-ax} x^k \sqrt{x^2-1} dx = \frac{k+1}{a} \int_1^{\infty} e^{-ax} x^{k-1} \sqrt{x^2-1} dx + \int_1^{\infty} e^{-ax} x^{k-2} \sqrt{x^2-1} dx - \frac{k-2}{a} \int_1^{\infty} e^{-ax} x^{k-3} \sqrt{x^2-1} dx. \quad (23)$$

Results of the computations

The integrals, the eigenvalue algorithm, and the optimization suite were coded in a new Fortran program. The linear parameters c_i were found by Choleski decomposition procedure. The nonlinear parameters were optimized using Powell algorithm [8]. Preliminary computations were performed for two small basis sets. First we optimized a 4-parameter wave function. Then, such a function was reoptimized with the relaxed 4K parameters, and finally, the optimization was performed with all 6K nonlinear parameters involved. The results, placed in Table I, show the potential power of reducing the energy error by an order of magnitude in comparison with the classic KW approach.

Table I. Born-Oppenheimer energy (in hartree) of the ground state hydrogen molecule at the equilibrium geometry ($R=1.4$ bohr). The energy error^a is given in parentheses in units of microhartree. K is the wave function expansion length.

K	Number of nonlinear parameters		
	4	4K	6K
5 ^b	-1.173 777 85 (697.86)	-1.174 264 18 (211.53)	-1.174 408 03 (67.68)
22 ^c	-1.174 434 11 (41.60)	-1.174 473 50 (2.21)	-1.174 474 77 (0.94)

^a The error is estimated with respect to $-1.174 475 714 0$ hartree computed by W. Cencek and J. Rychlewski, cited in [1].

^b Basis set definition ($\mu mk nl$): 0 00 00, 0 00 02, 0 01 01, 1 00 00, 0 00 10.

^c Basis set definition ($\mu mk nl$): 0 00 00, 0 00 02, 0 01 01, 1 00 00, 0 00 10, 0 10 10, 1 00 10, 2 00 00, 0 00 30, 0 10 02, 0 01 11, 1 00 20, 1 00 02, 1 10 10, 2 00 10, 0 00 22, 0 20 02, 0 02 02, 0 11 11, 1 01 11, 2 01 01, 0 01 13.

References

- [1] J. Rychlewski and J. Komasa, *Explicitly correlated functions in variational calculations* in: *Explicitly Correlated Wave Functions in Chemistry and Physics*, J. Rychlewski (ed.), Kluwer Academic Publishers (2003), p. 91.
- [2] H. H. James and A. S. Coolidge, *J. Chem. Phys.* **1**, 823 (1933).
- [3] W. Kołos and L. Wolniewicz, *J. Chem. Phys.* **43**, 2429 (1965).
- [4] E. T. Whittaker and G. N. Watson, *Kurs analizy współczesnej*, PWN, Warszawa (1968).
- [5] *Handbook of Mathematical functions*, M. Abramowitz and I. A. Stegun (ed.), Dover Publications, Inc., New York (1970).
- [6] <http://crd.lbl.gov/~dhbailey/mpdist/>
- [7] <http://web.comlab.ox.ac.uk/oucl/work/richard.brent/>
- [8] M. J. D. Powell, *Comput. J. (UK)* **7**, 155 (1964).