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Random tempering of Gaussian-type geminals. III. Coupled pair calculations on lithium hydride and beryllium

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We use random tempering formulas and a sorting procedure to produce basis sets of explicitly correlated Gaussian-type geminals for the calculation of the coupled pair energies of the beryllium atom and lithium hydride. These energies show rapid convergence and are comparable to calculations which use a basis set where all nonlinear parameters have been optimized. Our complete coupled pair energies are 92.95 and 82.65 mhartree for Be and LiH, respectively. When combined with literature values for single and triple excitations, our results provide the most accurate *ab initio* calculated energies to date for Be and LiH.

I. INTRODUCTION

In an earlier paper[1] we showed that random tempering is an efficient method of obtaining sets of explicitly correlated Gaussian-type geminals (GTGs) for atomic systems. A GTG basis set contains a large number of nonlinear parameters (Gaussian function exponents) which are optimized so as to minimize the energy of the system. Random tempering replaces the full optimization of these parameters by an optimization of a small number of tempering parameters. GTG exponents are generated by a mapping from a set of pseudo-random uniformly distributed numbers with the tempering parameters determining the shape of the mapping transformation. Using this technique we were able to compute the second-order energy of beryllium in considerably less time than earlier calculations which optimized all nonlinear parameters. In addition, we were able to obtain a relatively compact basis set by sorting the random tempered geminals according to energy increments. To reproduce the same second-order energy as that given by a full optimization we found that random tempered basis sets needed 2–3 times more geminals. In Ref. 2 we showed that random tempering could also be applied to molecular systems. With a relatively simple method of moving the geminal centers we were able to easily surpass the best second-order energy obtained from full optimizations.[3,4] In Ref. 2 we also introduced an improved sorting algorithm which generated basis sets of geminals only slightly larger (by a factor of 1 to 2) than those obtained by full optimization. In this paper we investigate the behavior of sorted random tempered basis sets in coupled pair calculations. Previous studies have shown that the coupled pair method produces very accurate correlation energies with basis sets optimized with respect to the second-order energy functional.[5–7] We show here that when combined with sorted random tempered basis sets, this method leads to accurate results in an efficient and systematic manner.

II. RANDOM TEMPERING

We use the following algorithm to produce a basis set of random tempered geminals:

(1) Select a tempering formula for each type of nonlinear parameter. This choice depends to some extent on the system to be investigated. For the beryllium atom we found that 9 tempering parameters were able to accurately describe the geminals[1] and for lithium hydrode a total of 38 tempering parameters were used.[2]

(2) Optimize these tempering parameters at the second-order energy level using a small SCF basis, a small number of geminals K and a small value for the strong orthogonality parameter.[3]

(3) Take these parameters and calculate the second-order energy using a large SCF basis, the strong orthogonality parameter set to zero, and an increasingly larger number of geminals until convergence is reached, linear dependence occurs or the calculation becomes computationally intractable. K's up to 400 and 700 were used for Be and LiH, respectively.

(4) Sort this expanded set of geminals according to their increasing contributions to the second-order energy. Although among K geminals there always exists an optimal subset of K' geminals, finding such a set requires $K!K'!/(K-K')!$ calculations. In Ref. 1 we outlined an efficient method for finding an approximate "best subset" of geminals. This algorithm reduces the size of the original basis set by a factor of 2 or more without significant change in the energy. The effectiveness of the sorting procedure shows that the random nature of our tempering algorithm places only a small fraction of the total number of geminals in the important regions of the geminal parameter space. In Ref. 2 we described an improved version of this sorting algorithm and demonstrated its effectiveness for LiH. The compact basis sets ($K' \ll K$) given by this method of sorting are particularly useful in calculations which go beyond second-order theory, e.g., in the coupled pair calculations of Sec. III. Because such calculations are more time consuming than a single second-order calculation, a reduction in the size of the GTG basis set will substantially reduce the amount of CPU time needed.

In order to employ the most compact basis sets in the coupled pair calculations described in the next section we have resorted the Be geminal basis sets from Ref. 1 using the improved sorting algorithm. A comparison of Table I (the new sorted set of Be geminals with tempering parameters

TABLE I. Comparison of sorted second-order pair energies for Be with fully optimized values. Values in mhartrees with signs reversed.

K^a	Pair 11	Pair[b] 12	Pair[b] 21	Pair 22	Total
Random tempered optimized + sorting[c]					
10	38.372	2.099	2.942	29.135	72.548
20	39.961	2.205	3.162	30.019	75.347
30	40.222	2.213	3.218	30.351	76.004
40	40.286	2.216	3.233	30.456	76.191
50	40.304	2.217	3.239	30.502	76.262
60	40.318	2.218	3.242	30.517	76.295
70	40.325	2.218	3.244	30.526	76.313
80	40.330	2.219	3.247	30.530	76.326
90	40.333	2.219	3.248	30.533	76.333
100	40.334	2.219	3.248	30.535	76.336
110	40.335	2.219	3.249	30.536	76.339
120	40.336	2.219	3.249	30.537	76.341
130	40.337	2.219	3.250	30.537	76.343
140	40.338	2.219	3.250	30.538	76.345
150	40.338	2.219	3.250	30.538	76.345
200	40.339	2.219	3.251	30.539	76.348
300	40.340	2.219	3.251	30.540	76.350
400	40.340	2.219	3.251	30.540	76.350
Fully optimized[d]					
10	39.663	2.199	3.087	30.166	75.115
20	40.252	2.210	3.225	30.404	76.091
30	40.321	2.216	3.245	30.494	76.276
40	40.333	2.218	3.250	30.523	76.324
60	40.341	2.219	3.252	30.536	76.348

[a] Number of geminals in the expansion.
[b] "12" and "21" pairs are triplet and singlet coupled $1s$–$2s$ electron pairs, respectively.
[c] Random tempered optimization and expansions described in Ref.1. The largest expanded set of $K = 400$ geminals was sorted using the improved sorting algorithm from Ref. 2. The value of the strong orthogonality parameter was equal to zero and the SCF orbitals were expanded into a 13-term basis.
[d] Full optimization calculations described in Refs. 3 and 4.

from Ref. 1) with Table V in Ref. 1 (the earlier sorted set) shows that this algorithm gives, as for LiH, more compact sets of geminals than our previous method.

III. CALCULATIONS

Since pair functions represent the bulk of the electron correlation effects, complete coupled pair (CCP) calculations provide a very accurate method of determining the correlation energy of atoms and molecules. This technique was proposed by Cizek[8] (and is often referred to as coupled cluster doubles or CCD) and was later reformulated for use with GTGs.[5] Because the leading perturbation correction to E_{CCP} is negative, this value can be viewed as a "perturbative" upper bound to the total correlation energy. We performed our calculations using the factorizable coupled pair (FCP) method which is an approximation to the CCP method and we used a super weak orthogonality plus projection (SWOP) approach to treat the strong orthogonality problem.[6] The FCP SWOP method has been shown to give energies which are practically equivalent to the CCP values.[5,6] The differences between FCP and CCP methods are only 0.03 and 0.01 mhartree for Be and LiH, respectively. Errors due to the SWOP treatment of strong orthogonality of pair

functions are smaller than 0.01 mhartree in large GTG basis sets.

In Table II we compare coupled pair calculations using sorted random tempered basis sets with similar calculations using basis sets from full optimizations. The $K = 40$ full optimization value for LiH was obtained with the basis produced in Ref. 2. This set of geminals is the result of an improved full optimization and gives a better coupled pair energy ($- 81.82$ mhartrees) than the previous $K = 40$ set ($- 81.50$ mhartrees[6]). For a small number of geminals the values from the sorted random tempered basis sets are in good agreement with the full optimization results and show a fast convergence. For a larger number of geminals the sorted random tempered basis sets produce essentially saturated energies. It should be noted, however, that the convergence for LiH around $K = 90$ is somewhat erratic. This behavior is due entirely to the sorting procedure. As Table VI in Ref. 2 shows, the same erratic convergence occurs in the second-order energy. Increasing the number of functions in the initial part of this procedure and/or iterations in the second part, would probably produce more compact basis sets and improve the convergence.

In Table II the pattern of convergence also contains information about the accuracy of our results. For example, if energies with K spaced by 10 are considered, we see that the convergence pattern is sometimes irregular, i.e., the increments do not decline monotonically. If, however, energies with K changing by 50 are used, the convergence is rapid. In

TABLE II. Comparison of the FCP SWOP pair energies from calculations with sorted random tempered basis sets and fully optimized basis sets. The value of the strong orthogonality parameter was equal to zero. SCF expansions of 13 and 20 terms were used for Be and LiH, respectively. An internuclear distance of 3.015 bohrs was used for LiH. Values in mhartrees with signs reversed.

K^a	Be Full[b]	Be Tempered	LiH Full[b]	LiH Tempered
5	83.211	73.603	···	67.858
10	88.454	82.075	···	75.254
20	90.667	89.673	80.505	80.243
30	91.986	91.577	···	81.355
40	92.305	91.910	81.820	81.833
50	···	92.559	···	82.030
60	92.895	92.739	···	82.146
70	···	92.800	···	82.280
80	···	92.872	···	82.355
90	···	92.890	···	82.386
100	···	92.910	···	82.453
110	···	92.921	···	82.478
120	···	92.933	···	82.504
130	···	92.944	···	82.531
140	···	92.954	···	82.569
150	···	92.963	···	82.586
160	···	92.965	···	82.596
200	···	92.973	···	82.635
250	···	92.978	···	82.663
Extrapolated	92.983 ± 0.002^c		82.71 ± 0.02^c	

[a] Number of geminals in the expansion.
[b] Reference 9. Basis sets from full optimizations described in Refs. 3 and 4. $K = 40$ calculation for LiH performed in this work using the improved basis described in Ref. 2.
[c] Extrapolation method described in the text.

such situations a simple extrapolation can be used to accurately estimate the basis set limit. For this reason we preformed a least-square fit of the formula $E_K = E_\infty + \gamma^K$ to the points $K = 150, 200, 250$. The extrapolated energies obtained from this calculation are $- 92.983 \pm 0.002$ and $- 82.71 \pm 0.02$ mhartree for Be and LiH, respectively. Therefore, our calculated FCP energies lie probably about 0.005 and 0.05 mhartree above the exact values. The error bars are rough estimates obtained by comparing the results of fittings with other formulas and other choices of points. A more detailed analysis of this extrapolation technique will be described in Ref. 10.

After adding a contribution of nonfactorizable terms[5] to our best FCP energies we obtain CCP energies of $- 92.95$ and $- 82.65$ mhartree for Be and LiH, respectively. The Be result is in a very good agreement with the extrapolated CCP energy of $- 92.96$ mhartree obtained by Lindgren and Salomonson.[11] The latter value was in fact obtained by a method which is an approximation to the CCP method, however, the error of this approximation should not exceed 0.02 mhartree. The above agreement may be to some extent fortuitous since Lindgren and Salomonson's[11] second-order energy (which is easier to calculate than the CCP energy) is 0.07 mhartree above the upper bound to this energy obtained in Ref. 4. The previous best CCP energy for LiH was calculated by Adamowicz and Bartlett.[12] The energy published by these authors contains, however, a contribution from single excitations. The value of this contribution should be identical to that obtained in their earlier work with a somewhat smaller basis set. Subtracting this value of $- 0.15$ mhartree from the CCSD energy of Table I in Ref. 12 we obtain a CCP (CCD) energy of $- 81.85$ mhartree which is 0.80 mhartree worse than our CCP energy.

It was shown in Ref. 6 that an FCP SWOP calculation takes only a few times longer than a single second-order calculation and need be performed only once for a given basis set. Since the optimization of N nonlinear parameters requires at least N^2 calculations of the functional, the computational bottleneck in this algorithm is clearly the selection of the GTG basis. We have shown in Refs. 1 and 2 that random tempering reduces the time of optimization by several orders of magnitude. Table II shows that sorted basis sets produce converged FCP results with a relatively small number of geminals. On average, a sorted random tempered basis set of a given size provides an FCP energy similar to that obtained with a fully optimized set of the same size. This means that the time of the FCP step is not increased when sorted random tempered basis sets are used. Thus, the time reduction factor obtained in Refs. 1 and 2 is fully preserved in the complete calculations.

In Table III we compare our coupled pair energies with the results of other accurate literature calculations and with the best available mixed experimental/theoretical estimations of the correlation energy of Be and LiH. Comparison with the latter values shows that *with only pair functions (or equivalently only double excitations)* we have obtained 99% of the correlation energy. In contrast, all the cited literature calculations included the effects of at least singles, doubles, and triples. Most of these calculations also included the ef-

TABLE III. Comparison of correlation energies obtained with various methods. An internuclear distance of 3.015 bohrs is used for LiH. Values are in mhartrees with signs reversed.

	Be	LiH
	92.85[a]	81.69[f]
	93.52[b]	
	93.88[c]	82.16[g]
	92.78 ± 0.5[d]	82.75 ± 0.4[d]
	94.31 ± 0.03[e]	
This work FCP	92.98	82.66
CCP[h]	92.95	82.65
Total (est)	94.29	82.96
Best estimate	94.37 ± 0.002[i]	83.2 ± 0.1[j]

[a] Numerical MCSCF result from Ref. 16.
[b] Hyllerass-CI result from Ref. 14.
[c] Full CI with $spd \cdots i$ STO basis set from Ref. 13.
[d] Fixed node Monte Carlo result from Ref. 17.
[e] Extrapolated full CI result from Ref. 13.
[f] Single and doubles CI off a multireference ground state. 132 015 C_{2v} symmetry adapted configurations with a $spd \cdots g$ GTO basis set from Ref. 18.
[g] CCSDT-1 calculation with 82 numerical orbitals from Ref. 12.
[h] Nonfactorizable pair contribution taken from Ref. 5
[i] Nonrelativistic correlation energy of ∞ Be. Value obtained from data of Ref. 13 by subtracting the theoretical values of relativistic, radiative, and mass polarization corrections from the experimental total energy. The error bar reflects only the experimental uncertainty. Uncertainties of the theoretical corrections are unknown but are probably at least one order of magnitude larger.
[j] Mixed experimental/theoretical value with very conservative estimate of error bounds—obtained using the theoretical energy of Li from Ref. 19, experimental dissociation energy from Ref. 20, and the SCF energy of LiH from Ref. 21.

fects of connected quadruples, thus taking into account all possible types of excitations in Be and LiH. Despite these high-level excitations, most of the literature energies are worse than our coupled pair energies. Two exceptions are the Be full CI energy of Bunge[13] and the Be Hylleraas-CI energy of Sims and Hagstrom.[14]

To compare our results with the experimental energy we must include the effects of singles and triples. By summing the energy contributions for Be reported by Bunge,[15] we found that singles and triples account for $- 0.33$ and $- 1.01$ mhartrees, respectively. According to Bunge,[13] this method of estimating the contribution of various configurations gives results in 99% agreement with those obtained by subtracting total energies obtained with and without these configurations. Therefore, the above singles/triples contribution should be within 0.01 mhartree of the true value obtainable with Bunge's expansion. The above value does not involve any extrapolations and therefore can be treated as a completely *ab initio* computed result. The disconnected quadruples are included in our CCP energy and the contribution of connected quadruples is certainly negligible. When the singles/triples contirbution is added to our CCP result, the total energy for Be is $- 94.29$ mhartree.

We now estimate the error of the Be total correlation energy. Above we argued that the error of the pair contribution was about 0.005 mhartree. The error of the singles and triples contribution is more difficult to determine. The major part ($- 0.407$ mhartree) of Bunge's $- 0.426 \pm 0.025$ mhartree correction for the incompleteness of the basis set is

the correction to the pair functions contribution. The only part of the correction which would affect the singles/triples contribution is the -0.019 ± 0.002 mhartree correction for the truncation of the CI expansion. Part of this correction is actually due to pair contributions but it is not possible to separate it using data published in Refs. 13 and 15. Thus, the possible truncation error of the singles/triples contribution is of the order of uncertainty introduced by the approximate method of extracting these contributions. Therefore, in the worst case, the exact nonrelativistic correlation energy of $^\infty$ Be may be 0.04 mhartree lower than -94.29 mhartree.

Our total energy for Be is 0.41 mhartree lower than the previous best *ab initio* calculated energy obtained by Bunge.[13] This means that the truncation error has been reduced by an order of magnitude. Our energy is 0.02 mhartree above Bunge's extrapolated energy.[13] Since the singles/triples contribution is within 0.03 mhartree the same in both energies, our results confirm the correctness of Bunge's extrapolation for pair contributions.

Our total energy lies 0.08 mhartree above the best mixed experimental/theoretical estimate of the beryllium atom correlation energy. This difference is larger than the estimated truncation error of our result. The discrepancy is probably due to the inaccuracy of the theoretical relativistic correction included in the estimate which does not take into account the L shell and intershell relativistic correlation.

For LiH our single/triples contribution comes from a calculation by Adamowicz and Bartlett[12] by subtracting their CCD energy as extracted by us (see above) from their CCSDT-1 energy we obtain a value of -0.31 mhartree for this contribution. When this result is added to our CCP energy, the total energy, -82.96 mhartree, is 0.24 mhartree within the best mixed experimental/theoretical estimation of the LiH correlation energy and it is 0.80 mhartree lower than the previous best theoretical result.[12] The error of the final energy is of course determined by the accuracy of the singles/triples correction. Since the singles contribution converges rapidly, this error is in fact due to the triples contribution. Therefore, the large scale, state-of-the-art calculation of Ref. 12 reproduced less than 50% of the triples contribution. This observation points out the difficulties of accurate computations beyond pair energies.

It is important to point out that our approach is entirely general and can be applied to any molecular system, in contrast to the methods which produced the previously best energies. The technique used by Bunge[13] is applicable only to atoms and the method of Adamowicz *et al.*[12] only to diatomic molecules.

IV. CONCLUSIONS

We have shown that a basis set of sorted random tempered geminals can produce extremely accurate coupled pair energies. These basis sets give results which are in good agreement with those obtained using sets of geminals where all nonlinear parameters have been optimized. The major disadvantage of the full optimizations is that they require a substantial computational effort. In contrast, random tempered geminals can easily and systematically produce increasingly larger basis sets. When these geminals are placed

into the coupled pair calculations, the energies show a rapid convergence. In both systems examined here the final value of the coupled pair energy is better than the full optimization results. These results are also better than most of the literature values, including those which employ higher-level excitations. This comparison shows that obtaining a saturated energy within a pair-only theory may be preferable to performing much more complicated calculations with triple and higher excitations.

When literature values for single and triple contributions are included, our energies agree very well with the best experimental/theoretical estimates for these systems and represent the best available *ab initio* calculated energies for Be and LiH.

For larger molecules, accurate calculation of the effect of triple excitations will be too difficult and one will have to rely on the coupled pair energies as the best available description of a system. It is now generally accepted that coupled cluster singles plus doubles (CCSD) calculations, if performed accurately, will provide about 99% of the correlation energy for the ground states of most molecules. However, the standard method of expansion of the pair functions into products of orbitals converges slowly and reproduces, in practice, only about 70% of the CCSD energy.[22] Therefore, the problem is in finding basis sets which make accurate calculations feasible. We have shown that such basis sets are now available. We believe that the combination of random tempering, sorting, and coupled pair calculations represents a powerful algorithm for performing highly accurate calculations on atoms and molecules. In our opinion, the coupled pair method will assume the role in the theoretical description of atoms and molecules similar to that held by the Hartree–Fock approximation in the past.

ACKNOWLEDGMENTS

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