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PIECEWISE POLYNOMIAL HYLLERAAS CONFIGURATION INTERACTION WAVEFUNCTIONS
FOR HELIUM

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ABSTRACT

The scientific problem treated in this work is that of describing the electronic structure of atoms and molecules with sufficient accuracy to be useful for predictions of chemical properties. The present activity consists of deriving computational solutions of the many-body Schrodinger equation for small chemical species. Two specific objectives are to explore the consequences of an explicit correlation term in the electronic wavefunction and to examine the effectiveness of certain mathematical forms as an expansion basis. The magnitude of the computational problem is massive and the existence of supercomputers like the CYBER 205 helps to bring these problems into a feasible range.

I. INTRODUCTION

The most widely used technique for representing electronic wavefunctions is "configuration interaction" (CI). CI trades accuracy for flexibility: the accuracy of CI energies has a practical limit¹ of 0.0005 eV. To go beyond this limit requires explicitly correlated wavefunctions (i.e., which depend on the interelectronic coordinate r_{12} , such as in the Hylleraas and the CI-Hylleraas methods.²

One "benchmark" for helium calculations is the value obtained by Pekeris³ using a Hylleraas wavefunction⁴ whose basis consisted of 1078 functions of the form, $(r_1+r_2)^i(r_1-r_2)^j r_{12}^k \exp[-c(r_1+r_2)]$, with $i+j+k < 21$. Pekeris' value was -2.903724375 a.u., whose error is 2×10^{-9}

a.u. A second benchmark is the Frankowski-Pekeris⁵ calculation, whose main difference from the Pekeris calculation was the use of powers of $\log(r_1+r_2)$: the result, -2.9037243770326 a.u.; the error, 2×10^{-12} a.u. A third and final benchmark is a slight modification of the Frankowski-Pekeris calculation by Freund, Huxtable, and Morgan,⁶ who obtained -2.90372437703407 a.u.

A methodological limitation of these three calculations is that they are difficult to apply to other atoms because of the problem of evaluating the multi-electron integrals that arise. For molecules the problem is exacerbated by the existence of multi-center multi-electron integrals involving exponentials.

The present work addresses the integrals problem by choosing a piecewise polynomial Hylleraas configuration interaction (PP-HY-CI) basis rather than the exponentials in the Pekeris expansion. More precisely, the PP-HY-CI wavefunction is constructed to have the form:

$$\text{CI-wavefunction} + r_{12} \times \text{CI-wavefunction}'$$

in which the radial parts of the orbitals are piecewise polynomials.^{1,7,8} For atoms, the radial integrals are reduced to localized, disjoint contributions, which are considerably fewer in number than would arise from bases of Slater or Gaussian functions of the same size.

In scope the PP-HY-CI wavefunction is similar to the Pekeris wavefunction, but with a distribution of exponentials. One aim of this work is to examine the rate of convergence of such expansions and to evaluate the need for additional logarithmic factors.

The next Section presents details of the PP-HY-CI method. Section III discusses some computational aspects of the problem. In Section IV, numerical results are given for the ground state of the helium atom. The final section contains some observations and conclusions.

II. THE PP-HY-CI METHOD

The HY-CI method has been developed principally by Hagstrom and coworkers.² The wavefunction, specialized for the ground state of helium, has the form

$$\psi = \psi_{\text{CI}} + r_{12} \times \psi'_{\text{CI}} \quad (1)$$

where

$$\psi_{CI} = \sum_{n_1 n_2 \ell m} C_{n_1 n_2 \ell m} R_{n_1 \ell}(r_1) R_{n_2 \ell}(r_2) Y_{\ell m}(\theta_1 \phi_1) Y_{\ell m}^*(\theta_2 \phi_2) \quad (2)$$

and where the $Y_{\ell m}$ are the usual spherical harmonics. ψ_{CI} is similar to ψ_{CI} , but with different expansion coefficients, $C_{n_1 n_2 \ell m}$. The radial orbitals $R_{n \ell}$ are here expanded on a piecewise polynomial basis set.¹

In particular, the piecewise polynomials are fixed by the "mesh" defining the subdivision of the r-axis into finite elements, the degree of the polynomials, and the degree of continuity at the mesh points. The most convenient organization of the raw polynomials is into "mesh-oriented unit-nth-derivative" (MOUND) functions which have the property that each basis function and its first s derivatives are zero at every mesh point, except for one derivative, say the n th, whose value is unity at only one mesh point, say r_p :

$$\left. (d/dr)^k \chi_{np}(r) \right|_{r=r_m} = \delta_{kn} \delta_{pm}, \quad (k < s). \quad (3)$$

These MOUND functions are given explicitly by a formula based on Hermite's interpolation formula:⁹

$$\begin{aligned} \chi_{np}(r) &\equiv 0, \quad (r < r_{p-1}, r > r_{p+1}) \\ &= \sum_{k=n}^s \binom{2k-n}{k} \frac{(-1)^n}{(2k-n)n!(r_p - r_{p-1})^{2k+1-n}} \quad (4) \end{aligned}$$

$$\begin{aligned} &\times [k(r-r_{p-1})^{k+1}(r_p - r)^k - (k-n)(r-r_{p-1})^k(r_p - r)^{k+1}], \\ &(r_{p-1} < r < r_p), \quad (5) \end{aligned}$$

$$\begin{aligned} &= \sum_{k=n}^s \binom{2k-n}{k} \frac{1}{(2k-n)n!(r_{p+1} - r_p)^{2k+1-n}} \\ &\times [k(r - r_p)^k(r_{p+1} - r)^{k+1} - (k-n)(r - r_p)^{k+1}(r_{p+1} - r)^k], \\ &(r_p < r < r_{p+1}). \quad (6) \end{aligned}$$

If $R(r)$ is any PP function of degree $2s+1$, then the expansion coefficients

of $R(r)$ on the MOUND basis are just the values of R and its first s derivatives at the N mesh points,

$$R(r) = \sum_{n=0}^s \sum_{p=0}^N R^{(n)}(r_p) \chi_{np}(r). \quad (7)$$

III. COMPUTATIONAL ASPECTS

With the form of the wavefunction specified by Eqs. (1)-(7), the problem is to calculate the expansion coefficients, $C_{n_1 n_2 \ell m}$ and $C'_{n_1 n_2 \ell m}$, and the expectation value for the energy. First one must calculate the matrix elements of the Hamiltonian H with respect to the $R_{n_1 \ell} R_{n_2 \ell}$ configurations and $r_{12} R_{n_1 \ell} R_{n_2 \ell}$ " r_{12} -configurations." The formulas are similar to those given in Ref. 1, Appendix A, but require here the expansion of r_{12} in spherical harmonics. Next the H matrix is transformed to an orthogonalized basis, and the lowest root is determined by standard methods.^{10,11} The transformation step is the most consumptive of computational effort and was accomplished by adaptations of a method described by Bender¹² involving successive quarter transformations.

The calculations were executed on the CYBER 205 at Colorado State University. For most of the work, double precision (128 bit word length) was required to eliminate numerical differencing arising from the inherent over-completeness (near linear dependence) of the HY-CI wavefunction. In selected subroutines, FORTRAN code was modified in order to permit vectorization of some DO loops. The overall increase in performance (i.e., decrease in execution time) from the original code to the final "optimized" version was a factor of two. Performance increases in selected subroutines were on the order of three to five.

The computer programs used in this work were originally written for use on a DEC 10 computer. For some small-scale comparison runs, the increase in execution speed was on the order of a factor of 50 faster on the CYBER 205 over the DEC 10. Larger-scale comparisons would be expected to yield even higher ratios of performance. Two additional aspects of the CYBER 205 made its use advantageous over the DEC 10: namely, the existence of 128 bit double precision (mentioned above) and virtual memory which facilitated the scaling-up of the calculations for higher-order cases.

Memory management became important during a matrix transformation procedure for the larger calculations performed. Since the matrix is hermitian, only a lower triangle of the matrix elements had been stored and

an indexing array had been used to identify terms. When the matrices became large (1800 x 1800), the efficiency of the virtual memory manager was thwarted because entire columns of the matrix were required in sequence. These were obtained by accessing an element per column until the column containing the diagonal element, then proceeding down that column. The solution was to produce a copy of the matrix that included the redundancies so that all elements of any given column would be available together. This yielded an efficient execution.

IV. NUMERICAL RESULTS

The calculated ground state energies of helium for PP-HY-CI wavefunctions with various polynomial degrees, mesh points, and maximum angular momentum quantum numbers are given in Table I. The maximum angular momentum quantum numbers are designated S, P, D and F. In each column, the energies (going downward) approach an "S-limit", "P-limit", etc. The convergence of these results is illustrated further in Table II where differences between these calculated energies and the "extrapolated energy" of Frankowski-Pekeris⁵ are tabulated.

Table I. Calculated ground state energy of helium for PP-HY-CI wavefunctions^a

Mesh ^b	S	P	D	F
3 x 5	-2.902576	-2.903627	-2.903664	-2.9036669
5 x 3	-2.90343133	-2.90371793	-2.90372043	-2.90372058
5 x 4		-2.90372134		
5 x 6		-2.90372414		
7 x 3	-2.90349584	-2.9037242176	-2.903724350	-2.9037243515
7 x 4	-2.90349783	-2.9037242611	-2.9037243741	
7 x 5	-2.90349807	-2.9037242665	-2.9037243766	
7 x 6	-2.90349823	-2.9037242679	-2.9037243769	
7 x 7	-2.90349827			

^a Energies in a.u.

^b Mesh is defined as the polynomial degree (2s + 1) x the number of mesh points (N).

Table II. Difference in energy between the calculated PP-HY-CI results and the extrapolated Frankowski-Pekeris^a energy for helium.^b

Mesh ^c	S x 10 ⁴	P x 10 ⁷	D x 10 ¹⁰	F x 10 ¹⁰
3 x 5	11.5	973.77	599,770	570,000
5 x 3	2.93	64.47	39,470	38,000
5 x 4		30.33		
5 x 6		23.34		
7 x 3	2.29	1.60	270	254
7 x 4	2.27	1.16	29.5	
7 x 5	2.26	1.11	4.05	
7 x 6	2.26	1.09	1.37	
7 x 7	2.26			

^a Ref. 5

^b Energies in a.u.

^c Mesh is defined as the polynomial degree (2s + 1) x the number of mesh points (N).

Table III. Comparison of selected configuration interaction energies for the helium atom^a

Energy	(year)	Author	[Ref.]	Basis ^b
-2.8992	(1928)	Hylleraas	[13]	SEL
-2.90170	(1963)	Davidson	[14]	NRO-SEL
-2.90322	(1966)	Ahlrichs et al.	[15]	NRO-STO
-2.90338	(1965)	Green et al.	[16]	STO
-2.90344	(1958)	Tycko et al.	[17]	SEL
-2.90370	(1979)	Carroll et al.	[1]	NRO-PP

^a Energies in a.u.

^b Definitions: SEL is single exponential Laguerre, NRO is natural radial orbital, STO is Slater-type orbital, PP is-piecewise polynomial.

Table IV. Comparison of selected non-configuration interaction energies for the helium atom^a

Energy	(year)	Author	[Ref.]	Basis ^b
-2.90324	(1929)	Hylleraas	[4]	HY
-2.903498	(1984)	This work		PP-HY-CI S-limit
-2.903624	(1976)	Morrell, et al.	[18]	HYPER-CO
-2.9037225	(1957)	Kinoshita	[19]	K
-2.9037239	(1963)	Davidson	[14]	K
-2.90372424	(1976)	Sims, et al.	[2]	HY-CI
-2.90372427	(1984)	This work		PP-HY-CI P-limit
-2.90372435	(1963)	Scherr-Knight	[20]	PT
-2.903724375	(1959)	Pekeris	[3]	HY-P
-2.90372437616	(1962)	Schwartz	[21]	HY-P
-2.9037243769	(1984)	This work		PP-HY-CI D-limit
-2.9037243770326	(1966)	Frankowski-Pekeris	[5]	HY-P
-2.90372437703407	(1983)	Freund, et al.	[6]	HY-P

^aEnergies in a.u.

^bDefinitions: HY is "Hylleraas," PP-HY-CI is piecewise polynomial Hylleraas configuration interaction, HYPER-CO is hyperspherical coordinates, K is "Kinoshita," PT is perturbation theory, HY-P is "Hylleraas-Pekeris."

Representative lists of total energies for helium are given in Table III for configuration interaction^{1,13-17} and in Table IV for non-configuration interaction^{2-6,14,18-21} approaches. The earliest CI calculation is that of Hylleraas,¹³ who quickly thereafter initiated non-configuration interaction techniques.⁴ Comparison of the two Tables indicates the slow convergence of the CI expansion for helium: the most accurate CI results¹ do not even reach the P-limit of the non-CI method.

V. OBSERVATIONS AND CONCLUSIONS

The convergence of the PP-HY-CI calculations for the energy of helium as a function of maximum angular momentum quantum number, L , appears to be on the following order: the S-limit residue is 10^{-4} a.u., the P-limit residue is 10^{-7} a.u., the D-limit residue is 10^{-10} a.u. An extrapolation to

the F-limit gives an estimate of 10^{-12} a.u. or better for this residue. Thus, the F-limit results might exceed the quality of the Frankowski-Pekeris⁵ limit. One implication of this situation is that it may not be necessary to include logarithmic factors in the HY-CI expansion to achieve the Frankowski-Pekeris result. The intrinsic flexibility arising from the disjoint nature of the piecewise polynomial basis functions is responsible.

A further observation from Tables I and II is that the wavefunction needs to be saturated with functions of low angular momentum quantum number, S and P, before the functions with higher L values can make a contribution in their own realm. This is especially evident for the D component of the wavefunction for each mesh represented, and the 5 x 3 mesh indicates that the effect is also present for the F components.

Work in progress is extending this work to an application to the hydrogen negative ion (H^-). The wavefunction for H^- needs to be more diffuse and extend to larger radial distances than needed for He. The initial indication is that the piecewise polynomial basis functions can yield this flexibility. The final accuracy of the H^- calculation is expected to be uniform with that found for He.

In principle, the configuration interaction technique offers an expansion of the wavefunction in a complete space of many-electron functions. Hence the addition of the r_{12} - CI factor, the second term in Eq. (1), produces an expansion that is over-complete. One advantage is faster convergence than for CI alone but linear dependence is a consequence. In the present work, this aspect led to the need for high precision numerical techniques.

The characteristics of piecewise polynomial basis functions combined with the Hylleraas configuration interaction expansion offer a useful approach to the determination of electronic wavefunctions. The ability of this approach to achieve high accuracy for the energy of helium and other two-electron systems makes it necessary to re-examine arguments related to the functional forms needed for a complete description of a wavefunction.

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