

Rational Function Approximation for Atomic and Molecular Wave Functions*

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Rational functions, the quotients of two polynomials, often provide uniformly accurate approximations for many of the classical functions of mathematical physics. Recently there has been renewed interest in the application of rational functions, especially the Padé approximant, to chemical and physical problems [1]. We propose here the use of rational functions to approximate electronic wave functions for atoms and molecules.

Rational functions will be useful only if they provide a more efficient representation than other basis functions, e.g., Slater-type orbitals. A simple test and illustration of the applicability of rational functions is the minimization of the energy of the helium atom with the orbital

$$(1) \quad \phi_a(\zeta r) \equiv (\zeta r + a)^{-1} \exp(-\zeta r) / \sqrt{4\pi}$$

and two-electron spatial wave function,

$$(2) \quad \psi_{\text{He}} = \phi_a(\zeta r_1) \phi_a(\zeta r_2)$$

ϕ_a has the simplest nontrivial rational function as a factor. The integrals necessary for the energy are,

$$(3) \quad \langle \phi_a | \phi_a \rangle = \zeta^{-3} a \exp(2a) [E_0(2a) - 2E_1(2a) + E_2(2a)]$$

$$(4) \quad \begin{aligned} \langle \phi_a | -\frac{1}{2}\nabla^2 - 2/r | \phi_a \rangle &= -\frac{1}{2} \{ \frac{1}{2} (\zeta a)^{-1} \exp(2a) [E_4(2a) - 2E_3(2a)] \} \\ &\quad - 2 \{ \zeta^{-2} \exp(2a) [E_1(2a) - E_2(2a)] \} \end{aligned}$$

$$(5) \quad \begin{aligned} \langle \phi_a \phi_a | 1/r_{12} | \phi_a \phi_a \rangle &= \zeta^{-5} \{ a - (1 + 4a + 8a^2) \exp(4a) E_1(4a) + (1 + 2a)^2 \exp(2a) E_1(2a) \\ &\quad - a(2a + 1)(2a + 2) \exp(4a) [E_1(2a)]^2 \} \end{aligned}$$

where [2]

$$(6) \quad E_n(x) \equiv \int_1^\infty dt t^{-n} \exp(-xt)$$

The energy obtained with $a = 1.371$ and $\zeta = 1.178$ (Bohr radii)⁻¹ is -2.8616375 a.u. As displayed in Table I, this energy is the lowest energy of any *two*-parameter orbital for helium known to date§, and it comes within 4.25×10^{-5} a.u. of the Hartree-Fock energy [3].

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§ Of course, many *three*-parameter orbitals give a better energy, e.g., the well-known "double zeta" orbital.

TABLE I. Single determinant ground-state energies for helium with various approximate orbitals with one and two parameters.

Orbital	Energy (a.u.)	Comment
$\exp(-1.6875 r)$	-2.847656	(Single parameter) screened 1s
$r^{-0.045} \exp(-1.61162 r)$	-2.85421[a]	Noninteger- n Slater-type orbital
$\exp\{-0.952273 r[1 + \exp(-0.134000 r)]\}$	-2.860451[b]	(Two-parameter) variable screening
$r^{-1}[\exp(-1.01657 r) - \exp(-2.81522 r)]$	-2.8608[c]	Os Slater-type orbital
$(1 + 2.81522 r^2) \exp(-1.01657 r)$	-2.86147[d]	Best two-Slater-type-orbital function with single exponential
$r^{-1}f(df/dr)^{1/2} \exp(-f)$ with $f = [-1 + (1 + 4\alpha\zeta r)^{1/2}]/2\alpha$	-2.8615[e]	Non-transparent approximation
$(1.178 r + 1.371)^{-1} \exp(-1.178 r)$	-2.8616375	Rational function—this work
ϕ_{HF}	-2.861680[f]	Twelve-basis function approximation to Hartree-Fock

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[f] Ref. [3].

Further indications of the quality of the two-parameter function $\phi_a(\zeta r)$ are the orbital energy and the cusp value. The orbital energy with ϕ_a is -0.917964 a.u., almost identical with the Hartree-Fock value [3], -0.917956 a.u. The cusp value is $(d/dr) \log \phi_a(\zeta r)_{r=0} = -2.037$, versus -2 for the exact Hartree-Fock orbital.

The success of this simple orbital suggests that rational functions* can furnish more efficient representations of electronic wave functions than the usual Slater-type orbitals.

Bibliography

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* We note in passing that $\phi_a(\zeta r)$ can be regarded as an integral transform function [4] with weight function $f(x) = 0, x < \zeta, f(x) = \zeta^{-1} \exp(a - \zeta^{-1} ax), x \geq \zeta$.