

# "Electronic Excited States from a Variance-Based Contracted Quantum Eigensolver"

## *Example Maple Worksheet for the H<sub>4</sub> Calculations*

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### Introduction

This Maple worksheet provides a Maple code for reproducing the H<sub>4</sub> calculations in the article "Electronic Excited States from a Variance-Based Contracted Quantum Eigensolver." To execute the worksheet, the user must have Maple, the add-on Quantum Chemistry Toolbox, and the file `mapletools.mp` in the directory returned by the command `currentdir()`.

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### Excited-state CQE

```
> ExcitedStateCQE := module()  
  option `Copyright David A. Mazziotti 2023`;  
  export N, nr, H;  
  local EnergyF, VarianceF, EnergyG, VarianceG, Iteration,  
    ModuleApply;  
  
  ModuleApply := proc(psi0, {maximum_iterations::posint := 100},  
    {tolerance::float := 1e-6})  
    local i, psi, out, e1, v1, c1;  
    psi := psi0;  
    for i to maximum_iterations do
```

```

print(`Iteration = `,i);
if i=1 then
  psi,out,e1,v1,c1 := Iteration(psi);
else
  psi,out,e1,v1,c1 := Iteration(psi,out);
fi;
if v1<tolerance then break fi;
od:
return [e1, v1, c1, psi];
end;

Iteration := proc(psi, ip::list := [])
local func, e0, v0, eg, vg, A2, A, ans, step, expM, psi2, e1,
v1, yk, c0, c1;
func := proc(t)
local expM, psi2, var;
expM := LinearAlgebra:-MatrixExponential(A,-t):
psi2 := expM.psi;
var := VarianceF(psi2);
return var;
end;
e0 := EnergyF(psi);
v0 := VarianceF(psi);
eg := EnergyG(psi);
vg := VarianceG(psi);
c0 := eg(..).eg(..)^%T;
print(`Initial Energy, Variance, and CSE LS = `,e0,v0,c0);
if ip=[] then
  A2 := vg;
else
  yk := -vg(..)-ip[1](..);
  A2 := vg+((-vg(..).yk^%T)/(yk.ip[2](..)^%T))*ip[2];
fi;
A := M2toM4(A2);
ans := Optimization:-Minimize('func(t)', t=-1..60, initialpoint
= {t = 0}, optimalitytolerance=1e-5, method=branchandbound);
step := rhs(op(ans[2]));
expM := LinearAlgebra:-MatrixExponential(A,-step):
psi2 := expM.psi;
e1 := EnergyF(psi2);
v1 := VarianceF(psi2);
c1 := EnergyG(psi2);

```

```

c1 := c1(...).c1(...)^%T;
print(`Final Energy, Variance, and CSE LS = `,e1,v1,c1);
return psi2,[-vg,A2],e1,v1,c1;
end:

EnergyF := proc(psi)
local e1;
e1 := binomial(N,2)*psi^%T.H.psi+nr;
return e1;
end;

VarianceF := proc(psi)
local e1, psi2, e2, var;
e1 := psi^%T.H.psi;
psi2 := H.psi;
e2 := psi2^%T.psi2;
var := binomial(N,2)^2*(e2-e1^2);
return var;
end:

EnergyG := proc(psi)
local psi2, E4, E2, acse;
psi2 := H.psi;
E4 := psi2.psi^%T;
E2 := binomial(N,2)*M4toM2(E4);
acse := E2-E2^%T;
return acse;
end:

VarianceG := proc(psi)
local psi2, E4, E2, acse;
psi2 := H.(H.psi);
E4 := psi2.psi^%T;
E2 := binomial(N,2)^2*M4toM2(E4);
acse := E2-E2^%T-2*(EnergyF(psi)-nr)*EnergyG(psi);
return acse;
end:

end module;

```

*ExcitedStateCQE* := module( ) ... end module

(3.1)

## Example

First, we set the Digits to 15,

```
> Digits := 15;
Digits := 15
```

(4.1)

load the Quantum Chemistry Toolbox, an add-on package for electronic structure in Maple,

```
> with(QuantumChemistry);
[AOLabels, ActiveSpaceCI, ActiveSpaceSCF, AtomicData, BondAngles, BondDistances,
Charges, ChargesPlot, ContractedSchrodinger, CorrelationEnergy, CoupledCluster,
DensityFunctional, DensityPlot3D, Dipole, DipolePlot, Energy, ExcitationEnergies,
ExcitationSpectra, ExcitationSpectraPlot, ExcitedStateEnergies, ExcitedStateSpins,
ExcitonDensityPlot, ExcitonPopulations, ExcitonPopulationsPlot, FullCI,
GeometryOptimization, HartreeFock, Interactive, Isotopes, LiteratureSearch,
MOCoefficients, MODiagram, MOEnergies, MOIntegrals, MOOccupations,
MOOccupationsPlot, MOSymmetries, MP2, MolecularData, MolecularDictionary,
MolecularGeometry, NuclearEnergy, NuclearGradient, OscillatorStrengths,
Parametric2RDM, PlotMolecule, Populations, Purify2RDM, QuantumComputing, RDM1,
RDM2, RTM1, ReadXYZ, Restore, Save, SaveXYZ, SearchBasisSets, SearchFunctionals,
SkeletalStructure, SolventDatabase, Thermodynamics, TransitionDipolePlot,
TransitionDipoles, TransitionOrbitalPlot, TransitionOrbitals, Variational2RDM,
VibrationalModeAnimation, VibrationalModes, Video]
```

(4.2)

and read some additional code required by the module

```
> read "mapletools.mp":
Let us define the linear molecule H4 with equal bond lengths of 1 Å
```

```
> mol := [{"H", 0, 0, 0}, {"H", 0, 0, 1}, {"H", 0, 0, 2}, {"H", 0, 0, 3}];
mol := [{"H", 0, 0, 0}, {"H", 0, 0, 1}, {"H", 0, 0, 2}, {"H", 0, 0, 3}]
```

(4.3)

Using the command *HartreeFock*, we perform a Hartree-Fock calculation in the minimal Slater-type orbital (STO-6G) basis set

```
> hf := HartreeFock(mol, basis="sto-6g", symmetry=true);
```

$$hf := \text{table} \left( \left[ \begin{array}{l} e_{\text{tot}} = -2.11246070, \\ mo\_coeff \end{array} \right] \right)$$
(4.4)

$$= \begin{bmatrix} 0.28112114 & 0.52805957 & 0.75651502 & -0.66286692 \\ 0.42596359 & 0.38421441 & -0.51300223 & 1.11739945 \\ 0.42596359 & -0.38421441 & -0.51300223 & -1.11739945 \\ 0.28112114 & -0.52805957 & 0.75651502 & 0.66286692 \end{bmatrix}, \text{converged} = 1, \text{group}$$

$$= \text{"Dooh"}, \text{populations} = \begin{bmatrix} 1.00767427 \\ 0.99232573 \\ 0.99232573 \\ 1.00767427 \end{bmatrix}, \text{aolabels} = \begin{bmatrix} \text{"0 H 1s"} \\ \text{"1 H 1s"} \\ \text{"2 H 1s"} \\ \text{"3 H 1s"} \end{bmatrix}, \text{dipole} = \begin{bmatrix} 0. \\ 0. \\ 0. \end{bmatrix},$$

*symmetry\_rotation*

$$\begin{aligned}
 &= \begin{bmatrix} 0.50000001 & 0.50000001 & -1.27481565 \times 10^{-8} \\ 0.50000001 & 0.50000001 & -1.27481565 \times 10^{-8} \\ 3.99442338 \times 10^{-9} & 3.99442338 \times 10^{-9} & 0.99999999 \end{bmatrix}, mo\_occ \\
 &= \begin{bmatrix} 2.00000000 \\ 2.00000000 \\ 0. \\ 0. \end{bmatrix}, mo\_symmetry = \begin{bmatrix} "A1g" \\ "A1u" \\ "A1g" \\ "A1u" \end{bmatrix}, mo\_energy = \begin{bmatrix} -0.62644895 \\ -0.38602074 \\ 0.29182906 \\ 0.85648398 \end{bmatrix}, rdm1 \\
 &= \begin{bmatrix} 0.71575201 & 0.64527093 & -0.16628145 & -0.39963561 \\ 0.64527093 & 0.65813138 & 0.06764853 & -0.16628145 \\ -0.16628145 & 0.06764853 & 0.65813138 & 0.64527093 \\ -0.39963561 & -0.16628145 & 0.64527093 & 0.71575201 \end{bmatrix}, charges \\
 &= \begin{bmatrix} -0.00767427 \\ 0.00767427 \\ 0.00767427 \\ -0.00767427 \end{bmatrix} \Bigg)
 \end{aligned}$$

With the command *MOIntegrals*, we compute the one- and two-electron integrals

```
> moint := MOIntegrals(mol, basis="sto-6g", symmetry=true,
  initial_mo=[hf[mo_coeff],hf[mo_symmetry]]):
```

The one-electron integrals are obtained from the sum of the kinetic energy and nuclear attraction integrals

```
> eil := moint[kinetic_energy_integrals]+moint
  [nuclear_attraction_integrals];
eil := [[ -1.83792362, 2.71947456 × 10-16, 0.16047144, -4.85874828 × 10-16 ],
  [ 1.22021239 × 10-16, -1.55516834, 7.02948397 × 10-16, -0.12979482 ],
  [ 0.16047144, 9.16770556 × 10-16, -1.25234913, -8.45411223 × 10-17 ],
  [ -6.69384397 × 10-16, -0.12979482, -4.56328773 × 10-16, -0.91421875 ]]
> ei2 := moint[electron_repulsion_integrals];
```

(4.5)

$$ei2 := \begin{bmatrix} 0.49667762 & 5.55111512 \times 10^{-17} & 0.43622512 & -0.08163536 & 1.110 \\ 1.73472348 \times 10^{-17} & 0.15765348 & -5.55111512 \times 10^{-17} & 4.16333634 \times 10^{-17} & 0 \\ 0.43622512 & -1.38777878 \times 10^{-17} & 0.45435086 & 0.00952649 & 1.249 \\ -0.08163536 & 5.55111512 \times 10^{-17} & 0.00952649 & 0.10805008 & 9.020 \\ 5.55111512 \times 10^{-17} & 0.09788880 & 1.11022302 \times 10^{-16} & 7.63278329 \times 10^{-17} & 0 \\ 0.44633025 & 8.32667268 \times 10^{-17} & 0.44846553 & -0.00733629 & -2.77 \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix}$$

We set the nuclear repulsion energy, the number of electrons, and the number of orbitals and compute the Hamiltonian

```
> ExcitedStateCQE:-nr := moimt[nuclear_energy];
ExcitedStateCQE:-N,r := round(add(hf[mo_occ])),2*op(1,hf
[mo_occ]);
ExcitedStateCQE:-H := MakeH(ei1,ei2)/binomial
(ExcitedStateCQE:-N,2);
nr := 2.29310125
N, r := 4, 8
```

$$H := \begin{bmatrix} -0.58828217 & 0 & 0 & 0 & 0 \\ 0 & -0.69602966 & 5.60220375 \times 10^{-17} & 0.01350438 & -5.4140616 \\ 0 & 3.10343347 \times 10^{-17} & -0.65560236 & 1.00967314 \times 10^{-16} & -0.0063 \\ 0 & 0.01350438 & 1.36604340 \times 10^{-16} & -0.60121270 & -3.0570060 \\ 0 & -8.47255450 \times 10^{-17} & -0.00634002 & -9.25346686 \times 10^{-17} & -0.5274 \\ 0 & -1.29686663 \times 10^{-16} & -0.02516681 & 6.79433361 \times 10^{-17} & -0.0068 \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix}$$

As a first example, we compute the ground-state energy and wave function from the excited-state contracted quantum eigensolver (CQE) by initializing the wave function to the ground state from the Hartree-Fock calculation

```
> psi := Vector(binomial(r,4)):
psi[18] := 1;
```

$$\Psi_{18} := 1$$

(4.8)

Executing the excited-state CQE, we obtain the ground-state energy after 20 iterations

```
> state0 := ExcitedStateCQE(psi);
Iteration = , 1
Initial Energy, Variance, and CSE LS = , -2.11246070, 0.08042650, 0.00446814
Final Energy, Variance, and CSE LS = , -2.15156616, 0.02898673, 0.00164269
Iteration = , 2
Initial Energy, Variance, and CSE LS = , -2.15156616, 0.02898673, 0.00164269
Final Energy, Variance, and CSE LS = , -2.16739047, 0.01205099, 0.00067934
```

Iteration = , 3  
 Initial Energy, Variance, and CSE LS = , -2.16739047, 0.01205099, 0.00067934  
 Final Energy, Variance, and CSE LS = , -2.17486122, 0.00443446, 0.00037556  
 Iteration = , 4  
 Initial Energy, Variance, and CSE LS = , -2.17486122, 0.00443446, 0.00037556  
 Final Energy, Variance, and CSE LS = , -2.17739307, 0.00222560, 0.00017162  
 Iteration = , 5  
 Initial Energy, Variance, and CSE LS = , -2.17739307, 0.00222560, 0.00017162  
 Final Energy, Variance, and CSE LS = , -2.17956731, 0.00121208, 0.00007240  
 Iteration = , 6  
 Initial Energy, Variance, and CSE LS = , -2.17956731, 0.00121208, 0.00007240  
 Final Energy, Variance, and CSE LS = , -2.18088646, 0.00011639,  $6.46141846 \times 10^{-6}$   
 Iteration = , 7  
 Initial Energy, Variance, and CSE LS = , -2.18088646, 0.00011639,  $6.46141846 \times 10^{-6}$   
 Final Energy, Variance, and CSE LS = , -2.18094174, 0.00003529,  $8.35023879 \times 10^{-7}$   
 Iteration = , 8  
 Initial Energy, Variance, and CSE LS = , -2.18094174, 0.00003529,  $8.35023879 \times 10^{-7}$   
 Final Energy, Variance, and CSE LS = , -2.18094785, 0.00002630,  $5.05578780 \times 10^{-7}$   
 Iteration = , 9  
 Initial Energy, Variance, and CSE LS = , -2.18094785, 0.00002630,  $5.05578780 \times 10^{-7}$   
 Final Energy, Variance, and CSE LS = , -2.18095177, 0.00002202,  $4.27920869 \times 10^{-7}$   
 Iteration = , 10  
 Initial Energy, Variance, and CSE LS = , -2.18095177, 0.00002202,  $4.27920869 \times 10^{-7}$   
 Final Energy, Variance, and CSE LS = , -2.18095860, 0.00001555,  $1.38381465 \times 10^{-7}$   
 Iteration = , 11  
 Initial Energy, Variance, and CSE LS = , -2.18095860, 0.00001555,  $1.38381465 \times 10^{-7}$   
 Final Energy, Variance, and CSE LS = , -2.18095976, 0.00001457,  $8.68353247 \times 10^{-8}$   
 Iteration = , 12  
 Initial Energy, Variance, and CSE LS = , -2.18095976, 0.00001457,  $8.68353247 \times 10^{-8}$   
 Final Energy, Variance, and CSE LS = , -2.18096102, 0.00001354,  $3.43033290 \times 10^{-8}$   
 Iteration = , 13  
 Initial Energy, Variance, and CSE LS = , -2.18096102, 0.00001354,  $3.43033290 \times 10^{-8}$   
 Final Energy, Variance, and CSE LS = , -2.18096129, 0.00001306,  $4.12051608 \times 10^{-8}$   
 Iteration = , 14  
 Initial Energy, Variance, and CSE LS = , -2.18096129, 0.00001306,  $4.12051608 \times 10^{-8}$   
 Final Energy, Variance, and CSE LS = , -2.18096205, 0.00001137,  $9.07861762 \times 10^{-8}$   
 Iteration = , 15  
 Initial Energy, Variance, and CSE LS = , -2.18096205, 0.00001137,  $9.07861762 \times 10^{-8}$   
 Final Energy, Variance, and CSE LS = , -2.18096266,  $9.85501955 \times 10^{-6}$ ,  $3.49352495 \times 10^{-8}$   
 Iteration = , 16  
 Initial Energy, Variance, and CSE LS = , -2.18096266,  $9.85501955 \times 10^{-6}$ ,  $3.49352495 \times 10^{-8}$   
 Final Energy, Variance, and CSE LS = , -2.18096291,  $9.30198078 \times 10^{-6}$ ,  $3.13475046 \times 10^{-8}$   
 Iteration = , 17  
 Initial Energy, Variance, and CSE LS = , -2.18096291,  $9.30198078 \times 10^{-6}$ ,  $3.13475046 \times 10^{-8}$

*Final Energy, Variance, and CSE LS* = ,  $-2.18096357, 6.19774531 \times 10^{-6}, 1.70468546 \times 10^{-7}$

*Iteration* = , 18

*Initial Energy, Variance, and CSE LS* = ,  $-2.18096357, 6.19774531 \times 10^{-6}, 1.70468546 \times 10^{-7}$

*Final Energy, Variance, and CSE LS* = ,  $-2.18096461, 2.81409595 \times 10^{-6}, 8.85335143 \times 10^{-8}$

*Iteration* = , 19

*Initial Energy, Variance, and CSE LS* = ,  $-2.18096461, 2.81409595 \times 10^{-6}, 8.85335143 \times 10^{-8}$

*Final Energy, Variance, and CSE LS* = ,  $-2.18096538, 1.34509806 \times 10^{-6}, 4.14268737 \times 10^{-8}$

*Iteration* = , 20

*Initial Energy, Variance, and CSE LS* = ,  $-2.18096538, 1.34509806 \times 10^{-6}, 4.14268737 \times 10^{-8}$

*Final Energy, Variance, and CSE LS* = ,  $-2.18096586, 7.98726708 \times 10^{-7}, 4.30095564 \times 10^{-8}$

$$state0 := \begin{bmatrix} -2.18096586, 7.98726708 \times 10^{-7}, 4.30095564 \times 10^{-8}, \\ \vdots \end{bmatrix} \quad \begin{bmatrix} 0. \\ 0. \\ 0. \\ 0. \\ 0. \\ 0. \\ \vdots \end{bmatrix} \quad (4.9)$$

70 element Vector[column]

As a second example, we compute the fifth excited-state energy and wave function from the excited-state CQE by initializing the wave function to a sin-adapted, triplet combination of two Hartree-Fock determinants

```
> psi := Vector(binomial(r,4)):
psi[21] := +1/sqrt(2);
psi[36] := -1/sqrt(2);
```

$$\Psi_{21} := \frac{\sqrt{2}}{2}$$

$$\Psi_{36} := -\frac{\sqrt{2}}{2}$$

(4.10)

Executing the excited-state CQE, we obtain the fifth excited-state energy after 9 iterations

```
> state5 := ExcitedStateCQE(psi);
Iteration = , 1
Initial Energy, Variance, and CSE LS = ,  $-1.64051290, 0.05015023, 0.00279716$ 
Final Energy, Variance, and CSE LS = ,  $-1.66179080, 0.03240698, 0.00172927$ 
Iteration = , 2
Initial Energy, Variance, and CSE LS = ,  $-1.66179080, 0.03240698, 0.00172927$ 
Final Energy, Variance, and CSE LS = ,  $-1.68395240, 0.02084602, 0.00117330$ 
```



$$\begin{aligned}
& \text{Iteration} = , 3 \\
& \text{Initial Energy, Variance, and CSE LS} = , -1.68395240, 0.02084602, 0.00117330 \\
& \text{Final Energy, Variance, and CSE LS} = , -1.70044563, 0.01606113, 0.00087455 \\
& \text{Iteration} = , 4 \\
& \text{Initial Energy, Variance, and CSE LS} = , -1.70044563, 0.01606113, 0.00087455 \\
& \text{Final Energy, Variance, and CSE LS} = , -1.72902969, 0.00575339, 0.00036814 \\
& \text{Iteration} = , 5 \\
& \text{Initial Energy, Variance, and CSE LS} = , -1.72902969, 0.00575339, 0.00036814 \\
& \text{Final Energy, Variance, and CSE LS} = , -1.73559733, 0.00114261, 0.00008980 \\
& \text{Iteration} = , 6 \\
& \text{Initial Energy, Variance, and CSE LS} = , -1.73559733, 0.00114261, 0.00008980 \\
& \text{Final Energy, Variance, and CSE LS} = , -1.73646474, 0.00007876, 4.35216877 \times 10^{-6} \\
& \text{Iteration} = , 7 \\
& \text{Initial Energy, Variance, and CSE LS} = , -1.73646474, 0.00007876, 4.35216877 \times 10^{-6} \\
& \text{Final Energy, Variance, and CSE LS} = , -1.73653391, 0.00001223, 7.64227184 \times 10^{-7} \\
& \text{Iteration} = , 8 \\
& \text{Initial Energy, Variance, and CSE LS} = , -1.73653391, 0.00001223, 7.64227184 \times 10^{-7} \\
& \text{Final Energy, Variance, and CSE LS} = , -1.73654479, 1.54062208 \times 10^{-6}, 1.01222654 \times 10^{-7} \\
& \text{Iteration} = , 9 \\
& \text{Initial Energy, Variance, and CSE LS} = , -1.73654479, 1.54062208 \times 10^{-6}, 1.01222654 \times 10^{-7} \\
& \text{Final Energy, Variance, and CSE LS} = , -1.73654560, 7.75491753 \times 10^{-7}, 3.92366180 \times 10^{-8}
\end{aligned}$$

$$\text{state5} := \begin{bmatrix} -1.73654560, 7.75491753 \times 10^{-7}, 3.92366180 \times 10^{-8}, \begin{bmatrix} 0. \\ 0. \\ 0. \\ 0. \\ 0. \\ 0. \\ \vdots \end{bmatrix} \end{bmatrix} \quad (4.11)$$

70 element Vector[column]