Tracking excited electronic states in nuclear coordinate space

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Introduction

Photochemistry

What happens after photoexcitation?

Electronically nonadiabatic processes

- Breakdown of the BO approximation
- Multiple coupled potential energy surfaces

Semiclassical approaches

- Ensemble of trajectories for nuclear motion $\mathbf{R}, \mathbf{v}$
- Electronic wave functions $|\psi_A(\mathbf{r}; \mathbf{R})\rangle$
- Surface hopping dynamics

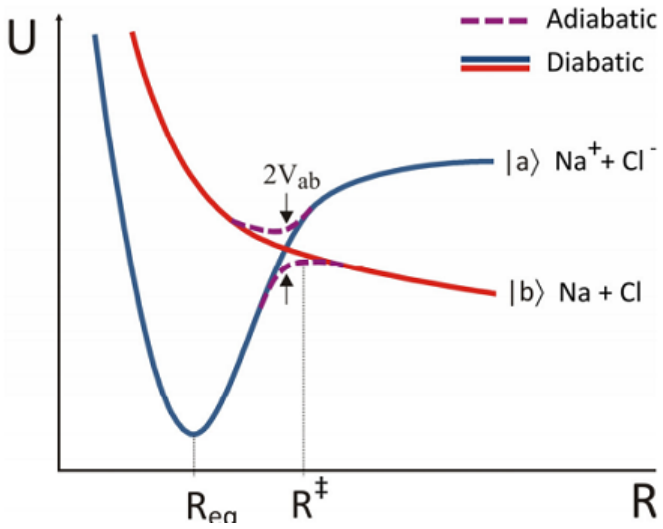
Adiabatic and diabatic states

Adiabatic states:

- Electronic structure methods
- Unique, well defined
- Conical intersections and avoided crossings (sudden changes in electronic properties)

Diabatic states:

- Smooth (stable electronic character)
- Useful for interpreting results
- ”Strict” diabatic states don’t exist
- Not unique, hard to construct



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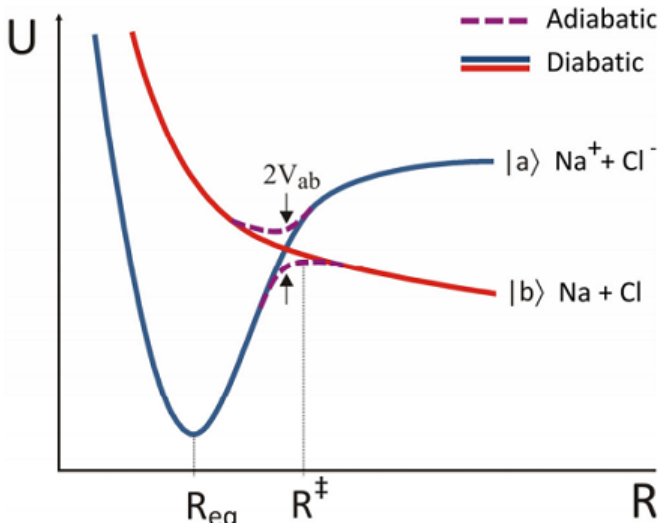

Diabatic states:

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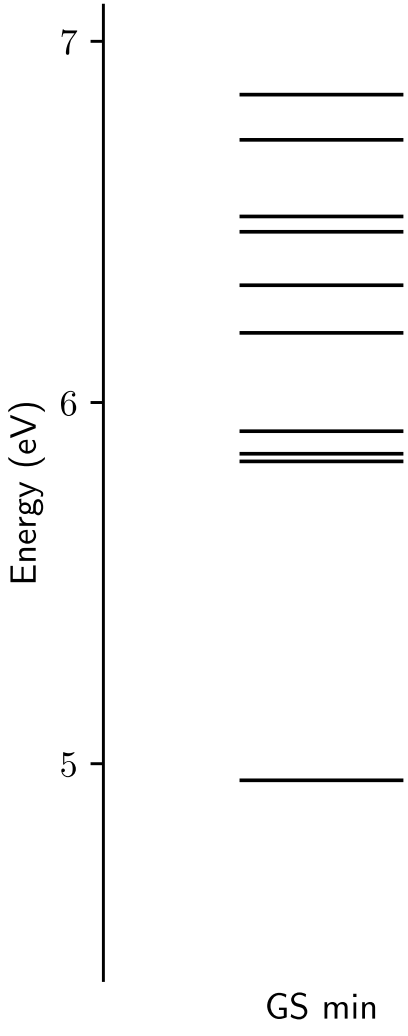
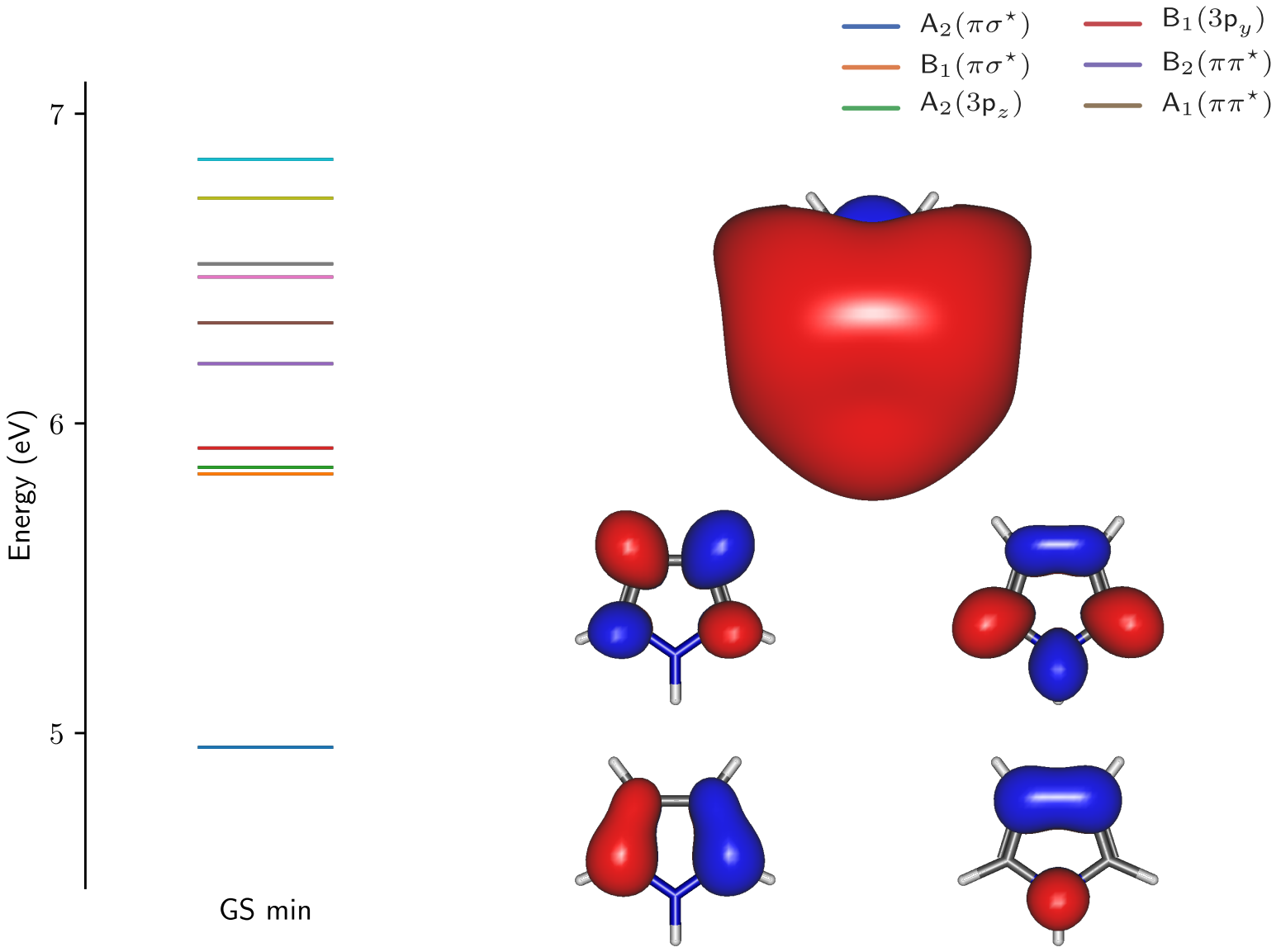
Goal: Use adiabatic states, but also keep track of electronic character

State assignment

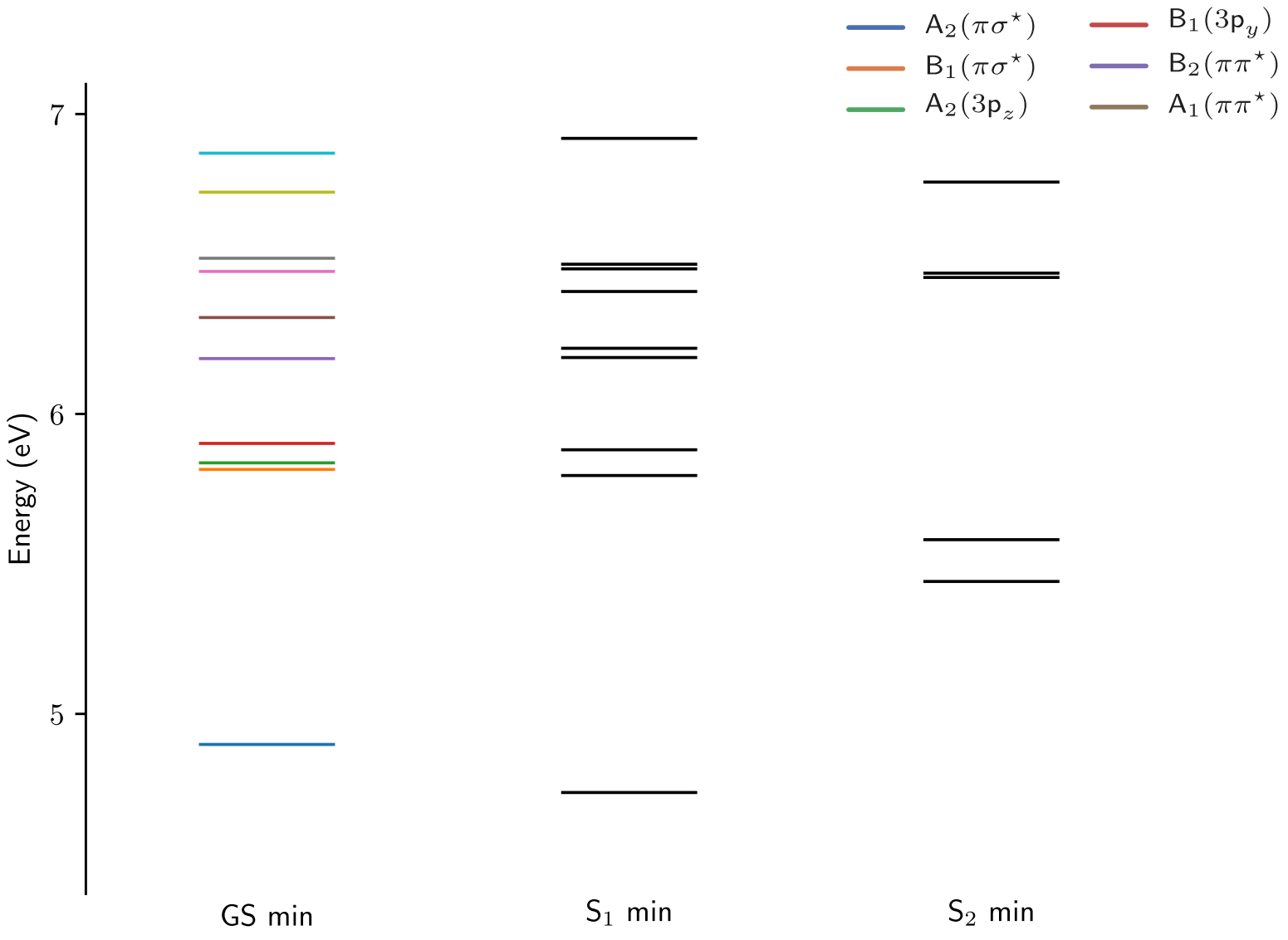
State assignment



State assignment



State assignment



Wave function overlaps

To compare wave functions at different geometries we need to be able to calculate matrix elements of the type:

$$\left\langle \psi_A(\mathsf{r};\mathsf{R}) \middle| \psi_B(\mathsf{r};\mathsf{R}') \right\rangle = \left\langle \psi_A \middle| \psi'_B \right\rangle$$

Assignment problem

```
Overlap matrix with phase matching between assigned bra/ket states:
       0.998  -0.000  -0.000   0.000   0.000  -0.000   0.000   0.000   0.069   0.000   0.000
       0.000   0.994   0.096   0.000   0.000  -0.000   0.040  -0.000  -0.000  -0.015   0.000
      -0.000   0.000   0.000  -0.536  -0.000   0.841   0.000   0.040   0.000  -0.000   0.059
      -0.000   0.093  -0.992  -0.000   0.000   0.000   0.044   0.000   0.000  -0.070   0.000
      -0.000   0.000  -0.000   0.842  -0.000   0.534   0.000   0.076   0.000   0.000  -0.010
      -0.000  -0.000   0.000   0.000   1.000   0.000  -0.000  -0.000  -0.000  -0.000   0.000
      -0.069   0.000   0.000   0.000   0.000  -0.000   0.000  -0.000   0.998   0.000  -0.000
      -0.000  -0.037   0.024  -0.000   0.000  -0.000   0.973  -0.000  -0.000   0.227  -0.000
       0.000   0.000   0.000  -0.058   0.000  -0.036  -0.000   0.817   0.000  -0.000  -0.573
      -0.000  -0.000   0.000   0.009   0.000  -0.080   0.000   0.570   0.000  -0.000   0.818
       0.000  -0.031   0.075   0.000  -0.000  -0.000   0.224  -0.000   0.000  -0.971  -0.000
```

Need to find pairs of adiabatic states at the two geometries which have the largest overlaps.

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      0.000  -0.031   0.075   0.000  -0.000  -0.000   0.224  -0.000   0.000  -0.971  -0.000
  Assignment:
      Rows: 1 2 3 4 5 6 7 8 9 10 11
      Cols: 1 2 6 3 4 5 9 7 8 11 10
```

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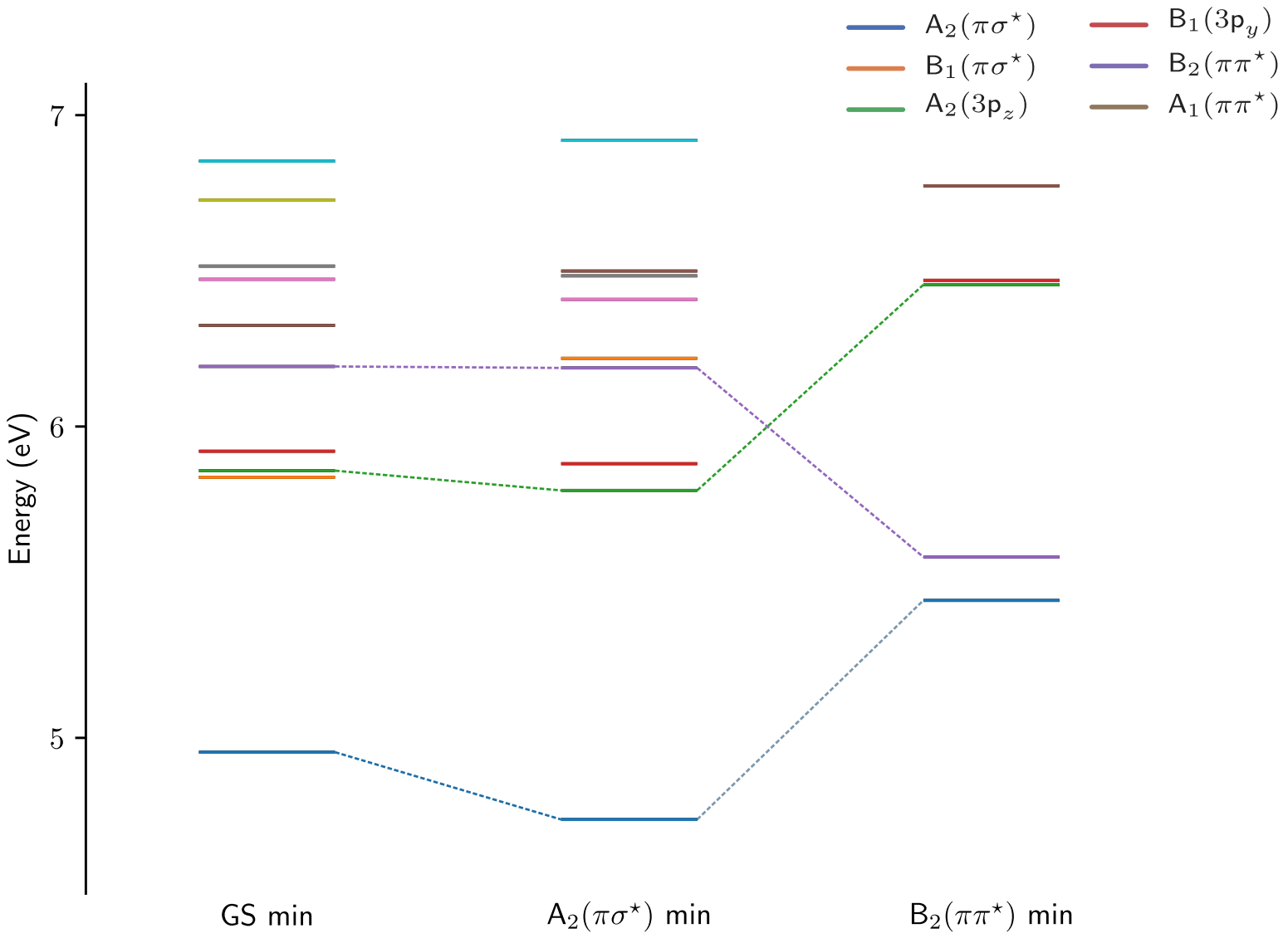
Assignment problem: Solved using the Hungarian algorithm

State assignment



Algorithm

Wave function overlaps

Overlap of two sets of wave functions at different nuclear geometries

$$|\psi_A\rangle = \sum_i^{n_{det}} d_i^A \, |\Phi_i\rangle \quad \text{and} \quad |\psi'_B\rangle = \sum_j^{n'_{det}} d_j'^B \, |\Phi'_j\rangle$$

$$\langle \psi_A | \psi'_B \rangle = \sum_i^{n_{det}} \sum_j^{n'_{det}} d_i^A d_j'^B \, \langle \Phi_i | \Phi'_j \rangle$$

Slater determinants built from MOs which

- are not orthogonal
- do not span the same space

$\langle \Phi_i | \Phi'_j \rangle$ is equal to the determinant of the overlaps of the orbitals.

Scaling: $n_{det} n'_{det} n_o^3$

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This quickly becomes very expensive!

Wave function overlaps

Solutions:

- Approximations
- More efficient algorithms

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Specific problem: Overlap of two CIS type wave functions

$$|\Psi_A\rangle = \sum_a^n \sum_i^m d_{ai}^A \left|\Phi_a^i\right\rangle \quad \text{and} \quad \left|\Psi'_B\right\rangle = \sum_b^n \sum_j^{m'} d'^B_{bj} \left|\Phi'^j_b\right\rangle$$

$$\left\langle \Psi_A \middle| \Psi'_B \right\rangle \propto \sum_a^n \sum_b^n \sum_i^m \sum_j^{m'} d_{ai}^A d'^B_{bj} \left\langle \Phi_a^i \middle| \Phi'^j_b \right\rangle$$

Scaling: $n^5 m m'$

OL2M Algorithm

Each overlap determinant is expanded into level 2 minors along the row/column corresponding to the virtual orbital to which the electron is excited.

$$\left\langle \Phi_a^i \middle| \Phi_b'^j \right\rangle = \sum_{c\neq a}^{n}\sum_{d\neq b}^{n} o_{cj} o_{id}\, \mathrm{sgn}(b-d)\,\mathrm{sgn}(c-a)(-1)^{a+b+c+d} \left\langle \Phi_{a,c} \middle| \Phi'_{b,d} \right\rangle + o_{ij}(-1)^{a+b} \left\langle \Phi_a \middle| \Phi'_b \right\rangle$$

These minors contain only rows/columns corresponding to occupied orbitals so they can be reused for all virtual orbitals.

Scaling: n^7

ONTO Algorithm

Alternative approach: Expand the wave functions in terms of natural transition orbitals (NTOs) before the overlap calculation

$$|\Psi_A\rangle = \sum_k^n \lambda_k^A \left|\Theta_k^A\right\rangle$$

$$|\Psi_B\rangle = \sum_l^n \lambda_l^B \left|\Theta_l^B\right\rangle$$

Now we need to calculate only n^2 overlap determinants.

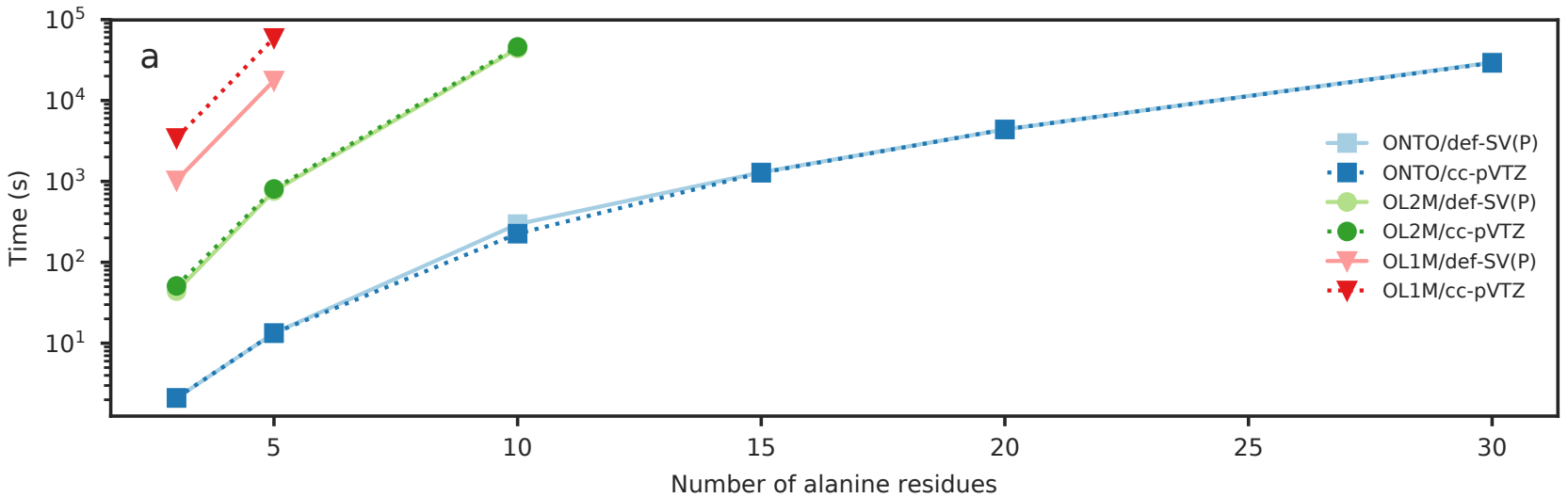
$$\sum_k^n \sum_l^n \lambda_k^A \lambda_l'^B \left\langle \Theta_k^A \middle| \Theta_l'^B \right\rangle$$

Scaling: $n^5 N_A N_B$

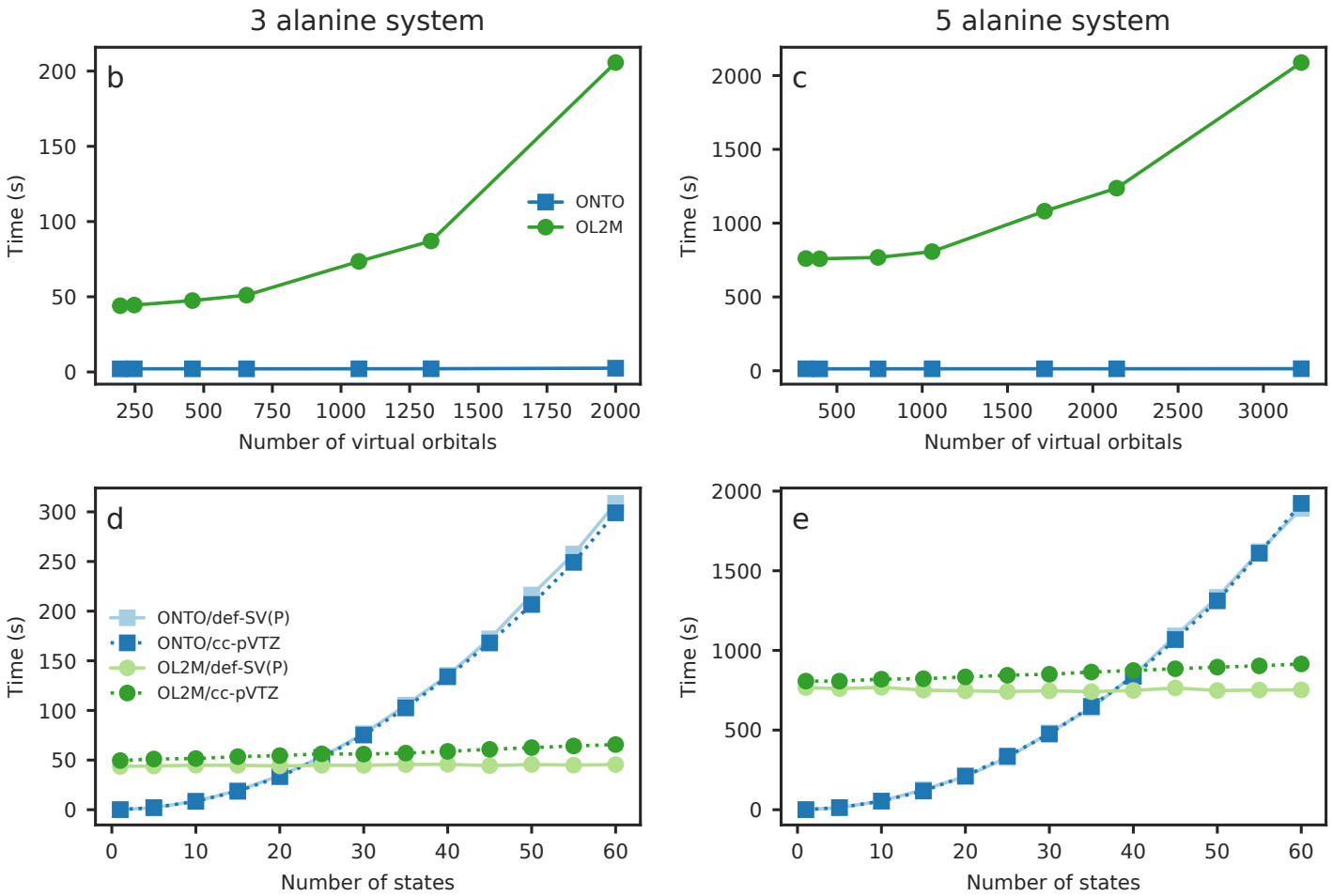
Scaling

Test case: alanine polypeptides

- 34 to 304 atoms
- 62 to 575 occupied orbitals
- 5 states (25 overlap matrix elements)



Scaling

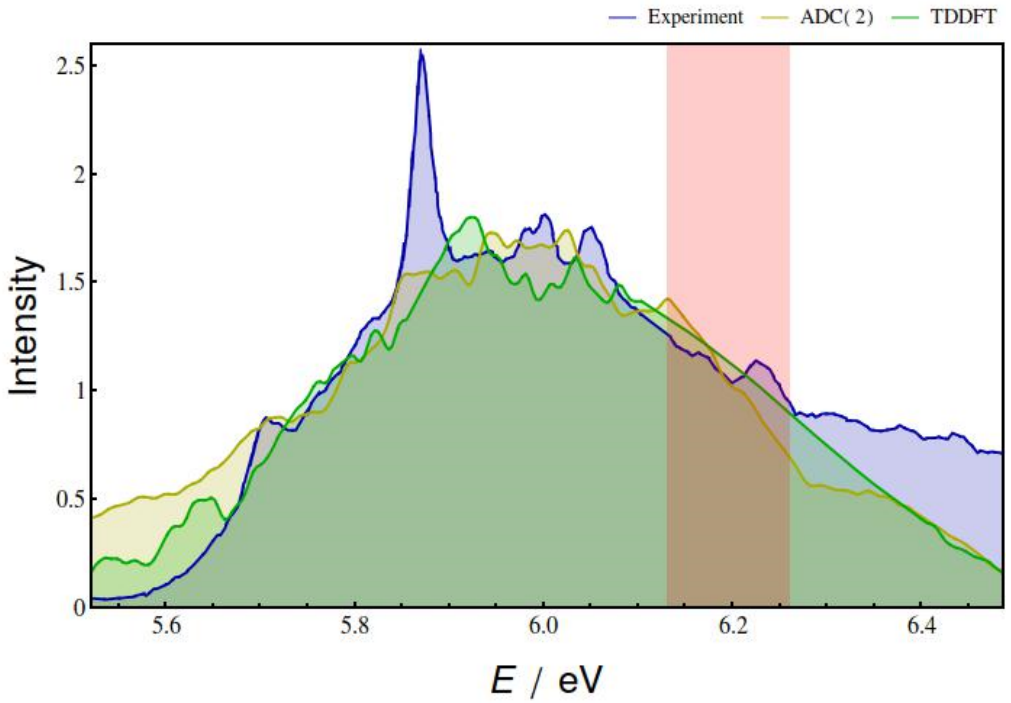

3 alanine system
5 alanine system
b
c
d
e
Time (s)
Number of virtual orbitals
Number of states
ONTO
OL2M
ONTO/def-SV(P)
ONTO/cc-pVTZ
OL2M/def-SV(P)
OL2M/cc-pVTZ

Overlaps in photochemical studies

Spectra using the nuclear ensemble method

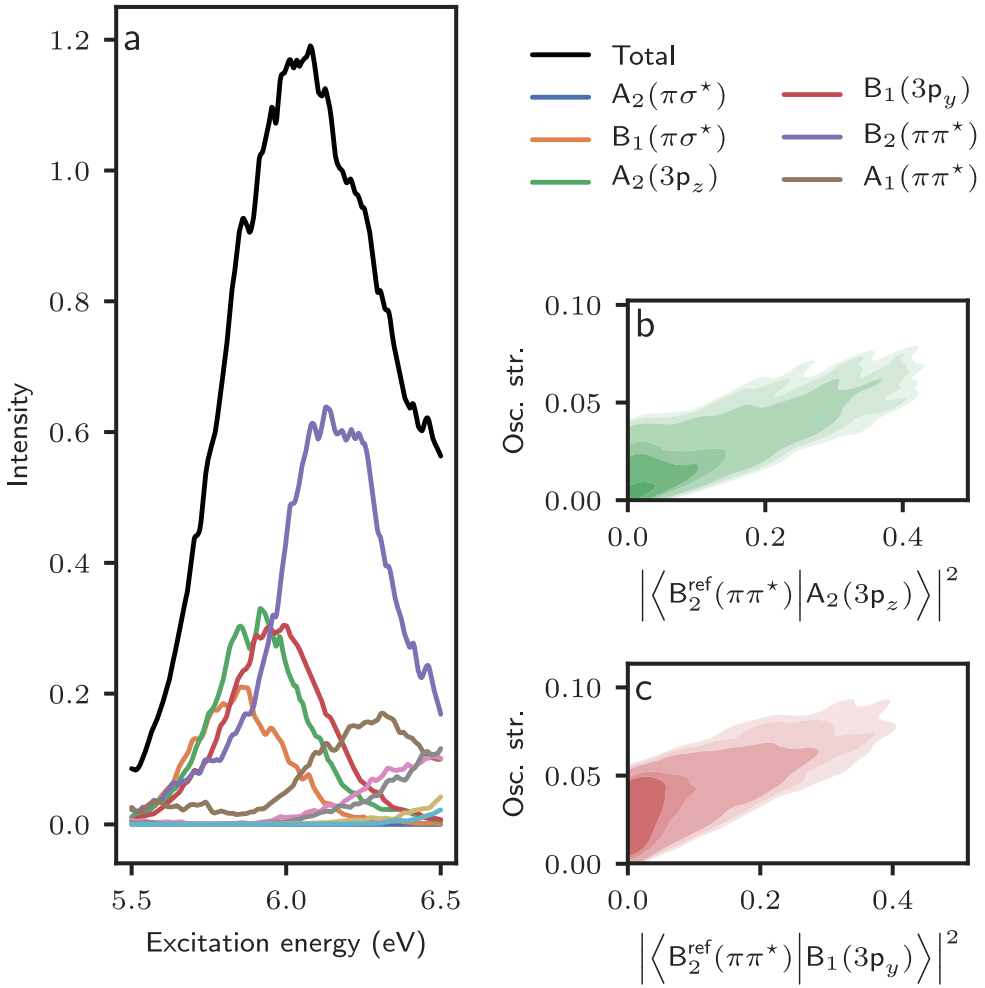
Excitation of an ensemble of nuclear geometries

- Low computational cost and conceptually simple
- No vibronic features
- Contributions from each state?

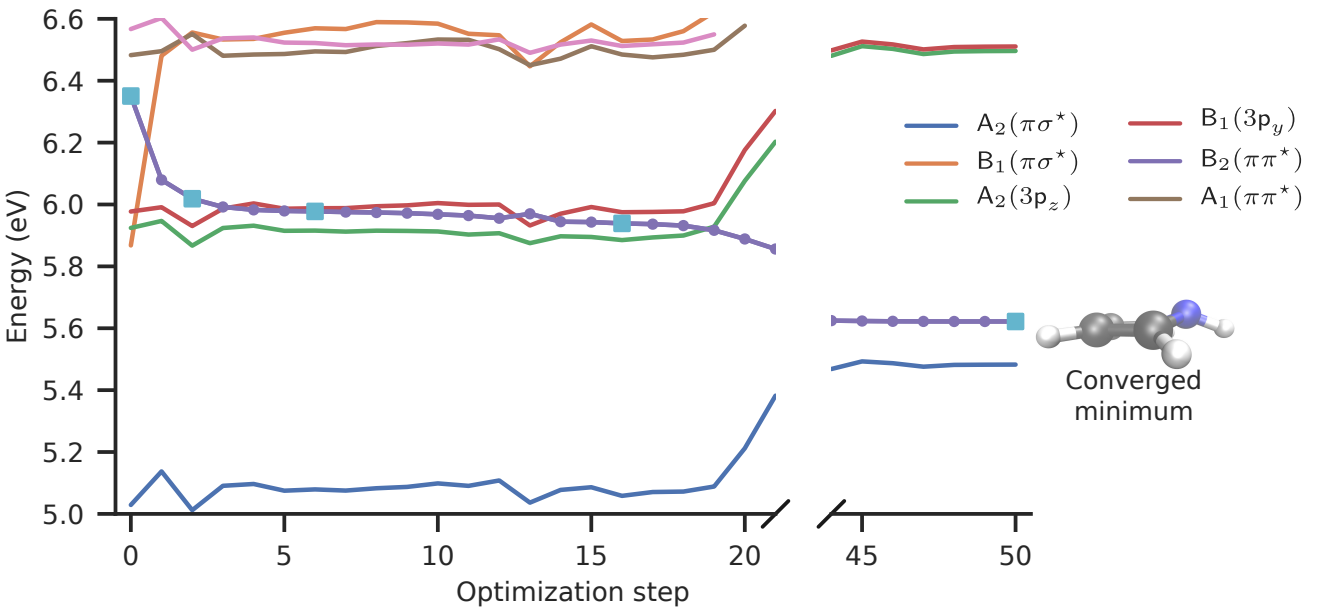


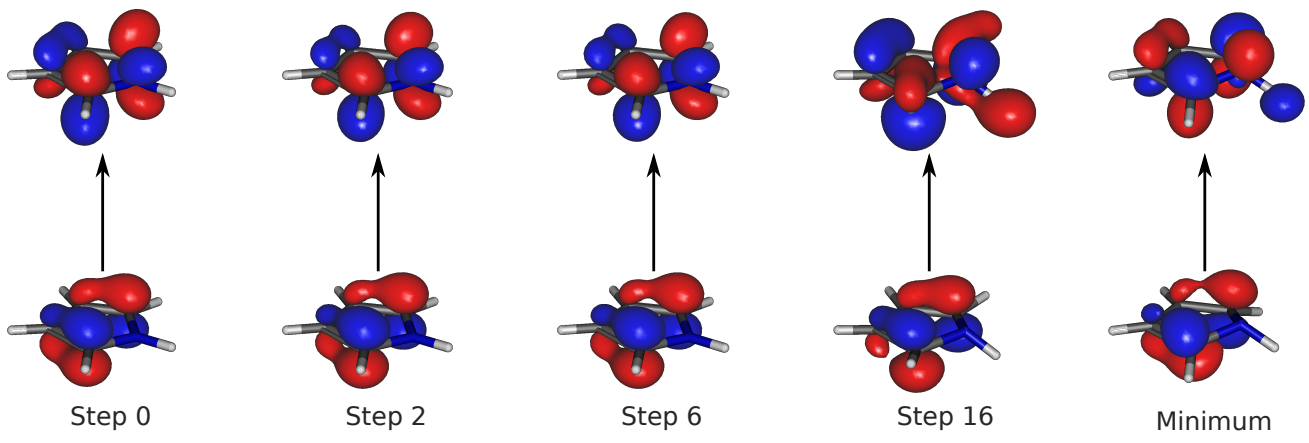
Spectrum decomposition

- Reference states at GS minimum geometry
- 8000 geometries from Wigner distribution
- Good agreement with MCTDH spectrum
- Evidence of intensity borrowing



Optimization with state switching

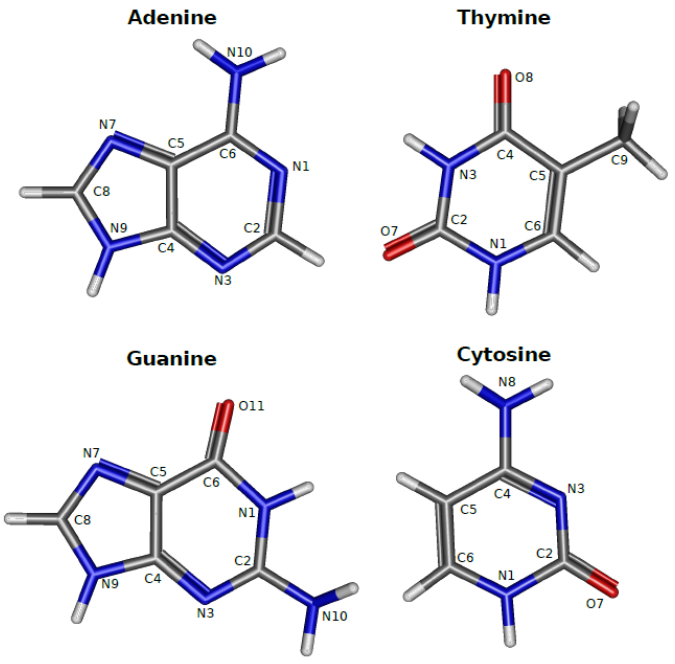




Solvation effects

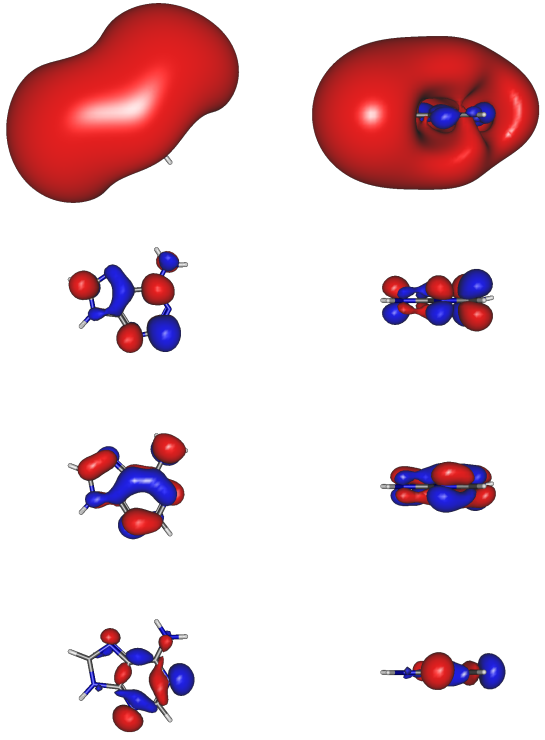
Study of effect of solvation on excited states of nucleobases

- ADC(2)/aug-cc-pVDZ
- Gas phase and COSMO comparison
- Ground state nuclear ensemble



Solvation effects

S	E_{ref}	NTO_1	E_ρ^V	E_ρ^C
S_1	4.99	$n_1\pi_1^*$	4.81± 0.28	5.09 ± 0.28
S_2	5.10	$\pi_1\pi_1^*$	4.92± 0.25	4.84 ± 0.26
S_3	5.12	$\pi_1\pi_2^*$	4.99± 0.18	4.97 ± 0.18
S_4	5.38	$\pi_1 Ryd_1$	5.29± 0.24	5.50 ± 0.21
S_5	5.63	$n_1\pi_2^*$	5.54± 0.25	5.76 ± 0.24
S_6	5.69	$\pi_1 Ryd_2$	5.63± 0.24	6.09 ± 0.21
S_7	5.96	$n_1 Ryd_1$	5.90± 0.26	6.35 ± 0.22
S_8	6.03	$n_2\pi_2^*$	5.89± 0.21	6.12 ± 0.22
S_9	6.17	$\pi_1 Ryd_3$	6.12± 0.24	6.25 ± 0.23
S_{10}	6.20	$\pi_2\pi_1^*$	6.05± 0.19	5.96 ± 0.18
S_{11}	6.40	$n_1 Ryd_2$	6.33± 0.25	7.01 ± 0.23
S_{12}	6.42	$\pi_1 Ryd_4$	6.36± 0.25	6.73 ± 0.24
S_{13}	6.46	$\pi_1\pi_3^*$	6.34± 0.22	6.39 ± 0.23
S_{14}	6.50	$\pi_2 Ryd_1$	6.41± 0.23	6.75 ± 0.20
S_{15}	6.56	$\pi_1 Ryd_5$	6.51± 0.24	6.80 ± 0.23



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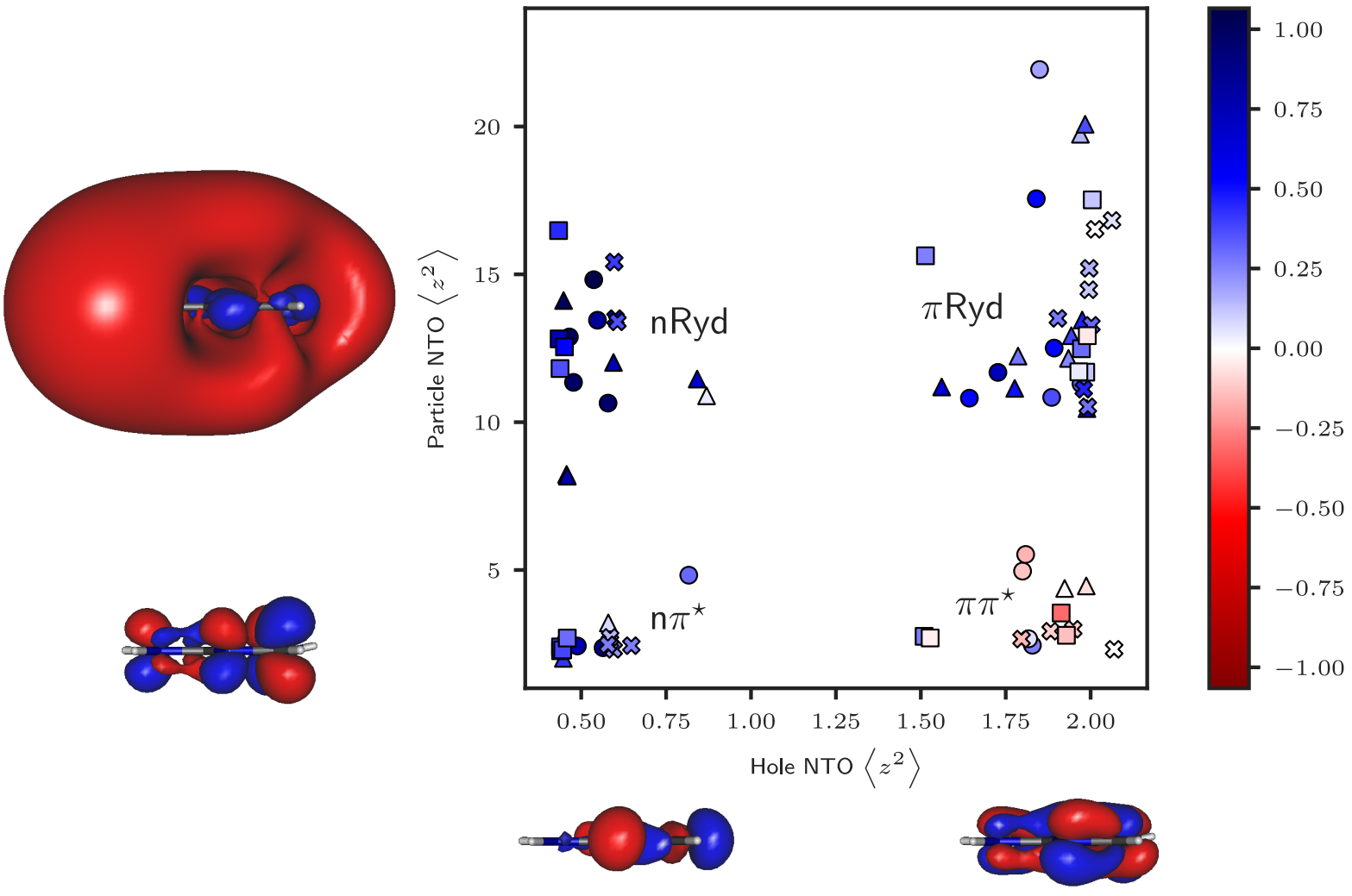

Conclusion

Summary

Wave function overlaps for TDDFT/ADC(2) can be calculated at almost no additional cost compared to the electronic structure calculation.

- Approximations are needed only for very large systems.

Overlaps are useful in all stages of studies of processes involving multiple electronic states.

- Electronic properties from nuclear ensemble
- Potential energy surface scans
- Method comparisons
- Dynamics

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Thank you for your attention!

Questions?