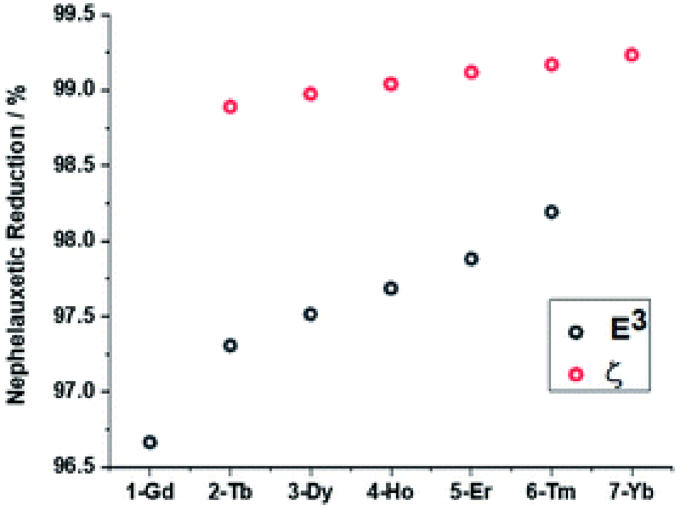
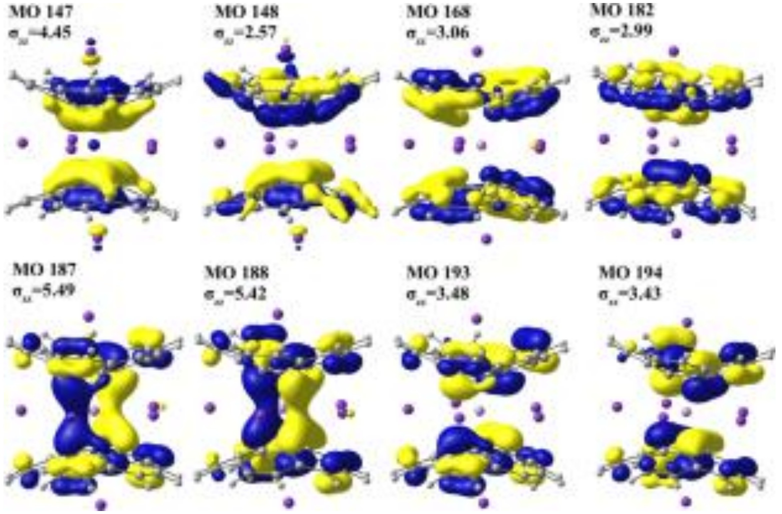
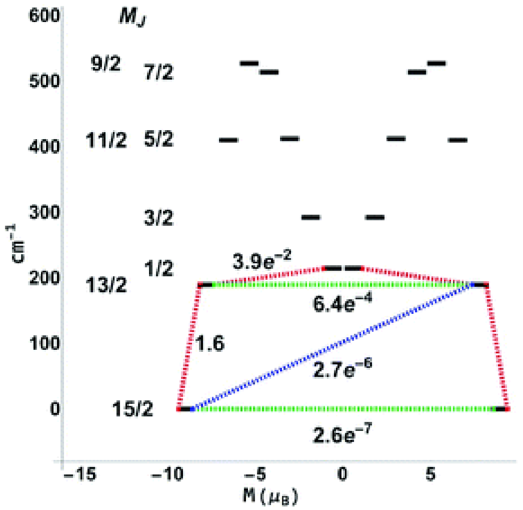
Orca

TD-DFT

NMR







Double Perturbation Theory

If we’re looking for the linear response of our molecule to two different perturbations, we can recast our Schrödinger equation using the following:

$$E = E^0 + \lambda_1 E^{10} + \lambda_2 E^{01} + \lambda_1 \lambda_2 E^{11}$$

$$\hat{H} = \hat{H}^0 + \lambda_1 \hat{H}^{10} + \lambda_2 \hat{H}^{01} + \lambda_1 \lambda_2 \hat{H}^{11}$$

$$\psi = \psi^0 + \lambda_1 \psi^{10} + \lambda_2 \psi^{01} + \lambda_1 \lambda_2 \psi^{11}$$

Also not that the perturbed wavefunctions are orthogonal to the ground state wavefunction

Double Perturbation Theory

We’re looking for a stationary state of E^{11}, so at first we can use the Time-Independent Schrödinger equation to find:

$$E^{11} = \frac{\partial^2 E}{\partial \lambda_1 \partial \lambda_2}$$

Plugging our perturbative expansion into the TISE, and only keeping terms in $\lambda_1\lambda_2$ followed by left multiplication and integration:

$$E^{11} = \langle \psi^0 | \widehat{H}^{11} | \psi^0 \rangle + \langle \psi^{01} | \widehat{H}^{10} | \psi^0 \rangle + + \langle \psi^0 | \widehat{H}^{10} | \psi^{01} \rangle$$

TD-DFT

The Time-Dependent Perturbation Theory gives us:

$$E^{11} = \lim_{\eta\to\infty} \sum_{j\neq 0} \left[\frac{\langle \Psi_0 | \hat{B} | \Psi_j \rangle \langle \Psi_j | \hat{A} | \Psi_0 \rangle}{\omega + i\eta - \Delta E_{0j}} - \frac{\langle \Psi_j | \hat{B} | \Psi_0 \rangle \langle \Psi_0 | \hat{A} | \Psi_j \rangle}{\omega + i\eta + \Delta E_{0j}} \right]$$

If we first invoke the independent particle model (IPM) and assume the operators are 1-electrons operators, then:

$$E^{11} = \lim_{\eta\to\infty} \sum_{k}^{occ} \sum_{a\neq k} \left[\frac{\langle \phi_k | \hat{B} | \phi_a \rangle \langle \phi_a | \hat{A} | \phi_k \rangle}{\omega + i\eta - \Delta E_{ka}} - \frac{\langle \phi_a | \hat{B} | \phi_k \rangle \langle \phi_k | \hat{A} | \phi_a \rangle}{\omega + i\eta + \Delta E_{ka}} \right]$$

$$= \lim_{\eta\to\infty} \sum_{ka} (n_k - n_a) \frac{\langle \phi_k | \hat{B} | \phi_a \rangle \langle \phi_a | \hat{A} | \phi_k \rangle}{\omega + i\eta - \Delta E_{ka}}$$

TD-DFT

We now allow the operator $\hat{A}$ to respond to the changes that the perturbation makes in the orbitals, rather than changing the orbitals themselves:

$$\hat{A}^{(1)} = \hat{A} + \hat{V}^{(1)C} + \hat{V}^{(1)XC}$$

If we first invoke the independent particle model (IPM) and assume the operators are 1-electrons operators, then:

$$E^{11} = \lim_{\eta \to \infty} \sum_{ka} (n_k - n_a) \frac{\langle \phi_k | \hat{B} | \phi_a \rangle \langle \phi_a | \hat{A} + \hat{V}^{(1)C} + \hat{V}^{(1)XC} | \phi_k \rangle}{\omega + i\eta - \Delta E_{ka}}$$

TD-DFT

To solve this equation, we now work with the perturbed first-order density matrix, which is easier to work with and can still be used to evaluate matrix elements:

$$E^{11}(\omega) = \int d\boldsymbol{x} \cdot \left[\hat{B}(\boldsymbol{x})\Gamma^{(1)}_{\hat{A}^{(1)}0}\right]$$

$$\mathrm{P}^{(1)}_{ak}(\omega) = \frac{n_k - n_a}{\omega - \Delta E_{ka}} \langle \phi_a | \hat{A}^{(1)} | \phi_k \rangle$$

$$\Gamma^{(1)}_{\hat{A}^{(1)}0} = \sum_{ka} \mathrm{P}^{(1)}_{ak}(\omega) \phi_a^*(\widetilde{\boldsymbol{x}}) \phi_k(\boldsymbol{x})$$

Note that $\langle \phi_a | \hat{A}^{(1)} | \phi_k \rangle$ also depends on $\mathrm{P}^{(1)}_{ak}(\omega)$ (it’s self-consistent), so we can’t solve directly…

TD-DFT

To get the $\mathrm{P}_{ak}^{(1)}(\omega)$, we explicitly write out the dependence of $\hat{A}^{(1)}$ on $\mathrm{P}_{ak}^{(1)}(\omega)$:

$$\hat{V}_{ak}^{(1)C} + \hat{V}_{ak}^{(1)XC} = \sum_{bj} \left(K_{ak,bj}^{C} + K_{ak,bj}^{XC}\right) \mathrm{P}_{bj}^{(1)}(\omega)$$

$$K_{ak,bj}^{C} = \left\langle \phi_a \phi_b \middle| |r_{12}|^{-1} \middle| \phi_k \phi_j \right\rangle$$

$$K_{ak,bj}^{XC} = \left\langle \phi_a \phi_b \middle| f_{XC}(\boldsymbol{x}_1, \boldsymbol{x}_2, \omega) \middle| \phi_k \phi_j \right\rangle$$

TD-DFT

Plugging the correlation functions into the expression for $\mathrm{P}_{ak}^{(1)}(\omega)$, we get the following for $\mathrm{P}_{ak}^{(1)}(\omega)$:

$$\sum_{b\neq j}\left[\delta_{ab}\delta_{kj}\frac{\omega-\Delta E_{jb}}{n_j-n_b}-K_{ak,bj}\right]P_{bj}^{(1)}(\omega)=\langle\phi_a|\hat{A}|\phi_k\rangle$$

TD-DFT

We can now imagine breaking this equation up...

If b,a is virtual and j,k is occupied:

$$\left[\delta_{ab}\delta_{kj}\left(\omega - \Delta E_{jb}\right) - K_{ak,bj}\right]P_{bj}^{(1)} = A_{ak}$$

If j,k is virtual and b,a is occupied:

$$\left[-\delta_{ab}\delta_{kj}\left(\omega - \Delta E_{jb}\right) - K_{ak,bj}\right]P_{bj}^{(1)} = A_{ak}$$

If b,k is virtual and j,a is occupied or j,a is virtual and b,k is occupied:

$$-K_{ak,bj}P_{bj}^{(1)} = A_{ak}$$

TD-DFT

If we now split into two parts, with $\mathrm{X} = P_{bj}^{(1)}$ (b vir, j occ) and $\mathrm{Y} = P_{bj}^{(1)}$ (b occ, j vir); and also $\mathrm{Q} = A_{ak}$ (a vir, k occ) and $\mathrm{R} = A_{ak}$ (a occ, k vir) :

$$\begin{pmatrix} A+\omega & B \\ B & A-\omega \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \begin{pmatrix} Q \\ R \end{pmatrix}$$

We can look back to see why this is true…

TD-DFT

We can now imagine breaking this equation up...

If b,a is virtual and j,k is occupied:

$$[\delta\delta(\omega - \Delta E) - K]X = Q$$

If j,k is virtual and b,a is occupied:

$$[-\delta\delta(\omega - \Delta E) - K]Y = R$$

If b,k is virtual and j,a is occupied or j,a is virtual and b,k is occupied:

$$-KX = R$$

$$-KY = Q$$

$$A = \frac{-\delta_{ab}\delta_{kj}\Delta E_{jb}}{n_b - n_j} - K_{ak,bj}$$

$$B = -K_{ak,bj}$$

TD-DFT

Our task is now to find the excitation energies using this equation:

$$\begin{pmatrix} A+\omega & B \\ B & A-\omega \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \begin{pmatrix} Q \\ R \end{pmatrix}$$

It’s important to recognize now that Q is simply the complex conjugate of R. $\langle \phi_a | \hat{A} | \phi_k \rangle = \langle \phi_a | \hat{A} | \phi_k \rangle^*$

Because the MOs are real, we can say that for real operators $\hat{A}$ we can represent $(Q+R)$ with $(X+Y)$, and with imaginary operators, $(Q+R)$ is represented with $(X-Y)$ (because everything on the left-hand side is real)

TD-DFT

Thus, after working out the algebra:

$$(X+Y) = S^{-1/2}\left[\omega^2 + S^{-1/2}(A+B)S^{-1/2}\right]^{-1} S^{-1/2}(Q+R)$$

$$S = I(A-B)^{-1}(-I)$$

For a singularity in $P^{(1)}$, therefore, it is clear that we need:

$$\omega^2 + S^{-1/2}(A+B)S^{-1/2} = 0$$

Now we have an eigenvalue equation, that we can use Davidson Diagonalization on:

$${\omega_{0j}}^2 F_{0j} = -S^{-1/2}(A+B)S^{-1/2} F_{0j}$$

TD-DFT (TDA)

In the TDA, our B term is approximated as zero:

$$\begin{pmatrix} A+\omega & 0 \\ 0 & A-\omega \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix} = \begin{pmatrix} Q \\ R \end{pmatrix}$$

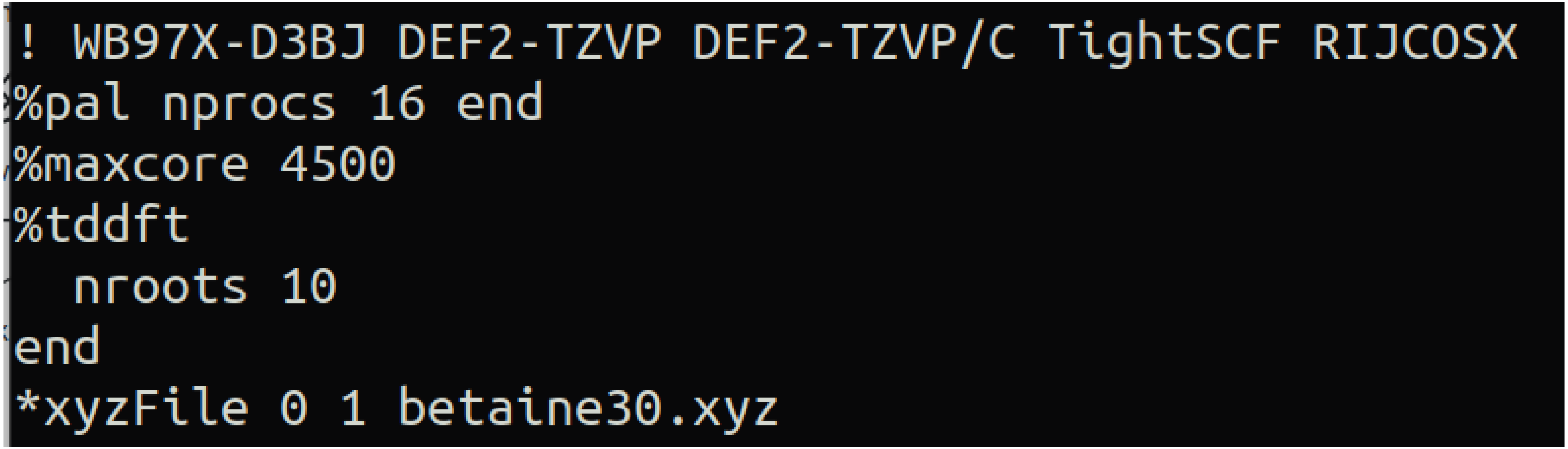
Why is this valid? Remember that our first-order density matrix is self-consistent, and as a first guess, it would be reasonable for us to assume that the density change is comprised entirely of excitations from the occupied to virtual orbitals (X) with Y=0. We don’t expect Y to get very large because it is entirely a correlation effect which ideally will have been appropriately treated in the ground state calculation

TD-DFT in Orca

- ORCA uses TDA by default in all TD-DFT equations, but it can be turned off if necessary.
- TD-DFT can be GREATLY sped up (up to 15) in ORCA with the use of an auxiliary basis set.

  This is similar to the RIJCOSX approximation in the ground state, but here a new auxiliary basis is introduced to fit densities of the excited states.
- Almost all DFT functionals have analytic gradients implemented for TD-DFT, so geometry optimization can be performed.

Let’s Run One



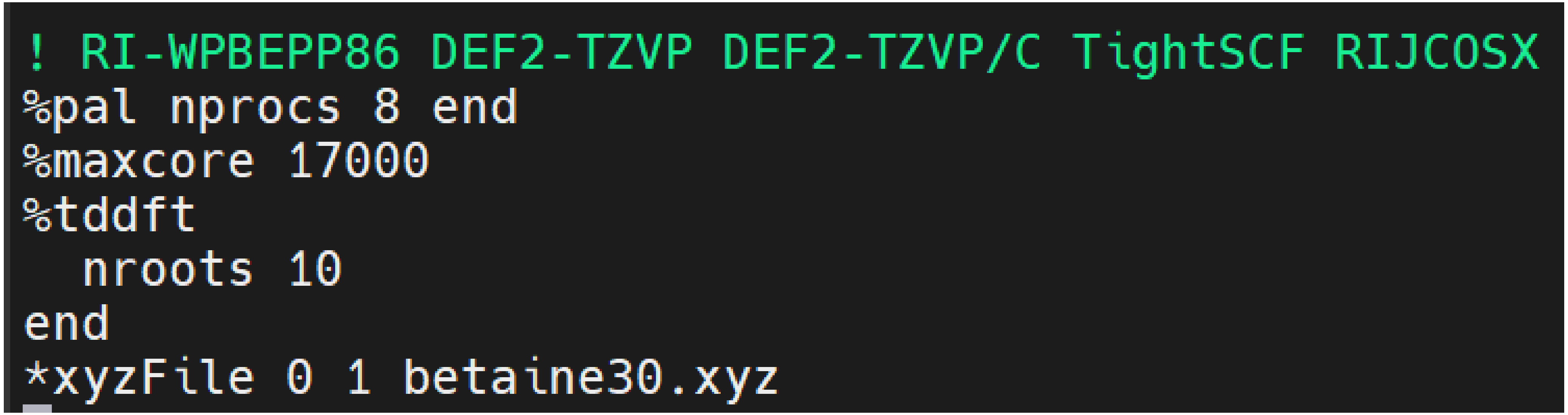
```
! WB97X-D3BJ DEF2-TZVP DEF2-TZVP/C TightSCF RIJCOSX
%pal nprocs 16 end
%maxcore 4500
%tddft
  nroots 10
end
*xyzFile 0 1 betaine30.xyz
```

My Recommendations

These are my personal functional recommendations:

- ωB97X-D3BJ has been shown to be very good for TD-DFT. A recent benchmark showed a RMSE of 0.29 eV which was the best among the tested functionals (B3LYP was worst, followed by PBE0, M06-2X, CAM-B3LYP, then ωB97X-D)
- PBE0 is still pretty reliable
- If you have the resources, there are new double-hybrid functionals specifically designed for excited states:
  - I have personally used wPBEPP86, and it is very good!

A Double-Hybrid Run



```
! RI-WPBEPP86 DEF2-TZVP DEF2-TZVP/C TightSCF RIJCOSX
%pal nprocs 8 end
%maxcore 17000
%tddft
  nroots 10
end
*xyzFile 0 1 betaine30.xyz
```

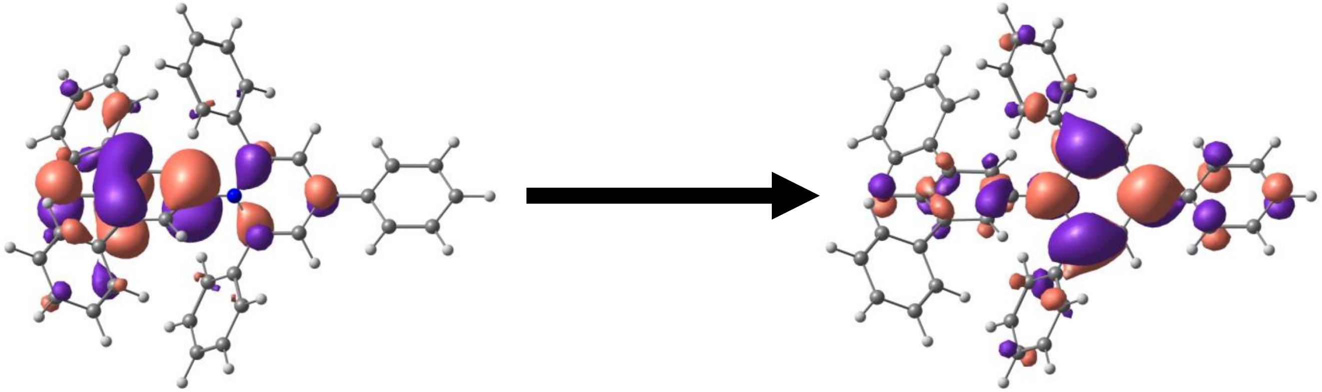
Natural Transition Orbitals

Natural orbitals are eigenvectors of the first-order perturbed density matrix:

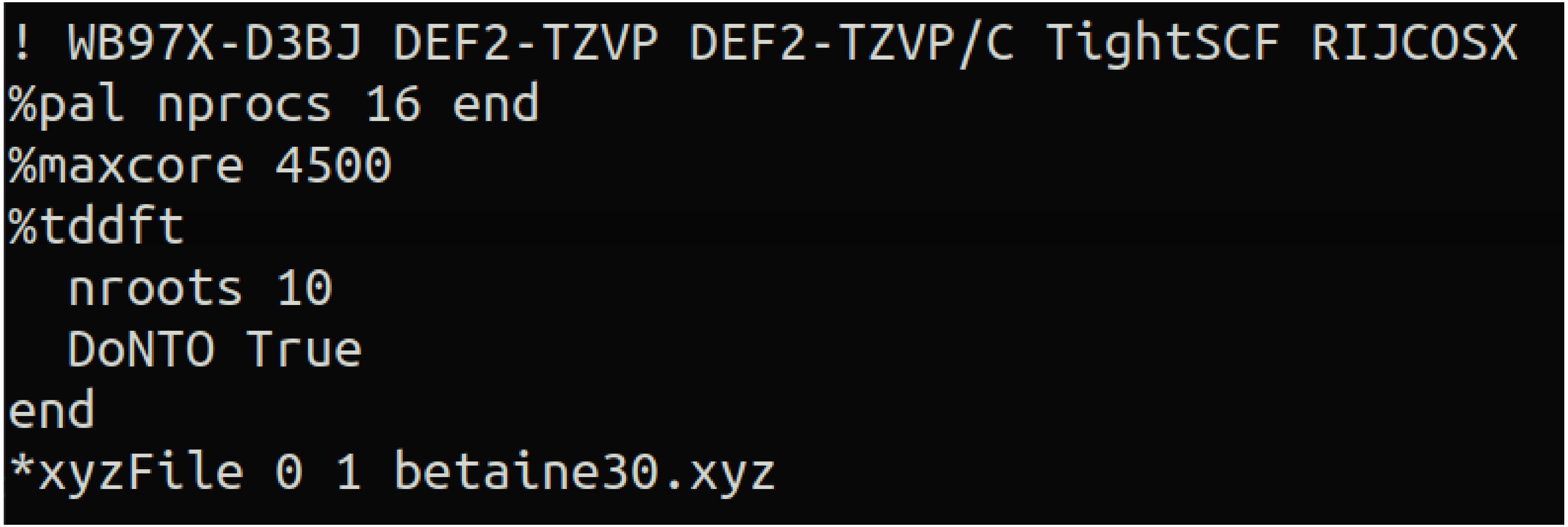
- We already saw this matrix!

$$\Gamma^{(1)}_{\hat{A}^{(1)}0} = \sum_{ka} \mathrm{P}^{(1)}_{ak}(\omega)\phi^{*}_{a}(\widetilde{\boldsymbol{x}})\phi_{k}(\boldsymbol{x})$$

- When visualized, these orbitals focus in on the regions of the molecule that are important for a given transition.

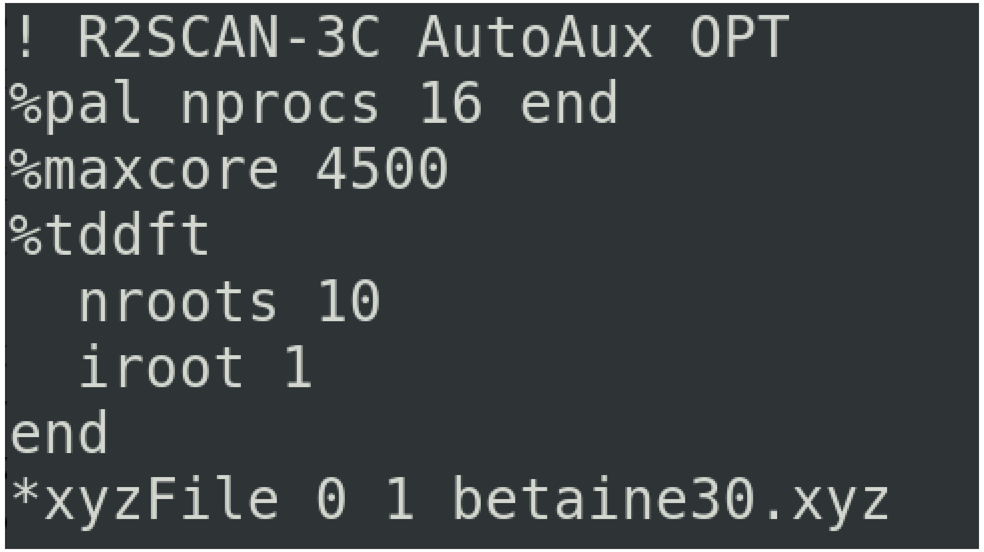


Generating NTOs

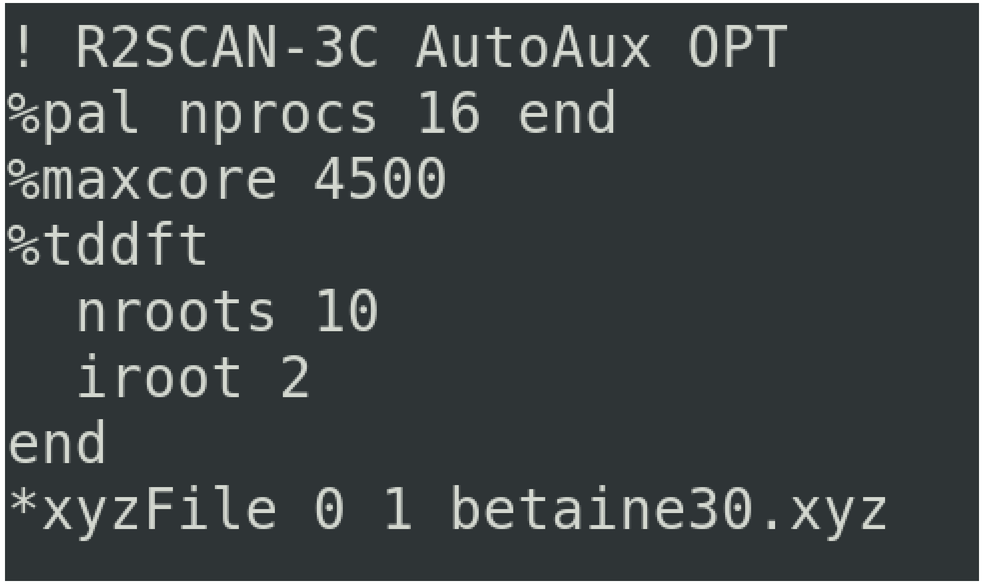


```
! WB97X-D3BJ DEF2-TZVP DEF2-TZVP/C TightSCF RIJCOSX
%pal nprocs 16 end
%maxcore 4500
%tddft
  nroots 10
  DoNTO True
end
*xyzFile 0 1 betaine30.xyz
```

Optimizing an Excited State



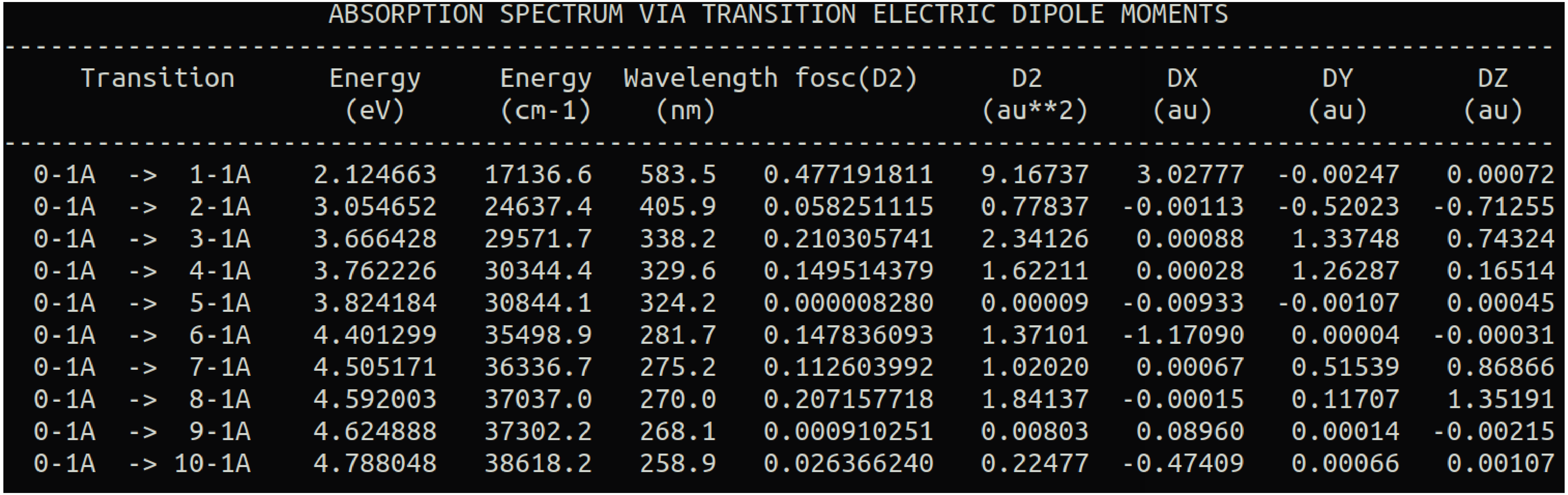
```
! R2SCAN-3C AutoAux OPT
%pal nprocs 16 end
%maxcore 4500
%tddft
  nroots 10
  iroot 1
end
*xyzFile 0 1 betaine30.xyz
```



```
! R2SCAN-3C AutoAux OPT
%pal nprocs 16 end
%maxcore 4500
%tddft
  nroots 10
  iroot 2
end
*xyzFile 0 1 betaine30.xyz
```

Looking at the results

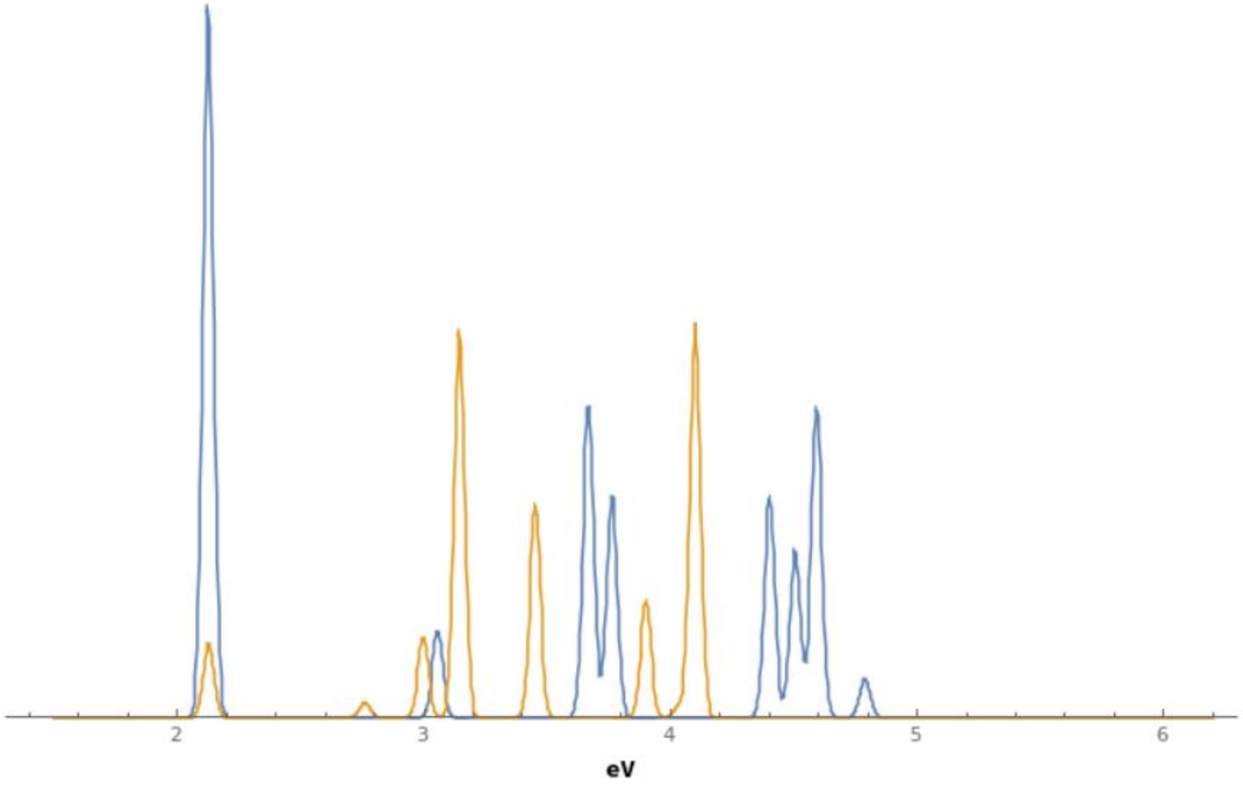
```
grep –A 15 ELECTRIC\ DIPOLE tddft.out | head –n16
```



```
                     ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS
-------------------------------------------------------------------------------------------
     Transition          Energy     Energy  Wavelength fosc(D2)       D2        DX        DY        DZ
                          (eV)      (cm-1)    (nm)                  (au**2)    (au)      (au)      (au)
-------------------------------------------------------------------------------------------
  0-1A  ->  1-1A    2.124663   17136.6   583.5   0.477191811   9.16737   3.02777  -0.00247   0.00072
  0-1A  ->  2-1A    3.054652   24637.4   405.9   0.058251115   0.77837  -0.00113  -0.52023  -0.71255
  0-1A  ->  3-1A    3.666428   29571.7   338.2   0.210305741   2.34126   0.00088   1.33748   0.74324
  0-1A  ->  4-1A    3.762226   30344.4   329.6   0.149514379   1.62211   0.00028   1.26287   0.16514
  0-1A  ->  5-1A    3.824184   30844.1   324.2   0.000008280   0.00009  -0.00933  -0.00107   0.00045
  0-1A  ->  6-1A    4.401299   35498.9   281.7   0.147836093   1.37101  -1.17090   0.00004  -0.00031
  0-1A  ->  7-1A    4.505171   36336.7   275.2   0.112603992   1.02020   0.00067   0.51539   0.86866
  0-1A  ->  8-1A    4.592003   37037.0   270.0   0.207157718   1.84137  -0.00015   0.11707   1.35191
  0-1A  ->  9-1A    4.624888   37302.2   268.1   0.000910251   0.00803   0.08960   0.00014  -0.00215
  0-1A  -> 10-1A    4.788048   38618.2   258.9   0.026366240   0.22477  -0.47409   0.00066   0.00107
```

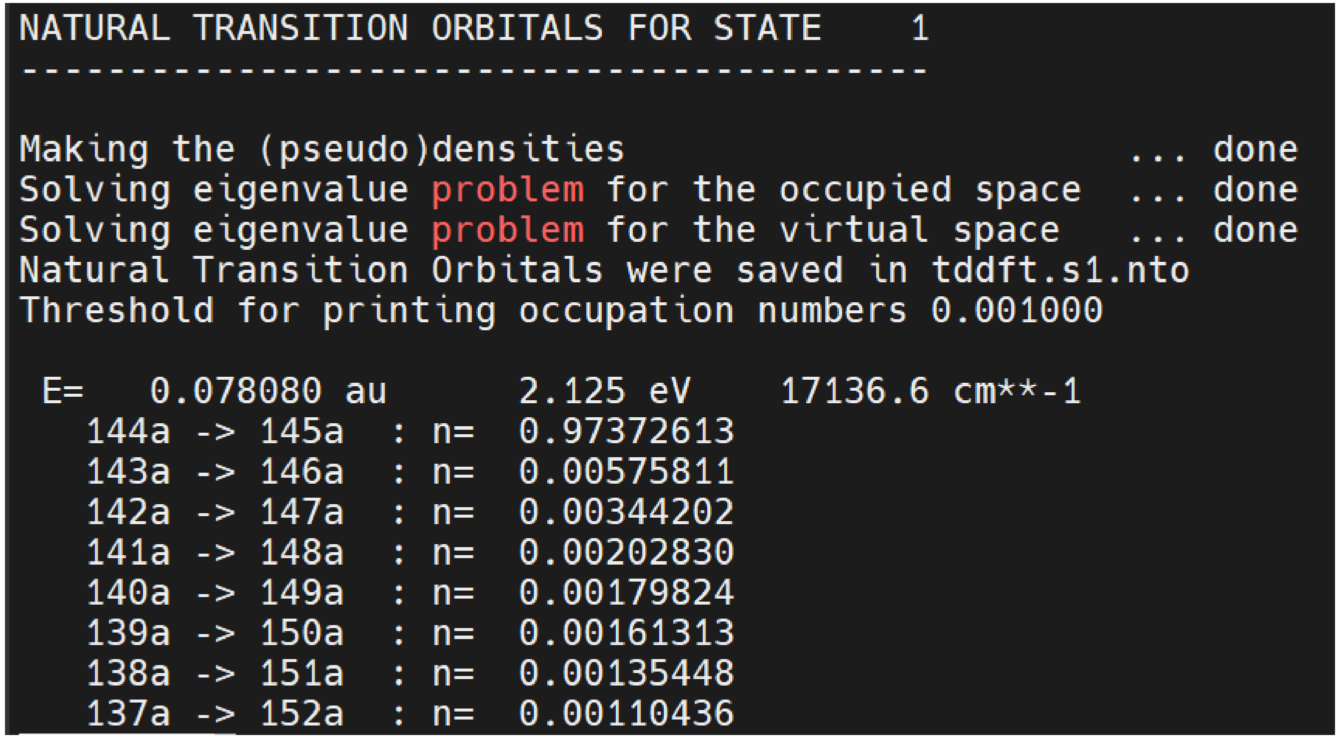
Plot Spectra

```
/projectnb/webmo/orca/6_0_0/orca_mapspc  tddft.out  ABS –eV –x01.5 –x16.2 –w0.05
```



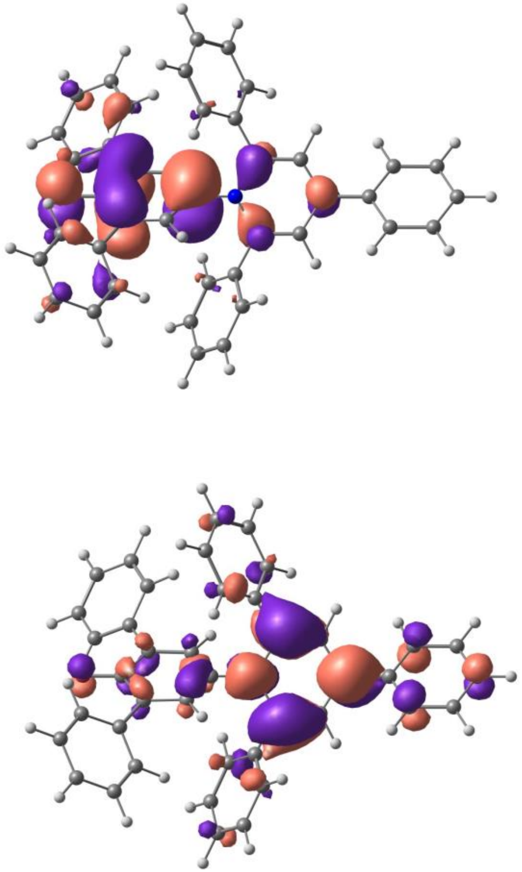
NTOs

```
grep –n NATURAL\ TRAN tddft.out
less +3735 tddft.out
```



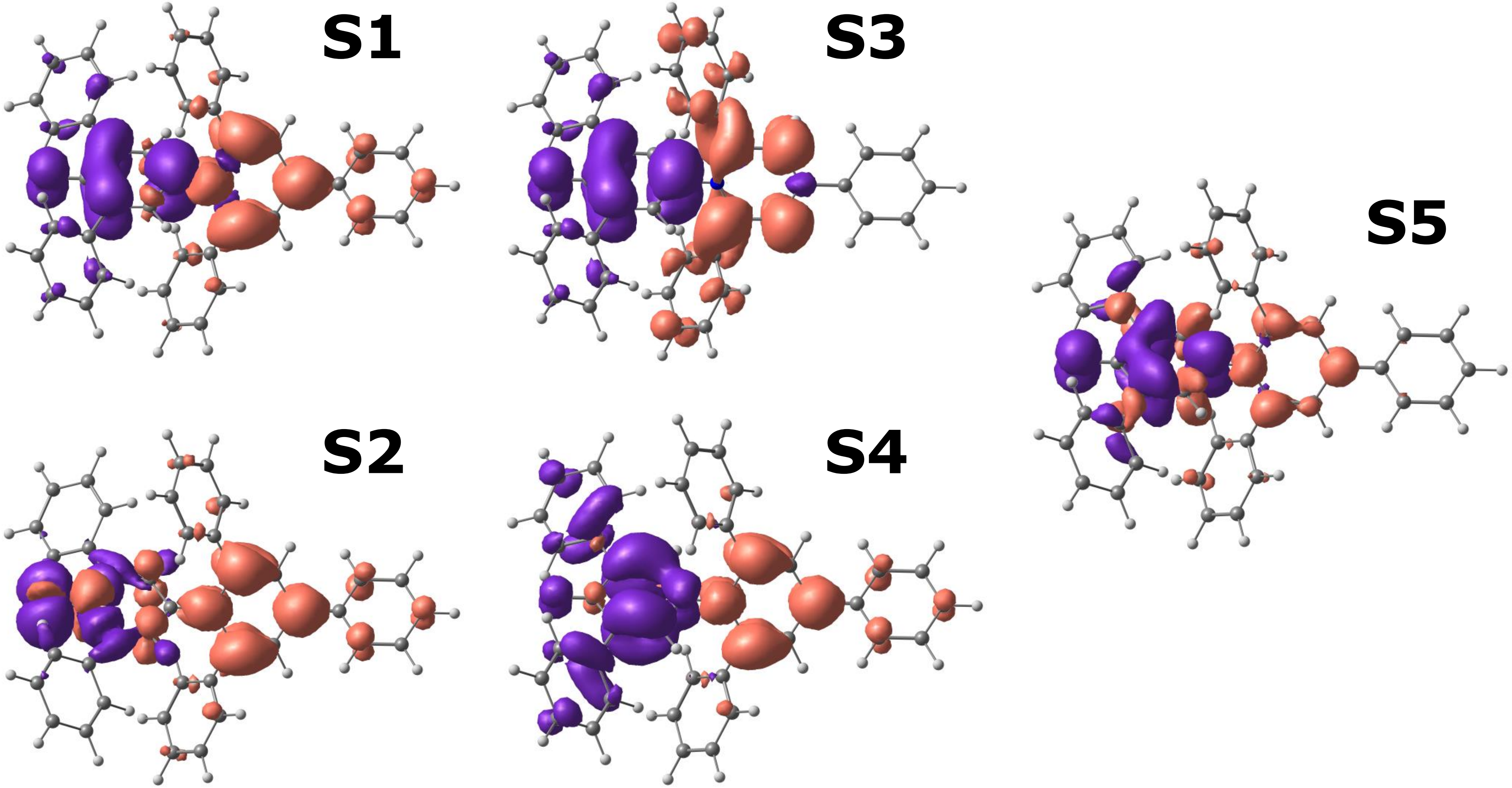
```
NATURAL TRANSITION ORBITALS FOR STATE    1
------------------------------------------

Making the (pseudo)densities                          ... done
Solving eigenvalue problem for the occupied space    ... done
Solving eigenvalue problem for the virtual space     ... done
Natural Transition Orbitals were saved in tddft.s1.nto
Threshold for printing occupation numbers 0.001000

 E=    0.078080 au      2.125 eV    17136.6 cm**-1
   144a -> 145a   : n=  0.97372613
   143a -> 146a   : n=  0.00575811
   142a -> 147a   : n=  0.00344202
   141a -> 148a   : n=  0.00202830
   140a -> 149a   : n=  0.00179824
   139a -> 150a   : n=  0.00161313
   138a -> 151a   : n=  0.00135448
   137a -> 152a   : n=  0.00110436
```

```
/projectnb/webmo/orca/6_0_0/orca_plot tddft.s1.nto –i << END
2
144
4
100
5
7
11
2
145
11
12
END
```



Difference Densities

```
/projectnb/webmo/orca/6_0_0/orca_plot tddft.gbw –I << END
4
100
5
7
6
y
1 2 3 4 5
12
END
```



NMR Theory

For the chemical shift, we have:

$$\boldsymbol{\sigma}_A = \left.\frac{\partial^2 E}{\partial \boldsymbol{B} \partial \boldsymbol{\mu}_A}\right|_{\boldsymbol{B}=0,\boldsymbol{\mu}_A=0}$$

The operators that end up contributing are the orbital Zeeman, paramagnetic orbital, and diamagnetic terms:

$$E^{11} = \left\langle \psi^0 \middle| \widehat{H}^{11} \middle| \psi^0 \right\rangle + \left\langle \psi^{01} \middle| \widehat{H}^{10} \middle| \psi^0 \right\rangle + + \left\langle \psi^0 \middle| \widehat{H}^{10} \middle| \psi^{01} \right\rangle$$

NMR Theory - Nonrelativistic

The following operators can be derived from Maxwell's Equations:

$$\hat{h}^{mag} = \boldsymbol{A}^{ext^2} + \hat{h}^{OZ} + \hat{h}^{SZ} + \hat{h}^{OP} + \hat{h}^{DS} + \hat{h}^{FC} + \hat{h}^{SD} + \hat{h}^{OD}$$

$$\hat{h}^{DS} = \frac{1}{2c^2}\sum_A \left[(\boldsymbol{\mu}_A \cdot \boldsymbol{B}^{ext})\left(\frac{\boldsymbol{r}_A}{r_A^3} \cdot \boldsymbol{r}\right) - (\boldsymbol{\mu}_A \cdot \boldsymbol{r})\left(\boldsymbol{B}^{ext} \cdot \frac{\boldsymbol{r}_A}{r_A^3}\right)\right]$$

$$\hat{h}^{OP} = \frac{1}{c^2}\sum_A \boldsymbol{\mu}_A\left(\frac{\boldsymbol{r}_A}{r_A^3} \times \hat{\boldsymbol{p}}\right) \qquad \hat{h}^{SZ} = -\hat{\boldsymbol{\mu}}_s \cdot \boldsymbol{B}^{ext} \qquad \hat{h}^{OZ} = -\hat{\boldsymbol{\mu}}_e \cdot \boldsymbol{B}^{ext}$$

$$\hat{h}^{FC} = \frac{8\pi}{3c^2}\delta(\boldsymbol{r}_A)\hat{\boldsymbol{\mu}}_A \cdot \boldsymbol{S} \qquad \hat{h}^{SD} = \frac{1}{c^2} \cdot \frac{3(\hat{\boldsymbol{S}} \cdot \boldsymbol{r}_A)(\boldsymbol{\mu}_A \cdot \boldsymbol{r}_A) - r_A^2\boldsymbol{\mu}_A \cdot \hat{\boldsymbol{S}}}{r_A^5}$$

NMR Theory - Nonrelativistic

The terms linear in $\boldsymbol{\mu}_A$, **B**, and $\boldsymbol{\mu}_A \boldsymbol{B}$

$$\hat{h}^{DS} = \frac{1}{2c^2} \sum_A \left[(\boldsymbol{\mu}_A \cdot \boldsymbol{B}^{ext}) \left(\frac{\boldsymbol{r}_A}{r_A^3} \cdot \boldsymbol{r} \right) - (\boldsymbol{\mu}_A \cdot \boldsymbol{r}) \left(\boldsymbol{B}^{ext} \cdot \frac{\boldsymbol{r}_A}{r_A^3} \right) \right]$$

$$\hat{h}^{OP} = \frac{1}{c^2} \sum_A \boldsymbol{\mu}_A \left(\frac{\boldsymbol{r}_A}{r_A^3} \times \hat{\boldsymbol{p}} \right)$$

$$\hat{h}^{OZ} = -\hat{\boldsymbol{\mu}}_e \cdot \boldsymbol{B}^{ext}$$

$$\hat{h}^{SZ} = -\hat{\boldsymbol{\mu}}_s \cdot \boldsymbol{B}^{ext}$$

Doesn’t contribute for diamagnetic molecules

NMR Theory – The Gauge

The magnetic field used in those operators has a problem, in that it has a “location” or an origin. This causes a problem for incomplete basis sets.

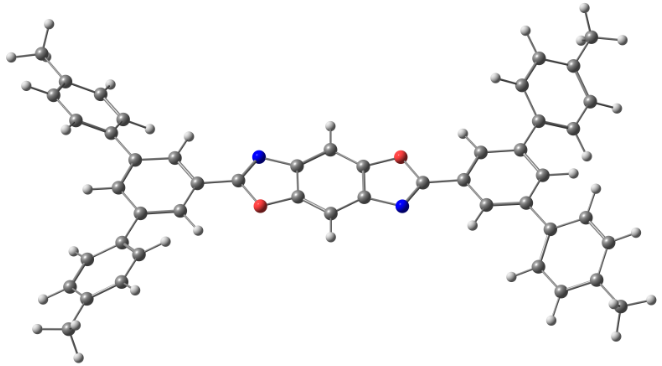
Orca by default uses so-called GIAO, or gauge-independent atomic orbitals to get over this problem.

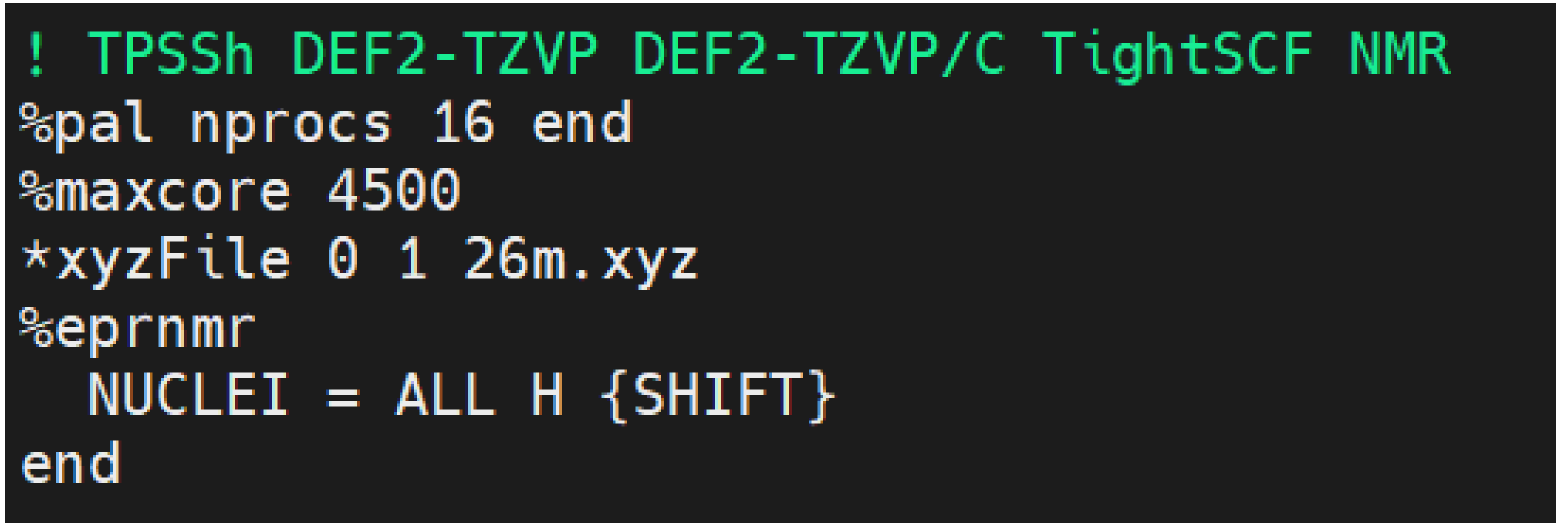
This adds a lot of math to the Coupled Perturbed equations but is worth the result!

For more information, see here:

McNeely, J., Rogachev, A.Y. Theoretical investigation of the record 7Li-NMR chemical shift in new sandwich-like aggregates of corannulene. Theor Chem Acc 139, 35 (2020). https://doi-org.ezproxy.bu.edu/10.1007/s00214-020-2549-4

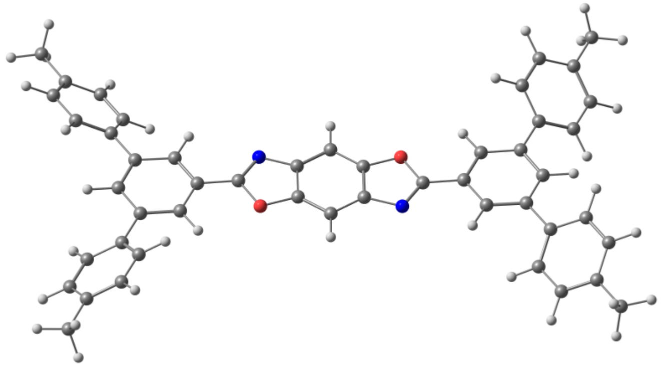
Running a Shielding Calculation (H)

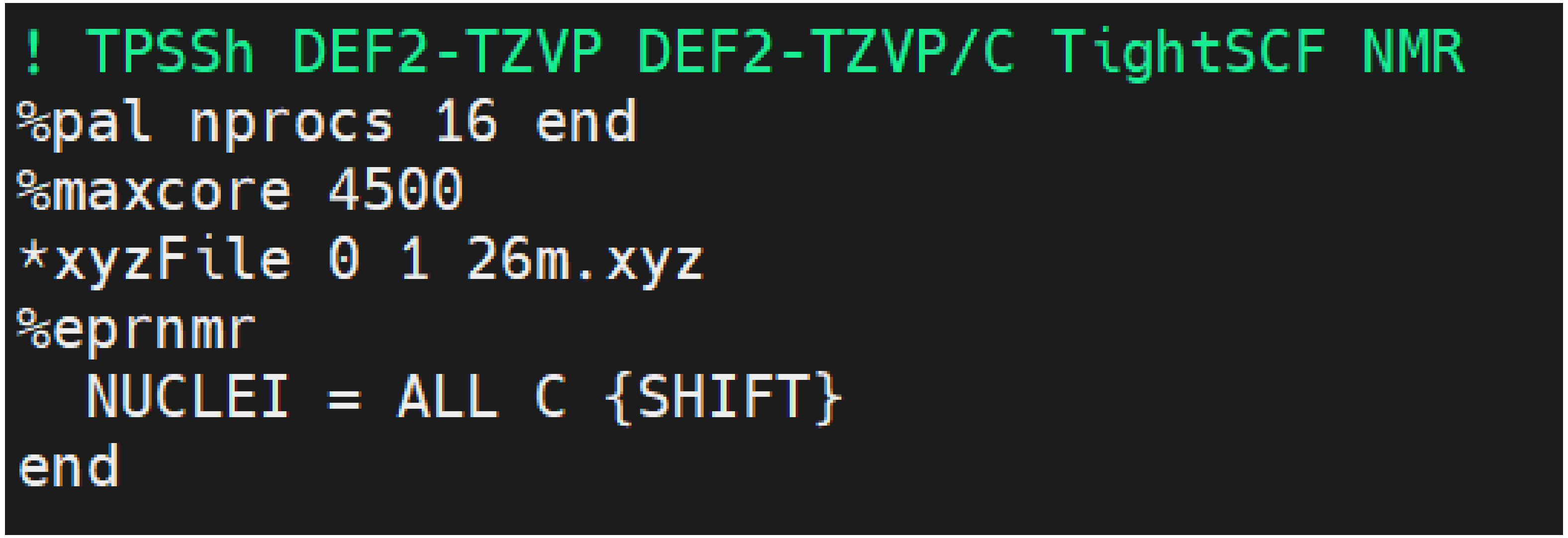




```
! TPSSh DEF2-TZVP DEF2-TZVP/C TightSCF NMR
%pal nprocs 16 end
%maxcore 4500
*xyzFile 0 1 26m.xyz
%eprnmr
  NUCLEI = ALL H {SHIFT}
end
```

Running a Shielding Calculation (C)





```
! TPSSh DEF2-TZVP DEF2-TZVP/C TightSCF NMR
%pal nprocs 16 end
%maxcore 4500
*xyzFile 0 1 26m.xyz
%eprnmr
  NUCLEI = ALL C {SHIFT}
end
```

NMR Theory

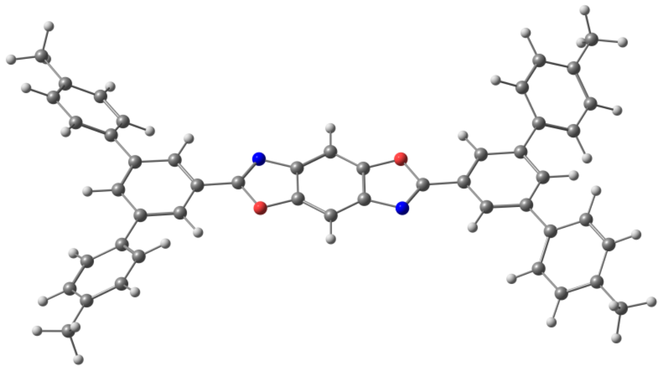
For the J-coupling, we have:

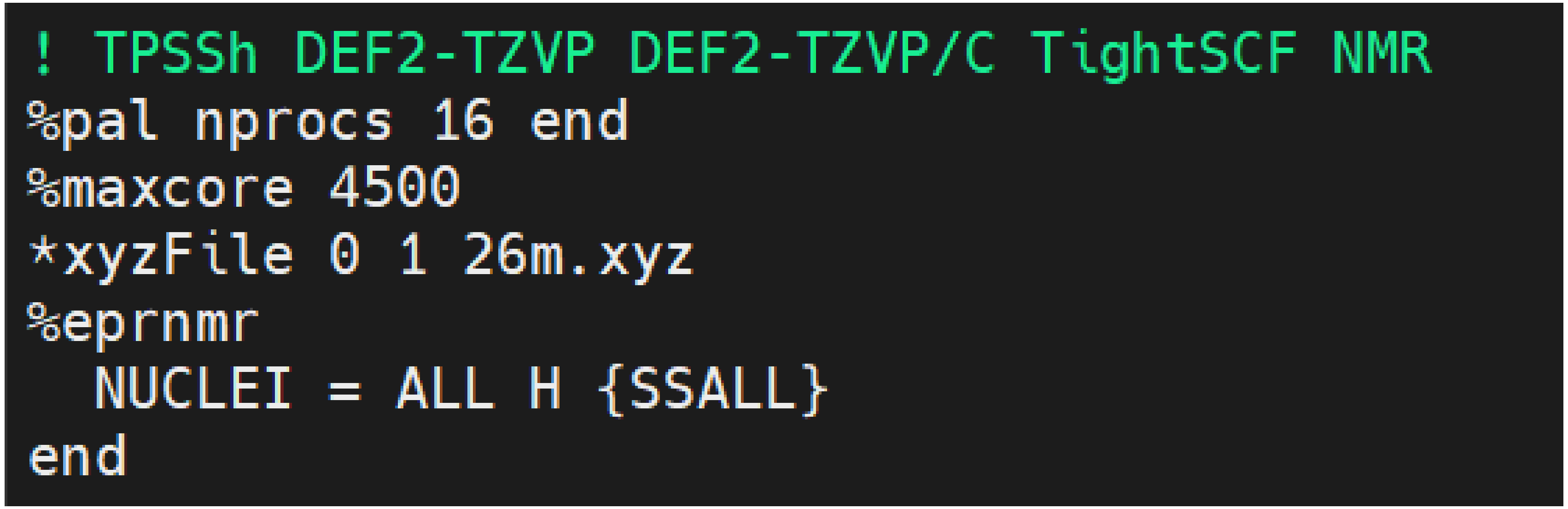
$$E = \boldsymbol{\mu}_A K_{AB} \boldsymbol{\mu}_B \qquad K_{AB} = \left.\frac{\partial^2 E}{\partial \boldsymbol{\mu}_B \partial \boldsymbol{\mu}_A}\right|_{\boldsymbol{B}=0,\boldsymbol{\mu}_A=0}$$

The operators that end up contributing are the orbital paramagnetic, Fermi contact, and spin dipole, and orbital diamagnetic:

$$E^{11} = \langle \psi^{01} | \widehat{H}^{10} | \psi^{0} \rangle + + \langle \psi^{0} | \widehat{H}^{10} | \psi^{01} \rangle$$

Running a Coupling Calculation (H)

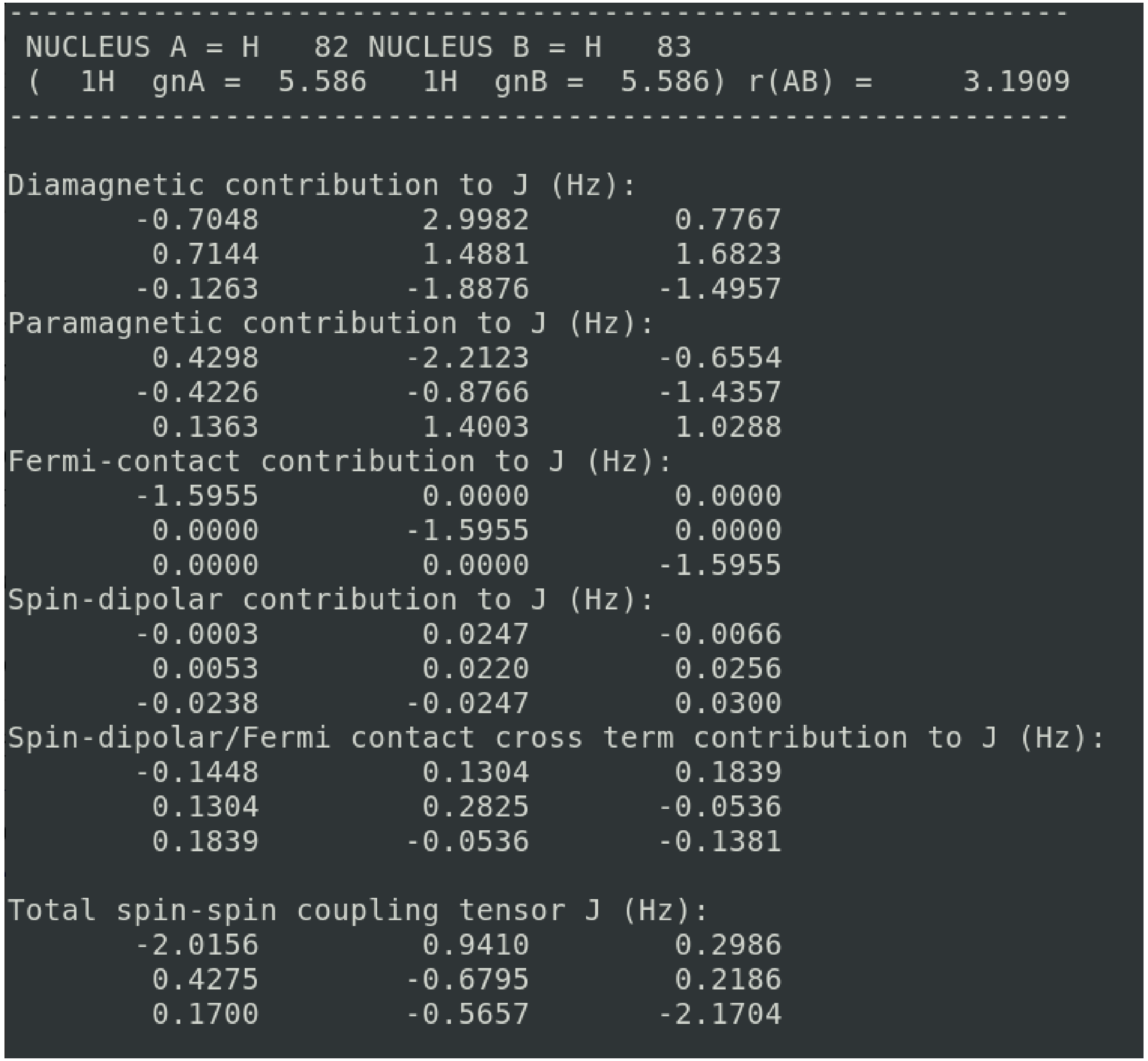




```
! TPSSh DEF2-TZVP DEF2-TZVP/C TightSCF NMR
%pal nprocs 16 end
%maxcore 4500
*xyzFile 0 1 26m.xyz
%eprnmr
  NUCLEI = ALL H {SSALL}
end
```

Looking at Results

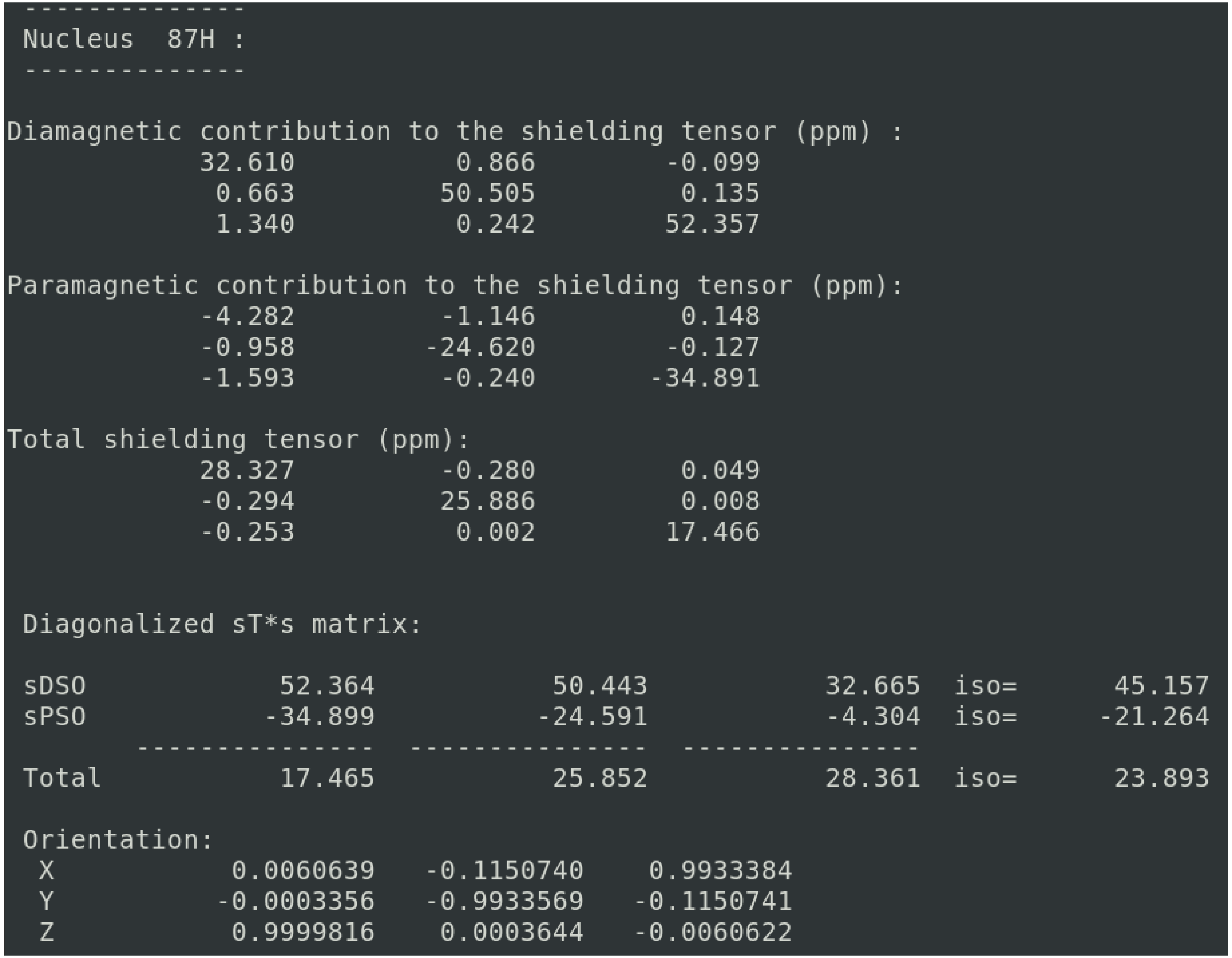
less +G nmr.out



```
-------------------------------------------------------------
 NUCLEUS A = H    82 NUCLEUS B = H    83
 (  1H  gnA =  5.586   1H  gnB =  5.586) r(AB) =     3.1909
-------------------------------------------------------------

Diamagnetic contribution to J (Hz):
       -0.7048          2.9982         0.7767
        0.7144          1.4881         1.6823
       -0.1263         -1.8876        -1.4957
Paramagnetic contribution to J (Hz):
        0.4298         -2.2123        -0.6554
       -0.4226         -0.8766        -1.4357
        0.1363          1.4003         1.0288
Fermi-contact contribution to J (Hz):
       -1.5955          0.0000         0.0000
        0.0000         -1.5955         0.0000
        0.0000          0.0000        -1.5955
Spin-dipolar contribution to J (Hz):
       -0.0003          0.0247        -0.0066
        0.0053          0.0220         0.0256
       -0.0238         -0.0247         0.0300
Spin-dipolar/Fermi contact cross term contribution to J (Hz):
       -0.1448          0.1304         0.1839
        0.1304          0.2825        -0.0536
        0.1839         -0.0536        -0.1381

Total spin-spin coupling tensor J (Hz):
       -2.0156          0.9410         0.2986
        0.4275         -0.6795         0.2186
        0.1700         -0.5657        -2.1704
```

Looking at Results

less +G nmr.out



```
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 Nucleus  87H :
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Diamagnetic contribution to the shielding tensor (ppm) :
            32.610          0.866         -0.099
             0.663         50.505          0.135
             1.340          0.242         52.357

Paramagnetic contribution to the shielding tensor (ppm):
            -4.282         -1.146          0.148
            -0.958        -24.620         -0.127
            -1.593         -0.240        -34.891

Total shielding tensor (ppm):
            28.327         -0.280          0.049
            -0.294         25.886          0.008
            -0.253          0.002         17.466


 Diagonalized sT*s matrix:

 sDSO            52.364           50.443           32.665  iso=      45.157
 sPSO           -34.899          -24.591           -4.304  iso=     -21.264
        ---------------  ---------------  ---------------
 Total           17.465           25.852           28.361  iso=      23.893

 Orientation:
  X           0.0060639   -0.1150740    0.9933384
  Y          -0.0003356   -0.9933569   -0.1150741
  Z           0.9999816    0.0003644   -0.0060622
```

Recommendations for NMR Calculations

These are my personal functional recommendations:

- PBE0 has long been recommended for NMR.
- Many groups also like the TPSSh functional.
- If you have the resources:
  - DSD-PBEP86 with the pcSseg-2 basis set