

# Piecewise polynomial basis functions for configuration interaction and many-body perturbation theory calculations. The radial limit of helium

Harris J. Silverstone and Dennis P. Carroll

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

David M. Silver

Applied Physics Laboratory, The Johns Hopkins University, Laurel, Maryland 20810

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Highly accurate configuration interaction and many-body perturbation theory calculations are shown to be possible with piecewise polynomial basis functions. In a preliminary calculation on the helium atom ground state, a new upper bound of  $-2.8790286$  a.u. is found for the radial limit.

## INTRODUCTION

Although the configuration interaction (CI) method is able to represent an electronic wavefunction to arbitrary accuracy, computational linear dependence, or numerical instability associated with the large bases required for accuracy, usually imposes a severe limitation. For example, the best conventional CI value in the literature for the radial limit of the helium ground state is  $-2.8790255$  a.u., obtained by Bunge<sup>1</sup> with a basis of ten Slater-type orbitals. The error, which is greater than  $3 \times 10^{-6}$  a.u., is enormous compared to the errors in non-CI calculations of the *total* energy of helium, namely the  $2 \times 10^{-9}$  a.u. error in the *total* nonrelativistic energy in Pekeris' "conventional" perimetric coordinate calculation,<sup>2</sup> and the estimated  $10^{-12}$  a.u. error in the Frankowski-Pekeris "logarithmic" calculation.<sup>3</sup> Attempts to use Slater-type orbital bases with much more than ten  $s$  orbitals for helium seem to have encountered practical difficulties.

Similarly, other methods, such as many-body perturbation theory<sup>4-6</sup> (MBPT), when finite basis set expansions are used, are no more accurate than their bases, whose practical limitation is often computational linear dependence.

Recently piecewise polynomial basis functions have been used to calculate the Hartree-Fock energy of helium.<sup>7</sup> Compared to Slater or Gaussian bases, piecewise polynomial bases are relatively free from computational linear dependence. Since the error in the best reported piecewise polynomial Hartree-Fock energy, which was estimated to be  $10^{-14}$  a.u., is small compared to the *total* energy errors in the Pekeris and Frankowski-Pekeris calculations, the possibility suggests itself that piecewise polynomial bases might permit CI and MBPT calculations of much higher accuracy than Slater or Gaussian bases.

The purpose of this paper is to show the potential of piecewise polynomial basis functions for high accuracy CI and MBPT calculations. In this preliminary study, we start from the Hartree-Fock calculations reported earlier<sup>7</sup> and carry out CI and MBPT calculations in the Hartree-Fock bases, obtaining in the end a new upper bound of  $-2.8790286$  a.u. for the helium radial limit.

The piecewise polynomial method is outlined in the next section. In succeeding sections the numerical results are given and discussed.

## PIECEWISE POLYNOMIAL WAVEFUNCTIONS AND HERMITE'S INTERPOLATION FORMULA

Of various piecewise polynomial methods, the "Hermite interpolation formula" (HIF) scheme is most convenient for high accuracy variational calculations.<sup>7</sup> The gist of the scheme is outlined here in a way intended to complement the more detailed discussion in Ref. 7.

We fix (a) a subdivision of the positive  $r$  axis by mesh points  $r_0 = 0 < r_1 < r_2 \cdots < r_n < \infty$ , and (b) the order of the polynomials, which is to be odd and denoted by  $2s + 1$ . We then define  $N \times (s + 1)$  radial basis functions  $\chi_{kn}(r)$ , indexed by  $k = 0, 1, \dots, s$ , and by  $n = 0, 1, \dots, N - 1$ , which have the special properties,

$$\chi_{kn}(r) \equiv 0, \quad (r \leq r_{n-1}, r \geq r_{n+1}), \quad (1)$$

$$(d/dx)^l \chi_{kn}(r) \Big|_{r=r_m} = \delta_{kl} \delta_{mn}, \quad (l \leq s). \quad (2)$$

The explicit definition of  $\chi_{kn}$  on the two subintervals (one in the case of  $\chi_{k0}$ ) on which it is not identically zero is a direct application<sup>7</sup> of Hermite's interpolation formula<sup>8</sup>:

$$\begin{aligned} \chi_{kn}(r) &= \frac{(-1)^k (r_n - r_{n-1})^k}{k!} \\ &\times \sum_{l=k}^s \left[ \binom{2l-1-k}{l-1} (r - r_{n-1}) \right. \\ &\quad \left. - \binom{2l-1-k}{l} (r_n - r) \right] \frac{(r - r_{n-1})^l (r_n - r)^{s-l}}{(r_n - r_{n-1})^{2l+1}}, \\ &\quad (r_{n-1} \leq r \leq r_n), \quad (3) \\ &= \frac{(r_{n+1} - r_n)^k}{k!} \sum_{l=k}^s \\ &\times \left[ \binom{2l-1-k}{l-1} (r_{n+1} - r) \right. \\ &\quad \left. - \binom{2l-1-k}{l} (r - r_n) \right] \frac{(r - r_n)^l (r_{n+1} - r)^{s-l}}{(r_{n+1} - r_n)^{2l+1}}, \\ &\quad (r_n \leq r \leq r_{n+1}), \quad (4) \end{aligned}$$

TABLE I. Radial limits for the helium ground state.

Author	Type of calculation	Basis	Radial limit (a.u.)
Davis <sup>a</sup>	CI	11 Laguerre polynomials times a common exponential	-2.8790248
Bunge <sup>b</sup>	CI	10 Slater-type orbitals	-2.8790255
Schwartz <sup>c</sup>	CI	45 terms of form $r_1^m r_2^n e^{-(r_1+r_2)}$	-2.8790264
present	MBPT	Raffenetti <sup>d</sup> eight term even-tempered Slater-type basis	-2.8788115
present	MBPT	Septic HIF polynomial, $N=7^e$	-2.8788223
present	MBPT	Septic HIF polynomial, $N=9^e$	-2.8788227
present	CI	Raffenetti <sup>d</sup> eight term even-tempered Slater-type basis	-2.8790174
present	CI	Septic HIF polynomial, $N=7^e$	-2.8790282
present	CI	Septic HIF polynomial, $N=9^e$	-2.8790286

<sup>a</sup>Reference 16.<sup>b</sup>Reference 1.<sup>c</sup>Reference 17.<sup>d</sup>Reference 9.<sup>e</sup>Reference 7.

where always ( $\bar{y}_k^{(h)}$ ) is to be taken as 0. If  $\bar{y}(r)$  denotes the HIF representation of a function  $y(r)$ , then the *expansion coefficients* are just the functional and derivative values of  $\bar{y}$  at the mesh points:

$$\bar{y}(r) = \sum_{n=0}^{N-1} \sum_{k=0}^s \bar{y}_k^{(h)}(r_n) \chi_{kn}(r). \quad (5)$$

Note that the largest value of  $n$  in Eq. (5) is  $N-1$ , so that by Eq. (4)  $\bar{y}(r)$  and its first  $s$  derivatives vanish at  $r_n$ . One is tempted to characterize this boundary condition by the term "spherical hyperbox."

The  $\chi_{kn}$  form an  $N \times (s+1)$  dimensional nonorthogonal basis of radial functions. After one obtains the matrix elements of  $\nabla^2$ ,  $1/r$ , and  $1/r_{12}$ , whose calculation is straightforward,<sup>7</sup> the nature of the basis is no longer apparent in a quantum mechanical calculation.

### CI AND MBPT CALCULATIONS

For a quick assessment of polynomial bases in CI and MBPT calculations, we took the Hartree-Fock occupied and virtual orbitals from the septic ( $s=3$ )  $N=7$  and  $N=9$  bases reported in Ref. 7, and we computed complete CI and MBPT energies. These bases have Hartree-Fock errors of  $3 \times 10^{-10}$  and  $1 \times 10^{-11}$  a.u., respectively, and have been chosen because of their balance of accuracy for the Hartree-Fock calculation and size (28 and 36 basis functions, respectively). For a parallel comparison with Slater-type orbitals, we carried out the same CI and MBPT calculations in the eight term even-tempered Hartree-Fock basis of Raffenetti.<sup>9</sup> We also tried to use Raffenetti's 12 term basis, but we encountered severe linear dependence problems. The results of all these calculations are summarized in Table I and are compared with other values for the radial limit in the literature.

The MBPT wavefunction contains all doubly excited configurations, with expansion coefficients given by

first order perturbation theory. For the unperturbed Hamiltonian  $\mathcal{H}_0$ , we used the sum of two one electron  $V^{N-1}$  Hamiltonians (cf. <sup>10-15</sup>) defined by

$$-\frac{1}{2} \nabla^2 - 2/r + J_{1s}(r), \quad (6)$$

where  $J_{1s}(r)$  is just the usual Coulomb operator associated with the occupied  $1s$  orbital. The Hartree-Fock  $1s$  orbital is an eigenfunction of this one-electron Hamiltonian, and there are rigorously no single excitations in the first order wavefunction. From an optimum mixture of the zeroth and first order wavefunctions, an energy upper bound was obtained as the expectation value of the full Hamiltonian.<sup>6</sup> The MBPT energies fall approximately  $2.06 \times 10^{-4}$  a.u. higher than the CI energies. This deficiency is the result of omitting higher order terms in the MBPT wavefunction, with 70% of the deficiency attributable to single excitations.

### DISCUSSION

One notes immediately that both of the piecewise polynomial bases give radial limits  $2 \times 10^{-6}$  a.u. lower than the best nonextrapolated value in the literature, and that  $-2.8790286$  a.u. is a new upper bound to the radial limit. No hint of numerical instability could be found in dealing with what are quite large basis sets in the  $1s^2$  radial limit context. We conclude that high accuracy CI and MBPT calculations can be readily carried out with piecewise polynomial basis functions.

The choice of mesh points is fundamental to the efficiency of a piecewise representation. The two sets used here were designed to suit the  $1s$  Hartree-Fock orbital and are by no means ideal for representing electron correlation. Although both give better radial limits than any previous calculation, the difference between them of  $4 \times 10^{-7}$  a.u., which is three orders of magnitude larger than the difference of their Hartree-Fock values, reflects the nonoptimization of the mesh. Further insight

can be gained from a natural orbital analysis<sup>1,18</sup>: we find only 13 (approximate) natural orbitals in the  $N=7$  case, and 16 in the  $N=9$  case, contributing greater than  $10^{-8}$  a.u. to the energy, and only the first eight or nine natural orbital energy contributions in the  $N=9$  case seem to have converged to within  $10^{-8}$  a.u. of their ultimate values. A more appropriate mesh, for which a greater number of natural orbitals would have converged, would have a greater point density for small  $r$ , the region in which the higher natural orbitals are rapidly oscillating [cf. Eq. (11) of Ref. 7].

With suitably chosen meshes, it is possible that piecewise polynomial basis functions will permit quantum mechanical treatments of atoms other than helium to an accuracy approaching that of a conventional Pekeris calculation.

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