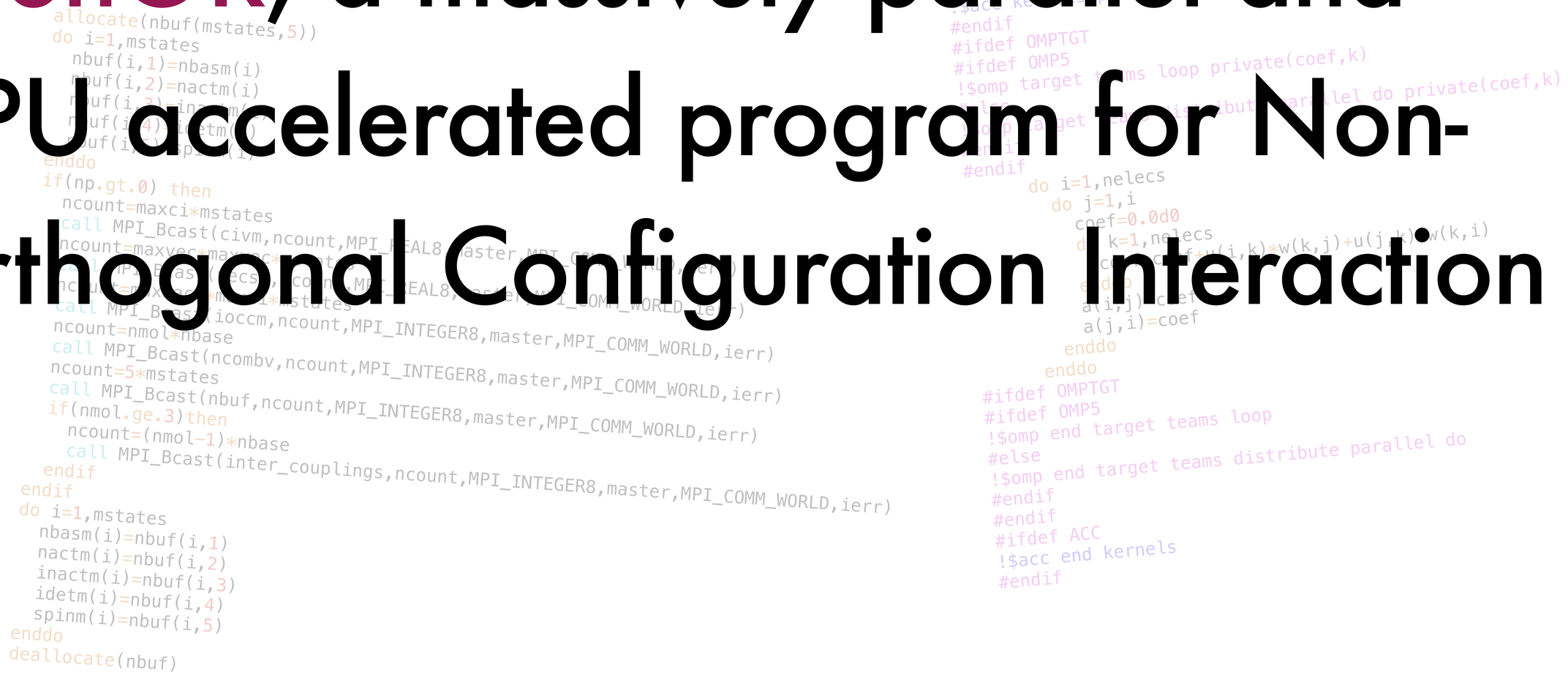
Universitat Rovira i Virgili

ICREA

# GronOR, a massively parallel and GPU accelerated program for Non-Orthogonal Configuration Interaction




Coen de Graaf

ADAC Paris, September 2023

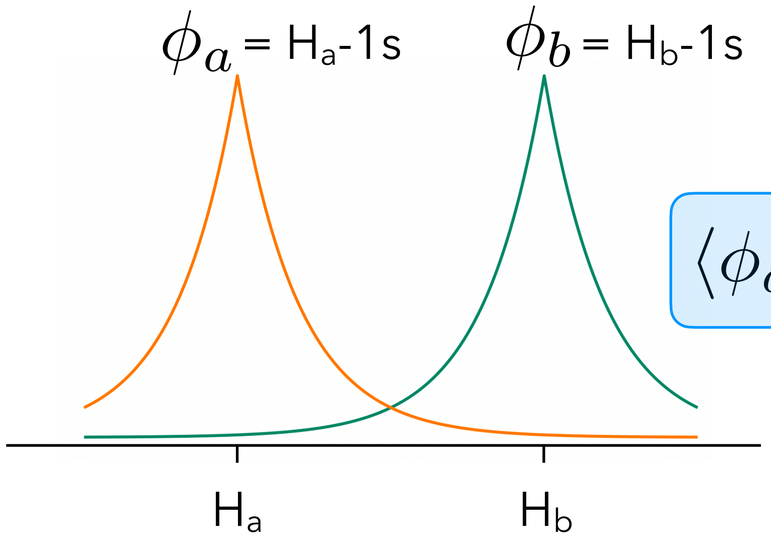
# Electronic structure calculations

*Heitler*

*London*

1927 – Quantum mechanical description of the chemical bond in $H_2$

$$\Psi = (\phi_a\phi_b + \phi_b\phi_a)(\alpha\beta - \beta\alpha)$$




$$\langle\phi_a|\phi_b\rangle = S_{ab} \neq 0$$

Evolved into **Valence Bond Theory**

- non-orthogonal atomic-like or bond-like orbitals
- stays close to the Lewis structures
- computationally elaborated

# Electronic structure calculations

*Hund*

*Mulliken*

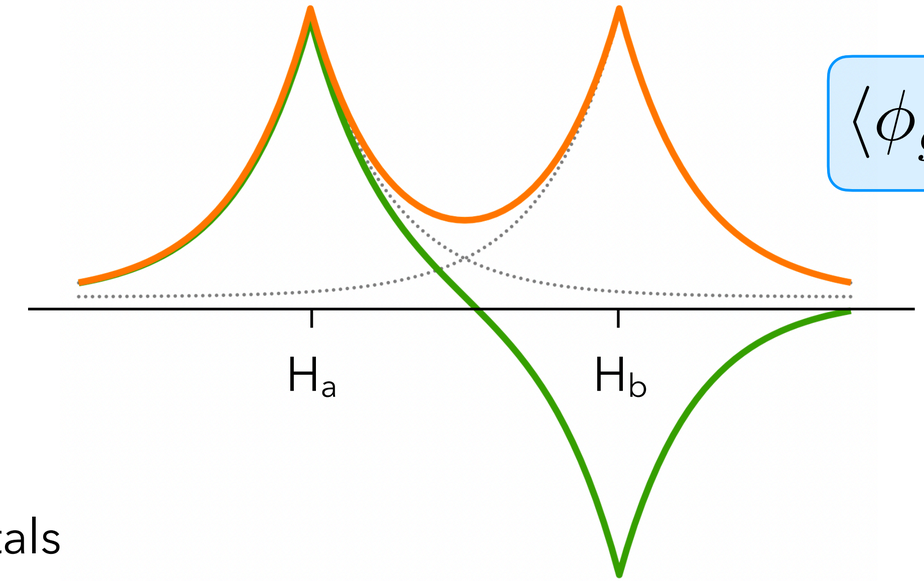
1928 – Foundations of **M**olecular **O**rbital theory

$$\Psi = c_1|\phi_g\overline{\phi}_g| + c_2|\phi_u\overline{\phi}_u|$$

$$= c_1\phi_g\phi_g(\alpha\beta - \beta\alpha) + c_2\phi_u\phi_u(\alpha\beta - \beta\alpha)$$

$$\phi_g = \phi_a + \phi_b$$

$$\langle\phi_g|\phi_u\rangle = 0$$




$$\phi_u = \phi_a - \phi_b$$

**MO Theory**

- orthogonal delocalized orbitals
- less intuitive
- computationally advantageous

**Electronic structure calculations: N**on-**O**rthogonal **C**onfiguration **I**nteraction

**NOCI-F:**

1. Full orbital relaxation
2. Static and dynamic electron correlation
3. Short wave functions : intuitive interpretation

*but*

4. Computationally demanding

**N**on-**O**rthogonal **C**onfiguration **I**nteraction with **F**ragments

**NOCI-F:** step by step

1 - Calculations on Fragment A and B

Multiconfigurational wave functions

A: **$S_0$, $T_1$, $S_1$, $D^+$, $D^-$, ...**

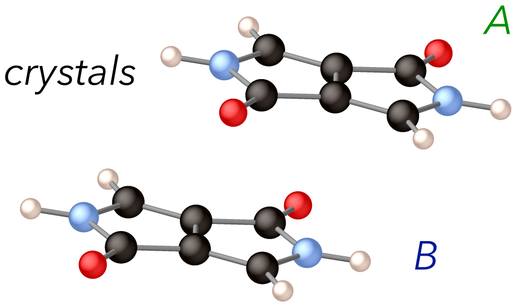
B: **$S_0$, $T_1$, $S_1$, $D^+$, $D^-$, ...**

***Orbital relaxation*** and ***Static correlation***

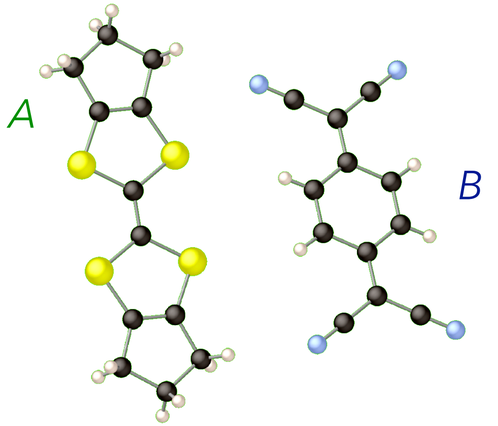
$$\Psi_{S_0} = c_0\Phi_0 + c_1\Phi_1 + c_2\Phi_2 + \dots$$

*linear combination of Slater determinants*

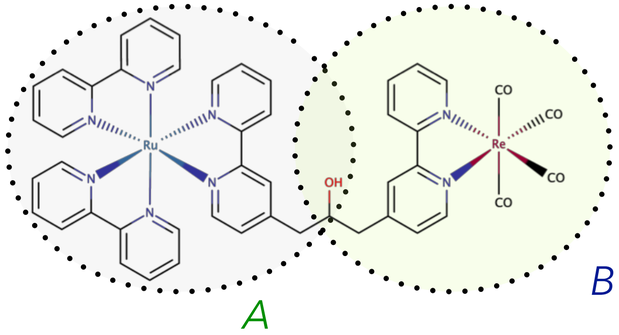
*Organic crystals*




*Charge transfer salts*




*Donor-Acceptor complexes*



# **N**on-**O**rthogonal **C**onfiguration **I**nteraction with **F**ragments

**NOCI-F:** step by step

1 - Calculations on Fragment A and B

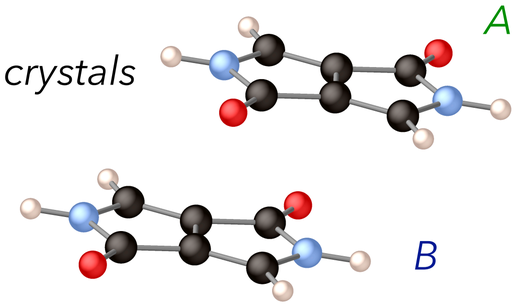
2 - Construction of multi-electron basis functions: **MEBF**s

Fragment A: $S_0$ $S_1$ $T_1$ $D^+$ $D^-$

Fragment B: $S_0$ $S_1$ $T_1$ $D^+$ $D^-$

MEBF for A – B: $S_0S_0$

*Organic crystals*

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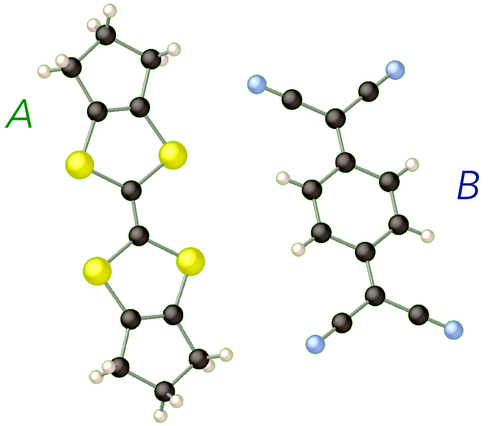


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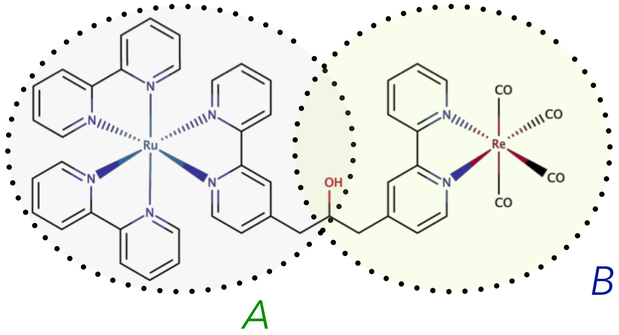

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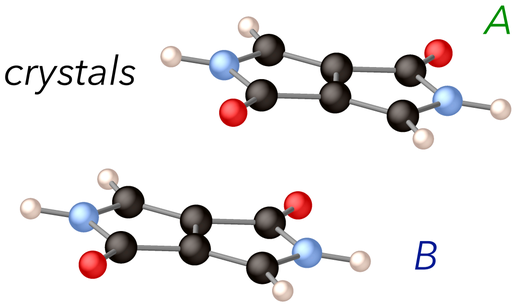


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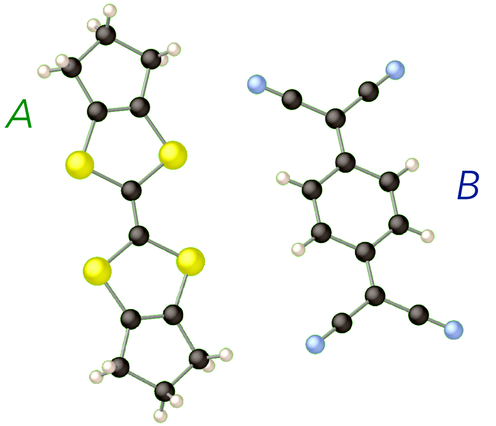


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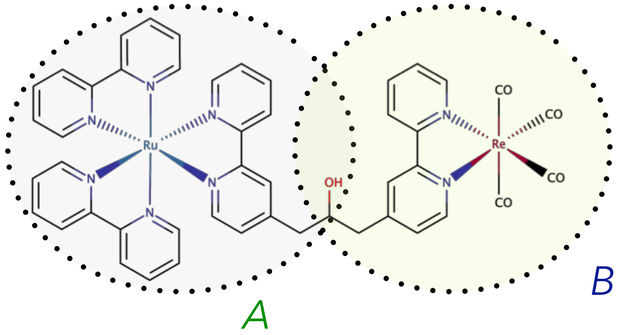

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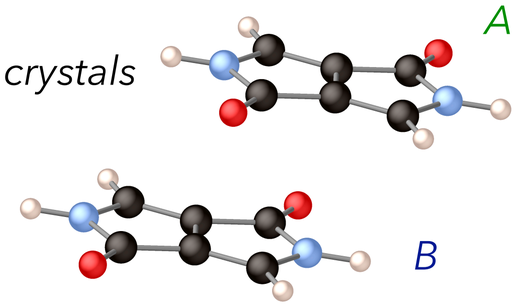


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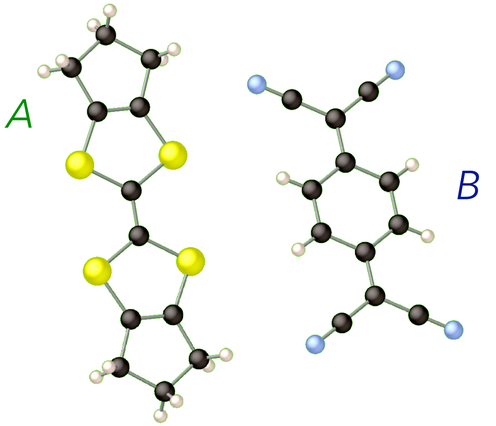


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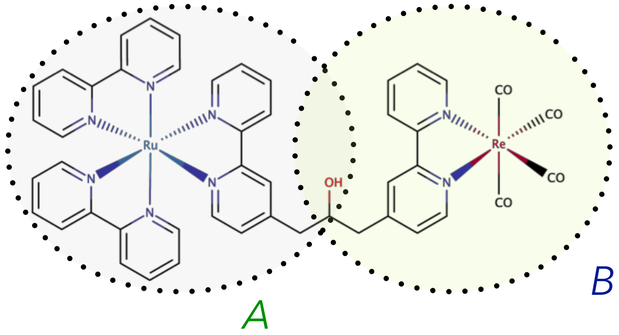

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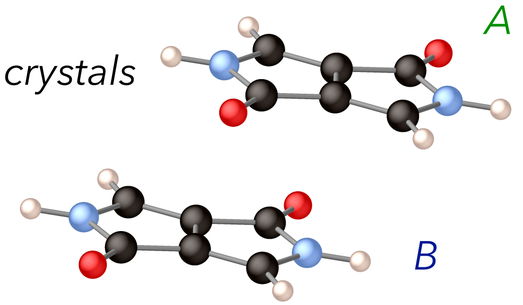


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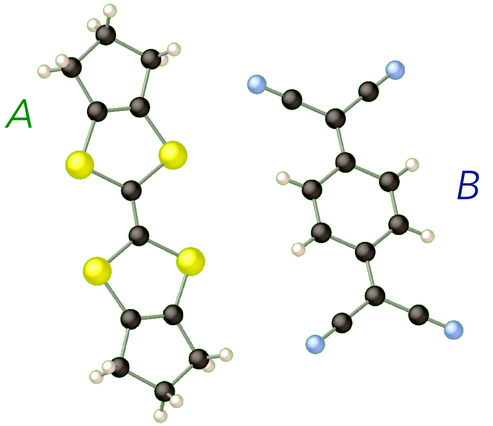


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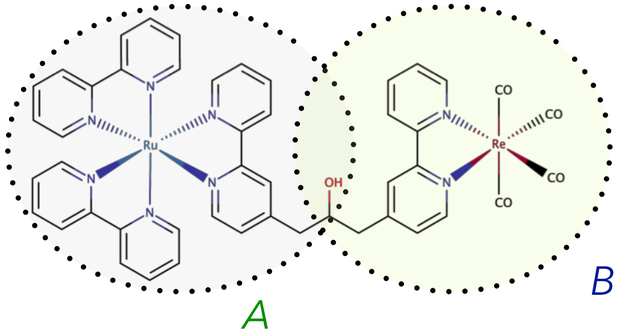

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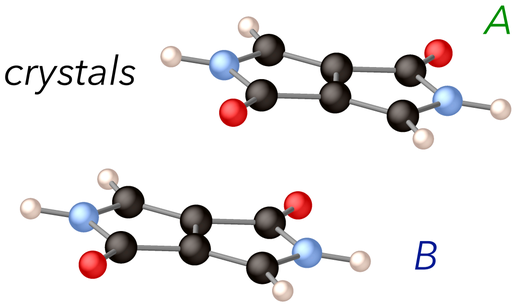
MEBF for A – B: $S_0S_0$ $S_0S_1$ $S_1S_0$ $T_1T_1$ $D^+D^-$ $D^-D^+$

***Diabatic*** states with full ***orbital relaxation***, but non-orthogonal

*Organic crystals*

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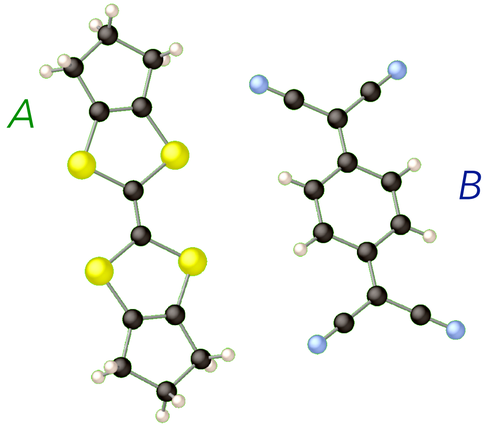
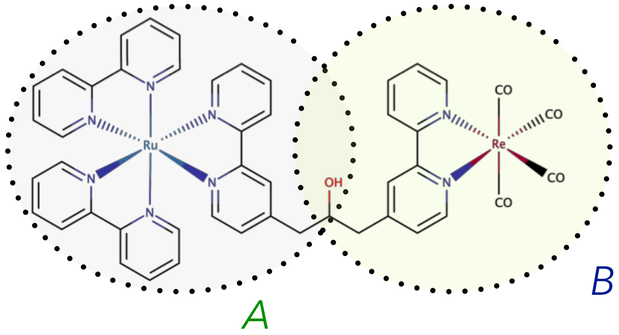



*Donor-Acceptor complexes*



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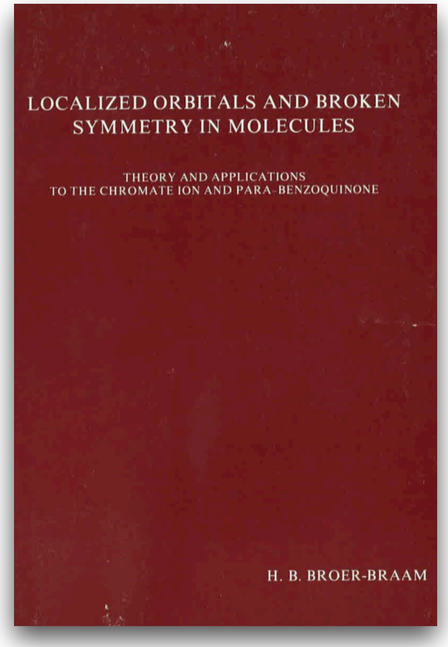



**NOCI-F:** step by step

1 - Calculations on Fragment A and B

2 - Construction of multi-electron basis functions: MEBFs

3 - Calculation of the non-orthogonal matrix elements

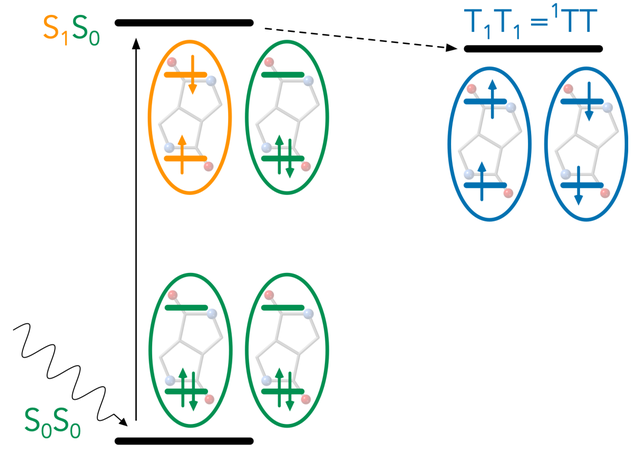
$\langle S_0 S_0|\hat{H}|S_0 S_0\rangle$ $\langle S_1 S_0|\hat{H}|T_1 T_1\rangle$ $\langle S_0 S_1|\hat{H}|D^+ D^-\rangle$ . . . and $\langle S_0 S_0|S_0 S_1\rangle$ $\langle D^+ D^-|D^- D^+\rangle$ . . .

**G**eneral **N**on-**O**rthogonal **M**atrix **E**lements (GNOME) algorithm

Ria Broer, PhD thesis, University of Groningen, 1981
R. Broer, W. C. Nieuwpoort, Chem. Phys. 54, 291-303 (1981)
R. Broer, W. C. Nieuwpoort, Theor. Chim. Acta 73, 405-418 (1988)

- ***Singular value decomposition***
- ***Symmetric eigenvalue problem***
- ***Processing a long list of integrals***

# **N**on-**O**rthogonal **C**onfiguration **I**nteraction with **F**ragments




**NOCI-F:** step by step

1 - Calculations on Fragment A and B

2 - Construction of multi-electron basis functions: MEBFs

3 - Calculation of the non-orthogonal matrix elements

$$\gamma_{\rho\sigma} = \frac{H_{\rho\sigma} - \frac{1}{2}(H_{\sigma\sigma} + H_{\rho\rho})S_{\rho\sigma}}{1 - S_{\rho\sigma}^2}$$

4 - Extract information from the NOCI matrix

- Electronic couplings
- NOCI wave functions

$\rho =$ $S_1S_0$ $\sigma =$ $T_1T_1$

$$\Psi_i = c_{i,\kappa}|S_0S_0\rangle + c_{i,\lambda}|S_1S_0\rangle + c_{i,\mu}|S_0S_1\rangle + c_{i,\nu}|T_1T_1\rangle + c_{i,\rho}|D^-D^+\rangle + c_{i,\sigma}|D^+D^-\rangle$$

*Compact expansion in diabatic states ; Intuitive interpretation*

# **N**on-**O**rthogonal **C**onfiguration **I**nteraction with **F**ragments

gitlab.com/gronor/gronor
www.gronor.org

## **NOCI-F:** step by step

1 - Calculations on Fragment A and B

2 - Construction of multi-electron basis functions: MEBFs

3 - Calculation of the non-orthogonal matrix elements

4 - Extract information from the NOCI matrix

Implemented in **GronOR**

- Massively parallel
- GPU-Accelerated
- Open source
- Under constant development
- latest release: **GronOR 23.07**
- Interfaced to OpenMolcas

T. P. Straatsma, R. Broer, A. Sánchez-Mansilla, C. Sousa, and C. de Graaf, *GronOR: Scalable and Accelerated Nonorthogonal Configuration Interaction for Molecular Fragment Wave Functions*, ***J. Chem. Theory Comput. 18, 3549–3565 (2022)***, *doi:10.1021/acs.jctc.2c00266*

NOCI-F in **GronOR**

$$\langle S_0 S_0 | \hat{H} | S_0 S_1 \rangle$$

Small CAS: ~20 determinants

NOCI-F in **GronOR**

Spin-adapted MEBF: 20 x 20 = 400 dets

$$\langle S_0 S_0 | \hat{H} | S_0 S_1 \rangle$$

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NOCI-F in **GronOR**

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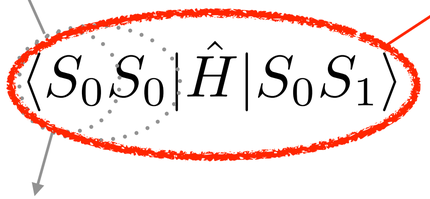



400 x 400 contributions to the matrix element

Small CAS: ~20 determinants

160.000 SVD, eigensolvers,

and integral processing

*Lot of work, but fully parallelised*

## GronOR

- Open source
- Fortran 90
- OpenMPI
- OpenACC, OpenMP

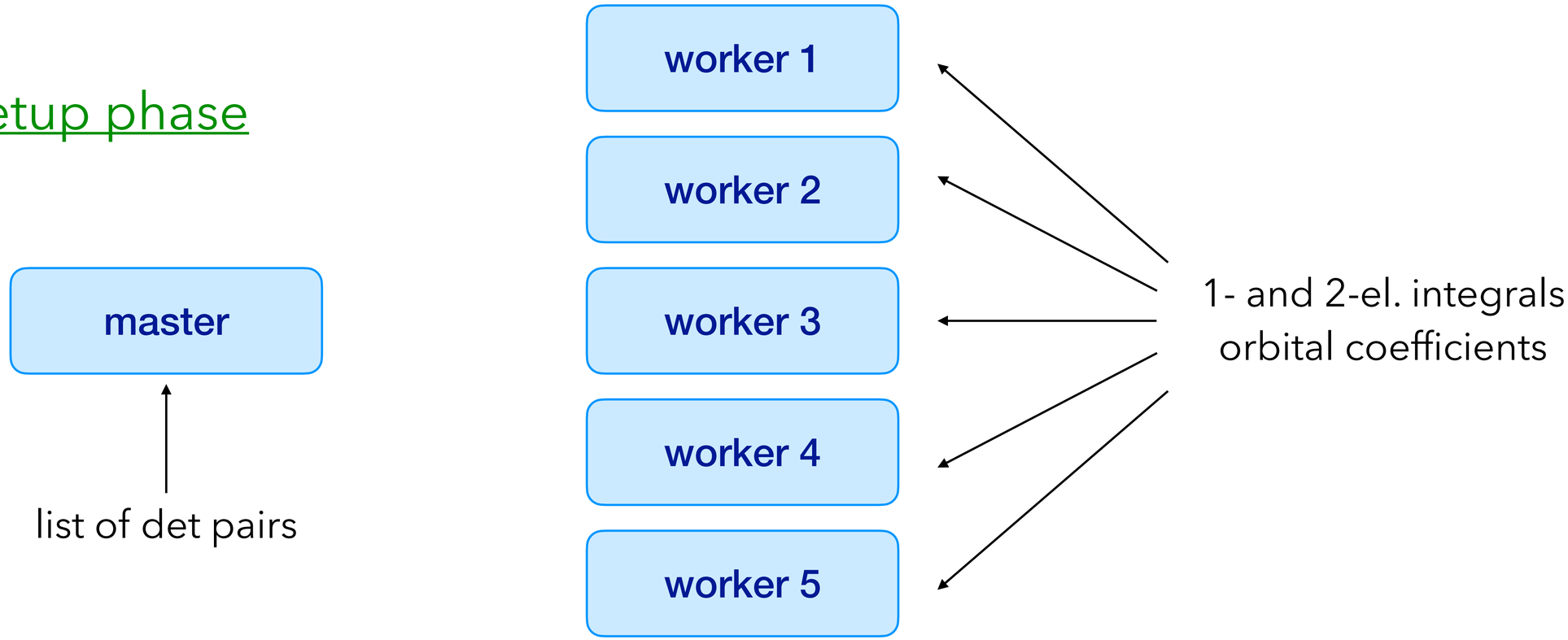
NOCI-F in **GronOR**

400 x 400 contributions to the matrix element

$\langle S_0 S_0 | \hat{H} | S_0 S_1 \rangle$

160.000 SVD and factorised co-factors

Setup phase



NOCI-F in **GronOR**

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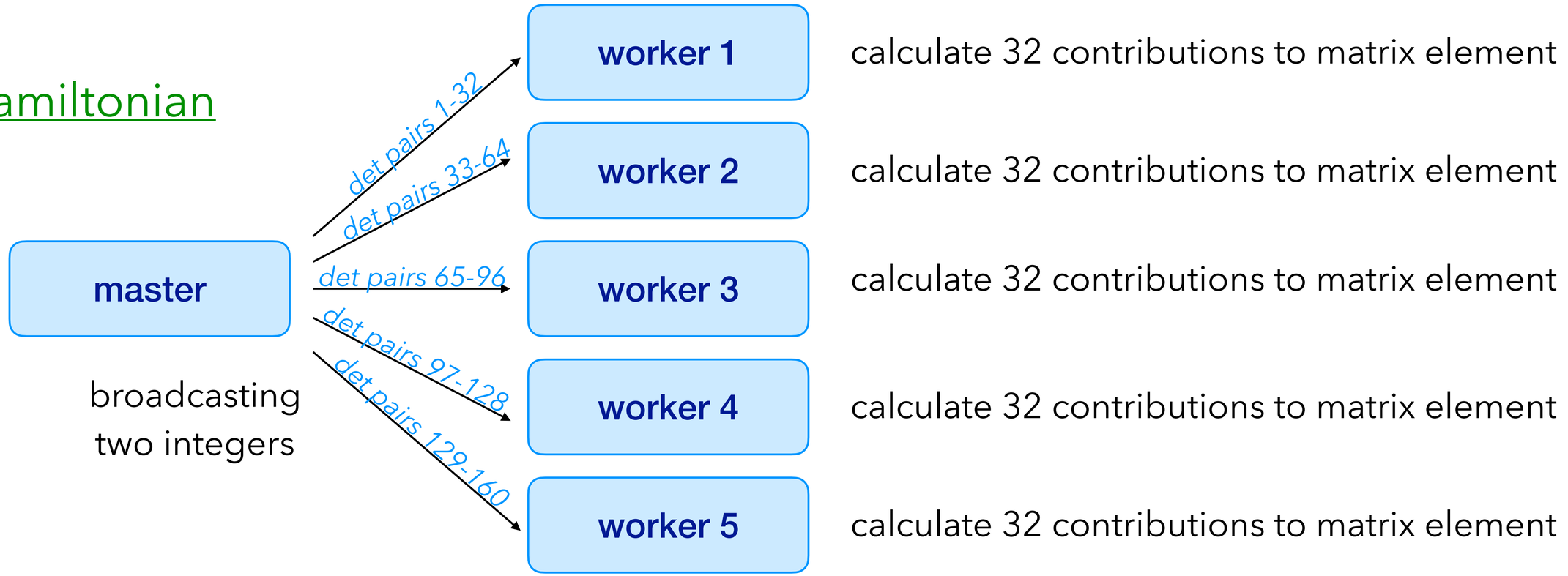
Hamiltonian



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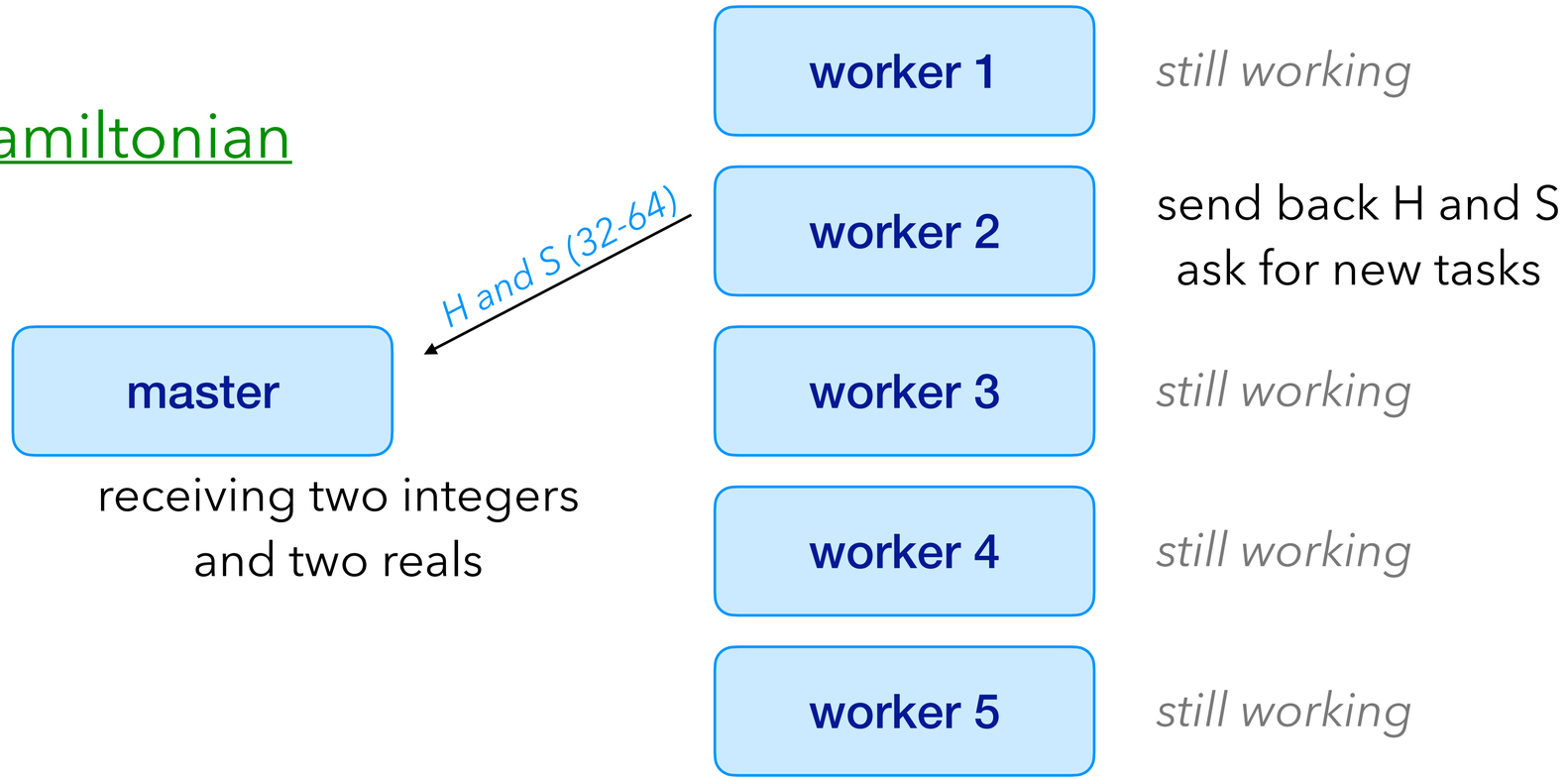


NOCI-F in **GronOR**

400 x 400 contributions to the matrix element

$\langle S_0 S_0 | \hat{H} | S_0 S_1 \rangle$

160.000 SVD and factorised co-factors

Hamiltonian

**master**

broadcasting
two integers

det pairs 161-192

| | |
|---|---|
| **worker 1** | *still working* |
| **worker 2** | calculate next 32 contributions to matrix element |
| **worker 3** | *still working* |
| **worker 4** | *still working* |
| **worker 5** | *still working* |

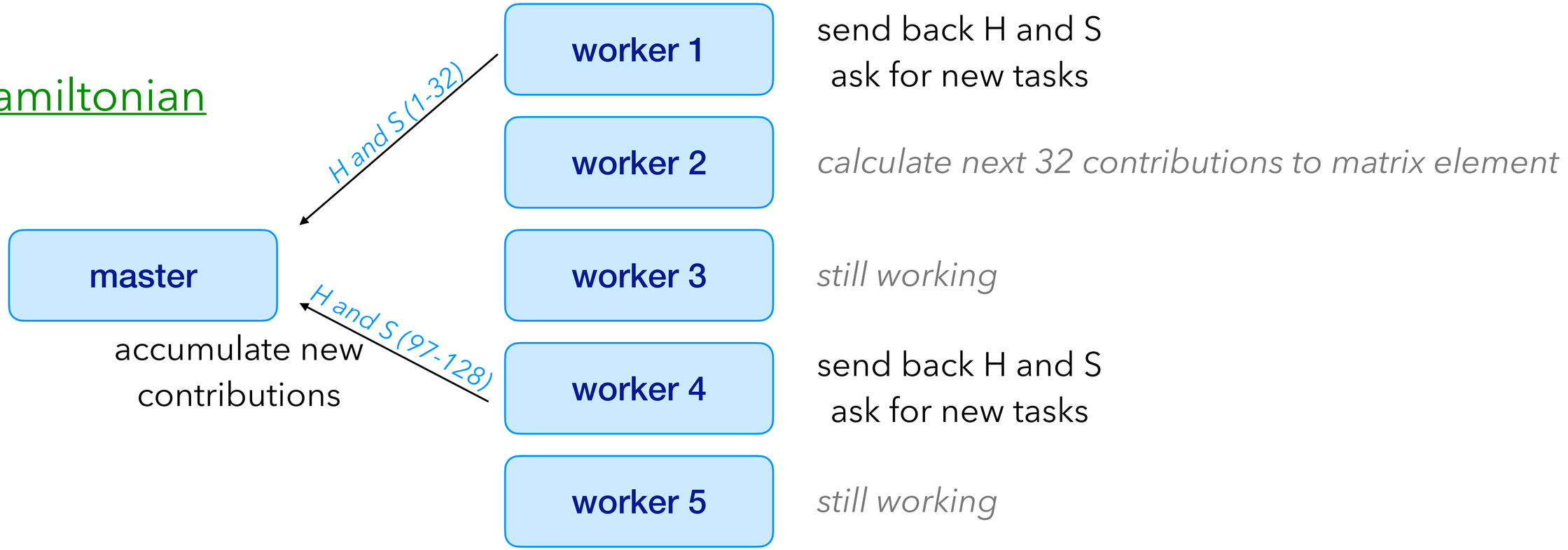
NOCI-F in **GronOR**

400 x 400 contributions to the matrix element

$\langle S_0 S_0 | \hat{H} | S_0 S_1 \rangle$

160.000 SVD and factorised co-factors

Hamiltonian



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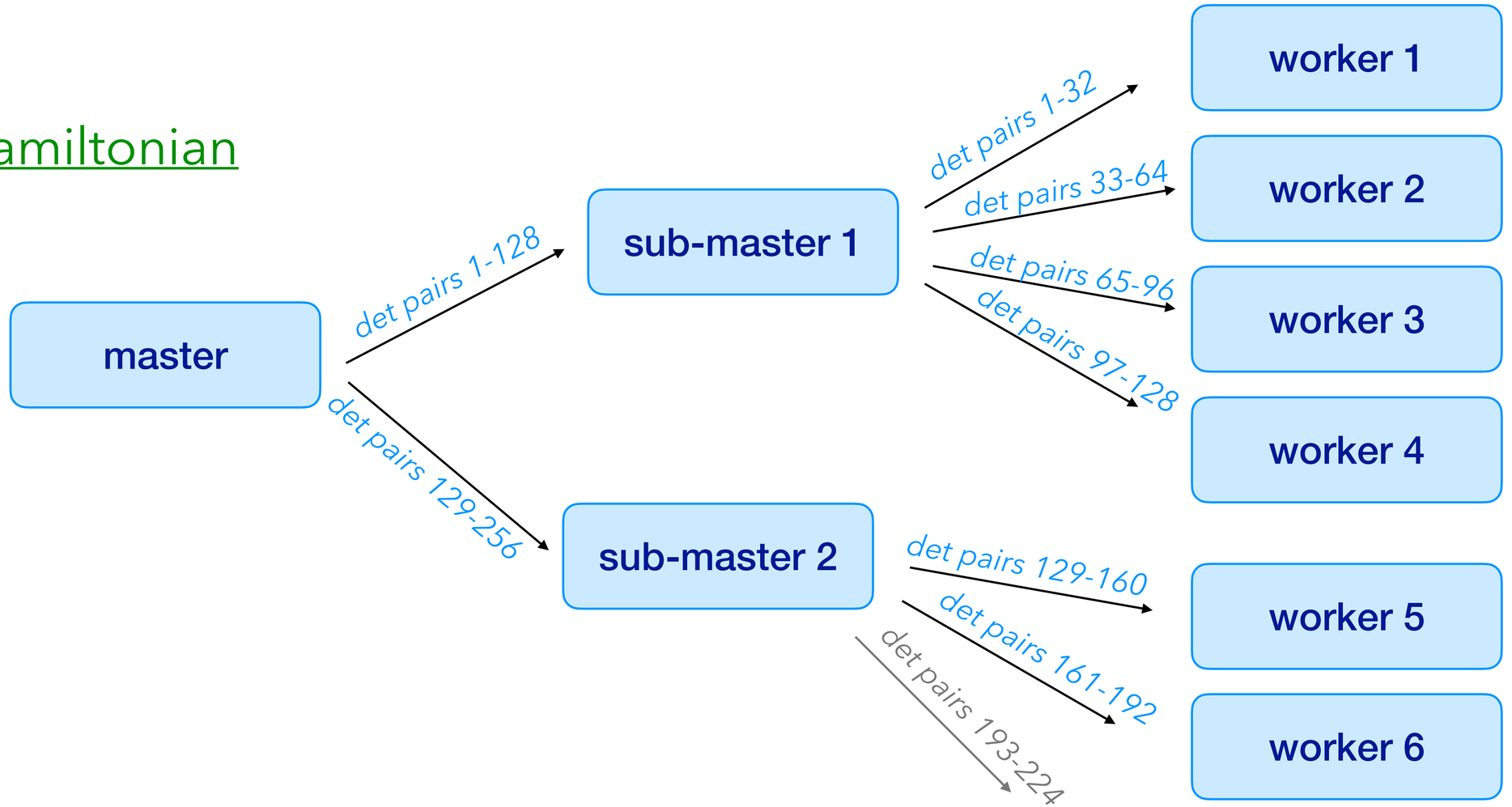


## Eigensolver / SVD

- CPU eispack, mkl
- Nvidia-GPU cusolver, cusolverj
- AMD-GPU hipsolver, rocsolver

```
interface
  integer(c_int) function cusolverDnDgesvdj(cusolver_Hndl,jobz,econ,m,n,a,lda,s,u,ldu,v,ldv, &
      work,lwork,devinfo,info ) bind(C,name='cusolverDnDgesvdj')
    use iso_c_binding
    import cusolverDnHandle
    import gesvdjInfo
    type(cusolverDnHandle), value :: cusolver_Hndl
    integer(c_int), value   :: jobz
    integer(c_int), value   :: econ,m,n,lda,ldu,ldv
    real(c_double), device  :: a(:,:),s(:),u(:,:),v(:,:),work(:)
    integer(c_int)          :: lwork
    integer(c_int)          :: devinfo
    type(gesvdjInfo)        :: info
  end function cusolverDnDgesvdj
end interface
```

NOCI-F in **GronOR**

## Eigensolver / SVD

- CPU eispack, mkl
- Nvidia-GPU cusolver, cusolverj
- AMD-GPU hipsolver, rocsolver

```
  ! ======== CUSOLVERJ =========

#ifdef CUSOLVERJ
  if(isolver.eq.SOLVER_CUSOLVERJ) then
    ndim=nelecs
    mdim=mbasel
    jobz=CUSOLVER_EIG_MODE_VECTOR
#ifdef ACC
!$acc data copy(dev_info_d,gesvdj_params) create(workspace_d)
!$acc host_data use_device(a,ev,u,w,dev_info_d,workspace_d)
#endif
#ifdef OMPTGT
!$omp target data use_device_addr(a,ev,u,w,dev_info_d,workspace_d,rwork)
#endif
    cusolver_status=cusolverDnDgesvdj(cusolver_handle,jobz,econ, &
                ndim,ndim,a,ndim,ev,u,ndim,w,ndim,workspace_d,    &
                lwork1,dev_info_d,gesvdj_params)
#ifdef ACC
!$acc end host_data
!$acc end data
#endif
#ifdef OMPTGT
!$omp end target data
#endif
    cusolver_status=cudaDeviceSynchronize()
    if(cusolver_status /= CUSOLVER_STATUS_SUCCESS) &
        write(*,*) 'cusolverDnDgesvdj failed',cusolver_status
    cusolver_status = cusolverDnXgesvdjGetSweeps &
        (cusolver_handle, gesvdj_params, exec_sweeps)
    cusolver_status = cusolverDnXgesvdjGetResidual &
        (cusolver_handle, gesvdj_params, residual)
  endif
#endif
```

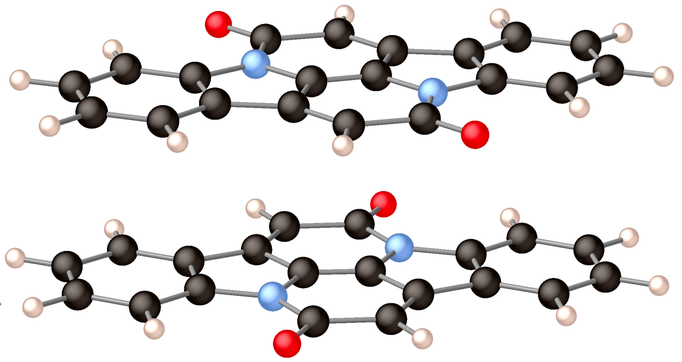
NOCI-F in **GronOR**

## Processing of the two-electron integrals

- openACC, openMP

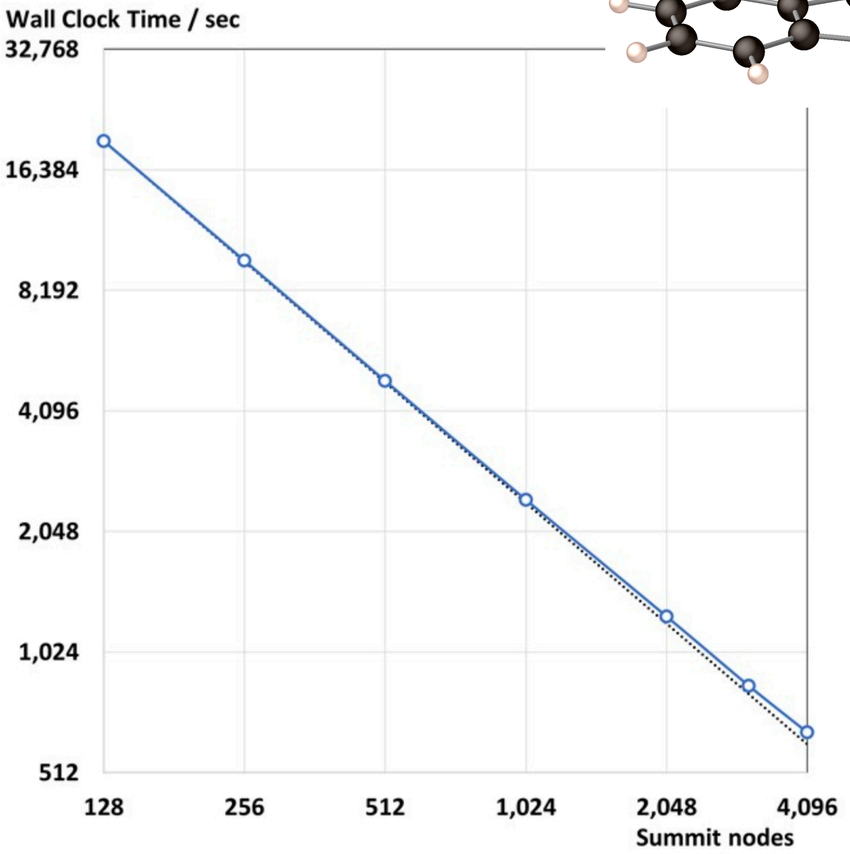
```
#ifdef ACC
!$acc kernels present(aat,aaa,tt,ta,sm,g,lab,ndx) copyin(kl,intndx,jntndx)
#endif
#ifdef OMPTGT
!$omp taskwait
#ifdef OMP5
!$omp target teams loop reduction(+:tst)
#else
!$omp target teams distribute parallel do reduction(+:tst)
#endif
#endif
    do ii=intndx,jntndx
      do jj=ii,kl
        intg=ndx(ii)+jj
        i=lab(1,ii)
        k=lab(2,ii)
        l=lab(1,jj)
        n=lab(2,jj)
        tst=tst+g(intg)*(sm(i,k)*sm(l,n) -aaa(i,n)*aaa(l,k)-ta(i,n)*ta(l,k) &
            -aat(i,n)*aat(l,k)-tt(i,n)*tt(l,k)-aat(l,i)*aaa(n,k)-tt(l,i)*ta(n,k) &
            -aaa(l,i)*aat(n,k)-ta(l,i)*tt(n,k))
      enddo
    enddo
#ifdef OMPTGT
#ifdef OMP5
!$omp end target teams loop
#else
!$omp end target teams distribute parallel do
#endif
#endif
#ifdef ACC
!$acc end kernels
#endif
```

NOCI-F in **GronOR**

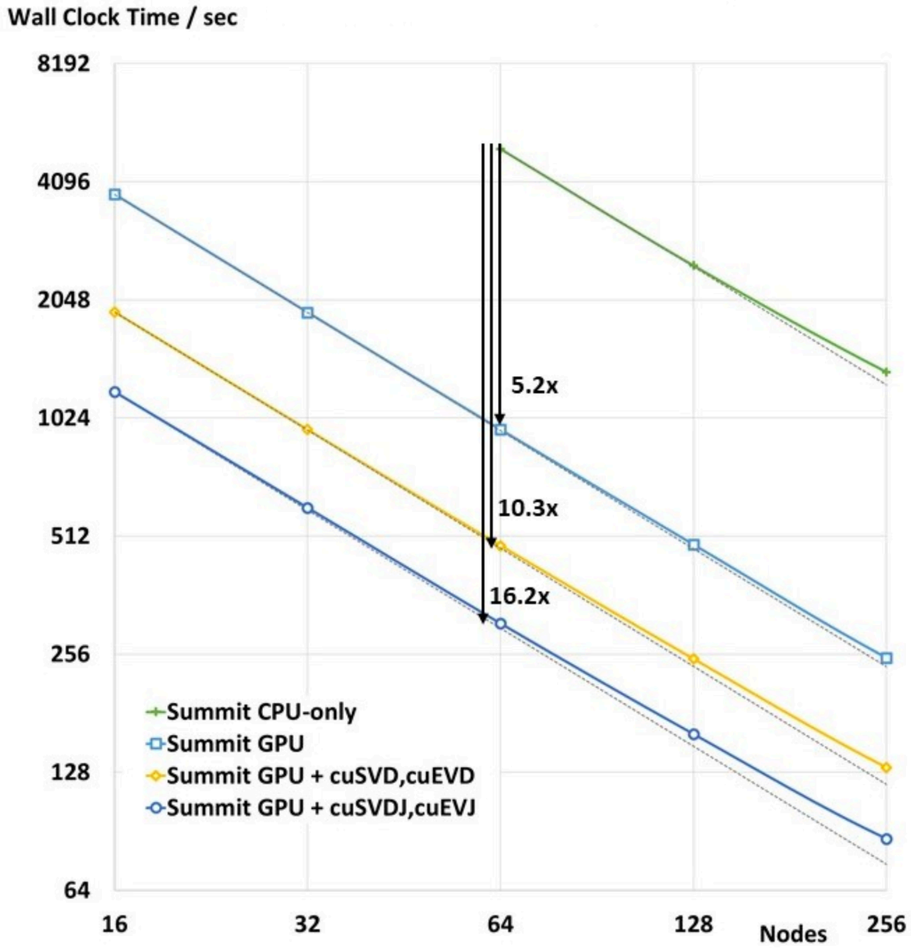


*indolonaphtheridine*

## Scaling on Summit




GPU acceleration





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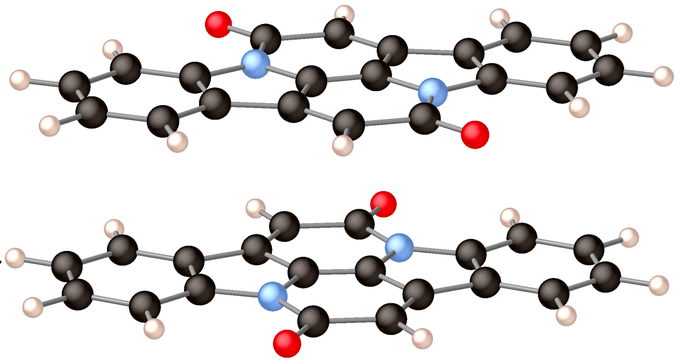
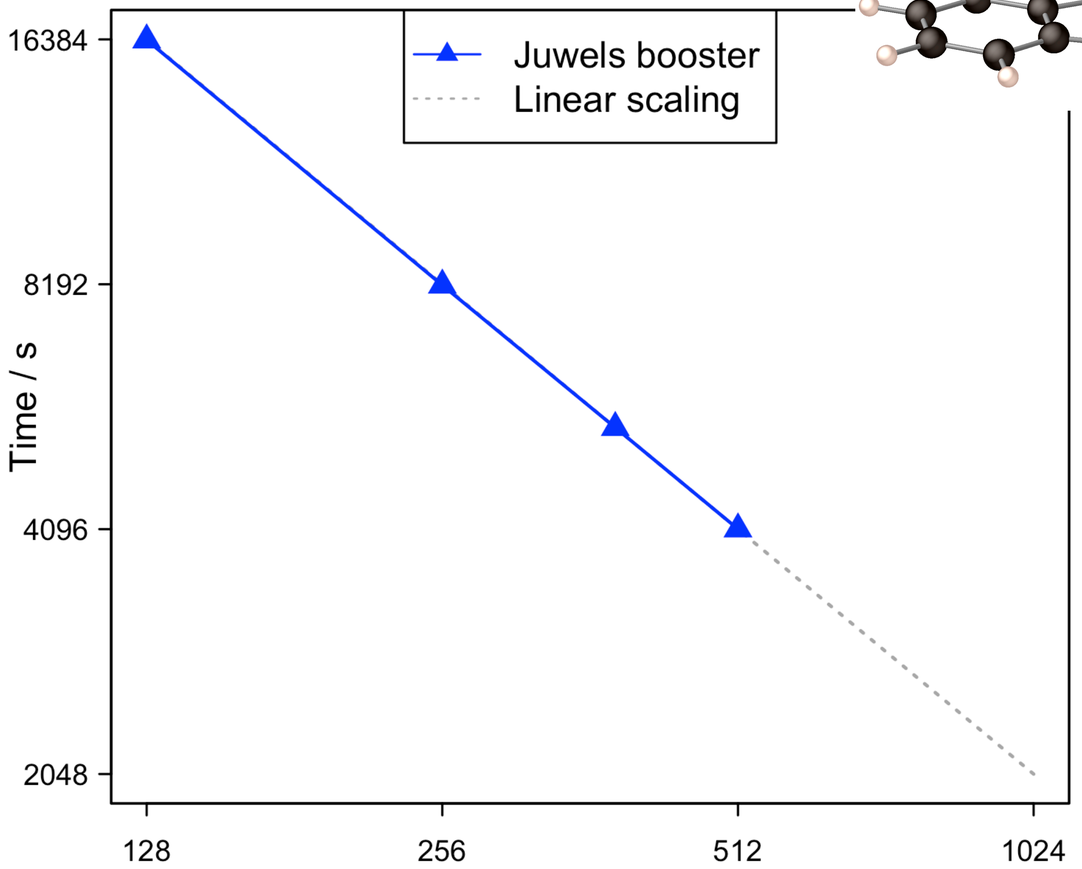
NOCI-F in **GronOR**



*indolonaphtheridine*

## Scaling on Juwels-Booster

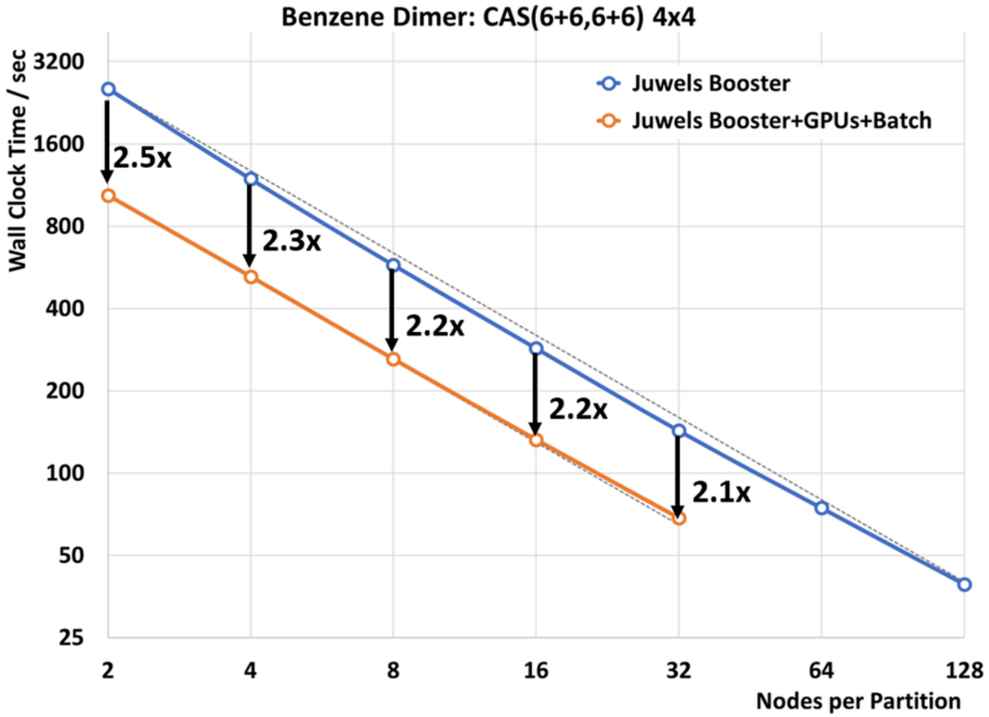




JÜLICH Forschungszentrum

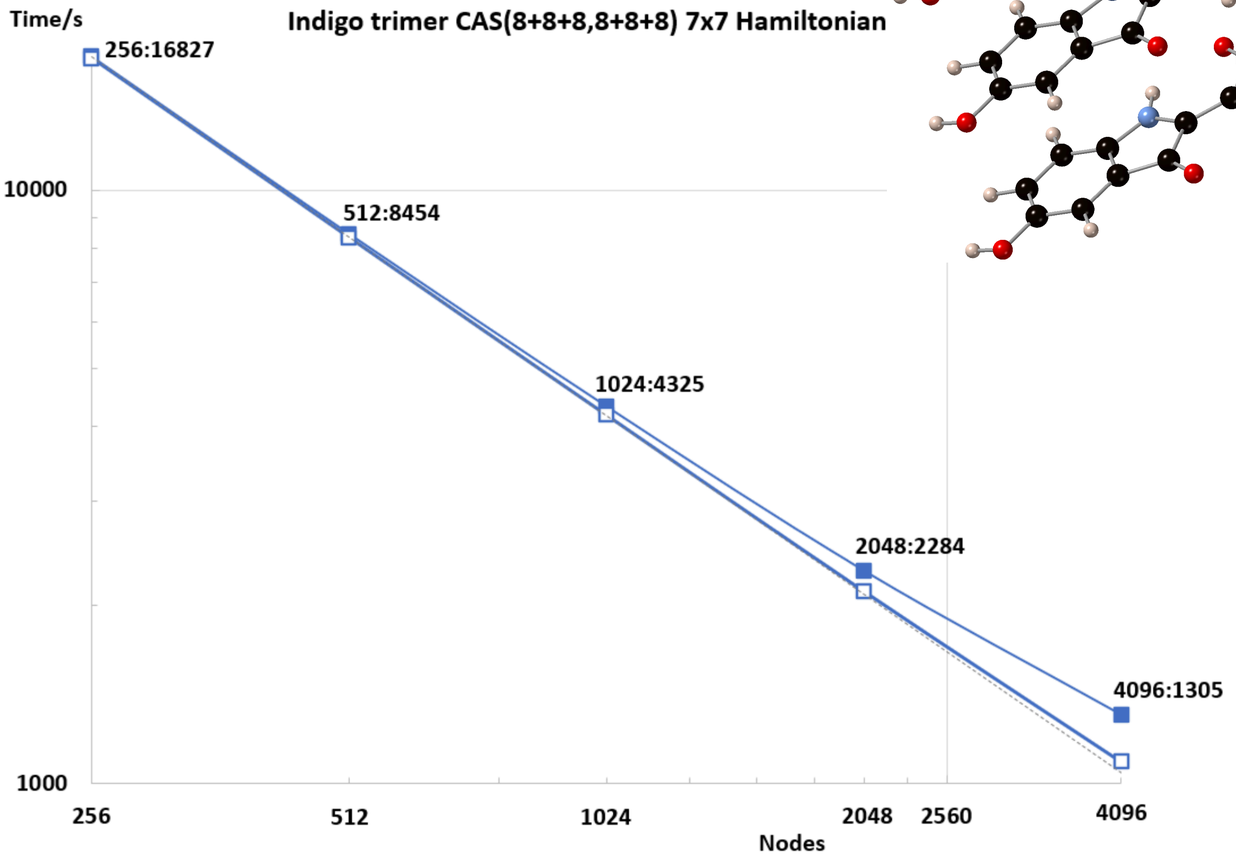
Heterogeneous cluster

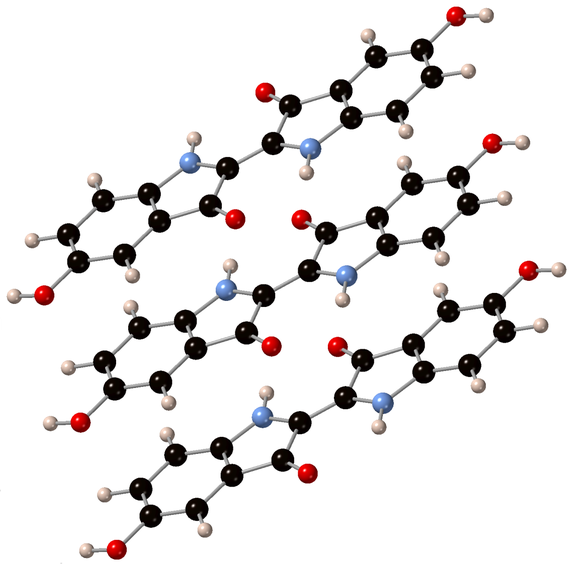
A100 + V100 + CPUs



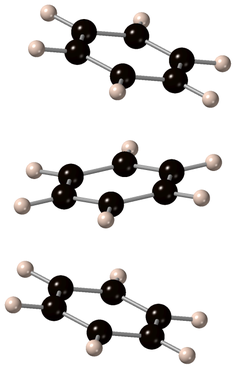
NOCI-F in **GronOR**

# Scaling on Frontier



benzene trimer



GPU acceleration

| | | |
|---|---|---|
| **Nodes** | 512 | 512 |
| **Ranks** | 4096 | 8196 |
| **CPU** | 3089 | 1740 |
| **GPU** | 163 | 86 |
| **speed-up** | **19.0** | **20.2** |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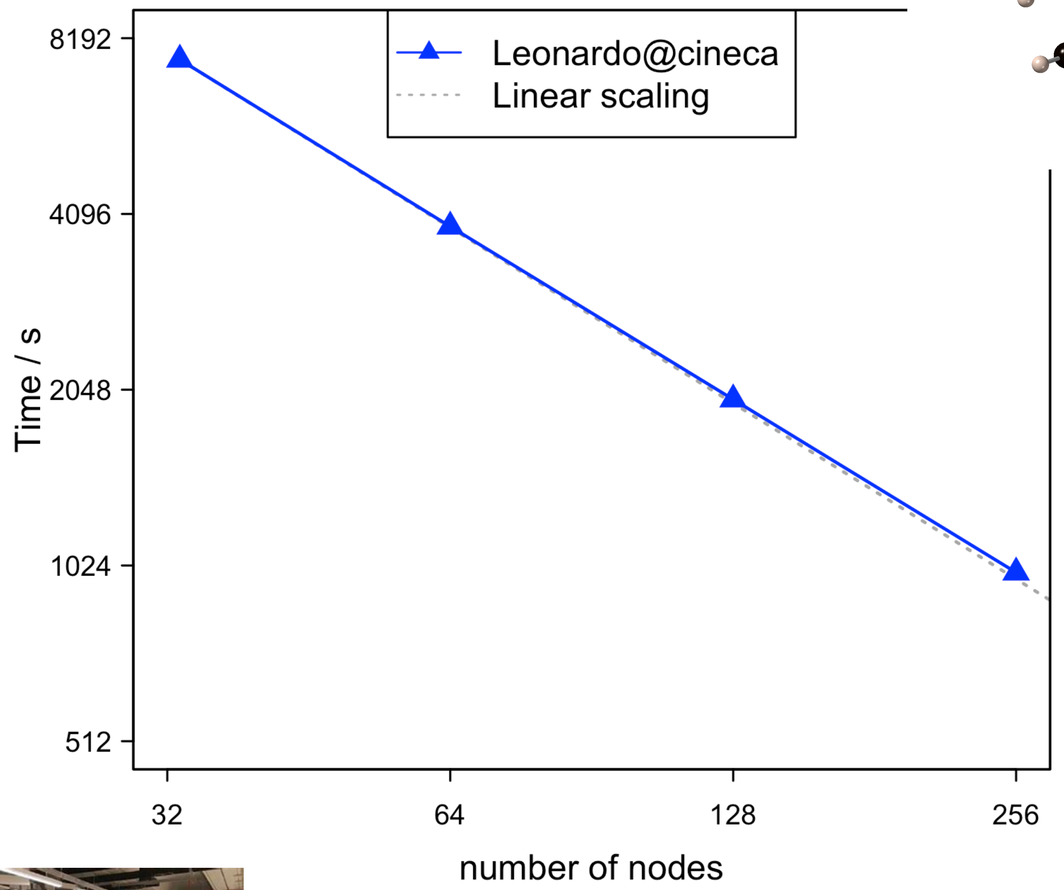
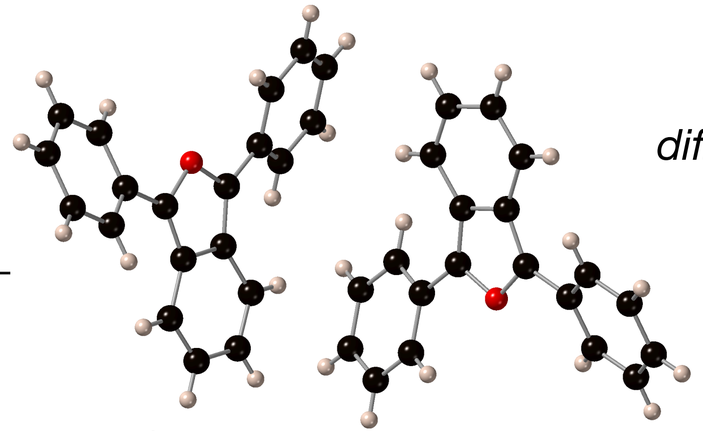
NOCI-F in **GronOR**

## Scaling on Leonardo



*difluorobenzofuran*


CINECA

*(preliminary results)*

# Current GronOR Team

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