

Current Studies of Few-Electron Systems

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Abstract: We review our current work on approaches to the description of three- and four-body systems using fully correlated exponential orbitals. This basis permits the construction of compact, yet surprisingly accurate wavefunctions, and is also useful (in more extended expansions) for highly precise studies of both adiabatic and nonadiabatic systems. Our presentation touches on both methodology and results.

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1 Fully Correlated Wavefunctions

The term *fully correlated wavefunction* refers to a description in which all the interparticle coordinates r_{ij} of a several-particle system occur explicitly in its wavefunction. Historically, such wavefunctions date back to work of Hylleraas on the He atom [1], and not long thereafter to the classic paper on H₂ by James and Coolidge [2]; both these works appended powers of the inter-electron distance r_{12} to a form exponential in the electron-nuclear distances r_i . A basis of this sort for atoms has become known as a Hylleraas basis, and a well-known example of its use is in the extremely precise studies of the He atom by Pekeris [3].

More recently a number of studies have used basis functions in which all the interparticle distances occur exponentially. We call these functions *fully correlated exponentials*; for a four-body system they have the generic form

$$\psi = \exp(-\alpha_{12}r_{12} - \alpha_{13}r_{13} - \alpha_{14}r_{14} - \alpha_{23}r_{23} - \alpha_{24}r_{24} - \alpha_{34}r_{34}). \quad (1)$$

The use of such functions in three-body problems was considered as long ago as 1962 by Calais and Löwdin [4]; early applications were by Delves and Kalotas [5] and Thakkar and Smith [6]. Our group has reported extremely compact versions of the integrals associated with their use in conventional energy calculations [7] (see also Abbott and Maslen [8]) and has also treated various singular integrals arising in properties calculations and in the study of relativistic effects [7, 9].

For four-body systems, analytical approaches for the necessary integrals seemed impossible until Fromm and Hill [10] reported general formulas. See also work by Remiddi [11], by the present author alone [12] and in work with Frolov and Vedene Smith [13], and by Pachucki, Puchalski, and Remiddi [14]. At this time there seems no hope of extending the machinery of fully correlated exponentials to more than four particles.

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Table 1: Properties of compact He ground-state wavefunctions: electronic energy E ; expectation values of position and momentum correlations $\mathbf{r}_1 \cdot \mathbf{r}_2$ and $\mathbf{p}_1 \cdot \mathbf{p}_2$, and of wavefunctions at points of particle coincidence; electron-nuclear (ν_1) and electron-electron (ν_{12}) cusps. The “exact” values are from [23].

	1 cfg	2 cfg	3 cfg	4 cfg	Exact
E	-2.899 534	-2.903 270	-2.903 629	-2.903 688 3	-2.903 724
$E - E_{\text{exact}}$	0.004 190	0.000 454	0.000 095	0.000 036 1	
$\langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle$	-0.085 010	-0.064 522	-0.064 373	-0.064 662	-0.064 737
$\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle$	0.192 818	0.160 746	0.158 308	0.158 902	0.159 069
$\langle \delta(\mathbf{r}_1) \rangle$	1.777 836	1.783 896	1.810 488	1.807 626	1.810 429
$\langle \delta(\mathbf{r}_{12}) \rangle$	0.129 494	0.111 481	0.108 729	0.108 367	0.106 345
$\langle \delta(\mathbf{r}_1)\delta(\mathbf{r}_2) \rangle$	2.000	1.803	1.849	1.885	1.869
ν_1	-1.962	-1.967	-2.001	-1.993	-2.000
ν_{12}	+0.207	+0.368	+0.427	+0.436	+0.500

For both three- and four-body systems, the formalism permits the use of complex parameters in the exponents (the α_{ij}). This has been found [15] to give the basis an important additional degree of flexibility, but has not yet seen comprehensive application to four-body systems.

An alternative to the use of fully correlated exponentials which does not have a firm four-body limit would be to employ fully correlated Gaussians. These have been used by a number of authors, including Vedene Smith [16, 17, 18]. Their main disadvantage is an inability to describe the cusps at interparticle coincidences; a less crucial problem is their incorrect long-distance limiting behavior. It has been proposed to improve the cusp behavior by augmenting the Gaussian basis with linear powers of the interparticle distances [19]. This increases the number of integrals which are required, and our recent efforts in developing a recursive formulation [20, 21] may be relevant.

The presentation will include a survey of our current work on integral evaluation methods.

2 Compact Wavefunctions

An extremely convenient use of a fully correlated exponential basis is in the compact representation of wavefunctions which, in other formulations, would require multiple terms to give even a zero-order representation of all the particle-particle interactions. An example is provided by our analysis of the ground states of the He isoelectronic series, which we studied for nuclei of infinite mass and for values of the nuclear charge Z from 1 through 10 [22]. To obtain optimum wavefunctions it is crucial to optimize all the nonlinear parameters for each basis member; we did so for wavefunctions consisting of one through four simultaneously optimized basis members (configurations), each (before symmetrization) of form $\phi_i = \exp(-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12})$. The results for neutral He ($Z = 2$) are shown in Table 1. The “exact” values with which we compare our results are from the highly accurate (and far more extensive) computations by Frolov and Smith [23], and are surely correct to all the digits shown.

In order to study trends in the isoelectronic series, we carried out meticulous optimizations of four-configuration wavefunctions for all the series members from $Z = 1$ through $Z = 10$, obtaining the electronic energies shown (for representative Z values) in Table 2. We note that the orderly trend exhibited in that table only emerged when the optimizations were in fact complete; various other studies with apparently less complete optimizations have not shown this degree of regularity.

The most striking feature of the data in Table 2 is that these highly compact functions are

Table 2: Ground-state energies computed for optimized four-configuration wavefunctions.

	$E(4 \text{ cfg})$	$E(\text{Exact})$	$E - E(\text{Exact})$
H^-	-0.527 713 1	-0.527 751 0	0.000 037 9
He	-2.903 688 3	-2.903 724 4	0.000 036 1
Be^{+2}	-13.655 532 2	-13.655 566 2	0.000 034 0
C^{+4}	-32.406 213 2	-32.406 246 6	0.000 033 4
O^{+6}	-59.156 562 2	-59.156 595 1	0.000 032 9
Ne^{+8}	-93.906 773 7	-93.906 806 5	0.000 032 8

capable of yielding energies within 40 microhartrees of the exact values, and that other properties (cf. Table 1) are reproduced to nearly quantitative accuracy.

The energy values can be analyzed in the context of the $1/Z$ expansion; they are consistent with the detailed analyses carried out some time ago by Midtdal and Aashamar [24] and more recently (and more accurately) by Baker, Freund, Hill, and Morgan [25].

3 Highly Precise Studies

The literature now contains a number of highly accurate studies of three-body systems. Using the Hylleraas basis, a good example is the detailed study by Drake, Cassar, and Nistor [26]. For the fully correlated exponential basis, the results obtainable are well illustrated by the work of Frolov and Smith cited in the previous section [23].

There are fewer high-precision studies of four-body systems. The atomic system that has been a focus of such investigations is the Li atom, the ground state of which has been the subject of an extensive review by King [27]. At this point the best calculations on Li have been carried out using a Hylleraas basis. Millihartree accuracy was first reached by Larsson in 1968 [28]; by the 1990's microhartree accuracy had been reached by a number of workers. At present the most precise published values, accurate to within a nanohartree, are those of Yan and Drake [29] and Puchalski and Pachucki [30].

Very few results have been reported in which a fully correlated exponential basis has been used for a four-body system. While such a basis may be expected to provide faster convergence as its size is increased, one could argue that this has not proved to be crucial for atomic systems (e.g. Li). However, the situation is different for nonadiabatic systems. It is therefore not a coincidence that the only four-body system for which comprehensive results have thus far been reported with a fully correlated exponential basis is the completely nonadiabatic quasimolecule Ps_2 ($e^+e^-e^+e^-$) [31].

We will report on our efforts in this area.

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