

NEO-XCHF1 Testing and Validation

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NEO-XCHF1 parallel version: Tests

The parallel XCHF1 code is an independent version, and has evolved to have several differences w.r.t the original GAMESS-XCHF1 code. I validated this new version against the one used for the JCP erratum by repeating some of the erratum calculations as well as a proton MO eigenvalue splitting calculation for HeH^+ at the XCHF1/ET5s5p_z2d_z/cc-pVDZ level—there was perfect agreement for these tests. Below, I will outline additional tests used to validate the parallel XCHF1 code. They are meant to form a logical progression for testing the Hartree-Fock, 2-, 3-, 4- and 5-particle integrals and energetic contributions to XCHF1.

1. Test NEO-HF/ET-5s5p2d/cc-pVDZ on Li-H-Li^+ .

Purpose: Test basis set normalization/contraction, basic NEOHF integrals, and second-order SCF by comparing to GAMESS-NEOHF calculation.

System: LiHLi^+ where $R_{\text{LiLi}} = 3.3776\text{\AA}$.

Electronic and nuclear overlap matrices and final energetic components are consistent. My SCF converges smoothly in 13 iterations beginning from core Hamiltonian electronic and nuclear guesses. Orbital gradients are consistent with those calculated using GAMESS-NEO.

NEOHF-Independent: -15.2718375740

NEOHF-GAMESS: -15.2718375739

2. Test against NEO-HF.

Purpose: Test Hartree-Fock build by reproducing the total energy of a NEO-HF calculation using a NEO-XCHF1 calculation where all $\gamma_i = 0$ and b_i are equal to their standard values.

Level of theory: XCHF1/1s/cc-pVDZ $N_{\text{gem}} = 3$ (XH^+ parameters). All $\gamma_{1-3} = 1.0d - 08$ and $R_{\text{HeHe}} = 1.955\text{\AA}$

NEO-HF Energy: -5.7643506712

NEO-XCHF1 Energy: -5.7643506736

3. Test XH^+ .

Purpose: Test 2-particle geminal components with s- p- d- functions by comparing to published results for XCHF1 and FGH. Test 2-particle geminal integrals using McMurchie-Davidson algorithms by me and Ari. Also tests NUCST keyword option. Note that frequencies are calculated using the difference in total energies between the ground and third excited proton vibrational state.

Level of theory: XCHF1/ET-5s5p3d/cc-pVDZ (UC) $R_{\text{XH}^+} = 1.0500211\text{\AA}$

Published result: NEOXCHF1: 1649 cm^{-1} . FGH: 1645 cm^{-1} .

Parallel code: 1636 cm^{-1}

xcOMP_MD_out.log_ST1 (Chet's Integrals):

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FINAL NEOXCHF ENERGY IS      -0.5942888644 AFTER 12 ITERATIONS
xcOMP_AEAC_out.log_ST1 (AC Integrals):
FINAL NEOXCHF ENERGY IS      -0.5942888630 AFTER 12 ITERATIONS

xcOMP_MD_out.log_ST4
FINAL NEOXCHF ENERGY IS      -0.5868349385 AFTER 19 ITERATIONS
xcOMP_AEAC_out.log_ST4
FINAL NEOXCHF ENERGY IS      -0.5868349371 AFTER 38 ITERATIONS

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4. Test for 3- and 4-particle integrals.

Purpose: Test 3- and 4-particle integral evaluation by calculating them using different algorithms.

System: He-H-He⁺ where $R_{HeHe} = 1.955\text{\AA}$

Level of theory: XCHF1/1s/cc-pVDZ $N_{gem} = 1$ (XH⁺ parameters).

2 test calculations were performed:

(a) All integrals evaluated using the McMurchie-Davidson approach implemented by CS.
Final Energy = -5.7675847093

(b) All Coulombic 3- and 4-particle integrals calculated using the auxiliary binomial expansion approach, and 3-particle kinetic energy integrals calculated using Ari's routines (with corrections to the overlap integrals).¹ All 2-particle geminal integrals were evaluated using Ari's routines. Note that the binomial expansion approach ultimately reduces the 3- and 4-particle integrals to sums over 2-particle integrals, and the 2-particle integrals were tested heavily in Test 3.
Final Energy = -5.7675847111

5. Test HeH⁺.

Purpose: Test 2-particle and 3-particle geminal components with s- p- d- functions by comparing to results from FGH. Level of theory: XCHF1/ET-5s5pz3dz/cc-pVDZ (UC) $R_{HeH^+} = 0.7728737\text{\AA}$

$N_{gem} = 3$ from HeH⁺ parameters.

FGH result: 2657 cm⁻¹.

Parallel code: 2516 cm⁻¹

GAMESS-XCHF1 (s-Harmonic): 2408 cm⁻¹

6. Test against GAMESS-NEOXCHF1 code for HeHHe⁺.

Purpose: Test full XCHF1 calculation against known result from JCP erratum. The erratum result was reproduced using the GAMESS version and a corrected version of Ari's code.

System: He-H-He⁺ where $R_{HeHe} = 2.25\text{\AA}$

Level of theory: XCHF1/ET-5s/STO-2G $N_{gem} = 3$ (XH⁺ params).

Total Energy (Independent) = -5.4788705945

Total Energy (GAMESS) = -5.4788706063

7. Size-consistent test using HeH⁺ — He.

Purpose: Test the 4- and 5-particle energetics by exploiting the size-consistency of NEOXCHF1.

The test was carried out as follows:

(a) Perform a NEO-XCHF1 calculation on He-H⁺ and a RHF calculation on He.

(b) Perform a NEO-XCHF1 calculation on [(He-H)⁺ - - - He] where R_{HeH^+} is the same as in the previous step and R_{HeH^+---He} is large—I used 22Å.

¹Ari and I evaluate the kinetic energy integrals differently, so this tests 2 different algorithms, not just two people coding the same algorithm. There were 2 bugs that needed to be fixed in Ari's overlap routines.

Table 1: Summary of “size-consistency” test for NEO-HF and NEO-XCHF1 calculations on the $\text{He-H}^+\text{---He}$ system. For this test $R_{\text{He-H}^+} = 0.783826314\text{\AA}$, which is the equilibrium distance at the HF/cc-pVDZ level, and $R_{\text{HeH}^+\text{---He}} = 22.0\text{\AA}$. All calculations used the cc-pVDZ electronic basis set and NEO calculations had a 1s nuclear basis function with $\alpha = 10.347$.

E Component	NEO-HF			NEO-XCHF1	
	He	HeH^+	$\text{HeH}^+\text{---He}$	HeH^+	$\text{HeH}^+\text{---He}$
E_{Nuc}			0.0930752387		0.0930752387
E_{ECORE}	-3.8820251026	-3.7612625064	-7.8299094536	-0.0400186197	-0.0829209385
E_{PCORE}		1.3586945232	1.4068933715	0.0143284208	0.0148367126
E_{ep}		-1.5253295413	-1.5735284950	-0.0137766748	-0.0142849677
E_{ee}	1.0268646254	1.0310794740	2.1514907604	0.0101727077	0.0219837401
2-PARTICLE				-0.7833686560	-0.7826236251
3-PARTICLE				-2.1013780405	-4.6118051169
4-PARTICLE					-0.7869823060
5-PARTICLE					0.3795198732
Total Energy	-2.8551604772	-2.8968180506	-5.7519785779	-2.9140408624	-5.7692013896
$\text{HeH}^+ + \text{He}$			-5.7519785278		-5.7692013396

(c) The following should hold: $E_{\text{HeH}^+\text{---He}} = E_{\text{HeH}^+} + E_{\text{He}}$.

(d) Note that the 4- and 5-particle contributions will be non-zero for the $E_{\text{HeH}^+\text{---He}}$ calculation, therefore this is a strong test of the code for these energy contributions.

The results from this test—as well as at the NEO-HF level—are presented in Table 1.

- Note that all tests I performed obey Mike’s test for the nuclear Fock matrix trace energy and trace overlap. Additionally, all calculations perform run-time checking of symmetry of electronic and nuclear Fock matrices and normalization of the NEO-HF component of the total wavefunction.

Validation: Parallel XCHF1 Calculations

Figure 1 presents a summary of XCHF1 H vibrational frequency calculations performed on XH^+ , HeH^+ , and HeHHe^+ . Despite the fact that the XCHF1 code has been solid during testing, the results for HeHHe^+ are clearly not what I would expect to see for a well-tested code. I elaborate on these calculations below.

Discussion of HeH^+ and XH^+ results

- The HARM results for both systems are below the corresponding FGH references. What is striking in comparison of the HeH^+ and XH^+ results in Figure 1 is that the EVAL results for XH^+ are spot-on with FGH, whereas for HeH^+ the EVAL results are lower than FGH, but agree with the HARM results. On one hand you can interpret the HARM and EVAL agreement for HeH^+ as an indication of things working properly—if the system is harmonic HARM and EVAL approaches should produce similar frequencies—but then why don’t we see the same spot-on agreement with FGH like we do for XH^+ ? But then this begs the question as to why the same agreement between HARM and EVAL is not observed for XH^+ , although the EVAL results agree very well with FGH. There is certainly a catch-22 here, but does it indicate some problem with the HeH^+ results?

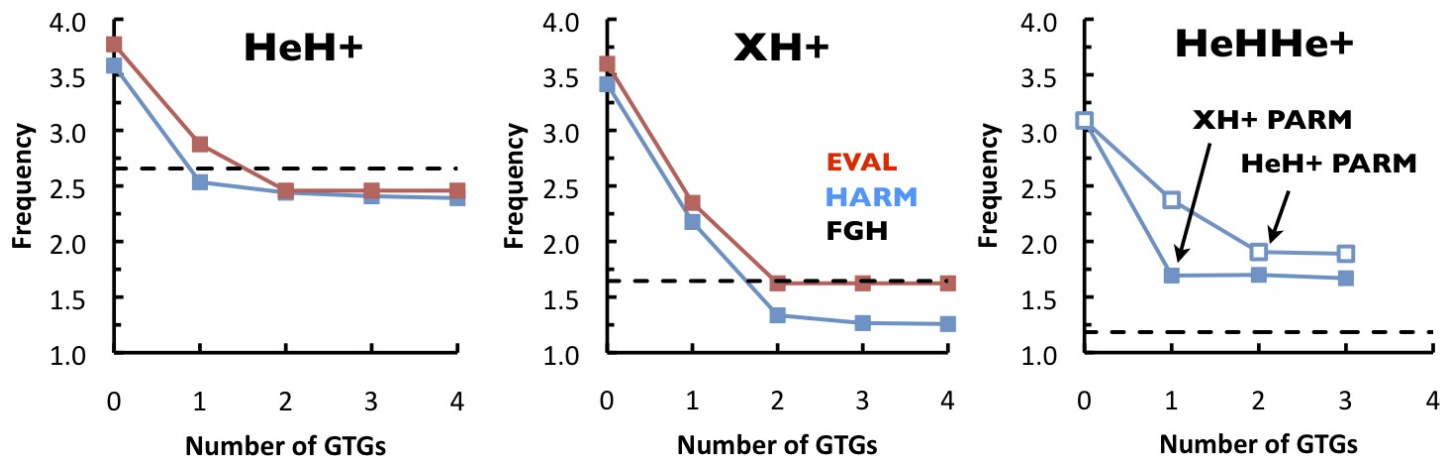


Figure 1: XCHF1 H vibrational frequencies as a function of $N_{gem} = 0 - 4$ for HeH^+ , XH^+ , and HeHHe^+ . The uncontracted (UC) cc-pVDZ electronic basis set was used for the HeH^+ and XH^+ calculations and the contracted cc-pVDZ basis set was used for HeHHe^+ . EVAL (red) values correspond to frequencies calculated as proton MO eigenvalue differences based on the the ET-5s5p_z3d_z proton basis set. HARM (blue) values correspond to converting a 1s proton basis function exponent to a harmonic frequency. For the HeH^+ and XH^+ HARM values, the geminal parameters and the proton basis function exponent were optimized in concert. For HeHHe^+ , the geminal parameters were either the XH^+ parameters, or HeH^+ parameters obtained with the contracted cc-pVDZ electronic basis set. The black dashed reference line corresponds to the FGH frequency value. Frequencies are in units of 1000 cm^{-1} .

- I also performed another set of EVAL frequency calculations for HeH^+ at the same level of theory, but using the XH^+ geminal parameters. These results are presented in Table 2. This doesn't clear up any of the questions posed in the previous bullet, but the results do demonstrate that the frequency is not very sensitive to using XH^+ or HeH^+ parameters—the XH^+ parameters appear (so far) to be transferable to many-electron systems.

Table 2: Comparison of XCHF1/ET-5s5p_z3d_z/cc-pVDZ(UC) level EVAL H vibrational frequencies and energies for HeH^+ using geminal parameters from HeH^+ and XH^+ . Frequencies are in cm^{-1} and energies are in au.

N_{gem}	XH^+ Parameters		HeH^+ Parameters	
	ν	E	ν	E
1	2458	-2.9058175	2875	-2.9071309
2	2568	-2.9118355	2480	-2.9163762
3	2436	-2.9159040	2458	-2.9181276
4	2414	-2.9169680	2458	-2.9181381

HeHHe⁺ Calculations

- HeHHe^+ calculations were performed at the XCHF1/1s/cc-pVDZ (contracted) level. For these calculations, the nuclear 1s exponent, α , was calculated variationally and used to calculate the vibrational frequency using the Harmonic approximation. Two sets of geminal expansion parameters were used:

1. XH^+ parameters calculated at the XCHF1/1s/cc-pVDZ (UC) level.
2. HeH^+ parameters calculated at the XCHF1/1s/cc-pVDZ contracted level.

The results for $N_{gem} = 1 - 3$ are presented in Table 4.

- The XH^+ parameters lead to the better α value, but the corresponding harmonic frequency is still 40% higher than the FGH stretching value. This is double the error observed for the JCP erratum calculations (which have similar bend/stretch FGH frequencies).
- In order to dissect the energetic behavior w.r.t. α , I performed two calculations—one with $\alpha = 7.0$ which is about the value obtained for $N_{gem} = 3$ using the XH^+ parameters, and the other with $\alpha = 4.95$ which is the target value. For both calculations I used the XH^+ parameters with $N_{gem} = 3$. These results are presented in Table 5.
- Considering the ΔE values in Table 5, the 4-PARTICLE contribution seems to make a large positive contribution going from $\alpha = 7.0 - 4.95$. All of the components listed above the 4-PARTICLE contribution come in to play in the HeH^+ 2-electron/1-proton system, and, since the HeH^+ results seem reasonable (based on Figure 1), any kind of bug/error would most likely be in the 4-PARTICLE component.²
- Since I’ve tested the 4-PARTICLE contribution—calculating the integrals using two different approaches, and with the size-consistency test—I’m left wondering if the geminal parameters need to be optimized along with α . This is contrary to the successes observed for XCHF2—which relies on geminal parameters from XH^+ —for the HeHHe^+ system. It’s also inconsistent with the transferrability of the XH^+ parameters to HeH^+ demonstrated in Table 2.

Table 3: Nuclear 1s exponents for HeHHe^+ . α^{fit} are obtained by fitting the effective proton density to a Gaussian based on the ET-5s proton basis set. α^{opt} are obtained by variationally optimizing 1 proton 1s exponent. The electronic basis set labeled cc-pVDZ (S-Only) indicated that the p-function in the cc-pVDZ basis set was replaced with an s-function. Exponent units are Bohr^{-2} .

Electronic Basis Set	Method	α^{fit}	α^{opt}
cc-pVDZ (S-Only)	NEO-HF	13.65	
cc-pVDZ	NEO-HF	13.71	
cc-pVDZ (S-Only)	NEO-XCHF1	6.62	6.75
cc-pVDZ	NEO-XCHF1	6.93	6.96

²Note: Although I’ve not presented them here, I performed the α optimization in Table 4 using a truncated XCHF1 where the 5-PARTICLE contribution was neglected. The α values I obtained for $N_{gem} = 1 - 3$ were very close to the corresponding ones obtained with the full XCHF1 calculations. Thus, it seems unlikely that the 5-PARTICLE contribution is a major player in the behavior of α .

Table 4: HeHHe⁺ XCHF1/1s/cc-pVDZ (contracted) level calculations. The nuclear 1s exponent, α , was calculated variationally and used to calculate the vibrational frequency using the Harmonic approximation. Geminal expansion parameters are derived either from HeH⁺ (using cc-pVDZ contracted electronic basis set), or from XH⁺ (with cc-pVDZ uncontracted basis set). For all calculations, $R_{HeHe} = 1.955\text{\AA}$ —FGH bend and stretch are 918 cm^{-1} ($\alpha = 3.84$) and 1184 cm^{-1} ($\alpha = 4.95$), respectively.

Source of geminal parameters	N_{gem}	α	ν / cm^{-1}	E / au
HeH ⁺	1	9.926	2373	-5.7808052
	2	7.970	1905	-5.7886500
	3	7.900	1889	-5.7898899
XH ⁺	1	7.083	1693	-5.7675854
	2	7.110	1699	-5.7782178
	3	6.980	1669	-5.7896372

Table 5: Comparison of XCHF1 energy components based on 2 1s nuclear exponent values. Geminal parameters are from XH⁺ with $N_{gem} = 3$. HeHHe⁺ at 1s/cc-pVDZ (contracted) level calculations. All values are in au.

Energy Component	$\alpha = 7.00$	$\alpha = 4.95$	ΔE
E_{Nuc}	1.0827156	1.0827156	0.0000000
E_{ECORE}	-0.0751628	-0.0757274	-0.0005646
E_{PCORE}	0.0165353	0.0166462	0.0001109
E_{ep}	-0.0164702	-0.0165571	-0.0000869
E_{ee}	0.0236109	0.0237817	0.0001708
2-PARTICLE	-0.3659060	-0.3702492	-0.0043432
3-PARTICLE	-5.1565816	-5.1613514	-0.0047698
4-PARTICLE	-1.6029571	-1.5932815	0.0096756
5-PARTICLE	0.3045789	0.3050142	0.0004353
Total Energy	-5.7896371	-5.7890089	0.0006282
HF Energy	-0.0514870	-0.0518566	-0.0003696
Geminal Energy	-6.8208657	-6.8198679	0.0009978

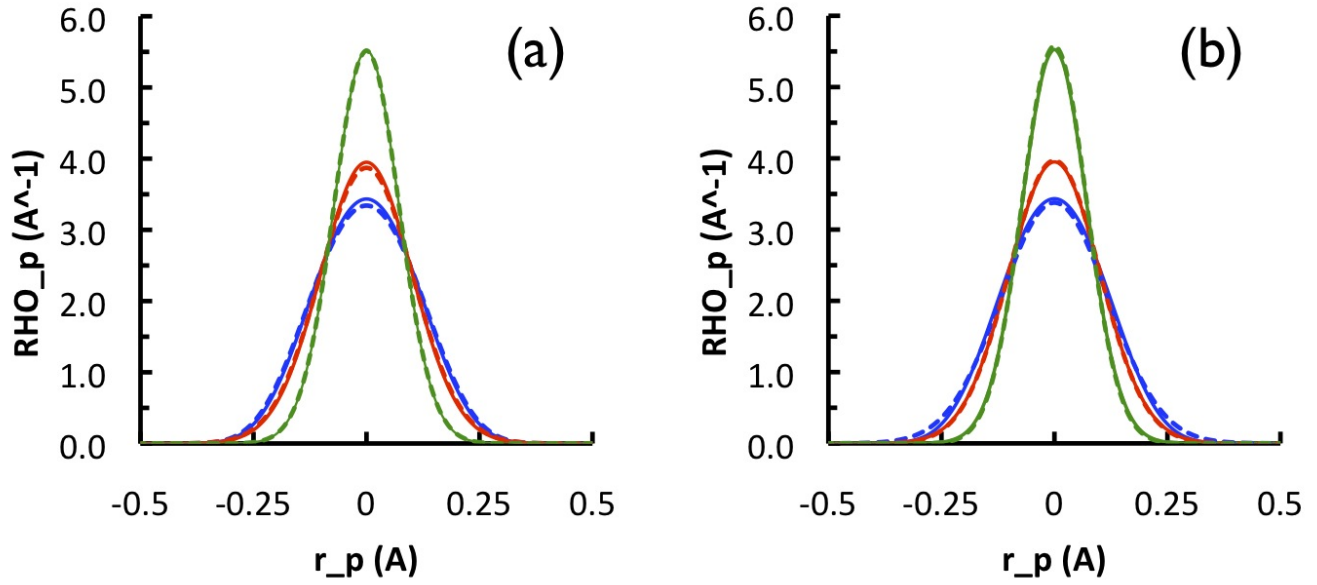


Figure 2: NEO-HF (green), NEO-XCHF1 (red), and 3D-FGH (blue) effective and harmonic proton densities for HeHHe^+ . In (a) the dashed lines are based on using the cc-pVDZ (SONLY) basis set and the solid lines correspond to the standard cc-pVDZ basis set. In (b) the dashed lines represent harmonic densities (based on tabulated frequency values) and the solid lines are effective densities—all values in (b) are based on the standard cc-pVDZ electronic basis set.

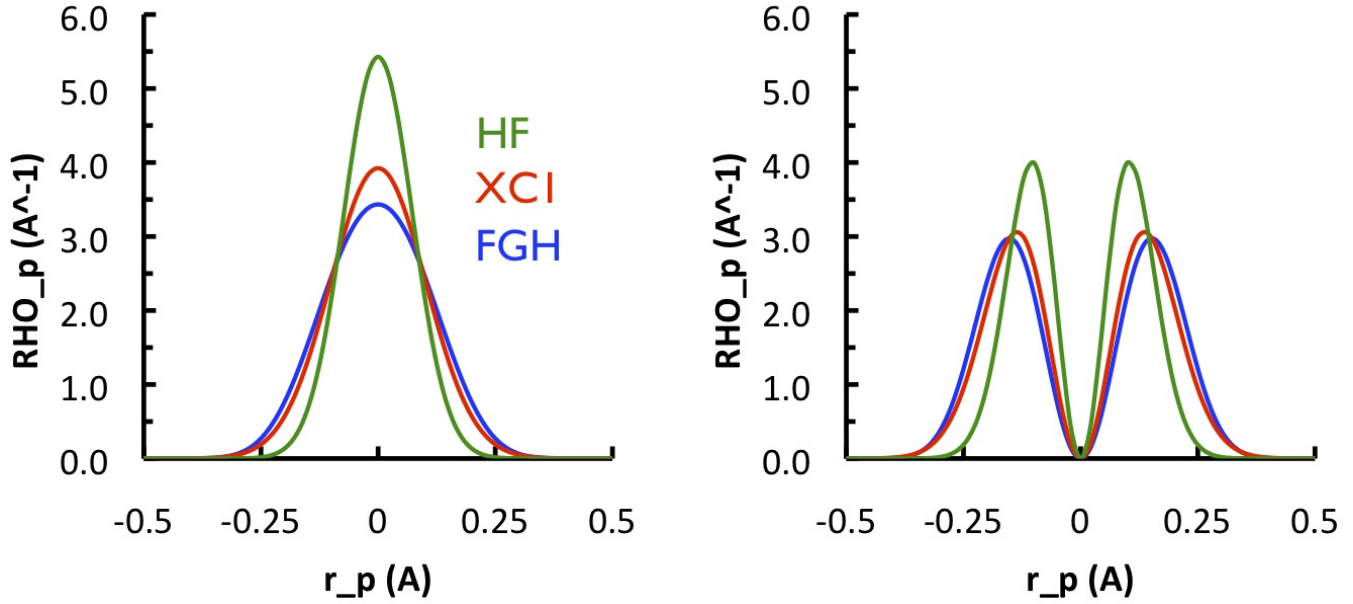


Figure 3: Ground and excited state NEO-HF (green), NEO-XCHF1 (red), and 3D-FGH (blue) effective proton densities for HeHHe^+ . The effective proton densities at the NEO levels are based on separate calculations for the ground and excited proton states. For the ground state NEO calculations a $1s$ nuclear basis function was used and the exponent was variationally optimized. The excited state NEO calculations were carried out in the same way using a single p_z function. All calculations employed the standard cc-pVDZ electronic basis set with $R_{\text{HeHe}} = 1.955\text{\AA}$. The NEO frequencies based on total energy differences are: 3450 and 2014 cm^{-1} for NEOHF and NEOXC1, respectively.

Routines Used for 4- and 5-Particle Contributions

```
subroutine GAM3_OMP_MD
  call xcalc_GAM3_MD
  call index_GAM_3PK

subroutine xcalc_GAM3_MD
  call pgiovlap
  call gfvee
  call gfke
  call gfvec
  call G3ovlap  --or-- call G3_MD_xggs
  call G4_MD_xgVepg  --or-- call G4Vep_AUX_g14g24V34
  call G4_MD_xgVeeg  --or-- call G4Vee_AUX_g14g34V12

subroutine GAM4_DSCF
  call read_GAM_ee
  call read_GAM_2s
  call loop_size
  call thread_gam4_DSCF
  call add2fock

subroutine thread_gam4_DSCF
  call symm_gam4

subroutine symm_gam4
  call i10

SUBROUTINE i10
  call calc_GAM_4_integral

subroutine calc_GAM_4_integral
  call pack_4D
  call underflow
  call index_GAM_2PK

subroutine read_GAM_2s
  call index_GAM_2PK

subroutine
  call E_from_GAM_3
  call GAM4_DSCF

subroutine E_from_GAM_3
  call zero_out
  call index_GAM_3PK
  call add2fock
```