High Precision Hy-CI Variational Calculations for the Ground State of Neutral Helium and Heliumlike ions

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Abstract

Hylleraas-Configuration Interaction (Hy-CI) method variational calculations with up to 4648 expansion terms are reported for the ground ^1S state of neutral helium. Convergence arguments are presented to obtain estimates for the exact nonrelativistic energy of this state. The nonrelativistic energy is calculated to be -2.9037 2437 7034 1195 9829 99 a.u. Comparisons with other calculations and an energy extrapolation give an estimated nonrelativistic energy of -2.9037 2437 7034 1195 9830(2) a.u., which agrees well with the best previous variational energy, -2.9037 2437 7034 1195 9829 55 a.u., of Korobov[1], obtained using the universal (exponential) variational expansion method with complex exponents[2]. In addition to He, results are also included for the ground ^1S states of H^-, Li^+, Be^{++}, and B^{+3}.

I. INTRODUCTION

In a review article on Computational Chemistry in 1996, Clementi and Corongiu [3] stated that using an Hy-CI [4, 5] expansion to solve the dynamical correlation is nearly impossible for more than 3 or 4 electrons. While that may have been true in 1996, its validity today is being challenged by the availibility of cheap CPUs which can be connected in parallel to significantly (orders of magnitude) enhance both the CPU power and the memory that can be brought to bear on the computational task. In this paper we address some of the issues arising from an attempt to come up with a good technique for obtaining very precise energies for few electron atomic systems using the Hy-CI formalism. Not only do we address the issue of choice of terms in the wave function, but we also address another fundamental mathematical issue arising in these types of calculations. In any attempt to get very precise energies, large basis sets have to be employed, which means that linear dependence in the basis set is never very far away. To proceed to several thousand terms in a wave function, extended precision arithmetic is needed to obviate the linear dependence problem, which in turn leads to high CPU costs. This work employs a novel wave function, namely, a wave function consisting of at most a single r_{12} raised to the first power combined with a conventional non-orthogonal CI basis. We believe that this technique can be extended to multielectron systems [6], where the use of at most a single r_{ij} (to the first power) retains the power of r_{ij} factors in the wave function without making the integral evaluation overly complicated. We use this technique to determine the nonrelativistic ground state energy of neutral helium more precisely than the best previous calculation [1][1], we discuss how we solved the extended precision problem, and we discuss the implications of this for 3 and 4 electron systems.

[1]Korobov[1] has done the best calculation to date on the ground state of neutral helium by considering variational basis functions of the type exp(-α_nr$_1$ - β_nr$_2$ - $\gamma_n r_{12}$) with complex exponents. See Thakkar and Smith[7] and Frolov and Smith[2] for a general discussion of this method.

II. METHOD OF CALCULATION

Variational methods based on explicitly correlated wave functions (wave functions including r_{ij} terms) are known to give the most accurate upper bounds to energy states, and the inclusion of r_{ij} terms in the wave function has become increasingly common, at least for few electron atomic systems (N $\leq$ 4). For example, standard Hylleraas (Hy) technique [8] calculations are perhaps best exemplified by the work of Drake and collaborators [9, 10, 11] and employ factors of powers of r_{ij} in the wave function. However, for four-electron atomic systems, there are already significant unresolved integration problems when Hylleraas basis sets are employed conventionally [12], in what may be referred to as an Hy-r_{ij} technique. In contrast, the Hy-CI method developed by us [4] and also independently by Woźnicki [13] does not suffer from this restriction. Woźnicki and coworkers refer to the method as SCC (Superposition of Correlated Configurations) and have employed it for an accurate Li ground state[14], and the approach has also been used to obtain accurate excited S states of Li [15]. For our part, we have used this method to calculate energies, oscillator strengths, and polarizabilities of two-, three-, and four-electron systems (see [16] and references therein). In these approaches, which we refer to as Hy-CI, the wave function is expanded as a linear combination of configurations, each of which contains at most one r_{ij} to some power. Using this type of wave function, the most cumbersome integrals that are needed for atoms with an arbitrary number of electrons are dealt with already in the four-electron problem. This point was noted by Clary and Handy [17] who demonstrated the utility of the Hy-CI method for N-electron atomic systems up to and including N = 10 by carrying out a calculation on atomic Ne. Clary [18, 19] and Clary and Handy [20] also demonstated the utility of the technique for systems other than atoms by performing Hy-CI calculations on one-positron atomic systems and on many-electron diatomic molecules. Nevertheless, in spite of all of the progress that has been made with Hy-r_{ij} and Hy-CI calculations in recent years, there still are practical issues to be resolved. Conventional Hy-r_{ij} calculations have proven to lead to better convergence estimates than Hy-CI calculations, which for 3 and especially 4 or more electrons can best be described as requiring educated guesswork to select the terms in the wave function, making it very hard to obtain good estimates of upper bounds to the exact nonrelativistic energies. In this work we show how an Hy-CI calculation can do as well as an Hy-r_{ij} calculation (indeed, we improve the Hy-r_{ij} energy estimate by two decimal places), while retaining the ability to give good convergence estimates for the upper bound to the exact nonrelativistic energy. In a future work we hope to make similar progress for three and four-electron systems [6].

We also note that the best previous calculation to date on the He ground state is neither Hy-r_{ij} nor Hy-CI, but one that employs a variational expansion in products of exponentials in the problem interparticle distances[1, 7, 2]. We made no real attempt in this work to minimize the number of expansion terms (one would certainly not have this luxury when dealing with larger atoms), resulting in an expansion that is approximately twice as long as Korobov's[1]. While the exponential products approach provides almost as good an energy and a more compact wave function for the He ground state and is straightforward to implement, it is not clear how useful it will be for atoms with more than two electrons.

III. WAVE FUNCTIONS

The Schrödinger equation for a three-body system consisting of a nucleus of Ze, mass M, and two electrons of charge -e and mass m_e has been treated thoroughly by Drake [21]. In this work, we focus on the nonrelativistic energy, using a hamiltonian which, for N electrons, is (in atomic units [2])

$$H_{NR} = \sum_{i=1}^{N} (-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}) + \sum_{i<j} \frac{1}{r_{ij}} \tag{1}$$

Note that this hamiltonian does not include mass polarization, which is commonly treated using first order perturbation theory [22].

For two electrons, the time-independent, nonrelativistic Schrödinger equation becomes

$$H_{NR}\Psi(\mathbf{r}_1, \mathbf{r}_2) = E\Psi(\mathbf{r}_1, \mathbf{r}_2) \tag{2}$$

Since the Schrödinger equation is not separable in the electron coordinates, basis sets which incorporate the r_{12} interelectronic coordinate are most efficient. The method we use to incorporate interelectronic coordinates in the calculations is our combined Hylleraas - Configuration Interaction (Hy-CI) method [4]. The Hy-CI method wave functions can be written in a form which is slightly different from conventional two-electron Hy-r_{ij} calculations [23, 24, 25, 26]

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{K=1}^{N} C_K \Phi_K(\mathbf{r}_1, \mathbf{r}_2), \tag{3}$$

where the terms Φ_K are specifically of the form

$$\Phi_K(\mathbf{r}_1, \mathbf{r}_2) = O(L^2)(1 \pm P_{12}) r_1^i r_2^j r_{12}^k Y_l^m(1) Y_{l'}^{m'}(2) e^{-\xi r_1 - \eta r_2}. \tag{4}$$

P_{12} is the operator which permutes electrons 1 and 2, and the plus sign is for singlet levels, the minus sign for triplet levels. In this work, the r_{12} power k is restricted to be either 0 or 1, i.e., in contrast to conventional Hy-CI calculations the r_{12} power is limited to the first power (a novel feature). Y_l^m is a normalized spherical harmonic in the Condon and Shortley phase condition [27].

Note that this form of the wave function differs from conventional two-electron Hy-r_{ij} calculations in that k is ≤ 1 and instead of higher powers of r_{ij} there are higher spherical harmonics in the basis set, with the $O(L^2)$ idempotent orbital angular momentum

[2]The atomic unit of energy is chosen as $\frac{\mu e^4}{\hbar^2}$ = 1 a.u. (of energy), where $\mu = m_e m_N/(m_e + m_N)$

projection operator [28] projecting out the proper symmetry. For two electrons, and ^1S,$^3S(L = 0)$ symmetry, $l' = l$. Furthermore, to within some constant factor,

$$O(L^2)Y_l^0(1)Y_l^0(2) = P_l(cos\theta_{12}) \tag{5}$$

where $P_l(cos\theta_{12})$ is a Legendre polynomial [5]. Therefore the wave function we actually used has

$$\Phi_K(\mathbf{r}_1, \mathbf{r}_2) = (1 \pm P_{12})r_1^i r_2^j r_{12}^k P_l(cos\theta_{12})e^{-\xi r_1 - \eta r_2}. \tag{6}$$

Note that the Legendre polynomials in Eq. (6) can be expressed in terms of spherical harmonics of (θ_1, ϕ_1) and (θ_2, ϕ_2) by the spherical harmonic addition theorem:[27].

$$P_l(cos\theta_{12}) = \frac{4\pi}{(2n+1)} \sum_{m=-l}^{l} Y_l^{-m}(1)Y_l^m(2) \tag{7}$$

Substituting this expression in Eq. (6) and taking k = 0 gives a conventional CI configuration for S states. There is also a close relationship between our (Hy-CI) wave function and Hy-r_{ij} wave functions. Since

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1r_2P_1(cos\theta_{12}), \tag{8}$$

r_{12}^k for k>1, when expanded out, gives a polynomial in powers of $P_l(cos\theta_{12})$ times 1 or r_{12} depending on whether k is even or odd. The powers of $P_l(cos\theta_{12})$ can in turn be expressed in terms of the $P_l(cos\theta_{12})$ polynomials, thus making explicit the connection between Hy-r_{ij} and Hy-CI. Although other (radial) factors will be different in the two methods, they are essentially equivalent methods, a fact we have used in coming up with our final wave function.

Drake[29] has pointed out the need for "doubling" basis sets so there is a natural partition of the basis set into two distinct distance scales - one appropriate to the complex correlated motion near the nucleus, and the other appropriate further out. Drake uses just two sets of orbitals to accelerate convergence; we use two sets of basis functions for each l, differing in the nonlinear parameters ξ and η. The first set has an orbital with an orbital exponent $\xi = \eta$ that makes it essentially a valence shell orbital. For the second set $\xi = \eta$ again, and the orbital has a large exponent. Valence (outer) orbitals are optimized whereas the inner orbital set is optimized for $s-$ and $p-$ but not beyond since the contributions for $l > 1$ are not large and the energy is a slowly varying function of the orbital exponents anyway.

To clarify this further, consider Table 1, where we list the basis set for our final 4648 term wave function. Each line in the table specifies both the {inner,inner} and {outer,outer} set for each l quantum number (= L_{max}). In the table, only the minimum information needed to specify the basis set is listed, namely, an exponent ζ ($\xi = \eta = \zeta$), the l quantum number for orbitals with that exponent, and the number of orbitals with that exponent (i and j in Eq. (4) range from l to n_{orbs} + l - 1). This gives rise to n_{orbs} (n_{orbs} + 1) / 2 terms without r_{12}, and the same number with r_{12}. There are 380 terms for l=0

Table 1: Hy-CI results for 1^1S He

L_{max}	n_{orbs}	ζ	n_{orbs}'	ζ'	N	Energy(E) in a.u.
0	19	2.20	19	25.0	760	-2.9034 9832 0585 8801 1976 93
1	19	3.05	19	40.5	1520	-2.9037 2426 8354 6045 9864 64
2	19	3.50	19	40.5	2280	-2.9037 2437 6954 6918 8919 88
3	18	3.90	18	40.5	2964	-2.9037 2437 7034 0541 4170 45
4	15	4.50	15	40.5	3444	-2.9037 2437 7034 1195 3899 21
5	14	5.20	14	40.5	3864	-2.9037 2437 7034 1195 9822 02
6	14	6.00	14	40.5	4284	-2.9037 2437 7034 1195 9829 62
7	13	6.50	13	40.5	4648	-2.9037 2437 7034 1195 9829 99

and ζ = 2.2, an $\{s^2\}r_{12}$ set. There are also 380 terms for l=0 and ζ = 25.0, an $\{s'^2\}r_{12}$ set. Since the orbital exponent is the same for all terms in a set, we refer to terms of the second one as {inner,inner} (large orbital exponent brings it in), and those of the first set as {outer,outer}.

Table 1 also lists our final energy value for the He ground state. In the table we give the energy as we progressively add in higher angular momentum basis sets. These are what might be referred to as s-wave, p-wave, ..., out to and including j-wave sets times both 1 and r_{12}. In the table, L_{max} = 0 refers to the l=0 {inner,inner} set plus the l=0 {outer,outer} set for a total of 380 + 380 = 760 terms. Similarly for succeeding rows in the table (L_{max} = 1 includes l=0 and l=1, etc). In all of the tables, we use N to refer to the number of terms in the wave function (see Eq. (3)).

In our final wave function, only {inner,inner} and {outer,outer} configurations were included. {inner,outer} were tried but were found to be unimportant in addition to greatly increasing the expansion size and degree of linear dependence in the configuration basis.

We have found the surprising result that one simply can't get to our answer without the {inner,inner} terms without a really massive increase in the expansion length. Many authors, starting perhaps with Roothaan and Weiss[30], have emphasized that the wave function should have a cusp-like behavior at $r_{12} = 0$ such that

$$(\frac{1}{\Psi}\frac{\partial\Psi}{\partial r_{12}})_{r_{12}=0} = \frac{1}{2} \tag{9}$$

and attributed the slow CI convergence to the necessity of piling up higher $s, p, d, ...$ angular terms in attempting to represent the details of this behavior. No one has emphasized the need for {inner,inner} terms at higher l values. Apparently, the need for these {inner,inner} terms at higher angular terms has not been evident in conventional CI up to now, because conventional CI doesn't describe the valence shell electron cusp properly either and anything put in near the nucleus will try to contribute to the valence shell cusp description (even an orbital with a large exponent will penetrate the valence region with a large enough power of r). In any event, including both {inner,inner} and {outer,outer} terms are key to the success of the current Hy-CI formalism. For example, if one just drops the {inner,inner} terms from the expansion in the last line of Table 1 and keeps all orbital exponents fixed, the result is E(2324 terms) = -2.9037 2437 7026 a.u., which is not as good as the Frankowski and Pekeris[31, 32] results obtained in 1966.

IV. NONRELATIVISTIC ENERGIES - RESULTS AND DISCUSSION

The wave function given by Eq. (3), $\Psi(\mathbf{r}_1, \mathbf{r}_2)$, is a linear combination of configurations Φ_K, where the coefficients C_K are those which minimize the total energy, E, given by

$$E = \frac{< \mathbf{\Psi}|\mathcal{H}|\mathbf{\Psi} >}{< \mathbf{\Psi}|\mathbf{\Psi} >} = \frac{\sum_{KL} C_K C_L H_{KL}}{\sum_{KL} C_K C_L S_{KL}}, \tag{10}$$

where

$$H_{KL} =< \mathbf{\Phi}_K|\mathcal{H}|\mathbf{\Phi}_L >; S_{KL} =< \mathbf{\Phi}_K|\mathbf{\Phi}_L > . \tag{11}$$

The condition for the energy to be an extremum, $\delta E = 0$, is the well-known matrix eigenvalue (secular) equation:

$$\sum_L H_{KL} C_L = \sum_L S_{KL} C_L. \tag{12}$$

Solving this equation is equivalent to solving the N-dimensional generalized eigenvalue problem

$$\mathbf{HC} = \lambda \mathbf{SC} \tag{13}$$

where $\mathbf{H}$ and $\mathbf{S}$ have matrix elements H_{KL} and S_{KL} given by Eq. (11). We solve this secular equation using both sequential and parallel inverse iteration algorithms, and using real*16 and real*24 arithmetic, as discussed below.

We started out writing our own Microsoft[3] ASM (MASM) quadruple precision (real*16, $\sim$ 32 digits) package simply because no Fortran 90 package for the PC had real*16 as a native data type. So much of our early experience was with real*16 arithmetic. Then, because of linear dependence problems (even at 32 decimal places), we extended the real*16 package to real*24 extended precision ($\sim$ 48 digits). Fortran 90, of course, has user defined datatypes and operator extensions which make implementation of real*16 and real*24 floating point operations essentially automatic once the appropriate interface MODULEs are constructed (i.e., no need to explicitly call subroutines to carry out the floating point operations). This is an important, very practical feature of the calculations.

Except for some of the shorter expansions reported in Table 2, all results reported in this paper were obtained using real*24 extended precision ($\sim$ 48 digits) floating point subroutines written in MASM including add, sub, mpy, div, exp, and log. There is a full

[3]The identification of any commercial product or trade name does not imply endorsement or recommendation by either the National Institute of Standards and Technology or Indiana University.

set of conversion routines between integers and single, double, and quad reals and our extended precision format, as well as output routines in the extended precision format.

The parallel calculations reported here were carried out at the National Institute of Standards and Technology on the instaNT.nist.gov NT Cluster, a 16 node cluster of Pentium II systems running Microsoft Windows NT [Server 4.0] with 100-Mbit Fast Ethernet for interconnection. The front-end machine is a 400MHz Pentium II with 780MB of RAM and 19GB of disk storage. The back-end nodes are single-cpu 400MHz Pentium IIs with 512MB of RAM and 8.4GB of local disk storage.

In the subsections that follow, we have endeavored to include all the data needed to reproduce the results reported in Tables 1, 2, and 5, should future workers want to do so.

A. Hy-r_{ij} results and comparison with earlier results

For a more detailed comparison with conventional Hy-r_{ij} methodology, we also undertook our own study of the Hy-r_{ij} method as applied to helium. Our results are summarized in Table 2.

n_1^{max},n_2^{max}, and n_{12}^{max} are the maximum powers of r_1, r_2, and r_{12}, respectively. N, the number of terms, can best be explained with an example. For row 1 in Table 2, what we did was to form all configurations from 4 outer s-orbitals with orbital exponent 2.0 and then split the orbital exponent to 2.0, 2.2. Otherwise, one gets linear dependence very quickly since 1s(2.0)1s(2.0), 1s(2.0)1s(2.2), and 1s(2.2)1s(2.2) are all very similar. The way we did it, only 1s(2.0)1s(2.2) arises. And similarly for the $\{$inner,inner$\}$ terms. Hence one does not have 4 x 4 x 5 = 80 $\{$outer, outer$\}$ terms but only [4(4+1)/2] x 5 = 50 terms, with a similar number of $\{$inner, inner$\}$ terms, giving 100 terms in all.

These are real*16 (128 bit) calculations except for the last 5, which are real*24 (192 bit) calculations (and they are only a partial listing of our results). Our 2184 term result agrees quite well with the 2114 term result of Drake[29] in Table 3, the best previous Hy-r_{ij} calculation. As problem size increased, run times became a problem, especially for the generalized eigenvalue problem step, so we decided to develop a portable parallel inverse iteration solver. Since the inverse iteration solver matrix representation is a blocked one, we modified the secular equation step to generate H and S in the appropriate block order. Then MPI[33] was used to run the same program on multiple processors (on the same or different hosts) and give each host a block of the H (and S) matrix, with no need to redistribute the matrices for the inverse iteration step. The MPI code uses blocking sends and receives to do the equivalent of an MPI_reduce and then an MPI_gather (on to the root process) in real*24 arithmetic. We have this parallel inverse iteration solver running on the NIST NT cluster instaNT.nist.gov.

On a 3052 term calculation, run times were 41.51 seconds to construct the secular equation and 6425.73 seconds to solve for one root using inverse interation. On 16 processors, solving the secular equation took only 555.66 seconds, i.e, a two hour run on one processor became 10 minutes running on the cluster. We found that the processing speed could be predicted, as a function of cluster size, by the simple scaling law T = constant (s + (1 - s) /N_{proc}), where T is the runtime in seconds, constant = 6419 in this case, and s is the inherently sequential part of the calculation. This function is plotted in Fig. 1. We find that the sequential fraction s = 0.022, indicating that the scaling is excellent and we could go to a larger number of processors (if we had them). Finally, one last reason for going parallel is to circumvent the executable image size limitation for sequential programs under both Windows and NT DOS modes. To go beyond about 3300 terms in our calculations involves either writing intermediate results out to disk or spreading the calculation (and memory requirements) across a

Table 2: Hy-r_{ij} results for 1^1S He (including orbital basis)

n_1^{max}	n_2^{max}	{outer,outer} {inner,inner}	n_{12}^{max}	N	Energy(a.u)
4	4	{2.0,2.2} {6.0,6.2}	4	100	-2.9037 2280 7177 558
6	6	{2.0,2.2} {6.0,6.5}	4	210	-2.9037 2437 3077 229
6	6	{2.0,2.2} {6.0,6.5}	6	294	-2.9037 2437 6814 373
6	6	{2.0,2.2} {6.0,6.5}	7	336	-2.9037 2437 6900 260
6	6	{2.0,2.2} {6.0,6.5}	8	378	-2.9037 2437 6947 786
7	7	{2.0,2.2} {6.0,6.5}	8	504	-2.9037 2437 7033 120
8	8	{2.0,2.2} {6.0,6.5}	8	648	-2.9037 2437 7033 898
8	8	{1.85,2.05} {8.6,8.8}	9	720	-2.9037 2437 7034 0967 2287
9	9	{1.95,2.15} {9.8,10.0}	9	900	-2.9037 2437 7034 1150 3
10	10	{1.95,2.15} {11.0,11,2}	9	1100	-2.9037 2437 7034 1184 93
10	10	{1.95,2.15} {11.0,11,2}	10	1210	-2.9037 2437 7034 1189 65
11	11	{2.10,2.30} {12.4,12.6}	10	1452	-2.9037 2437 7034 1194 42
11	11	{2.10,2.30} {12.4,12.6}	11	1584	-2.9037 2437 7034 1194 90
12	12	{2.20,2.40} {16.0,16.2}	11	1872	-2.9037 2437 7034 1195 8414
13	13	{2.20,2.40} {16.0,16.2}	11	2184	-2.9037 2437 7034 1195 9090
13	13	{2.20,2.40} {19.5,19.7}	12	2366	-2.9037 2437 7034 1195 9567
14	14	{2.20,2.40} {21.5,21.7}	12	2730	-2.9037 2437 7034 1195 9725 15
15	15	{2.20,2.40} {22.0,22.2}	12	3120	-2.9037 2437 7034 1195 9793 92
16	16	{2.20,2.40} {23.5,23.7}	12	3536	-2.9037 2437 7034 1195 9815 09

number of processors.

B. Extrapolation of Hy-CI results

The Hy-r_{ij} results gave us the insight we needed to do the actual Hy-CI runs discussed previously. Table 3 compares our final energy value for the He ground state with previous results. The calculated value is a rigorous upper bound to the exact nonrelativistic energy of this state. In Table 3, we have also included our extrapolation of the energies given in Table 1, obtained using a formula from Pekeris and co-workers[24]

$$E_{extrapolated} = E_1 + \frac{(E_1 - E_0)(E_2 - E_1)}{2E_1 - E_0 - E_2}, \tag{14}$$

where E_0, E_1, and E_2 are the values at L_{max} = 5, 6, and 7 respectively. This formula gives -2.9037 2437 7034 1195 9830 01 a.u for the extrapolated energy. Based on the fact that extrapolations tend to undershoot the exact result, the sensitivity of E to the non-linear parameters and the convergence in L, we estimate the exact nonrelativistic energy to be 2.9037 2437 7034 1195 9830 a.u. with an uncertainty of 1 or 2 in the last digit. This result is in complete agreement with the landmark calculations of Korobov[1]. In addition to values for He, we have also included results for other members of the He isoelectronic sequence, namely, H^-, Li^+, Be^{++} and B^{+3}. For these results, no exponent minimization was done, just a simple nuclear charge based scaling of the wave function of Table 1. For example, the results for Li^+ were obtained by scaling the orbital exponents by a factor of 3.0 / 2.0 and for Be^{++} the orbital exponents were scaled by a factor of 4.0 / 2.0. For Li^+ we varied the orbital exponents extensively using shorter expansions and the result was that orbital exponent variations are important in the 20th decimal place. Our results for H^-, Li^+, and Be^{++} agree with the results of Drake[21] [4] to the 16 decimal places he reports (he doesn't have a value for B^{+3}) and, except for H^- [5], are more precise by at least three decimal places. These results were easy to obtain, which points out how flexible our expansion is.

We would like to point out again the close relationship between Hy-r_{ij} and Hy-CI. In Table 4 we show this by tabulating E_l results for l = 0,1,2,... levels of truncation of the wave function expansion used in Table 1 versus the equivalent Hy-r_{ij} truncation results for the best wave function in Table 2[6]. The two energy columns are clearly related, the minor differences being easily explained by the different functional forms, methods of optimization of non-linear parameters, and the fact that these limits are not rigorously defined (except for the first one).

[4] Drake's value for Be^{++} contains a misprint. -13.1... should be -13.6...

[5] Convergence is slow for H^-

[6] There is no entry on the Hy-r_{ij} side corresponding to l = 6 since 12 is the upper limit to n_{12}^{max} in our code.

Table 3: Comparison with previous explicitly correlated calculations for 1^1S He and He-like ions

Author	N	Energy(a.u.)
Frankowski and Pekeris[31, 32]	246	-2.9037 2437 7032 6
Freund $et.al.$[34]	230	-2.9037 2437 7034 0
Thakkar and Koga[35]	308	-2.9037 2437 7034 1144
Baker $et.al.$[36]	476	-2.9037 2437 7034 1184
Goldman[37]	8066	-2.9037 2437 7034 1195 9382
Bürgers $et.al.$[38]	24497	-2.9037 2437 7034 1195 89
Drake[29]	2114	-2.9037 2437 7034 1195 9582
Korobov[1]	2200	-2.9037 2437 7034 1195 9829 55
Korobov[1] Extrapolated		-2.9037 2437 7034 1195 9830 6(10)
This work	4648	-2.9037 2437 7034 1195 9829 99
Extrapolated	∞	-2.9037 2437 7034 1195 9830 01
Estimated		-2.9037 2437 7034 1195 9830(2)
This work, H^-	4640	-0.5277 5101 6544 3771 2249
This work, Li^+	4284	-7.2799 1341 2669 3059 6489
This work, Be^{++}	4648	-13.6555 6623 8423 5867 0206
This work, B^{+3}	4648	-22.0309 7158 0242 7815 4163

Table 4: Comparison of Hy-r_{ij} and Hy-CI results for 1^1S He

l	E_l(Hy-CI) in a.u.	n_{12}^{max}	E(Hy-r_{ij}) in a.u.
0	-2.9034 9832 0585	1	-2.9034 9825 7090
1	-2.9037 2426 8354	3	-2.9037 2426 8491
2	-2.9037 2437 6954 6918	5	-2.9037 2437 6955 3843
3	-2.9037 2437 7034 0541	7	-2.9037 2437 7034 0553
4	-2.9037 2437 7034 1195 3899	9	-2.9037 2437 7034 1195 4000
5	-2.9037 2437 7034 1195 9822	11	-2.9037 2437 7034 1195 9796
6	-2.9037 2437 7034 1195 9830	13	

C. Configuration Interaction

As a test of our integral and eigenvalue routines and also to investigate the basis set linear dependence problem, we have carried out a number of conventional configuration interaction calculations on He. In this connection, in Table 5 we report the results of a 4699 term expansion carried out using real*24 arithmetic. A typical symmetry adapted configuration has the form

$$(1 + P_{12})r_1^i e^{-\xi r_1} r_2^j e^{-\eta r_2} P_l(cos\theta_{12}) \tag{15}$$

where $\xi = \eta$ for all configurations except the 49 ss terms in the third row. Non-linear parameters were carefully chosen for terms up through ff. For this part of the calculation there were considerable problems with linear dependence in real*16 mode, forcing us to move to real*24 arithmetic. For higher l values we used an approximate linear relationship between orbital exponent and l-value, with occasional checks on the accuracy of the approximation. In any case, the energy contributions for the higher l-values are very insensitive to the orbital exponents and depend much more on the number of basis orbitals (powers of r) for a given l-value, even as the contribution for an l-value decreases to less than microhartree values (e.g., l=16-18). The upper limit on l of 18 was set by program and operating system limitations of the PC used to do these particular calculations.

Also included in Table 5 for comparison purposes are the excellent recent results of Jitrik and Bunge[39] for the He ground state. These results were obtained with much smaller basis sets for each l-value but with essentially a separately optimized exponent for each basis orbital. Our approach, however, has been to use a basis with as few non-linear parameters as possible, that is, a basis very like that used in our Hy-r_{ij} and Hy-CI calculations. Note that although one can get spectroscopic accuracy (1 cm^{-1} is approximately 5 microhartrees) for He using CI, microhartree accuracy is still not available. We estimate that to get microhartree accuracy would require terms up to l=30 and maybe up to 1200 more terms, although with a more efficient basis (more non-linear parameters) the overall expansion length could be shortened considerably. This and other options are currently being investigated[40]. Nevertheless, after some 70 years of trying, the best CI treatment for He is still accurate to only 5 decimal places!

Table 5: CI results for the ^1S ground state of neutral He (a.u.)

	l	n	ζ	N	E_l(a.u.)	Previous work[39]
ss	0	19	4.1	190		
ss	0	21	20.3	421		
ss	0	7	4.1, 20.3	470	-2.8790 2875 65	2.8790 2862 7
pp	1	17	4.7			
pp	1	21	20.9	854	-2.9005 1621 99	-2.9005 1577 4
dd	2	16	6.1			
dd	2	21	22.5	1221	-2.9027 6680 53	-2.9027 6612 6
ff	3	16	7.0			
ff	3	21	24.0	1588	-2.9033 2101 62	-2.9033 2011 0
gg	4	21	14.0	1819	-2.9035 1846 49	-2.9035 1734 1
hh	5	21	16.0	2050	-2.9036 0551 51	-2.9036 0419 6
ii	6	21	18.0	2281	-2.9036 4964 42	-2.9036 4818
jj	7	21	19.0	2512	-2.9036 7432 76	-2.9036 7269
kk	8	21	21.0	2743	-2.9036 8919 34	-2.9036 8741
ll	9	21	22.0	2974	-2.9036 9865 63	-2.9036 9675
mm	10	21	23.0	3184	-2.9037 0497 38	-2.9037 0296
nn	11	20	24.0	3415	-2.9037 0932 48	-2.9037 0720
oo	12	20	25.0	3625	-2.9037 1243 32	-2.9037 1019
pp	13	20	27.0	3835	-2.9037 1470 34	-2.9037 1237
qq	14	20	28.0	4045	-2.9037 1640 56	-2.9037 1396
rr	15	20	29.0	4255	-2.9037 1769 92	-2.9037 1515
ss	16	18	30.0	4426	-2.9037 1869 56	
tt	17	17	31.0	4579	-2.9037 1948 04	
uu	18	15	32.0	4699	-2.9037 2009 19	
"Exact"					-2.9037 2437	
Error					-0.0000 0428	

V. CONCLUSIONS

The renewed interest in r_{ij}s is coming from the incredible accuracy of experiments these days. To do as well theoretically requires explicitly correlated wave functions, in general. Goldman's [37] work is the exception for He, as he gets an energy of -2.9037 2437 7034 1195 938(50) a.u. (8066 term expansion). His estimate is in agreement with our calculated result, -2.9037 2437 7034 1195 9829 99 a.u. However Goldman's CI is not the conventional kind of CI. Instead of powers of r_1 and r_2 he uses powers of $r_<$ and $r_>$, which is fine for He but leads to 3- and 4-electron integrals for Li and Be (unlike conventional CI). Only Li has been done essentially as accurately as He, and that only with a 6000 fold increase in CPU requirements[7]. And the integrals get messier with conventional r_{ij} techniques. We have always thought that the idea behind the Hy-CI technique was to **marry** the relative ease of doing CI with the better convergence obtained when r_{ij} factors are used. We have pointed out, for He, the close connection between Hy-r_{ij}. It seems to us that the Hy-CI method selects the important term types in a more natural manner. Also, the calculation, at least for He, is easier. If one restricts the wave function to a single r_{ij} in each term (n$\leq$1) then the most difficult integrals are already dealt with at the N = 4 level and the calculation is greatly simplified. The only problem has been figuring out a systematic technique for choosing basis orbitals and configurations that leads to good energy estimates with a reasonable number of expansion terms.

One of the results of this study has been a detailed comparison of Hy-r_{ij} and Hy-CI techniques so that we are able to move on to calculations of Li and possibly Be atom states to very good accuracy. As we move on to larger systems, computational times will increase greatly, as well as memory requirements, so it is imperative to program these routines using parallel programming techniques and MPI (for portability).

[7] Drake [21] says that only for He and Li have results of spectroscopic accuracy been obtained. He says the demand on computer resources increases by a factor of about 6000 to reach spectroscopic accuracy for Li over He.

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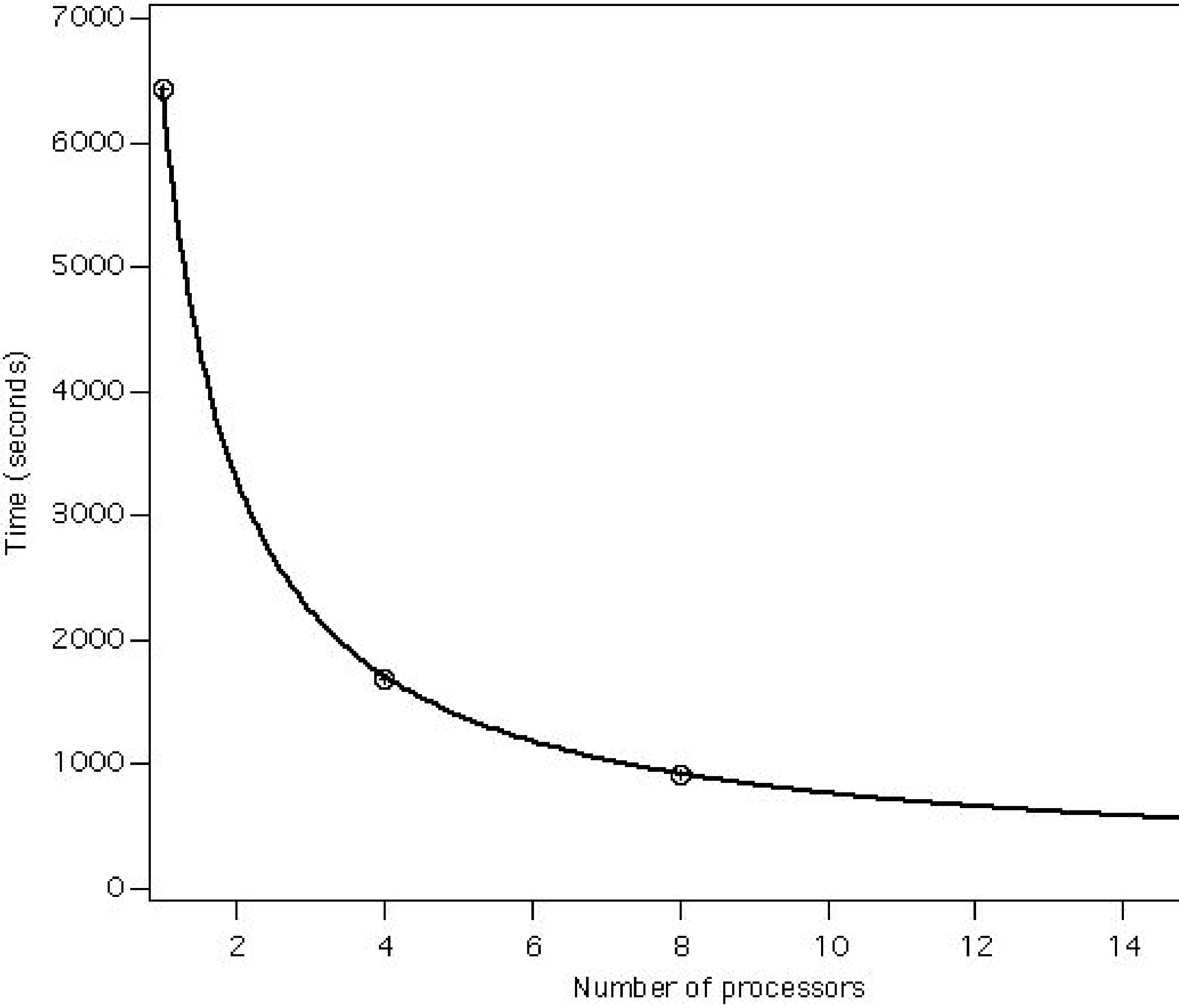

Figure 1: He Hy-CI Scaling with Cluster Size