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Mixed Basis Functions in Molecular Quantum Mechanics

IV. The Linear, Equidistant System of Four Interacting Hydrogen Atoms

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A series of calculations have been carried out for the linear system of four equidistant hydrogen atoms for an internuclear separation of 1.7 a.u. The configuration interaction technique was used, the orbital basis consisting of a mixed set of 1*s* Slater and floating spherical Gaussian functions. The results obtained are encouraging although the effects of unoptimized non-linear parameters are noticeable.

Es wurde eine Reihe von Rechnungen für ein lineares System von vier äquidistanten Wasserstoffatomen (Kernabstand jeweils 1.7 a.u.) durchgeführt. Dabei benutzt man die Konfigurationswechselwirkungs-Technik, die Orbitalbasis bestand aus einem gemischten Satz von 1*s* Slater- und "floating" sphärischen Gauß-Orbitalen. Die Resultate sind ermutigend, obwohl die Effekte der nicht optimierten nichtlinearen Parameter merklich sind.

Introduction

In the previous papers a series of calculations were reported on 2 and 3 electrons systems, using mixed sets of functions as orbital bases [1–3]. The results were encouraging and as a further test of the method a series of calculations have been carried out on the linear, equidistant system of four hydrogen atoms. Extensive theoretical work on H_4 has been hindered by the difficulties involved in the calculation of the three- and four-centre integrals; so much so that the most sophisticated configuration interaction calculation to date has only made use of a 1*s*, 1*s*′ STO basis [4]. Another, less formidable problem is the large number of configurations which arise, even if only a moderately small basis were used. Linear H_4 has been used as a convenient model for a one-dimensional metallic crystal [5], although as yet it has not been experimentally observed.

The basis sets used in the current H_4 calculation consist of a 1*s*, 1*s*′ STO basis enlarged by Gaussians, much the same way as for H_2 and H_3, so as to improve both the SCF and correlation parts of the CI wavefunction [2, 3]. The calculation of the integrals does not present any fresh problems. The geometry is taken to be identical to the optimum one calculated by Rubinstein and Shavitt [4], i.e. linear, equidistant with an internuclear separation of 1.7 a.u.

Calculations and Results

A series of configuration interaction type calculations have been carried out for the ground state ($^1\Sigma_g^+$) of the linear, equidistant H_4 system, for a fixed internuclear distance of 1.7 a.u., in the Born-Oppenheimer approximation. The orbital bases used consist of a $1s$, $1s'$ type set of Slater orbitals, gradually enlarged by the addition of spherical Gaussian functions arranged spatially so as to allow for both axial and angular correlation, as well as to improve the SCF part of the wavefunction.

In order to keep the number of configurations at a reasonably low level an iterative procedure, very similar to the interative natural orbital method of Bender and Davidson [6], was introduced and found to function successfully. As a first approximation a CI wavefunction is constructed containing a limited number of configurations, the basis consisting of orthonormal symmetry orbitals. After the computation of the energy expectation value and corresponding eigenvector the spinless first order reduced density matrix is calculated and diagonalized resulting in a set of "approximate" natural orbitals; approximate because they were calculated using a limited CI wavefunction. In the next calculation the original symmetry orbital basis is replaced by the set of natural orbitals. The process is then repeated, gradually dropping those configurations which make too small a contribution to the wavefunction after a given iteration, until there is no change in the energy and in the natural orbitals. Hence a self-consistent set of orbitals are determined which are hopefully a good approximation to the exact natural orbitals. The process is essentially a multiconfigurational SCF technique, although a great deal simpler to implement on the computer than the more conventional schemes hitherto proposed [7–9].

The Hamiltonian matrix elements between the configurations and the natural orbitals were calculated by the procedure already used in H_3 calculations [3]. There are two linearly independent spin eigenfunctions for the singlet state and four types of configurations, listed in the Appendix together with the representation matrices $\boldsymbol{U}(P)$ which were used in these calculations.

The numerical and geometrical details of the various bases used in these calculations are given in Table 1 and in Figs. 1 and 2. The exponents of the orbitals were chosen on the basis of the H_3 results, since H_3 and H_4 have very similar geometries, as were the spatial distributions of Gaussians. No optimization of the non-linear parameters was undertaken at any stage of the calculations. The results are summarized in Table 2.

In calculation Ref. [1] from the $1s$, $1s'$ STO's eight symmetry orbitals were constructed and orthonormalized by the Schmidt method. The first CI wavefunction was taken to consist of a dominant single determinantal function

Table 1. The orbital bases used in the H_4 calculations
($1S = 1s$-type Slater orbital, $G =$ Spherical Gaussian function)

Calculation Ref.	Number of basis functions	Number of configurations	Orbital basis and exponents
1	8	48	$1S_A = 1S_D = 1.19$, $1S_B = 1S_C = 0.96$, $1S_{A'} = 1S_{D'} = 1.24$, $1S_{B'} = 1S_{C'} = 0.90$
2	11	55	STO basis as for calculation $1 + G_1 = G_2 = G_3 = 1.00$
3	15	69	As for calculation 2, $+ G_4 = G_5 = G_6 = G_7 = 0.40$
4	19	90	As for calculation 2, $+ G_4 = G_5 = \cdots = G_{11} = 0.40$

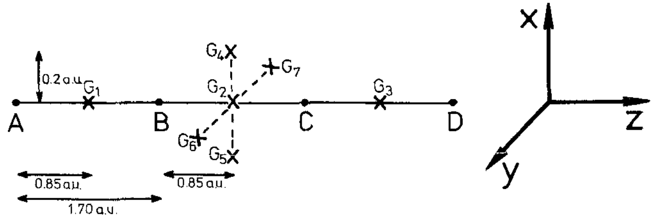

Fig. 1. Positions of the Gaussians in the 11 and 15 orbital H_4 calculations [2, 3]

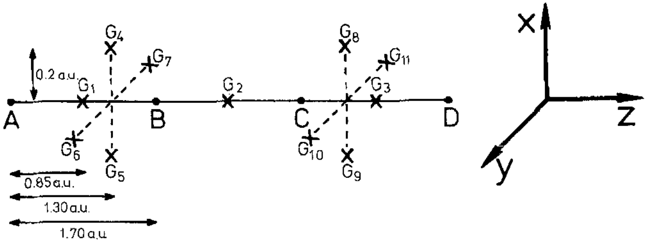

Fig. 2. Positions of the Gaussians in the 19 orbital H_4 calculation [4]

Table 2. Summary of the H_4 calculations (the energies, with the exception of those in the last column, given in atomic units); the H_2 energies required for the last entry were taken from calculations with comparable basis sets, namely the 4, 5 and 9 orbital calculations respectively [2]

Calculation Ref.	Number of basis functions	Number of configurations	Total energy	Kinetic energy	Nuclear attraction energy	Electron repulsion energy	Energy of dominant configuration	Apparent correlation energy	$E_{H_4} - 2E_{H_2}$ (kcal/mole^{-1})
1	8	48	−2.23723	2.23480	−9.33888	2.31783	−2.17833	−0.05890	43.08
2	11	55	−2.24302	2.22775	−9.34315	2.32336	−2.18282	−0.06020	44.30
3	15	69	−2.24720	2.22925	−9.34104	2.31557	−2.18282	−0.06438	
4	19	90	−2.25810	2.23210	−9.33559	2.29637	−2.18282	−0.07528	49.81
8 orbital calculation of Rubinstein and Shavitt [4]			−2.234						

Table 3. Natural orbitals expressed in terms of the original basis,

Natural orbital and its symmetry	Occupation number	Coefficient of atomic orbital			
		$1S_A$	$1S_B$	$1S_C$	$1S_D$
1 σ_g	1.973563	0.304797	0.363791	0.363791	0.304797
2 σ_u	1.937014	0.269596	−0.007723	−0.007723	−0.269596
5 σ_g	0.063171	0.573758	−0.334194	−0.334194	0.573758
7 σ_u	0.017150	−0.078872	−0.166240	0.166240	0.078872
3 σ_g	0.00380	1.070388	1.952159	1.952159	1.070388
4 σ_u	0.003616	4.272493	0.277069	−0.277069	−4.272493
6 σ_g	0.000620	5.473303	−2.835818	−2.835818	5.473303
9 σ_g	0.000591	−2.325916	−0.256812	−0.256812	−2.325916
10 σ_u	0.000274	−3.626281	−1.229978	1.229978	3.626281
8 σ_u	0.000196	4.672738	−9.311377	9.311377	−4.672738
11 σ_g	0.000006	0.300176	4.57332	4.575332	0.300176

$|1\bar{1}2\bar{2}|$, plus all the configurations which could be obtained by single and double substitutions in the above determinant, resulting in a total of 49 configurations. Orbitals 1 and 2 are simply given as

$$1 = a + b + c + d + a' + b' + c' + d'$$

$$2 = a + b - c - d + a' + b' - c' - d'$$

where a, b, c, d and a', b', c', d' are the $1s$ and $1s'$ STO's centred on nuclei a, b, c, d.

The resulting energy was −2.23416 a.u., the coefficient of the leading determinant being 0.945926, all the other coefficients an order of magnitude smaller. This seemed a clear indication that the determinant $|1\bar{1}2\bar{2}|$ was a fair approximation to the SCF wavefunction, hence the 49 term CI expansion was also expected to be a reasonable approximation to the full CI wavefunction. Next, the natural orbitals were used to construct the same set of configurations, the leading determinant constructed from the two NO's with the highest occupation numbers. After 3 iterations the change in the total energy was less than 10^{-5}, while the change in NO's was of the order of 10^{-4}, dropping to less than 10^{-8} after 6 iterations. In the final wavefunction the coefficient of the leading determinant was 0.977610, while the configurations obtained by single substitutions all had coefficients less than 10^{-6} and could be omitted from the expansion without a significant increase in the energy. Hence it appears that the iterative procedure used gives a set of Brueckner type orbitals such that all single excitations have vanishingly small coefficients [10, 11]. Next, the configuration wavefunction was extended to include triple and quadruple excitations as well, resulting in a total of 64 configurations. The iterations were then repeated, omitting those configurations which had sufficiently small ($\leq 10^{-3}$) coefficients, some of them double excitations, finally resulting in a 48 configuration wavefunction. This final wavefunction contains 4 triple and 4 quadruple excitations. Although these new configurations have zero matrix elements with the leading determinant, they make a small contribution to the energy (~0.38 kcal/mole) through second order effects. The energy terms calculated by this 48 configuration wavefunction are given in Table 2.

In calculation Ref. [2] three Gaussians, placed on the molecular axis, as shown in Fig. 1, were added to the 8 orbital basis. The symmetry orbitals formed from and their occupation numbers, from the 11 orbital H_4 calculation

Coefficient of atomic orbital						
$1S_{A'}$	$1S_{B'}$	$1S_{C'}$	$1S_{D'}$	G_1	G_2	G_3
−0.063644	0.042099	0.042099	−0.063644	0.022785	0.022593	0.022785
0.220148	0.489810	−0.489810	−0.220148	0.030459	0.0	−0.030459
0.302971	−0.268651	−0.268651	0.302971	−0.000002	0.0	−0.000002
1.087010	−1.747110	1.747110	−1.087010	−0.000164	0.0	0.000164
−0.758486	−2.023819	−2.023819	−0.758486	0.000478	0.000018	0.000478
−4.420480	−0.224360	0.224360	4.420480	−0.004076	0.0	0.004076
−6.470700	3.630527	3.630527	6.470700	−0.000004	0.0	−0.000004
1.777873	0.041838	0.041838	1.777873	1.108409	−0.524337	1.108409
3.443406	−0.780154	0.780154	−3.443406	1.648924	0.0	−1.648924
−6.846303	14.24447	14.24447	6.846303	0.000078	0.0	−0.000078
0.165227	−2.970354	−2.970354	0.165227	−1.205726	−2.552824	−1.205726

these new orbitals were Schmidt orthogonalized to the set of natural orbitals from calculation Ref. [1] and used to construct 37 configurations which were added to the 48 of the previous calculation. Four iterations were performed, resulting in a 55 configuration wavefunction, all other configurations found to be negligible. The natural orbitals and their occupation numbers from this calculation are presented in Table 3.

In calculation Ref. [3] four off axial Gaussians were added to the orbital basis, as shown in Fig. 1. As in the analogous H_2 and H_3 calculations [2, 3], the point group of the molecule was taken to be D_{4h}, hence two e_{1u}, one b_{1g} and one a_{1g} symmetry orbitals could be formed from these new Gaussians. The a_{1g} orbital was Schmidt orthogonalized to the NO basis from calculation Ref. [2], the other three already orthogonal by virtue of their symmetry properties. 69 configurations were found significant enough to be included in the expansion.

The final H_4 calculation [4] employed two sets of four off-axial Gaussians, as shown in Fig. 2, in addition to the 11 orbitals from calculation Ref. [2]. The orthonormal basis, however, contained only 16 molecular orbitals, since orbital 11 from the 11 orbital NO set and the a_{1g} and a_{2u} Gaussian lobe functions were discarded from the set. The omission of these orbitals was not expected to increase the energy by more than 0.0002 a.u., this belief based on similar results for H_3. The molecular orbitals, constructed from the off-axial Gaussians, are listed in Table 4. The final wavefunction contains 90 configurations, these were selected after a few trial runs testing which new configurations would be important enough to be used. The occupation numbers of the natural orbitals resulting from this calculation are listed in Table 5, while in Table 6 the 90 configurations and their coefficients are presented.

The wavefunctions from the other H_4 calculations are given elsewhere [12][1].

Discussion

The results of calculation Ref. [1] represent a slight improvement (~2 kcal/mole in the total energy) over the results of Rubinstein and Shavitt [4], despite the small number of configurations in the wavefunction. Clearly, the orbital

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[1] Also available from G. B. Bacskay on request.

Table 4. Additional molecular orbitals, expressed in terms of the original basis, for the 19 orbital H_4 calculation (the first 10 orbitals are orbitals 1–10, as listed in Table 3)

Molecular orbital and its symmetry	Coefficient of atomic orbital							
	G_4	G_5	G_6	G_7	G_8	G_9	G_{10}	G_{11}
11 e_{1u_x} (π_{u_x})	2.404816	−2.404816			2.404816	−2.404816		
12 e_{1u_y} (π_{u_y})	0.0	0.0	2.404816	−2.404816	0.0	0.0	2.404816	−2.404816
13 e_{1g_x} (π_{g_x})	3.335528	−3.335528	0.0	0.0	−3.335528	3.335528	0.0	0.0
14 e_{1g_y} (π_{g_y})	0.0	0.0	3.335528	−3.335528	0.0	0.0	−3.335528	3.335528
15 b_{1g} (Δ_g)	19.63822	19.63822	−19.63822	−19.63822	19.63822	19.63822	−19.63822	−19.63822
16 b_{1u} (Δ_u)	26.3699	26.3699	−26.3699	−26.3699	−26.3699	−26.3699	26.3699	26.3699

Table 5. The occupation numbers of the natural orbitals from the 19 orbital H_4 calculation

Natural orbital and its symmetry	Occupation number
1 σ_g	1.966401
2 σ_u	1.933892
5 σ_g	0.060481
7 σ_u	0.016261
11 π_{u_x}	0.004195
12 π_{u_y}	0.004195
3 σ_g	0.003638
4 σ_u	0.003501
13 π_{g_x}	0.002857
14 π_{g_y}	0.002857
6 σ_g	0.000602
9 σ_g	0.000550
10 σ_u	0.000262
8 σ_u	0.000176
15 Δ_g	0.000082
16 Δ_u	0.000066

Table 6. Configurations and their coefficients from the 19 orbital H_4 calculation

Configuration		Coefficient
Orbitals	Type	
Dominant configuration		
1 1 2 2	1	0.974926
Double substitutions		
1 1 3 3	1	−0.013578
1 1 4 4	1	−0.024375
1 1 5 5	1	−0.144772
1 1 3 5	2	−0.0182899
1 1 6 6	1	−0.007985
1 1 3 6	2	−0.008532
1 1 5 6	2	0.007147
1 1 7 7	1	−0.033975
1 1 4 7	2	0.004494
1 1 8 8	1	−0.003537
1 1 4 8	2	−0.001029
1 1 7 8	2	0.004358
2 2 3 3	1	−0.019727
2 2 4 4	1	−0.009980
2 2 4 8	2	0.001990
2 2 5 5	1	−0.056799
2 2 3 5	2	0.021110
2 2 6 6	1	−0.004344
2 2 3 6	2	0.003026
2 2 5 6	1	−0.011914
2 2 7 7	2	−0.039707
1 1 12 12	1	−0.014631
2 2 12 12	1	−0.031911
1 2 12 14	3	0.038480
1 2 12 14	4	0.012622
1 1 13 13	1	−0.020239
2 2 13 13	1	−0.013440
1 1 14 14	1	−0.020240
2 2 14 14	1	−0.013443
1 1 15 15	1	−0.001788
2 2 15 15	1	−0.004499
1 1 16 16	1	−0.003188
2 2 16 16	1	−0.002294
1 2 15 16	3	0.005738
1 2 15 16	4	0.001621
2 2 4 7	2	0.007694
2 2 8 8	1	−0.004610
2 2 7 8	2	−0.007631
1 3 2 4	3	−0.019882
1 3 2 4	4	−0.020626
1 3 2 7	3	0.016904
1 3 2 7	4	0.021685
1 5 2 4	4	−0.032073
1 5 2 7	3	−0.084147
1 5 2 7	4	−0.048863
1 6 2 4	3	−0.005128
1 6 2 4	4	−0.009776
1 6 2 7	3	−0.001704
1 6 2 7	4	−0.002517
1 6 2 8	3	−0.004026
1 1 9 9	1	−0.009064
1 1 10 10	1	−0.005558
2 2 9 9	1	−0.010441
2 2 10 10	1	−0.004503
1 9 2 10	3	−0.007572
1 9 2 10	4	−0.010026
1 1 11 11	1	−0.014683
2 2 11 11	1	−0.031975
1 2 11 13	3	0.038503
1 2 11 13	4	0.012605
Triple substitutions		
7 7 1 3	2	0.002077
1 6 2 8	4	−0.003923
7 7 1 5	2	−0.001513
7 4 1 5	3	−0.003339
7 4 1 5	4	0.003554
1 5 11 11	2	0.001457
1 7 11 13	3	0.001140
2 5 11 13	4	−0.001465
1 5 12 12	2	0.001464
2 7 12 12	2	−0.000729
1 7 12 14	3	0.001133
2 5 12 14	4	−0.001459
1 5 13 13	2	−0.001912
2 7 13 13	2	0.000909
1 5 14 14	2	−0.001912
2 7 14 14	2	0.000933
Quadruple substitutions		
5 5 7 7	1	0.013058
5 5 4 4	1	0.003677
7 4 5 3	4	0.002806
5 5 3 3	1	0.004505
9 9 5 5	1	0.002191
10 10 5 5	1	0.000986
5 5 11 11	1	0.005652
7 7 11 11	1	0.001697
5 5 12 12	1	0.005765
5 5 13 13	1	0.003126
7 7 13 13	1	0.001253
5 5 14 14	1	0.003120
7 7 14 14	1	0.001298

exponents used in our calculation are closer to the optimum values. Rubinstein and Shavitt used the exponents 1.230 and 0.615 for the $1s$ and $1s'$ orbitals respectively, their ratio kept fixed as 2:1 during the optimization procedure, judged too large by the authors themselves. Furthermore, it appears that the 48 configuration wavefunction may be very close to a good multiconfigurational SCF wavefunction. Hence, no significant improvement in the energy would be expected, were the wavefunction of the full CI type, i.e. containing 176 configurations.

The introduction of Gaussians with σ symmetry resulted in a relatively small decrease in the total energy (0.00579 a.u.), most of it appearing as an improved energy for the leading configuration, i.e. the "SCF part" of the wavefunction. Compared to the H_3 results [3] where the analogous energy decrease was ~ 0.009 a.u., the above change seems too small. Optimization of the exponents in this case is probably desirable to improve the above results.

The effect of the first set of functions with angular dependence is disappointingly little (calculation Ref. [3]). Obviously the π_u functions are unable to bring about sufficient angular correlation between electrons delocalized over a molecule which is far too long to be efficiently covered by the simple π_u functions. A smaller orbital exponent should have been used for the off-axial Gaussians, or more functions with angular dependence. In the final calculation Ref. [4] we chose the second alternative by the addition of another set of four off-axial Gaussians. The effects are quite marked, obviously the new π_u orbitals especially are much more successful in allowing for angular correlation than the earlier ones, which consisted of only two Gaussians.

The H_4 wavefunctions in these calculations were developed in terms of a dominant configuration (that is expected to approximate to the SCF wavefunction in the given basis) and double, triple and quadruple substitutions in the above single determinant. As pointed out earlier, the absence of single excitations implies Brueckner self-consistency, since in the case of Hartree-Fock self-consistency single excitations could still appear, even though Brillouin's theorem was satisfied, due to second order effects. Quadruple excitations seem an order of magnitude more important than triple excitations, this is not unexpected, since the latter are thought to correspond to unlinked clusters of electrons, or "simultaneous binary collisions" between electrons in different regions of space [13].

Unfortunately, no definite new value has been produced for the upper bound of the energy difference of H_4 and two H_2 molecules, apart from the very first entry in Table 2, i.e. 43.08 kcal/mole, resulting from the simplest calculation in this series. As the basis for the H_4 calculations was increased the above energy difference increased also, indicating that the H_4 basis was becoming progressively poorer than the comparable H_2 basis. As pointed out earlier, optimization of the nonlinear parameters should definitely be carried out to improve these results.

Conclusion

It has been demonstrated again that mixed basis sets could be very useful for future work on multicentre systems of this kind. The iterative scheme used in this work has proved very useful too; all the CI expansions were successfully kept reasonably short. It would be very interesting and profitable to do some calculations for H_4, using the set of basic integrals computed for the present work, but employing SCF and multi-configurational SCF techniques. A full CI calculation would also be worth attempting. Such calculations will be undertaken shortly.

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Appendix

The Representation Matrices $\boldsymbol{U}(P)$, Used in the Evaluation of Matrix Elements between the 4 Electron Configurations

The four types of configurations with $S=0$ are defined as

$$\Phi^1 = (i\,i\,j\,j)^1 = |i\,\bar{i}\,j\,\bar{j}|\,,$$

$$\Phi^2 = (i\,i\,j\,k)^2 = 1/\sqrt{2}\,\{|i\,\bar{i}\,j\,\bar{k}| + |i\,\bar{i}\,k\,\bar{j}|\}\,,$$

$$\Phi^3 = (i\,j\,k\,l)^3 = 1/2\,\{|i\,\bar{j}\,k\,\bar{l}| + |j\,\bar{i}\,k\,\bar{l}| + |i\,\bar{j}\,l\,\bar{k}| + |j\,\bar{i}\,l\,\bar{k}|\}\,,$$

$$\Phi^4 = (i\,j\,k\,l)^4 = 1/\sqrt{12}\,\{|i\,\bar{j}\,k\,\bar{l}| + |j\,\bar{i}\,k\,\bar{l}| + |i\,\bar{j}\,l\,\bar{k}| + |j\,\bar{i}\,k\,\bar{l}| - 2\,|i\,\bar{k}\,j\,\bar{l}| - 2\,|j\,\bar{l}\,i\,\bar{k}|\}\,,$$

Φ^2 could also be written as $(j\,k\,i\,i)^2$.

The $\boldsymbol{U}(P)$ matrices are:

$$\boldsymbol{U}(1) = \boldsymbol{U}(23.14) = \begin{pmatrix} 1 & \sqrt{2} & 2 & 0 \\ \sqrt{2} & 1 & \sqrt{2} & 0 \\ 2 & \sqrt{2} & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix},$$

$$\boldsymbol{U}(12.34) = \boldsymbol{U}(13.24) = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & \sqrt{2} & 0 \\ 0 & \sqrt{2} & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix},$$

$$\boldsymbol{U}(12) = \boldsymbol{U}(34) = \boldsymbol{U}(14.12.13) = \boldsymbol{U}(13.12.14) = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix},$$

$$\boldsymbol{U}(13) = \begin{pmatrix} -2 & -1/\sqrt{2} & -1 & \sqrt{3} \\ -1/\sqrt{2} & -1/2 & -1/\sqrt{2} & \sqrt{3}/\sqrt{2} \\ -1 & -1/\sqrt{2} & -1/2 & \sqrt{3}/2 \\ \sqrt{3} & \sqrt{3}/\sqrt{2} & \sqrt{3}/2 & 1/2 \end{pmatrix},$$

$$\boldsymbol{U}(24) = \begin{pmatrix} 0 & -1/\sqrt{2} & -1 & \sqrt{3} \\ -1/\sqrt{2} & -1/2 & -1/\sqrt{2} & \sqrt{3}/\sqrt{2} \\ -1 & -1/\sqrt{2} & -1/2 & \sqrt{3}/2 \\ \sqrt{3} & \sqrt{3}/\sqrt{2} & \sqrt{3}/2 & 1/2 \end{pmatrix},$$

$$\boldsymbol{U}(14.13.12)=\boldsymbol{U}(12.13.14)\begin{pmatrix}0&0&0&0\\0&-1/2&-1/\sqrt{2}&\sqrt{3}/\sqrt{2}\\0&-1/\sqrt{2}&-1/2&\sqrt{3}/2\\0&\sqrt{3}/\sqrt{2}&\sqrt{3}/2&1/2\end{pmatrix},$$

$$\boldsymbol{U}(13.12)=\boldsymbol{U}(34.14)=\boldsymbol{U}(24.34)=\boldsymbol{U}(24.12)=\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&0&-1/2&-\sqrt{3}/2\\0&0&\sqrt{3}/2&-1/2\end{pmatrix},$$

$$\boldsymbol{U}(13.14)=\boldsymbol{U}(23.34)=\boldsymbol{U}(23.12)=\boldsymbol{U}(14.12)=\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&0&-1/2&\sqrt{3}/2\\0&0&-\sqrt{3}/2&-1/2\end{pmatrix},$$

$$\boldsymbol{U}(14)=\boldsymbol{U}(23)=\begin{pmatrix}0&-\sqrt{2}&-1&-\sqrt{3}\\-\sqrt{2}&-1/2&-1/\sqrt{2}&-\sqrt{3}/\sqrt{2}\\-1&-1/\sqrt{2}&-1/2&-\sqrt{3}/2\\-\sqrt{3}&-\sqrt{3}/\sqrt{2}&-\sqrt{3}/2&1/2\end{pmatrix},$$

$$\boldsymbol{U}(13.14.12)=\boldsymbol{U}(12.14.13)=\begin{pmatrix}0&0&0&0\\0&-1/2&-1/\sqrt{2}&-\sqrt{3}/\sqrt{2}\\0&-1/\sqrt{2}&-1/2&-\sqrt{3}/2\\0&-\sqrt{3}/\sqrt{2}&-\sqrt{3}/2&1/2\end{pmatrix},$$

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