Presentation on Calculations of Excited Electronic states by converging to saddle points on the electronic energy surface using density functionals or Hartree-Fock

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Methodology:

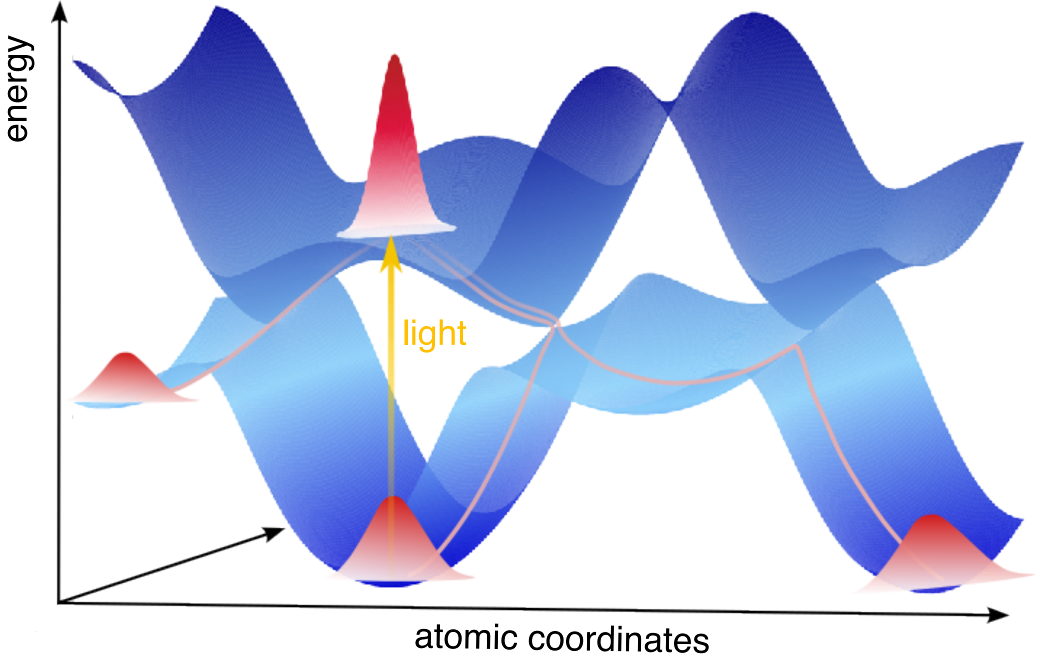
- Variational, time-***in***dependent calculations using density functionals to find solutions of Kohn-Sham eqns. corresponding to higher energy ("delta SCF", state-specific, …).
- Orbitals optimised for excited states by converging on *saddle points* on the electronic energy surface.

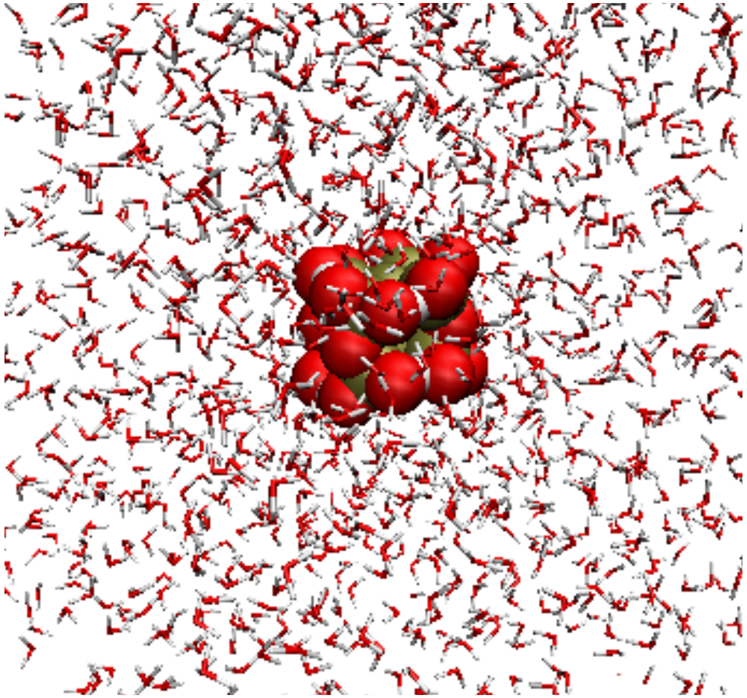
Applications:

- Twisting of C=C bond, avoided crossing, conical intersection (molecular motors).
- Rydberg excited states of molecules.
- Charge transfer excitations in molecules.
- Nitrogen-vacancy defect in diamond, optical preparation of a pure spin state.

Simulations of light-induced bond breaking / bond formation

Curchod and Agostini J. Phys. Chem. Lett, **8**, 831 (2017)





Goal:

Identify and optimise the mechanisms of solar energy conversion to harness sunlight in sustainable ways

Need to calculate the variation of the energy as a function of atomic coordinates in excited electronic states as well as ground st.

Condensed phase systems are large, need to represent 10^3 electrons.

Calculate the dynamics of atoms on the energy surfaces (e.g. Newton eqn. of motion or wave packet propagation).

Can use QM/MM to take solvation effects into account
(SAFIRES for handling of the interface, SCME potential energy function, …).

[1]

Variational calculation of the ground electronic state

Recall, variational calculation of the ground state

Given a time-independent Hamiltonian, *H*, with eigenstates $|\phi_n>$

$$H|\phi_n >= E_n|\phi_n >$$

where *n=0* for ground state, *n=1* for first excited state, etc.

then for any arbitrary state vector $|\psi >$ in the space spanned by the eigenstates, i.e.

$$|\psi >= \sum_n c_n|\phi_n > \ ,$$

we have

$$< H >= \frac{< \psi|H|\psi >}{< \psi|\psi >} \ \geq \ E_0 \ .$$

The best estimate of the energy of the ground state is obtained by finding the minimum in the expectation value of the energy, and the corresponding state vector is the best estimate of the ground state.

Most optimisation methods are designed to find a minimum (or maximum), for example self-consistent field (SCF) procedures of various sorts.

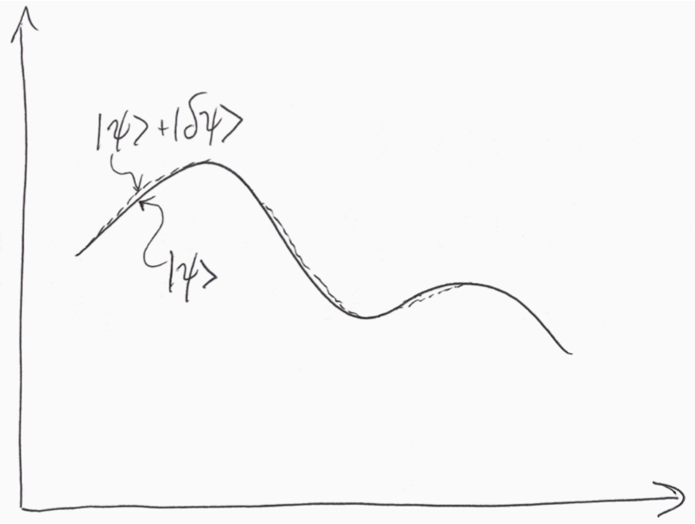
More general variational optimisation (calculus of variations)

When an infinitesimal change in the state vector is made

$$|\psi> \rightarrow \ |\psi> + |\delta\psi>,$$

expectation value of energy changes by $\delta < H >$

$$< H > \rightarrow < H > + \delta < H > .$$



See, for example:
"Quantum Mechanics" by
Cohen-Tannoudji, Diu and Laloe.

If $|\psi >$ is such that $\delta < H >= 0$ for all $|\delta\psi >$,

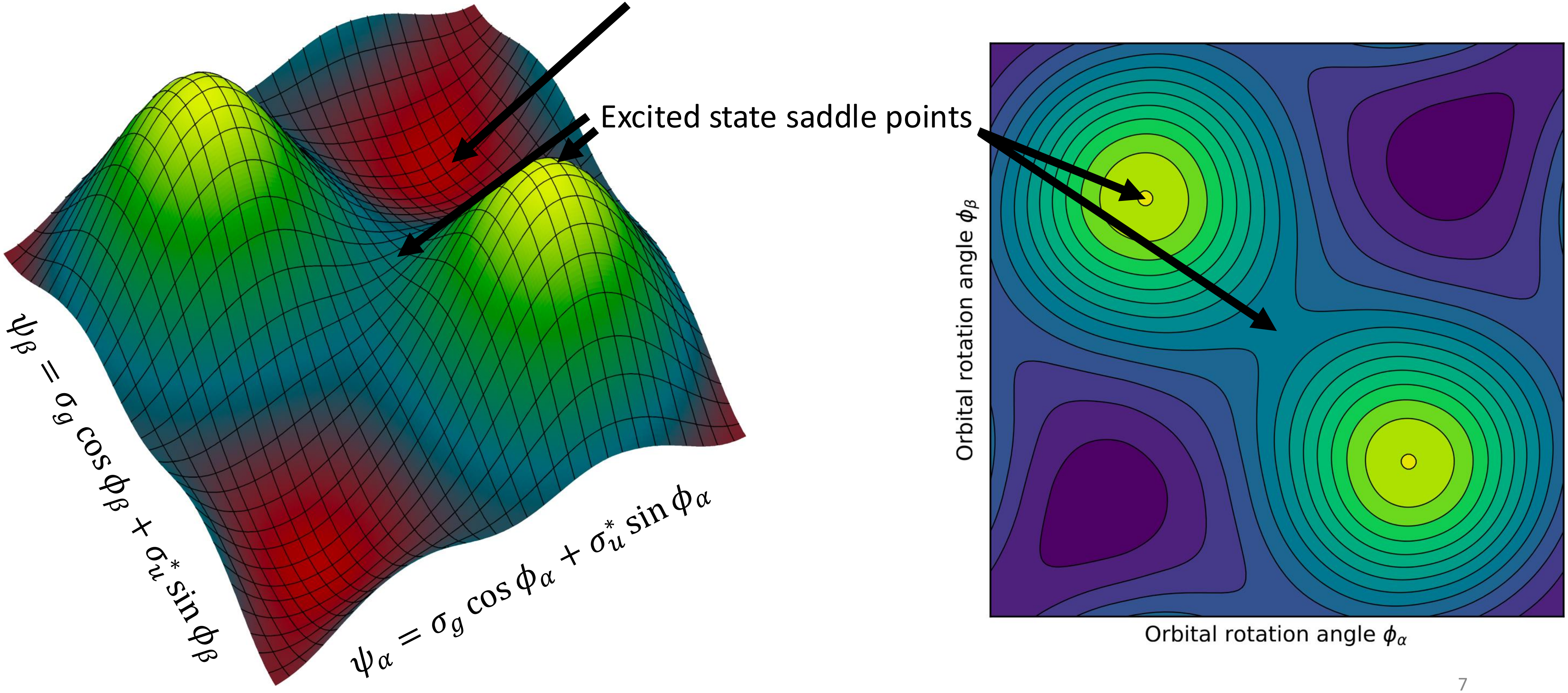
then $$H|\psi >=< H > |\psi >$$

i.e. $|\psi >$ is an eigenvector of *H* with an eigenvalue < *H* > ,
a solution to the Schrödinger equation.

This applies to *excited states* as well as the ground state.

Excited states are also stationary with respect to variations in $|\psi >$ but correspond to ***saddle points*** on the energy surface representing the variation of $< H >$ with respect to the various electronic degrees of freedom.

Time-*in*dependent excited state calculations – Concept


Ground state minimum

Excited state saddle points

Need to find saddle points on the electronic energy landscape in order to converge on excited electronic states.

[4]

CI: Exact solutions to the Schrödinger equation

Start with the simplest form for an N-electron wave function, a single Slater determinant (SD).

Variational minimisation of the energy with respect to orbitals gives the Hartree-Fock approximation, $|\psi_0>$.

Exact solution can then be obtained by taking a linear combination of all SDs that can be formed with these orbitals and variationally optimise, configuration interaction (CI)

$$|\Phi>= \underbrace{C_0|\psi_0>}_{\text{Hartree-Fock SD}} + \underbrace{\sum_r \sum_a C_a^r|\psi_a^r>}_{\text{single excitation SDs}} + \underbrace{\sum_a \sum_{b>a} \sum_r \sum_{s>r} C_{ab}^{rs}|\psi_{ab}^{rs}>}_{\text{double excitation SDs}} + \ldots .$$

CI: Exact solutions to the Schrödinger equation

Configuration interaction (CI)

$$|\Phi >= \underbrace{C_0|\psi_0>}_{\text{Hartree-Fock SD}} + \underbrace{\sum_r \sum_a C_a^r|\psi_a^r>}_{\text{single excitation SDs}} + \underbrace{\sum_a \sum_{b>a} \sum_r \sum_{s>r} C_{ab}^{rs}|\psi_{ab}^{rs}>}_{\text{double excitation SDs}} + \ldots.$$

The expectation value of the energy as a function of the linear expansion coefficients defines an *electronic energy surface*,

$$< \Phi|H|\Phi >_{(C_0,\{C_a^r\},\{C_{ab}^{rs}\}\ldots)}$$

Near a stationary point corresponding to an excitation to state k
the eigenvalues of the Hessian matrix are $2(E_n - E_k)$ where $n = 0, 1, 2, \ldots.$
and $E_0 \leq E_1 \leq E_2\ldots$

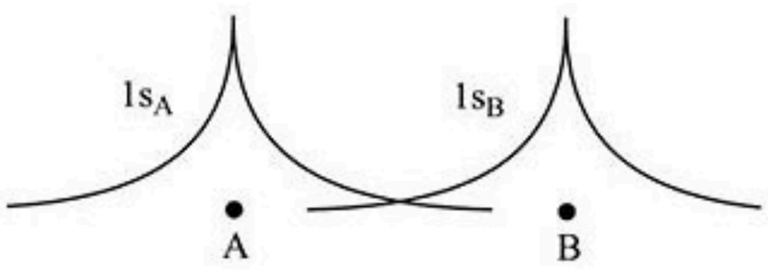
So, the ground state, $k = 0$, corresponds to a minimum,
first excited state, $k = 1$, corresponds to a 1st order saddle point,
second excited state, $k = 2$, corresponds to a 2nd order saddle point,
etc. (see T. Helgaker, P. Jørgensen and J. Olsen
Molecular Electronic-Structure Theory, Chapter 4 (Wiley, 2000))

Electronic energy surface

An electronic energy surface describes how a system's energy varies as a function of the electronic degrees of freedom (i.e. expansion coefficients)

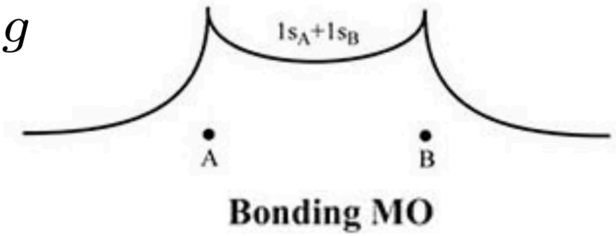
Example, H_2

use minimal basis set,
1s atomic orbital on each atom

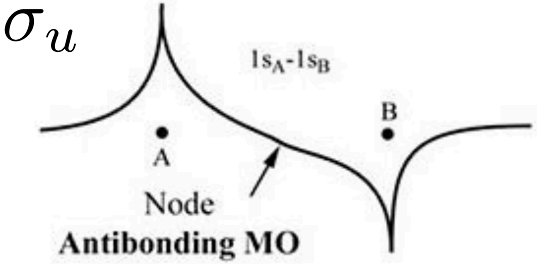


Molecular orbitals for spin-up, α , and spin-down, β

σ_g

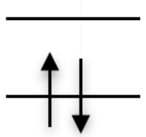


σ_u



The ground state wave function is

$$\psi = \sigma_g(1)\sigma_g(2)(\alpha(1)\beta(2) - \alpha(2)\beta(1))$$



LUMO, σ_u

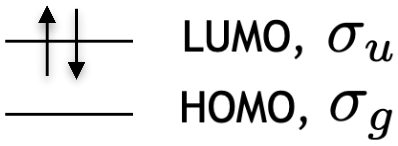
HOMO, σ_g

Electronic energy surface

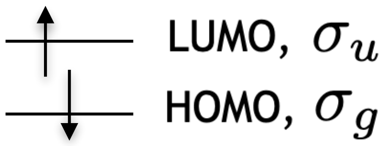
Calculate the expectation value of the energy for an arbitrary linear combination of the two molecular orbitals of an H_2 molecule.

$$\begin{pmatrix} \psi^{1,\alpha} \\ \psi^{0,\alpha} \\ \psi^{1,\beta} \\ \psi^{0,\beta} \end{pmatrix} = \begin{pmatrix} \cos\phi_\alpha & \sin\phi_\alpha & 0 & 0 \\ -\sin\phi_\alpha & \cos\phi_\alpha & 0 & 0 \\ 0 & 0 & \cos\phi_\beta & \sin\phi_\beta \\ 0 & 0 & -\sin\phi_\beta & \cos\phi_\beta \end{pmatrix} \begin{pmatrix} \sigma_g^\alpha(r) \\ \sigma_u^\alpha(r) \\ \sigma_g^\beta(r) \\ \sigma_u^\beta(r) \end{pmatrix}$$

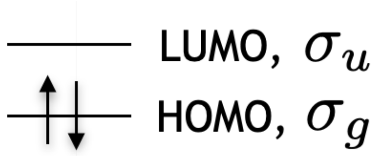
2nd order SP:


LUMO, σ_u
HOMO, σ_g

1st order SP:

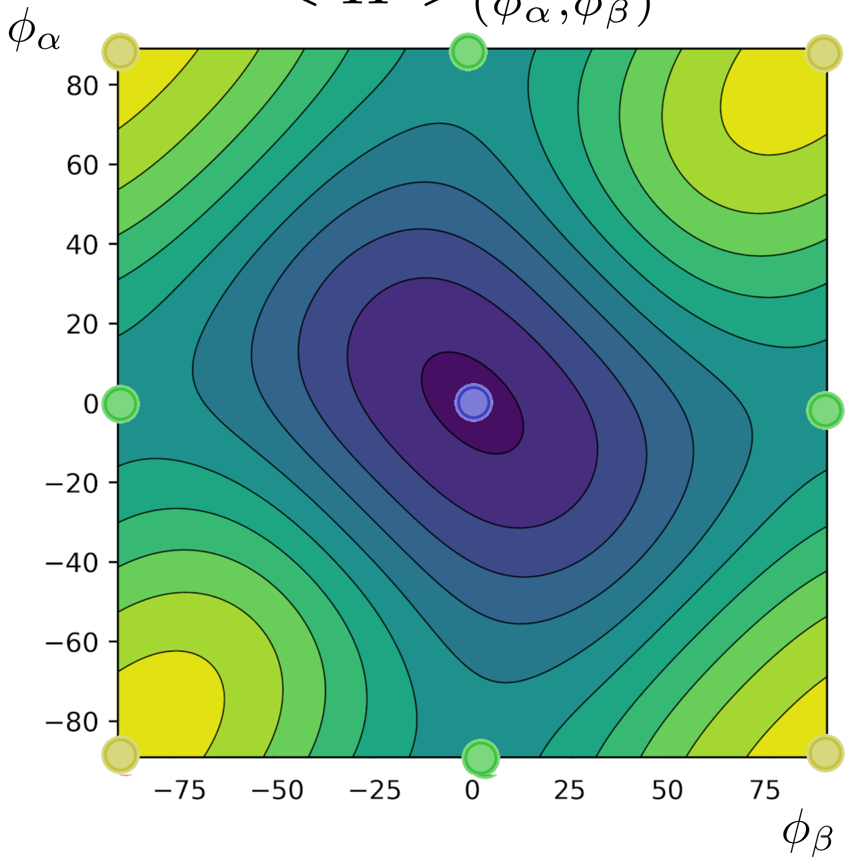

LUMO, σ_u
HOMO, σ_g

Minimum:


LUMO, σ_u
HOMO, σ_g

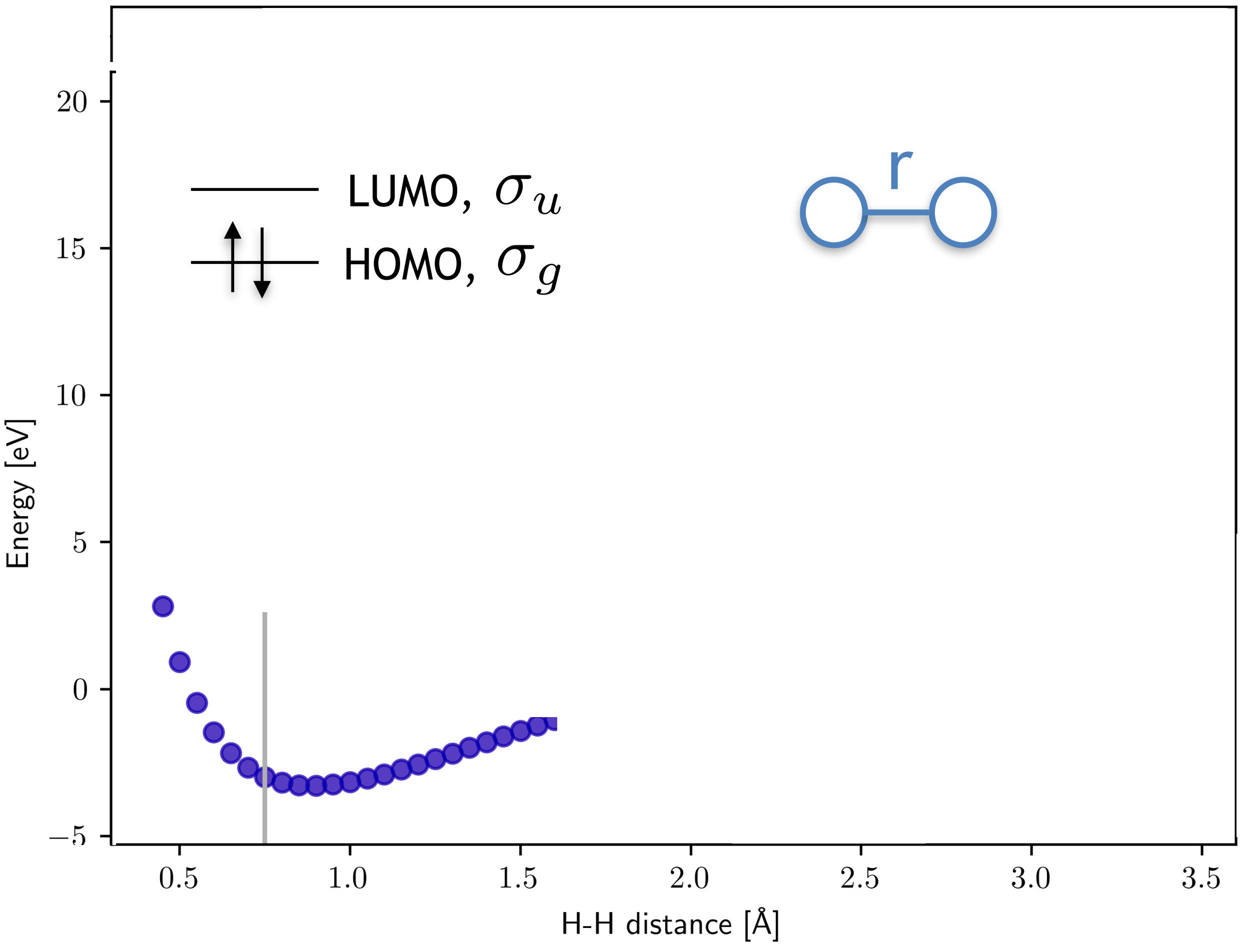
Electronic energy surface:

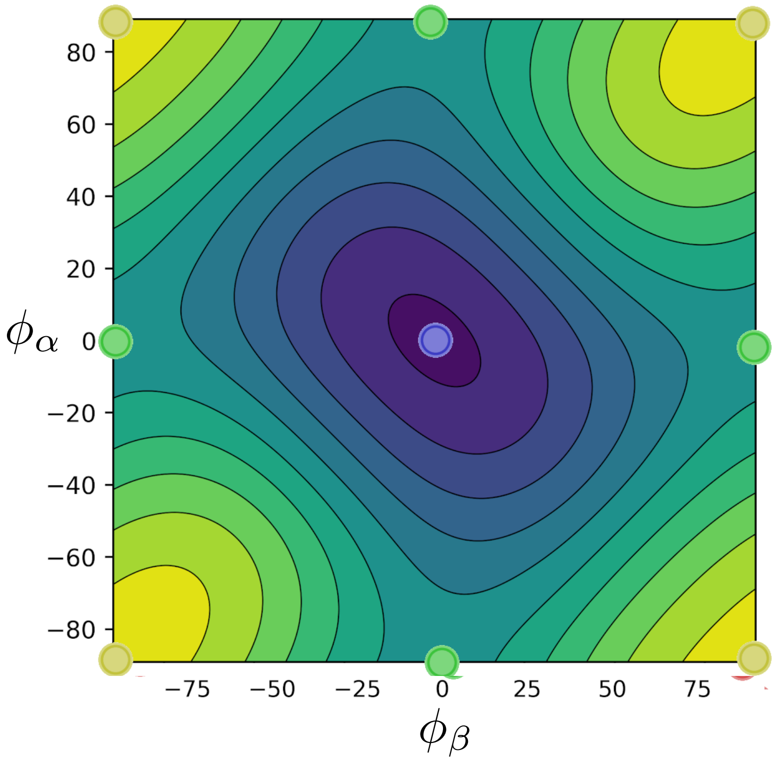
$$< H >_{(\phi_\alpha, \phi_\beta)}$$



Stretch the H-H bond

H_2 molecule,
minimal basis set



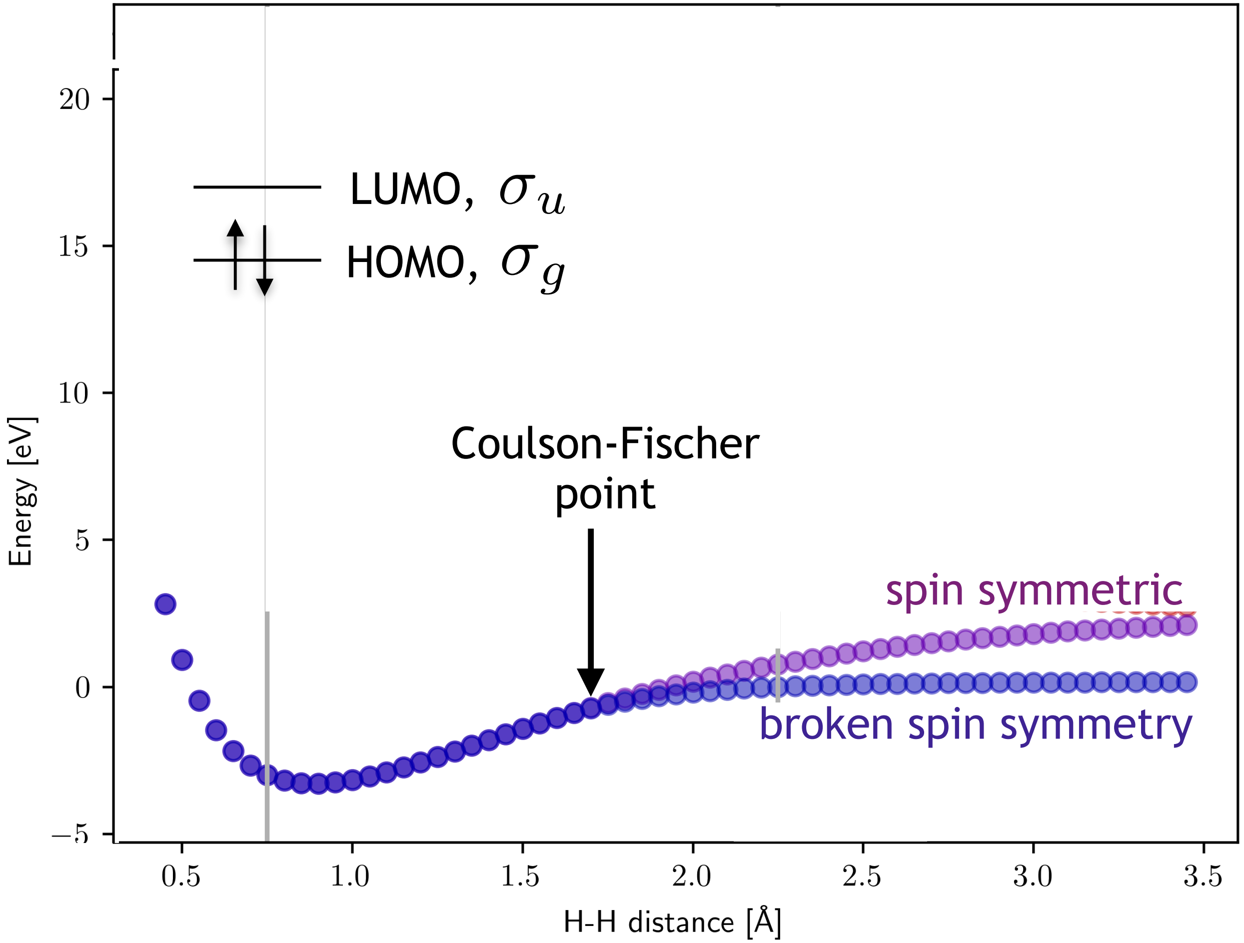


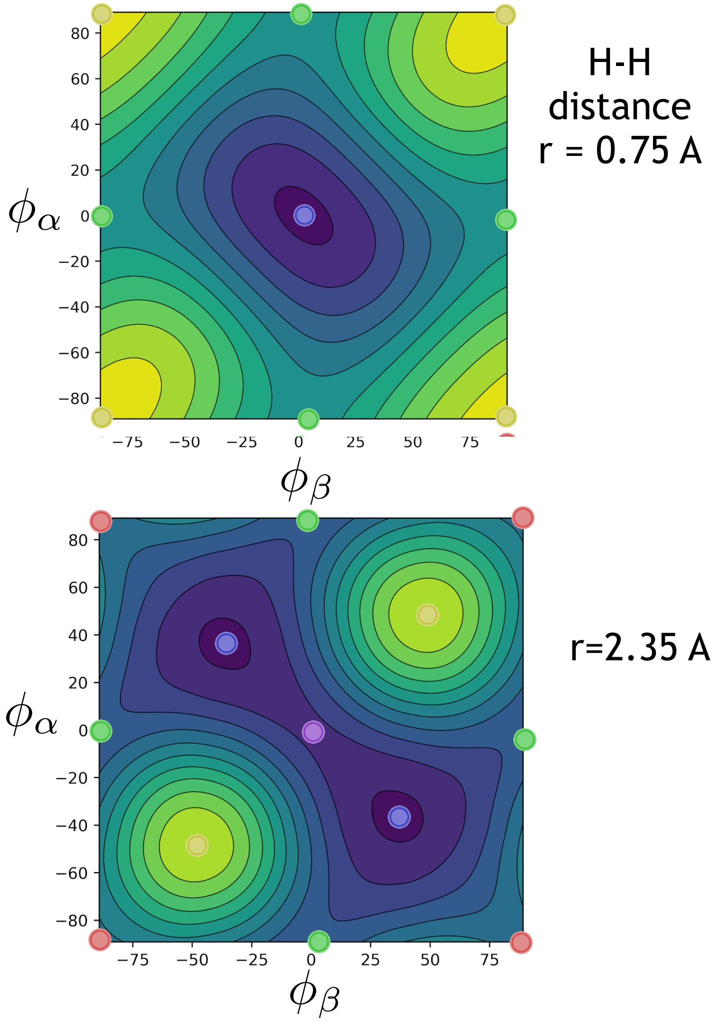
$$\begin{pmatrix} \psi^{1,\alpha} \\ \psi^{0,\alpha} \\ \psi^{1,\beta} \\ \psi^{0,\beta} \end{pmatrix} = \begin{pmatrix} \cos\phi_\alpha & \sin\phi_\alpha & 0 & 0 \\ -\sin\phi_\alpha & \cos\phi_\alpha & 0 & 0 \\ 0 & 0 & \cos\phi_\beta & \sin\phi_\beta \\ 0 & 0 & -\sin\phi_\beta & \cos\phi_\beta \end{pmatrix} \begin{pmatrix} \sigma_g^\alpha(r) \\ \sigma_u^\alpha(r) \\ \sigma_g^\beta(r) \\ \sigma_u^\beta(r) \end{pmatrix}$$

Symmetry breaking in a single Slater determinant wave function can effectively account for static correlation to some extent

H_2 molecule,

minimal basis set



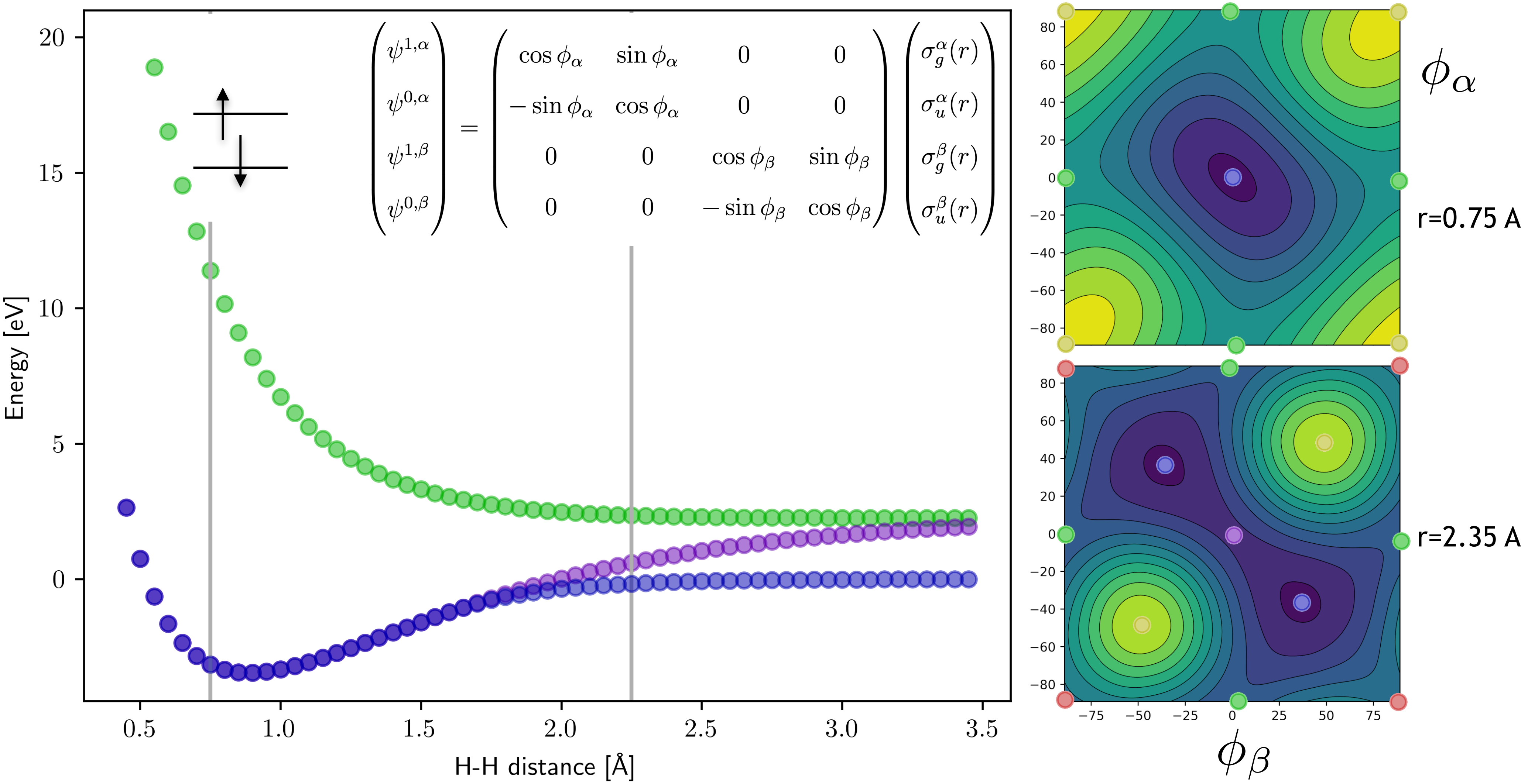


At larger H-H distance than 1.6 Å, a broken spin symmetry state gives lower energy

[10]

Energy curve for the first excited state

A first order saddle point at, for example, (0, 90 deg.) corresponds to an open shell singlet excited state, where an electron has been excited from HOMO to LUMO



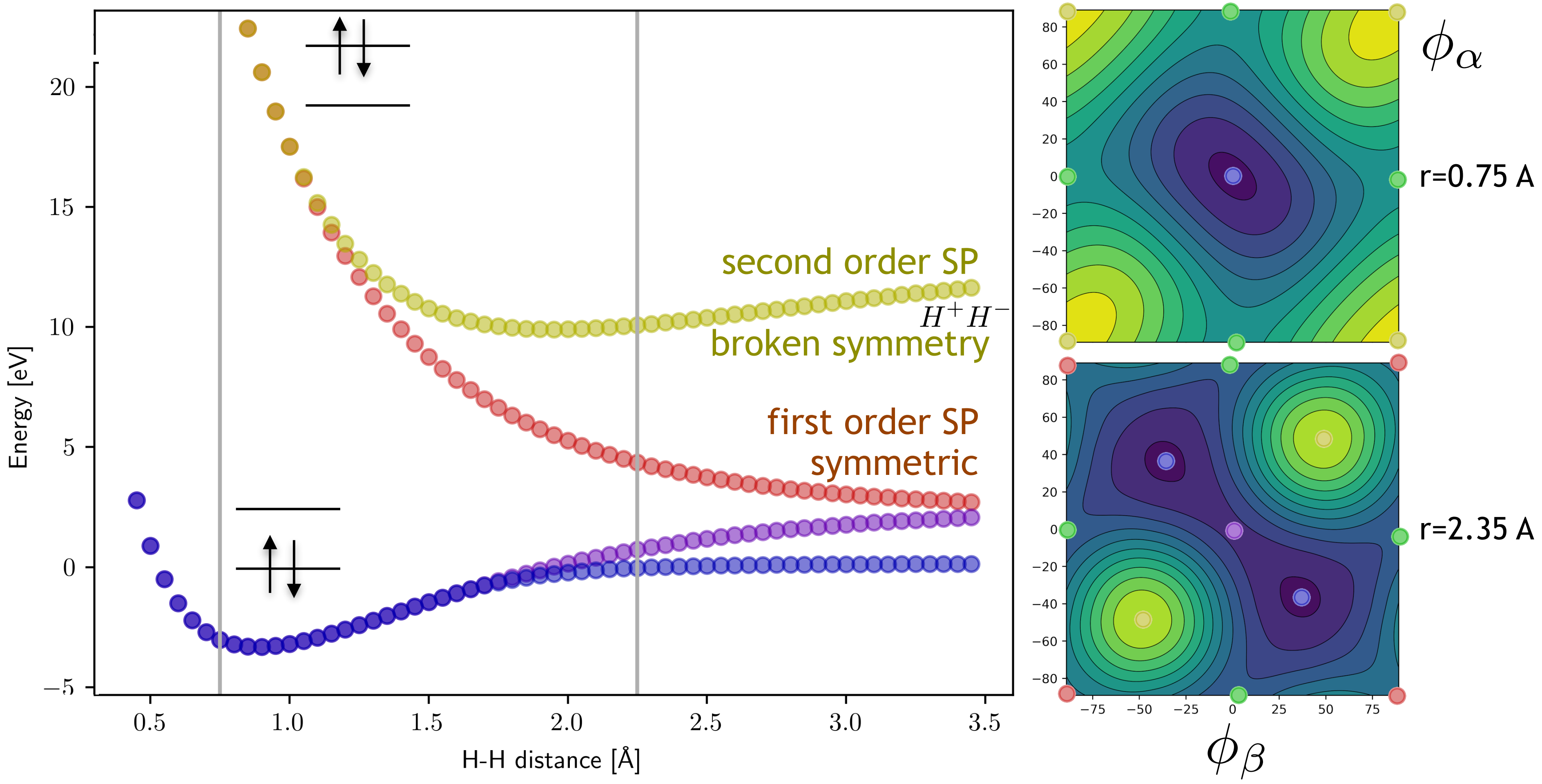
$$\begin{pmatrix}\psi^{1,\alpha}\\ \psi^{0,\alpha}\\ \psi^{1,\beta}\\ \psi^{0,\beta}\end{pmatrix} = \begin{pmatrix}\cos\phi_\alpha & \sin\phi_\alpha & 0 & 0\\ -\sin\phi_\alpha & \cos\phi_\alpha & 0 & 0\\ 0 & 0 & \cos\phi_\beta & \sin\phi_\beta\\ 0 & 0 & -\sin\phi_\beta & \cos\phi_\beta\end{pmatrix}\begin{pmatrix}\sigma_g^\alpha(r)\\ \sigma_u^\alpha(r)\\ \sigma_g^\beta(r)\\ \sigma_u^\beta(r)\end{pmatrix}$$

[11]

Energy curve for the second excited state

A second order saddle point (here maximum) at, for example, (90, 90) corresponds to a double excitation.

When r > 1.0 Å, a *higher energy* broken symmetry solution exists.



To follow the broken symmetry solution for the second excited state, need to target the 2nd order saddle point (not the lower energy solution)

Calculations with density functionals

Can the Kohn-Sham equations be used to calculate excited electronic states?

Can Kohn-Sham functionals, developed for ground state calculations, give accurate estimates of excited electronic states?

By converging on a saddle point on the electronic energy surface,

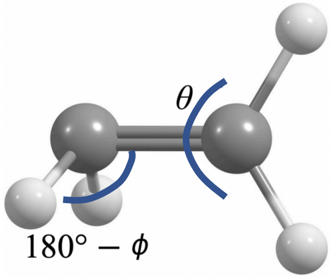
- a solution to the Kohn-Sham equations is found that corresponds to higher energy than the ground state,
- the orbitals are optimised for the *excited* electronic state.
- equivalent to solving the full TD-DFT equations for the exact functional.

Application 1: Rotation and pyramidalization in the V state of ethylene

Conical intersection between ground state, N, and excited singlet state, V, in ethylene

θ: double bond torsion

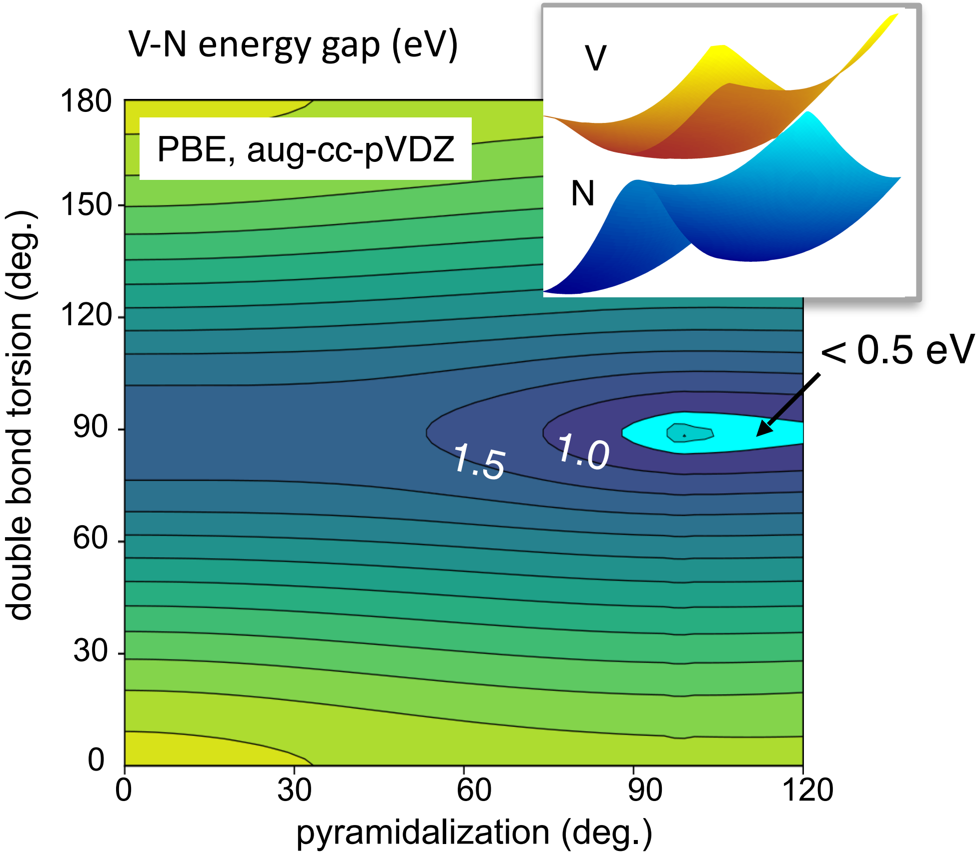
ϕ: pyramidalization



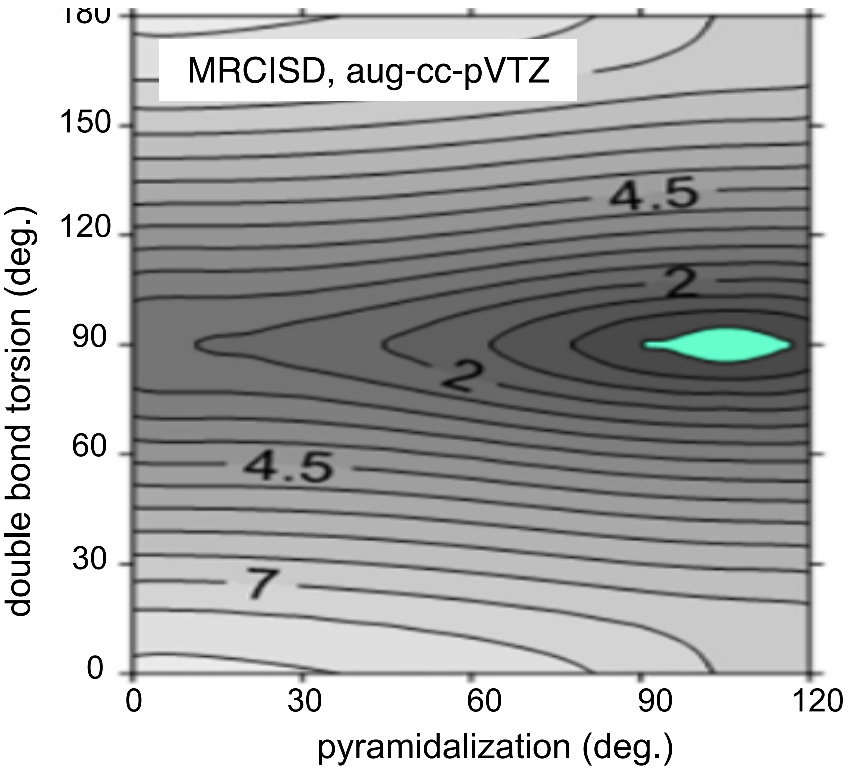
V state is open shell singlet,
so need to carry out spin purification

$$E_{\mathrm{V}} = 2E(|x\bar{y}\rangle) - E(|xy\rangle)$$

Yorick L. A. Schmerwitz



Schmerwitz, Ivanov, Jónsson, Jónsson, Levi, *JPC-L* (2022)



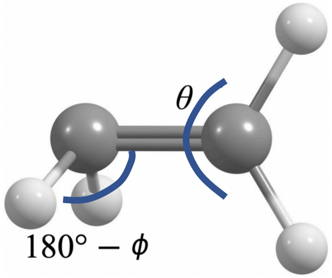
Barbatti & Crespo-Otero, *Top Curr Chem* **368**, 415 (2016)

Application 1: Rotation and pyramidalization in the V state of ethylene

Conical intersection in ethylene

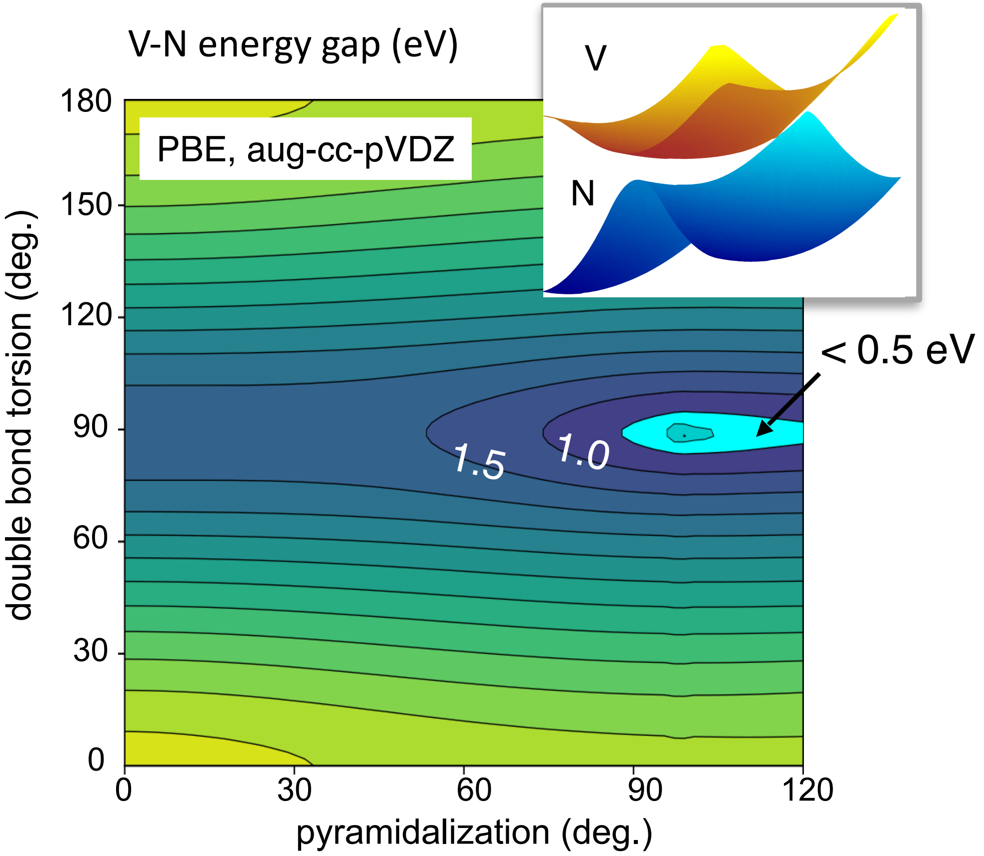
θ: double bond torsion

ϕ: pyramidalization



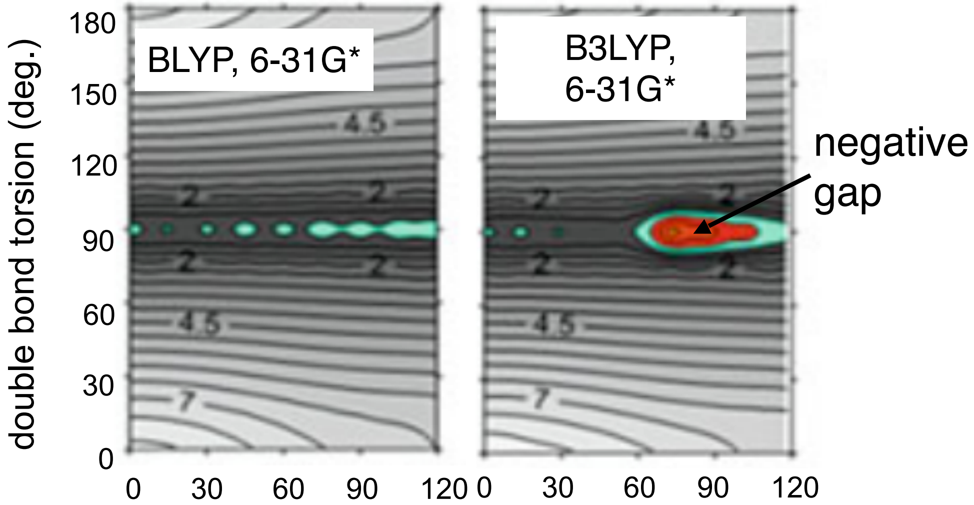
spin purification $E_{\mathrm{V}} = 2E(|x\bar{y}\rangle) - E(|xy\rangle)$

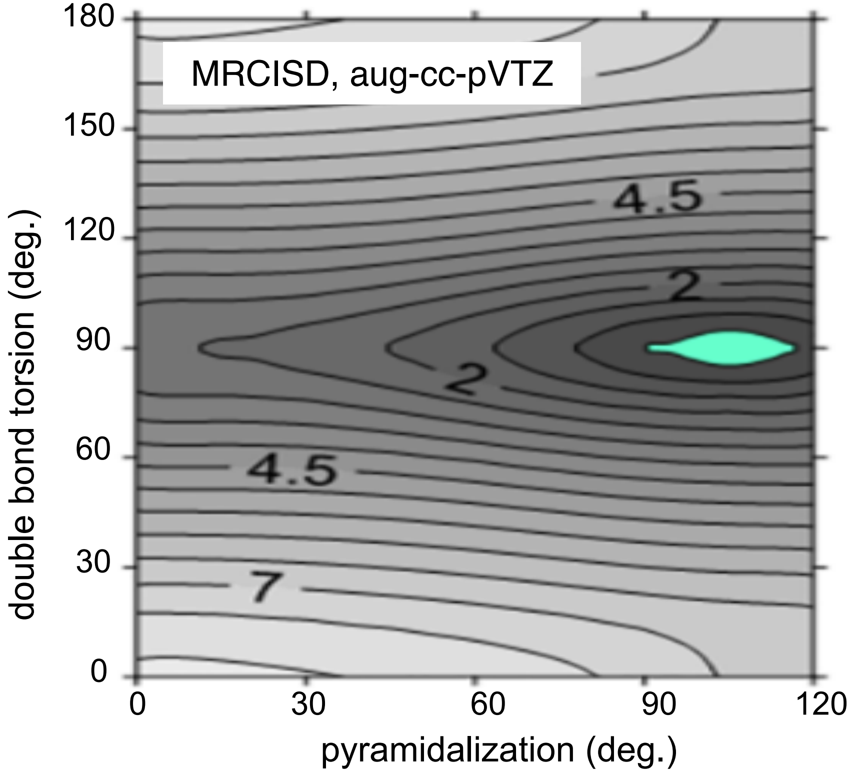
V-N energy gap (eV)



Schmerwitz, Ivanov, Jónsson, Jónsson, Levi, *JPC-L* (2022)

Linear-response TDDFT



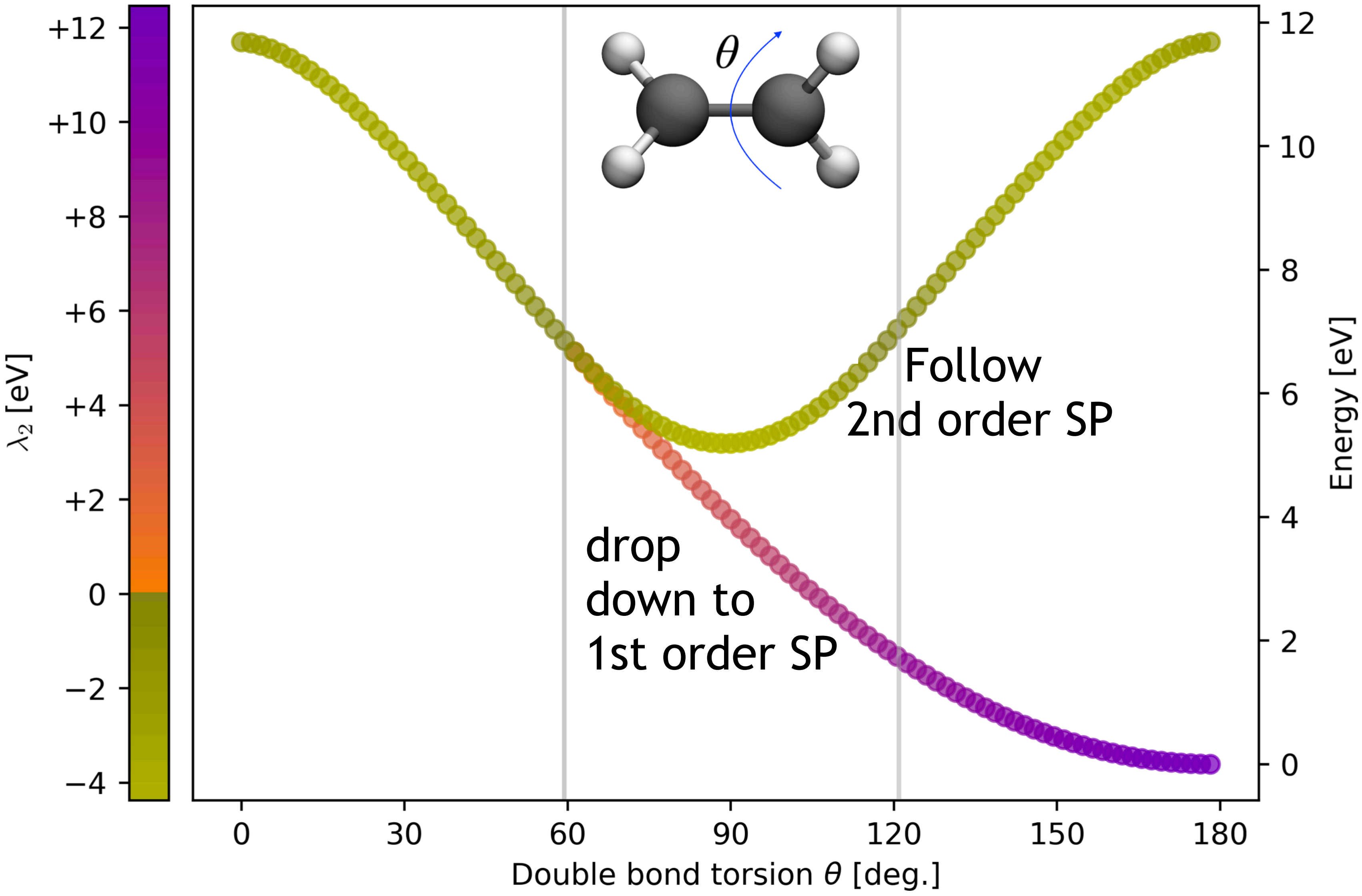


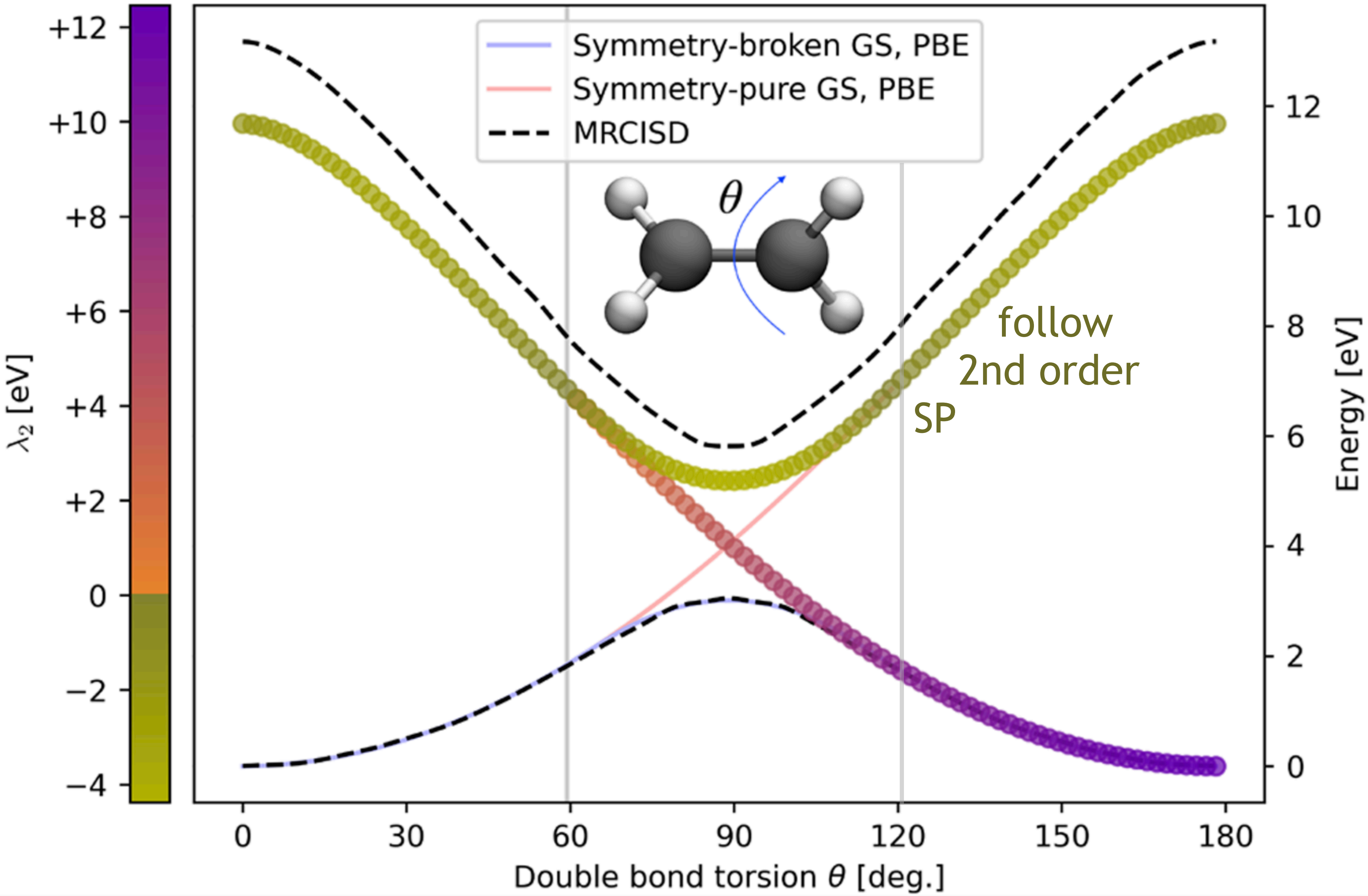
Barbatti & Crespo-Otero, *Top Curr Chem* **368**, 415 (2016)

Application 1: Rotation of the double-bond in the Z state of ethylene

Second excited singlet state, Z

By consistently converging on the second order saddle point on the energy surface, a broken symmetry solution is followed when the torsion angle is larger than ca. 60 deg.

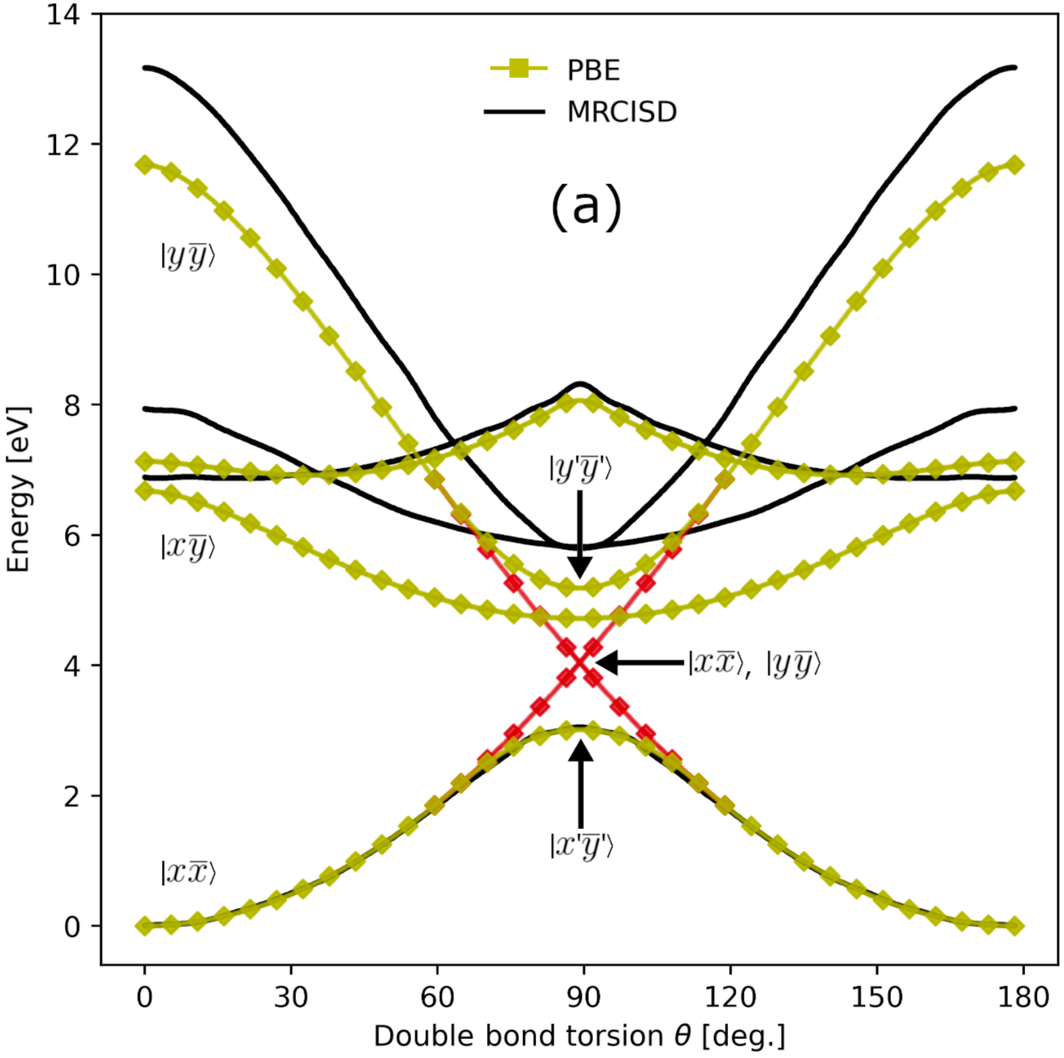




An avoided crossing can be reproduced nicely when the excited state is consistently found by converging on a second order saddle point.

MRCISD calculations from: Barbatti, M.; Paier, J.; Lischka, H. *J. Chem. Phys.* 2004.

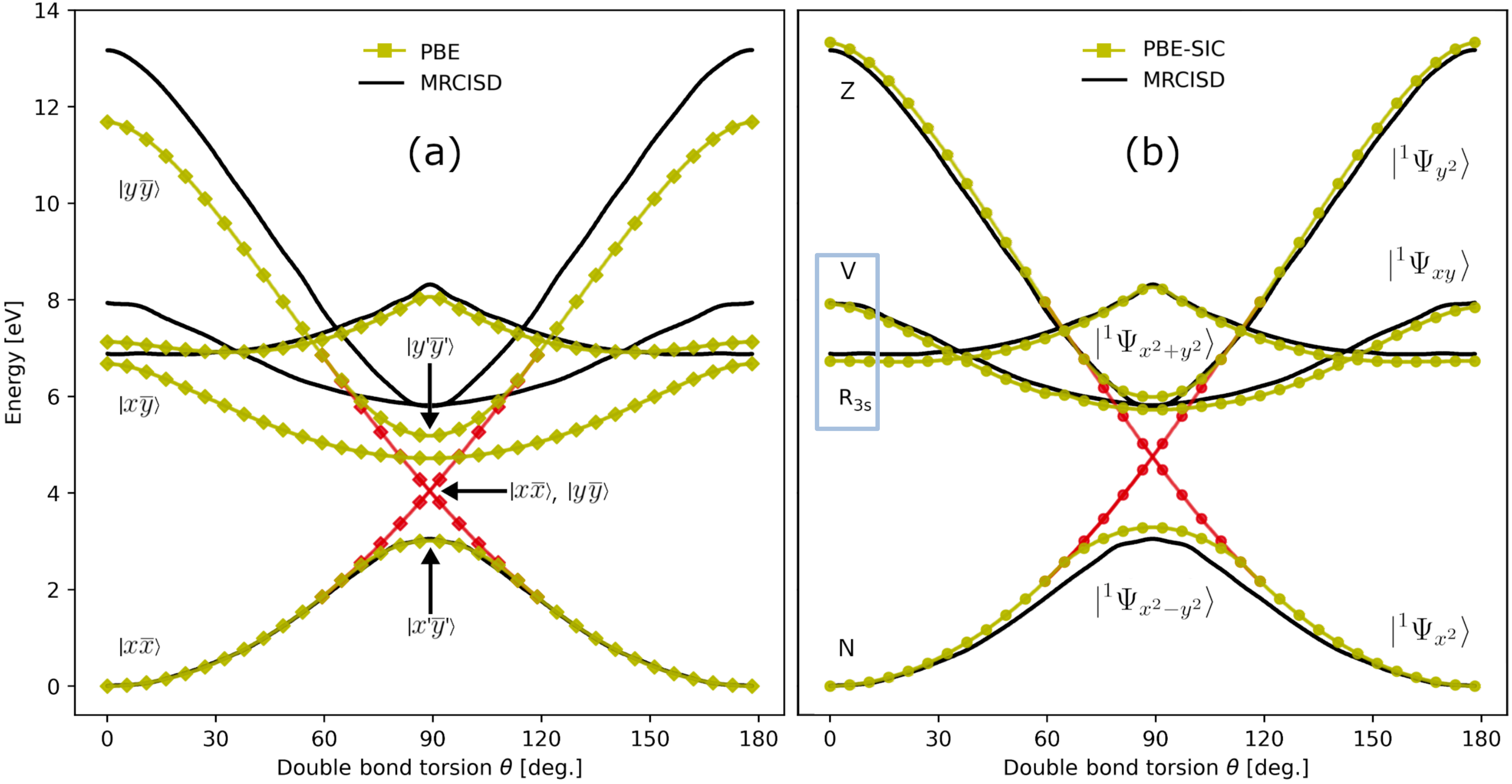
use PBE functional



MRCISD calculations from: Barbatti, M.; Paier, J.; Lischka, H. *J. Chem. Phys.* 2004.

Schmerwitz, Ivanov, Jónsson, Jónsson, Levi, *JPC-L* (2022) use PBE functional

use self-interaction corrected PBE

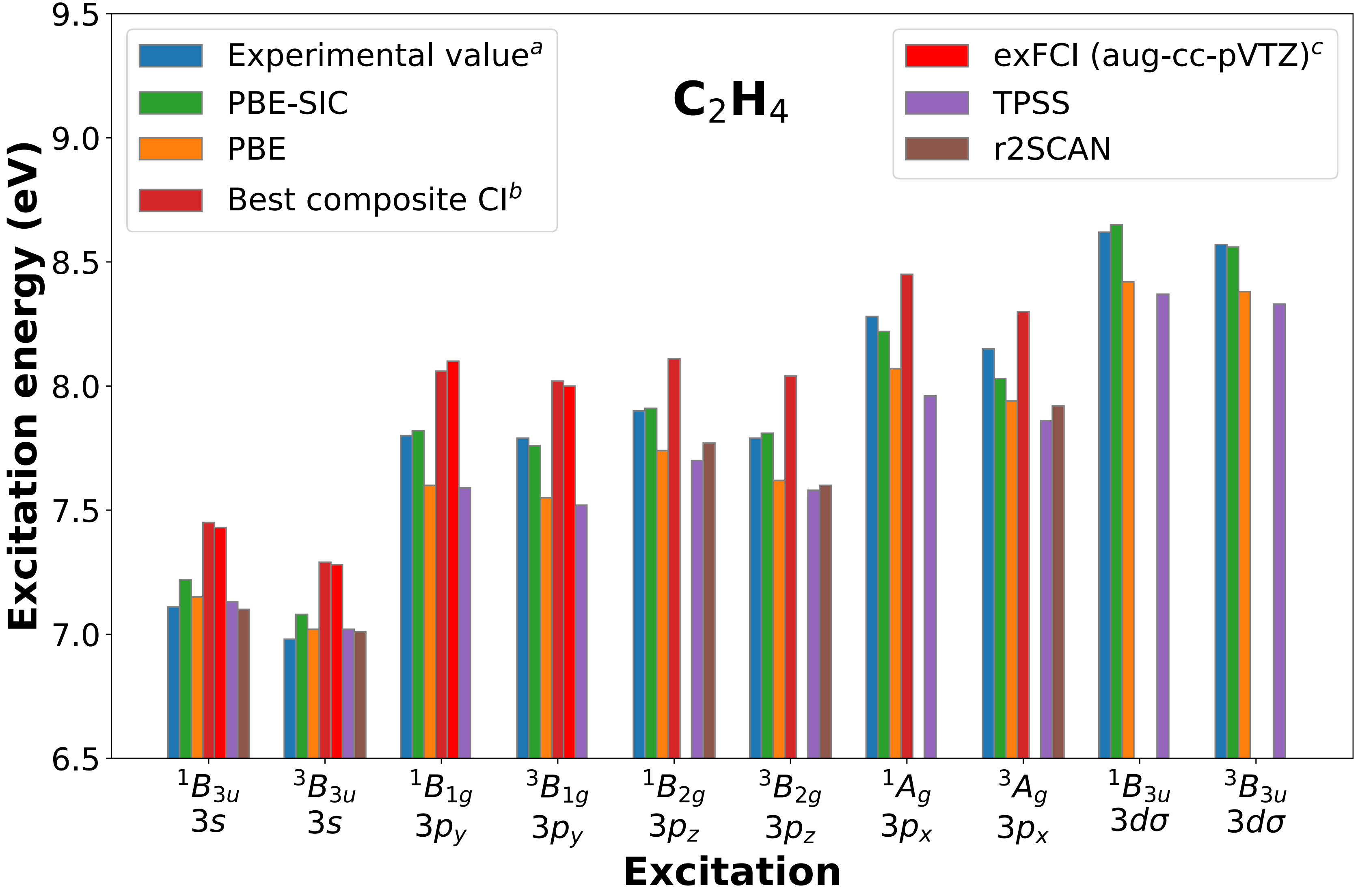


PZ self-interaction correction makes the agreement with MRCISD nearly quantitative!

MRCISD calculations from: Barbatti, M.; Paier, J.; Lischka, H. *J. Chem. Phys.* 2004.

Schmerwitz, Ivanov, Jónsson, Jónsson, Levi, *JPC-L* (2022)

Rydberg excited states of ethylene



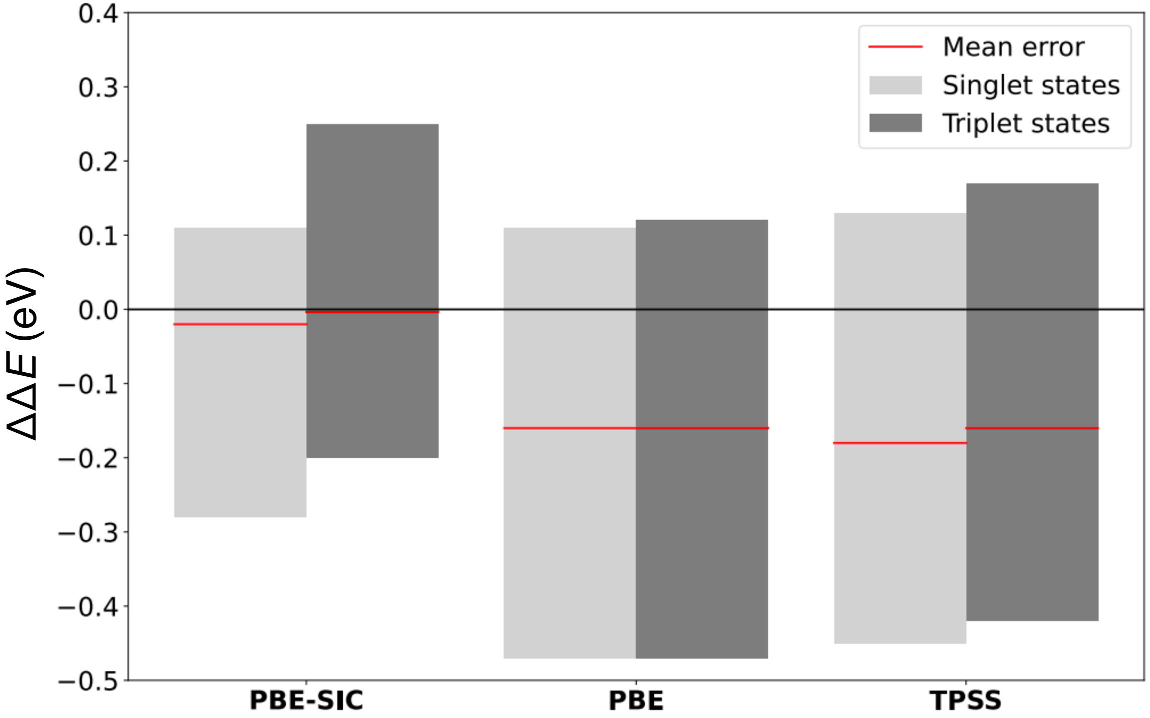
a. Melvin B. Robin. Higher excited states of polyatomic molecules. Vol. 3. Academic Press, Inc. 1985.

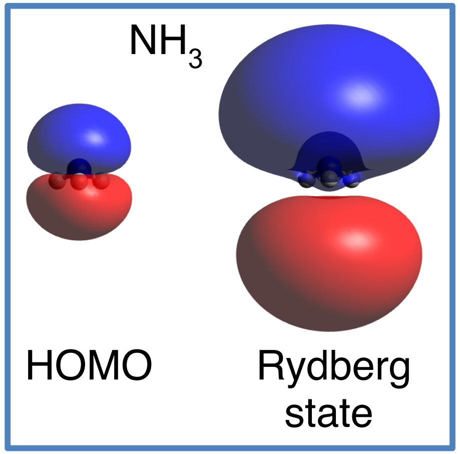
b. D. Feller, K. A. Peterson and E. R. Davidson, “A systematic approach to vertically excited states of ethylene using configuration interaction and coupled cluster techniques”, *JCP* (2014).
Use correlation consistent basis set sequence cc-pVnZ, (n = D, T, Q, 5) extended with carbon spd (VDZ), spdf (VTZ), spdfg (VQZ), and spdfgh (V5Z) diffuse functions.

Side note: Summary of calculations of Rydberg excited states of molecules

Over **30** singlet and triplet Rydberg excitations of $H_2C{=}CH_2$,$H_2C{=}O$, NH_3 and H_2O calculated using a real space grid basis with projector augmented-wave (PAW) approach.

Alec E. Sigurðarson



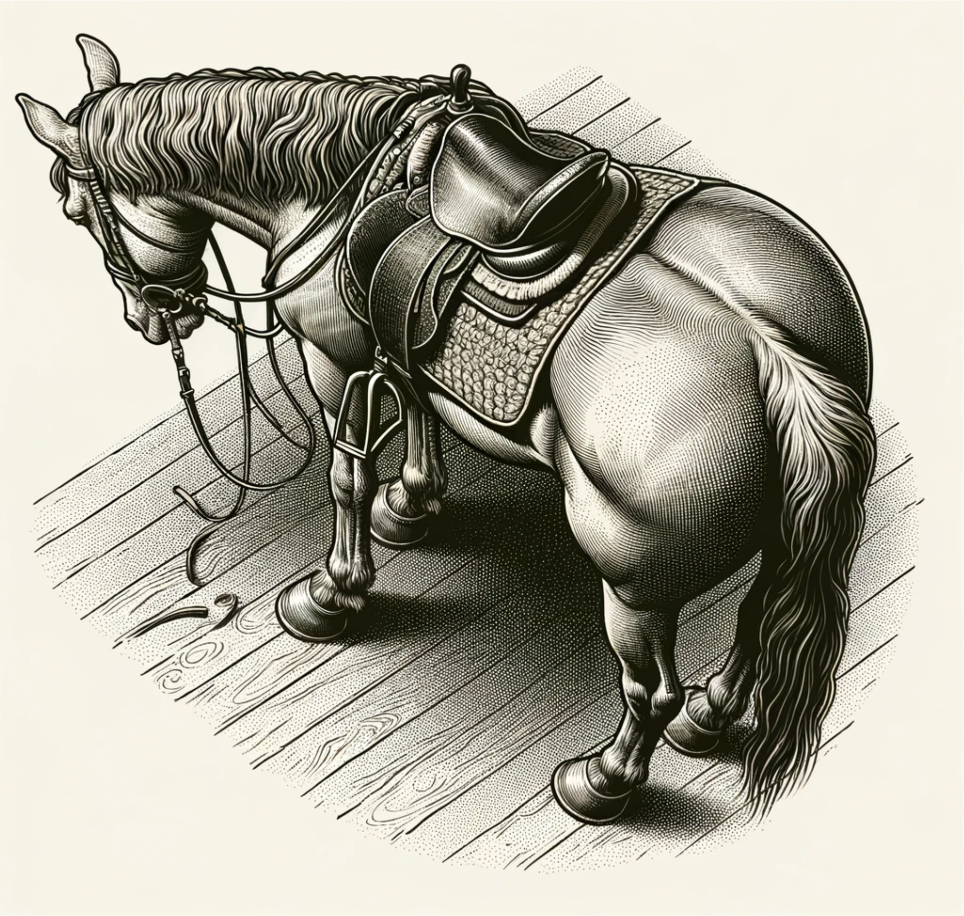


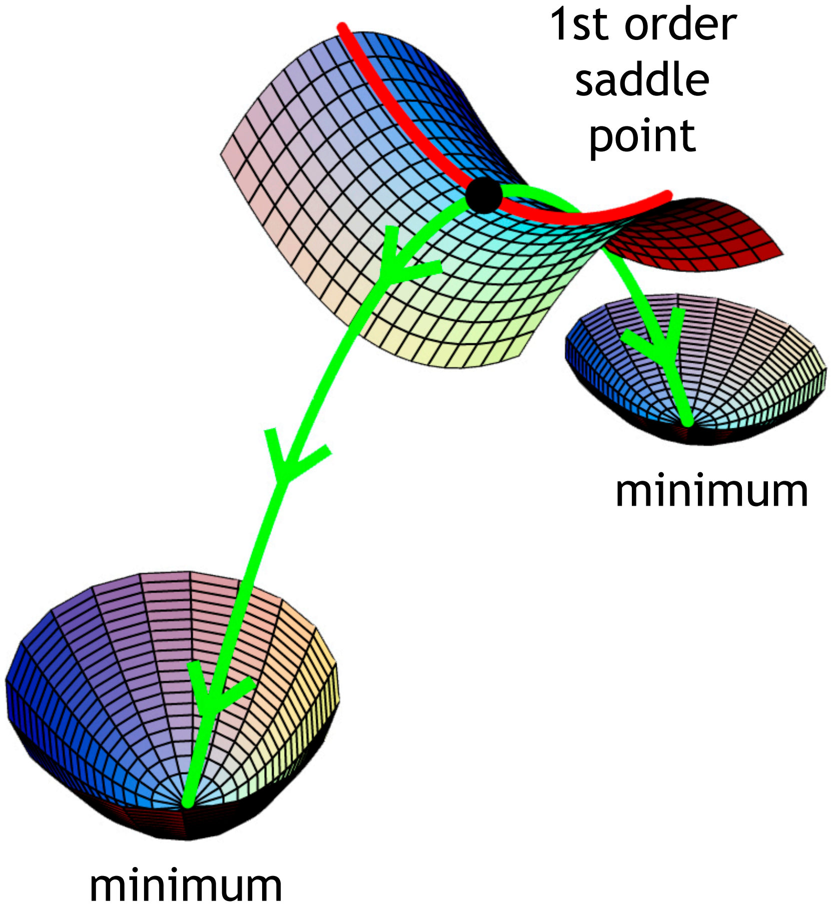
$\Delta\Delta E = \Delta E - \Delta E(\mathrm{exp})$ (Error on the excitation energy with respect to experimental estimates)

PBE-SIC: orbital-by-orbital Perdew-Zunger self-interaction correction applied to PBE.

A. E. Sigurðarson, Y.L.A. Schmerwitz, D.K.V. Tveiten, G. Levi and H Jónsson *J. Chem. Phys.* **159**, 214109 (2023)

Saddle point



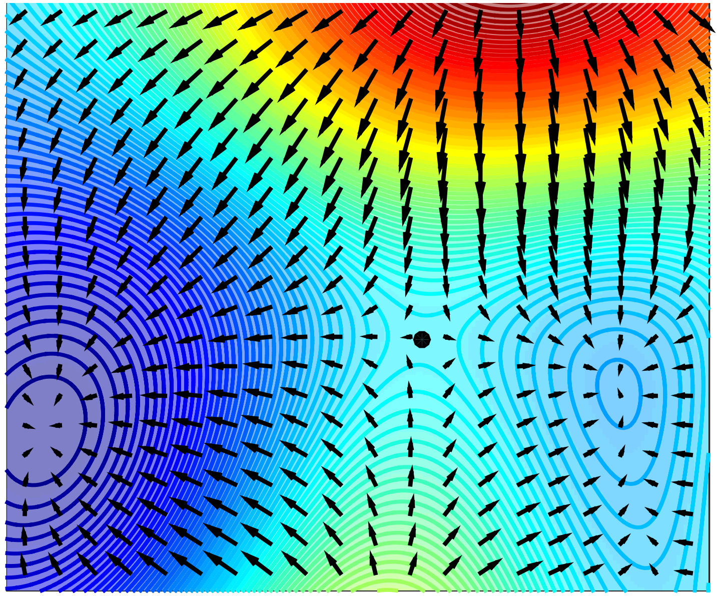


At a 1st order saddle point, the gradient is zero and the Hessian (matrix of second derivatives) has one and only one negative eigenvalue.

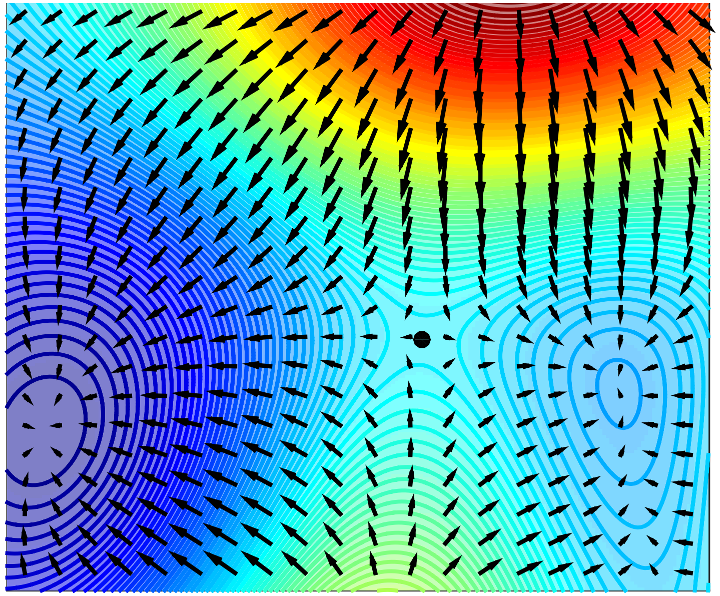
At an *n*-th order saddle point, the Hessian has *n* negative eigenvalues.

Methodology:
Simple method for converging on a first order saddle point

The negative gradient,$-g$, around a first order saddle point



Methodology:
Simple method for converging on a first order saddle point

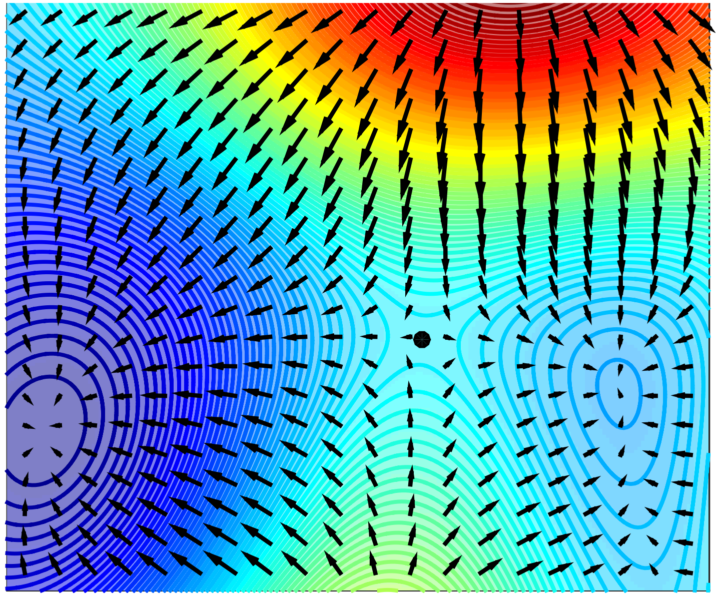


The negative gradient,-g, around a first order saddle point

Find the eigenvector corresponding to the lowest eigenvalue of the Hessian, v_1, the so-called “minimum mode”.

Methodology:
Simple method for converging on a first order saddle point

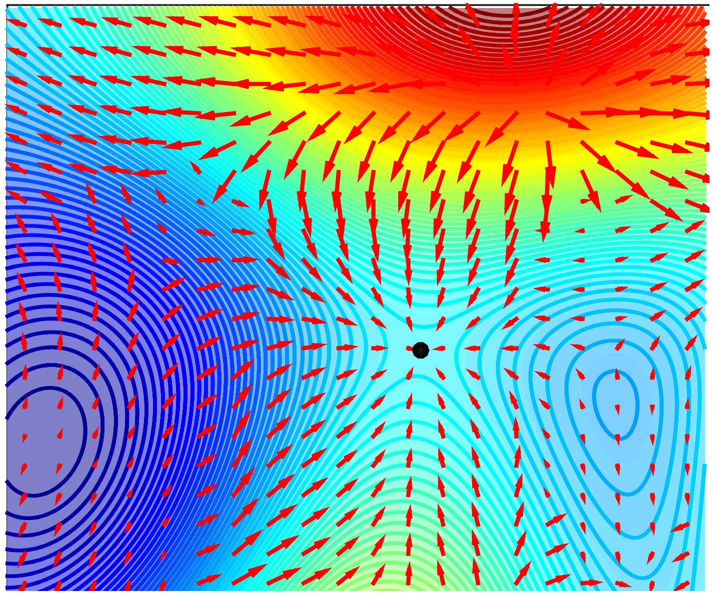
The negative gradient, -g, around a first order saddle point



Find the eigenvector corresponding to the lowest eigenvalue of the Hessian, v_1, the so-called "minimum mode".

Invert that component of the gradient

$$g^{mod} = g - 2(v_1 \cdot g)v_1$$



the transformed negative gradient, -g_{mod}, corresponds to a minimum

This projection locally transforms a first order saddle point to a minimum

[22c]

Minimum mode following (MMF) method

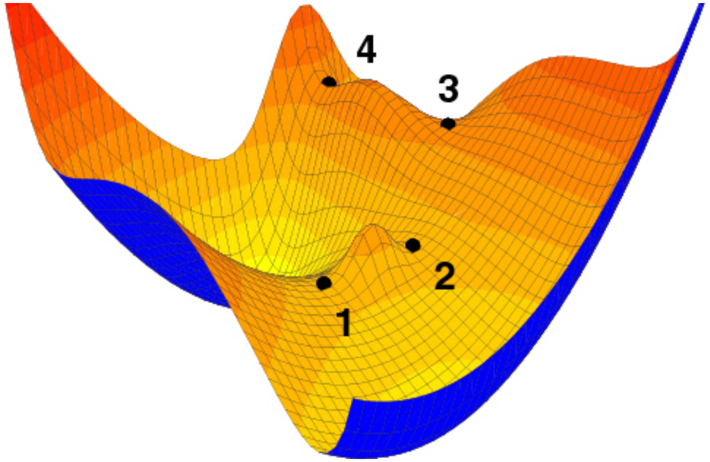
Minimum mode found using Davidson algorithm, requires only first derivatives, no need to even construct the Hessian matrix.

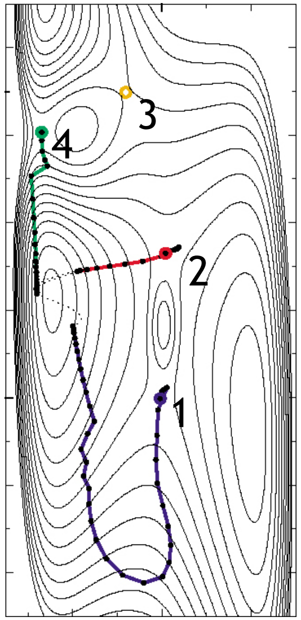
If all eigenvalues are positive, move uphill along the minimum mode, else invert the component of the gradient:

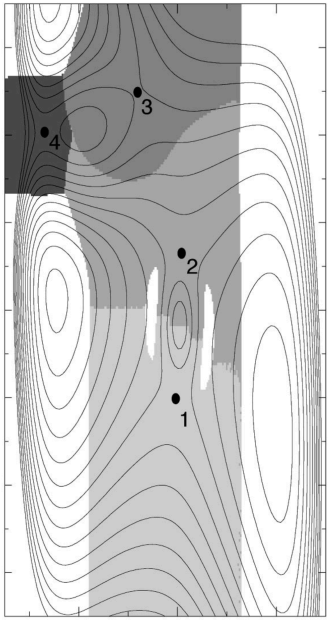
$$
\begin{aligned}
g^{mod} &= -(v_1 \cdot g)v_1 && \text{if min eigenvalue > 0} \\
&= g - 2(v_1 \cdot g)v_1 && \text{else}
\end{aligned}
$$

Then, can use any force-based minimisation to converge on the saddle point.

Example







basins of attraction

Generalized mode following method for finding an *n*-th order saddle point

Find the eigenvectors corresponding to the *n* lowest eigenvalues of the electronic Hessian (need more Davidson iterations).

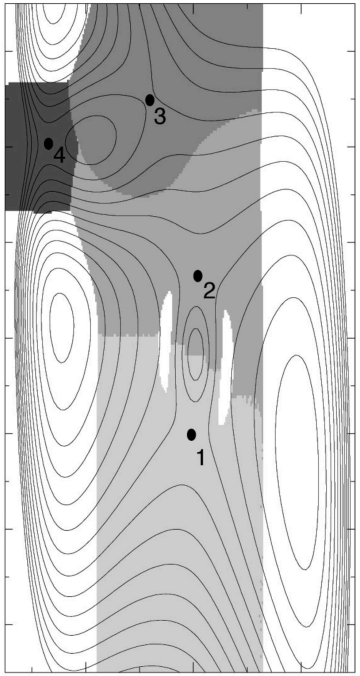
If all *n* eigenvalues are negative, invert the component of the gradient along each of the eigenvectors

$$g^{mod} = g - 2\sum_{i=1}^{n}(v_i \cdot g)v_i \quad if\ \lambda_n < 0$$

Otherwise, replace the gradient with the projection onto the sum of eigenvectors corresponding to the positive eigenvalues in this set

$$g^{mod} = -\sum_{\substack{i=1 \\ \lambda_i \geq 0}}^{n}(v_i \cdot g)v_i \quad if\ \lambda_n \geq 0$$

Thereby move uphill in directions that are not consistent with the basin of attraction to an *n*-th order saddle point.



basins of attraction

Yorick L. A. Schmerwitz, Gianluca Levi and Hannes Jónsson, *JCTC* **19**, 3634 (2023).

Implementation of this methodology

Use direct orbital optimisation (**DO**) to calculate optimal orbitals

$$\boldsymbol{\psi} = e^{\boldsymbol{A}}\boldsymbol{\psi}_0 \qquad \boldsymbol{A} = -\boldsymbol{A}^\dagger$$

'Direct energy minimization based on exponential transformation in density functional calculations of finite and extended systems',
A.V. Ivanov, E.Ö. Jónsson, T. Vegge and H. Jónsson,
Comp. Phys. Commun. 267, 108047 (2021).

Can be applied to non-unitary invariant functionals, such as Perdew-Zunger self-interaction corrected functionals.

A.V. Ivanov, G. Levi, E.Ö. Jónsson and H. Jónsson,
J. Chem. Theory Comput. 17, 5034 (2021).

Implemented in the main branch of the ***GPAW*** code using
real space grid, plane waves or atomic basis sets,
PAW (projector augmented wave),
periodic or fixed boundary conditions.

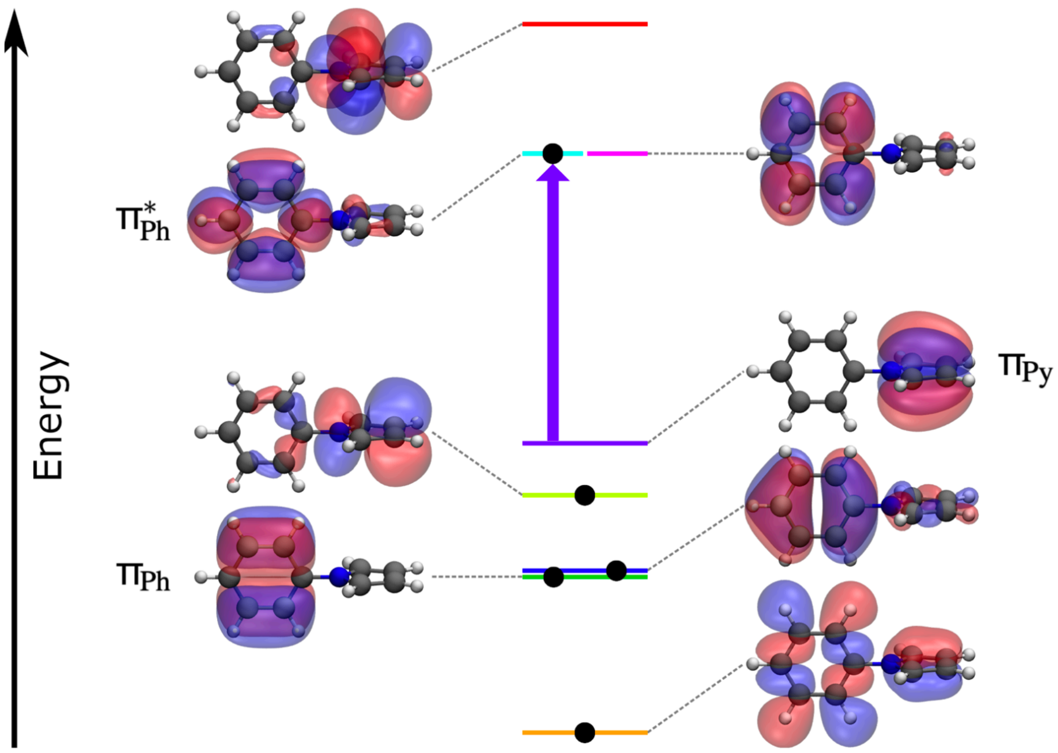
J.J. Mortensen, A.H. Larsen, M. Kuisma, A.V. Ivanov *et al.*,
J. Chem. Phys. 160, 092503 (2024).

Also implemented in the ***ORCA*** code for calculations of molecules, now the default time-independent excited state method.

Application 2: Charge transfer in N-phenylpyrrole

Transfer of electron density from the pyrrole group to the phenyl group,
appears to be a HOMO to LUMO excitation based on the ground state orbitals

Initial guess, 1st order SP



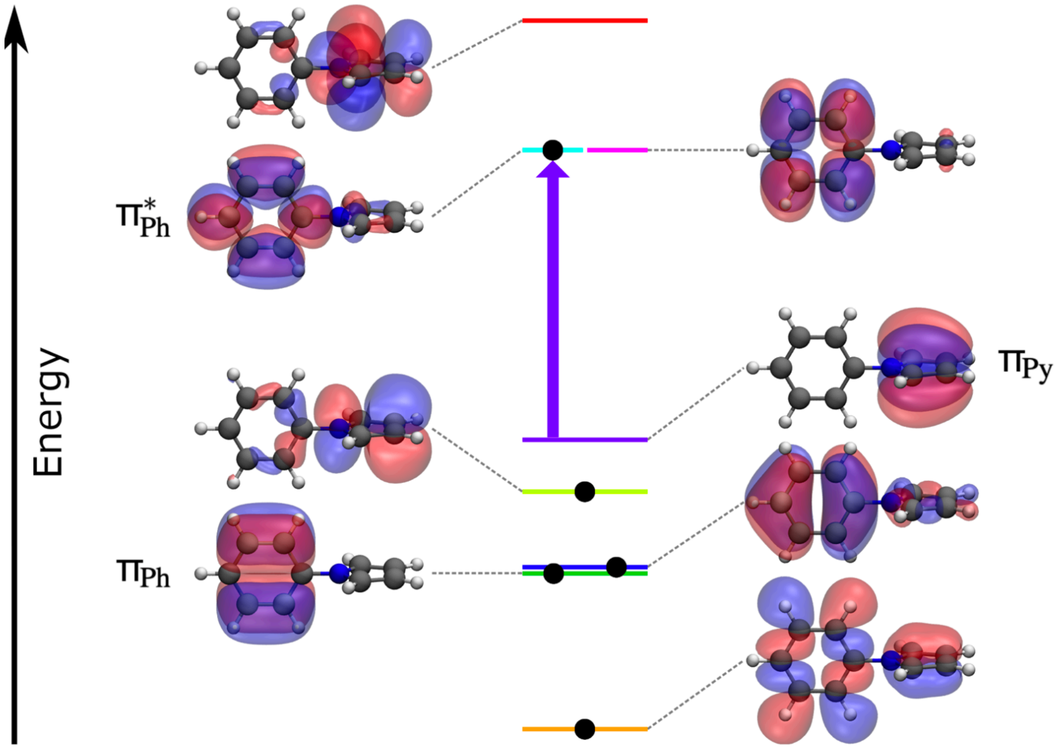
ground state orbitals

After optimising all but the electron/hole orbitals,
by minimizing the energy to allow for response
to the excitation,
the Hessian has 7 negative eigenvalues,
one larger than -1 eV.

Application 2: Charge transfer in N-phenylpyrrole

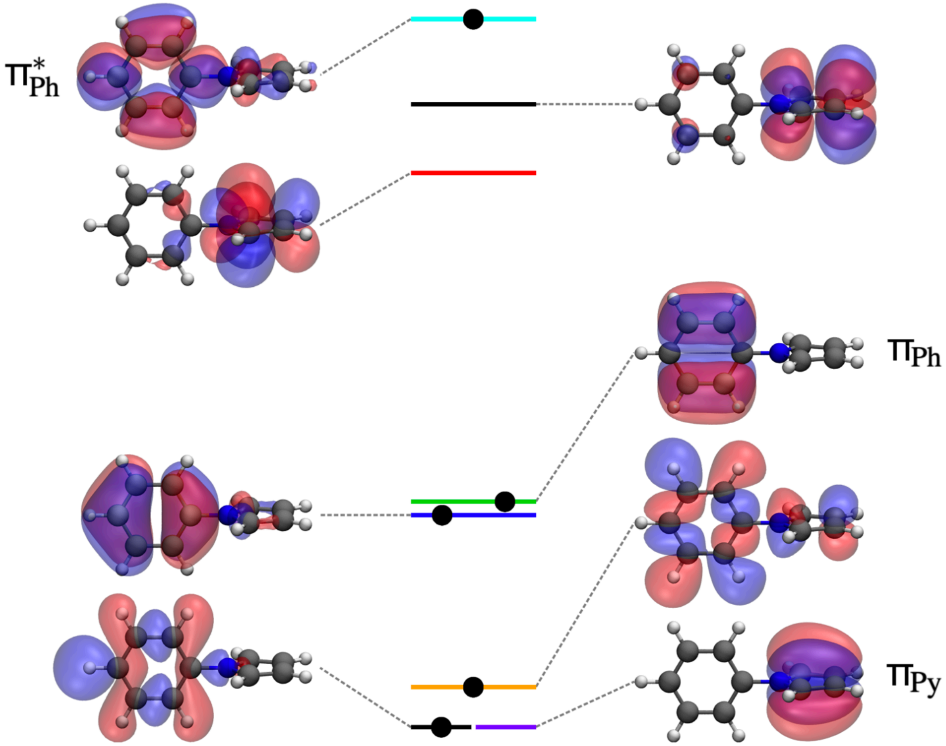
Appears to be a HOMO to LUMO excitation based on the ground state orbitals, but turns out to be a 6th order saddle point after convergence.

Initial guess 1st order SP



ground state orbitals

Turns out to be 6th order SP



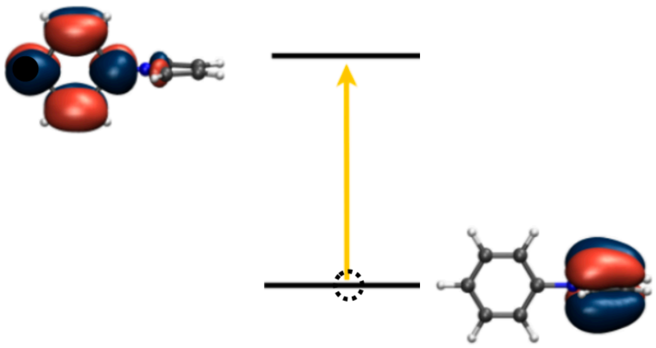
excited state orbitals

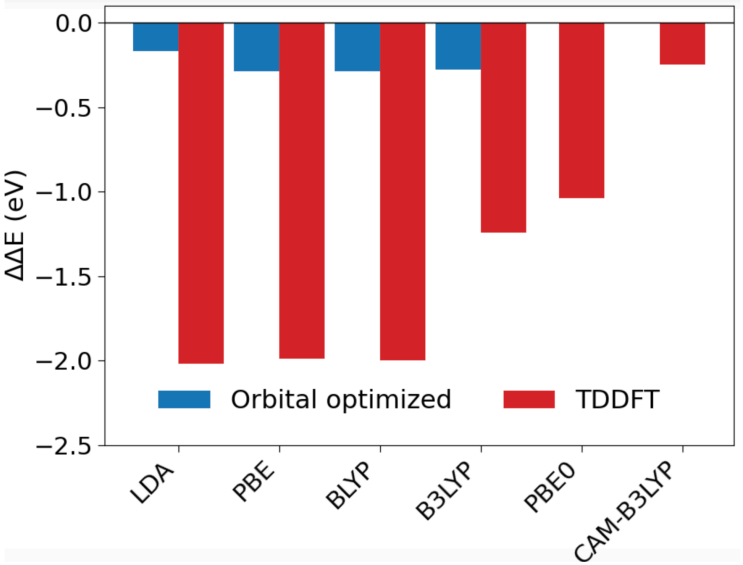
Guess 7 +/- 1 order saddle point, i.e. try also 6th order and 8th order

Large changes in the orbitals, not HOMO → LUMO anymore

Y.L.A. Schmerwitz, G. Levi and H. Jónsson, *J. Chem. Theory Comput*. 19, 3634 (2023).

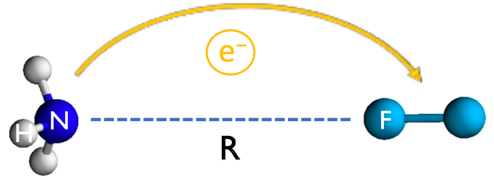
The calculated excitation energy is 5.39 eV using PBE,
while theoretical best estimate is 5.58 eV as obtained by Loos *et al*. in Toulouse
“Reference Energies for Intramolecular Charge-Transfer Excitations” *J. Chem. Theory Comput.* 17, 3666 (2021).



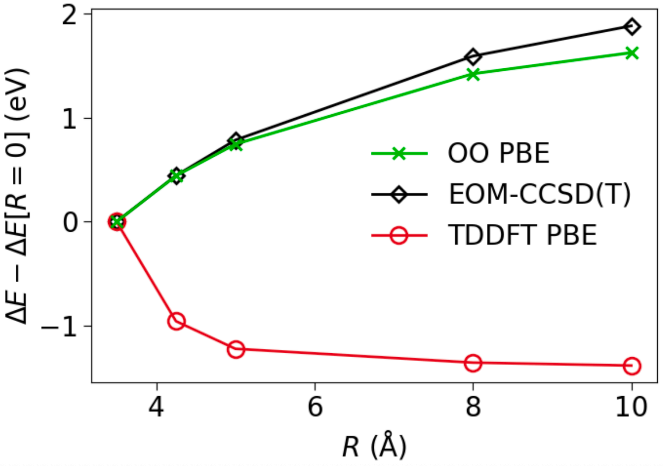


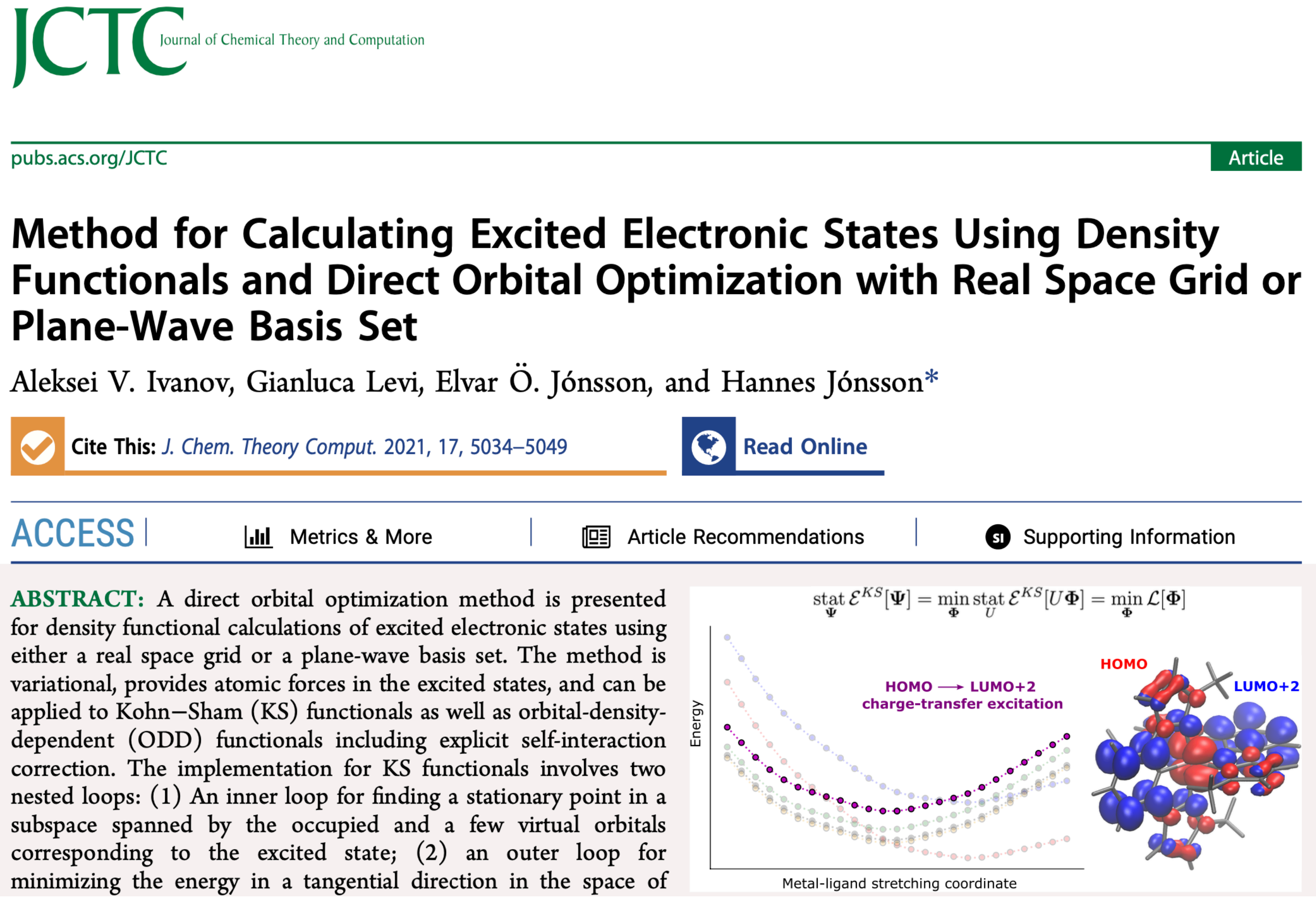
Gianluca Levi

In a benchmark study of 27 excitations in 15 organic molecules the time-INdependent orbital optimised calculations give on average results with half as large error than LR-TDDFT when long range charge transfer occurs [E. Selenius *et al*., *JCTC* 20, 3809 (2024)].



Intermolecular charge transfer excitation





JCTC Journal of Chemical Theory and Computation

pubs.acs.org/JCTC Article

Method for Calculating Excited Electronic States Using Density Functionals and Direct Orbital Optimization with Real Space Grid or Plane-Wave Basis Set

Aleksei V. Ivanov, Gianluca Levi, Elvar Ö. Jónsson, and Hannes Jónsson*

Cite This: *J. Chem. Theory Comput.* 2021, 17, 5034–5049 Read Online

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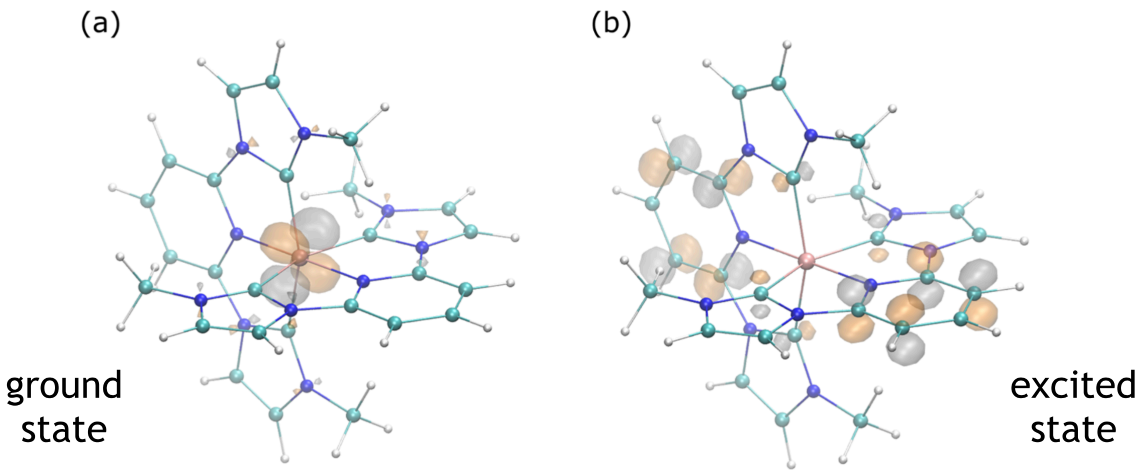
ABSTRACT: A direct orbital optimization method is presented for density functional calculations of excited electronic states using either a real space grid or a plane-wave basis set. The method is variational, provides atomic forces in the excited states, and can be applied to Kohn–Sham (KS) functionals as well as orbital-density-dependent (ODD) functionals including explicit self-interaction correction. The implementation for KS functionals involves two nested loops: (1) An inner loop for finding a stationary point in a subspace spanned by the occupied and a few virtual orbitals corresponding to the excited state; (2) an outer loop for minimizing the energy in a tangential direction in the space of

$$\underset{\Psi}{\mathrm{stat}}\,\mathcal{E}^{KS}[\Psi] = \min_{\Phi}\,\underset{U}{\mathrm{stat}}\,\mathcal{E}^{KS}[U\Phi] = \min_{\Phi}\mathcal{L}[\Phi]$$

Aleksei Ivanov

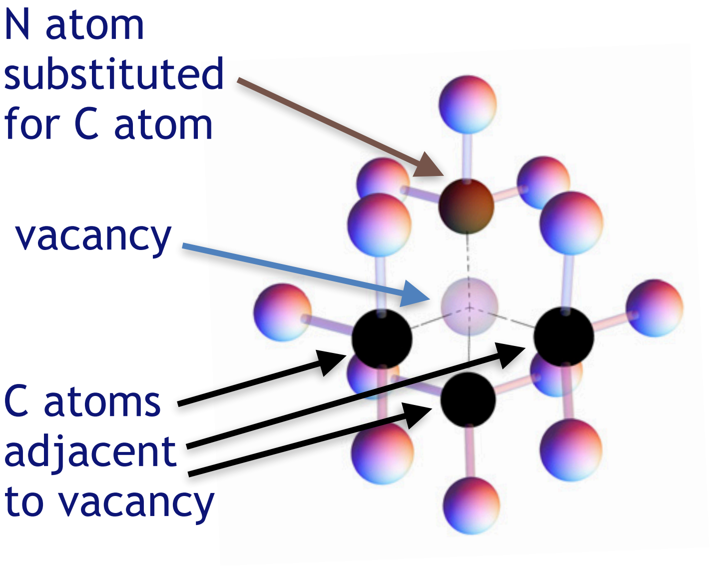


[28]

Application 3: Negatively charged nitrogen-vacancy defect in diamond

Well suited for many applications,
e.g. quantum information processing.

An optical cycle can be used to prepare a *pure spin* state
even at room temperature.

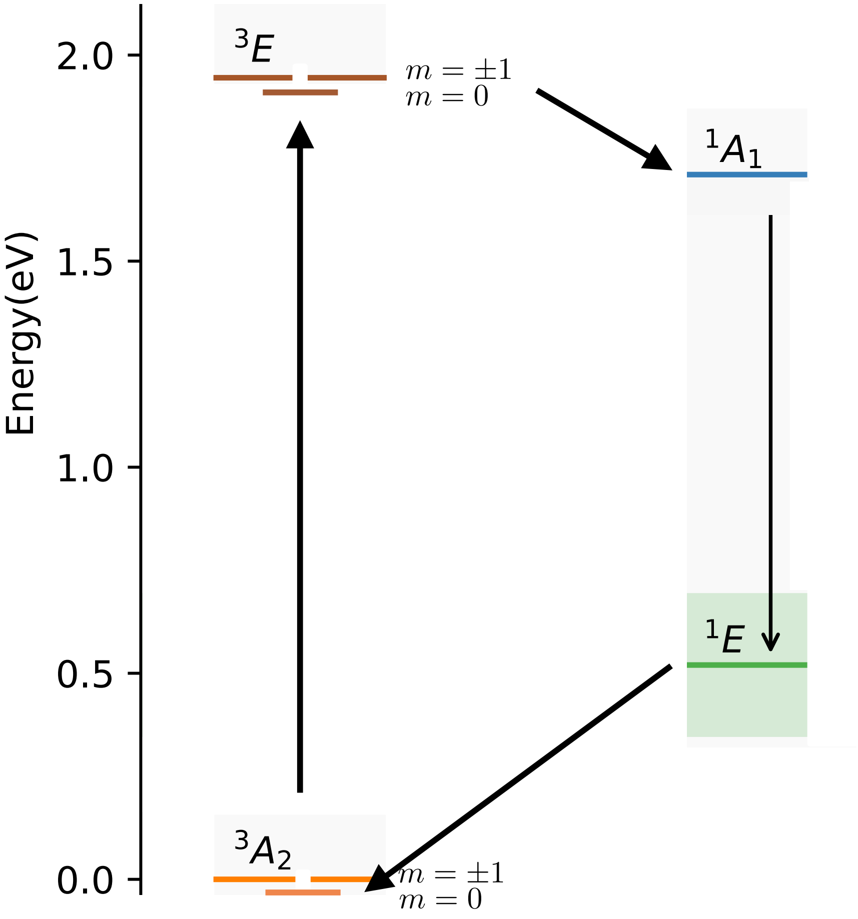


N atom substituted for C atom

vacancy

C atoms adjacent to vacancy

C_{3V} symmetry



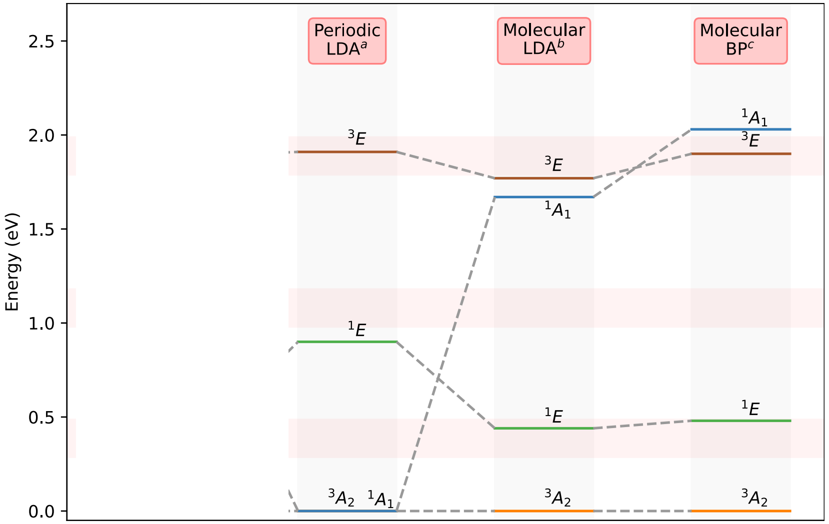
This picture has emerged from various experiments and high level calculations.

Can density functional calculations be useful for such systems?

Negatively charged nitrogen-vacancy defect in diamond

Quote from C. Bhandari, A.L. Wysocki, S.E. Economou, P. Dev, and K. Park, *Multiconfigurational study of the negatively charged nitrogen-vacancy center in diamond*, Physical Review B, 103, 014115 (2021):

> "Furthermore, DFT could not correctly predict either the ordering or the energy difference between the excited spin-triplet and spin-singlet states of the NV-center defect [28,38,39]. The aforementioned incorrect predictions of DFT highly influence our understanding of ..."



a. A. Gali, M. Fyta, and E. Kaxiras, *Ab initio supercell calculations on nitrogen-vacancy center in diamond: Electronic structure and hyperfine tensors*, Phys. Rev. B **77**, 155206 (2008).

b. P. Delaney, J. C. Greer, and J. A. Larsson, *Spin-polarization mechanisms of the nitrogen-vacancy center in diamond*, Nano Lett. **10**, 610 (2010).

c. J. P. Goss, R. Jones, S. J. Breuer, P. R. Briddon, and S. Öberg, *The Twelve-Line 1.682 ev Luminescence Center in Diamond and the Vacancy-Silicon Complex*, Phys. Rev. Lett. **77**, 3041 (1996).

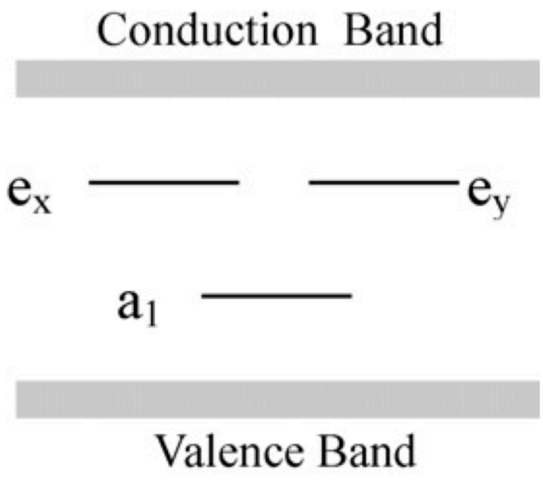
Negatively charged nitrogen-vacancy defect in diamond

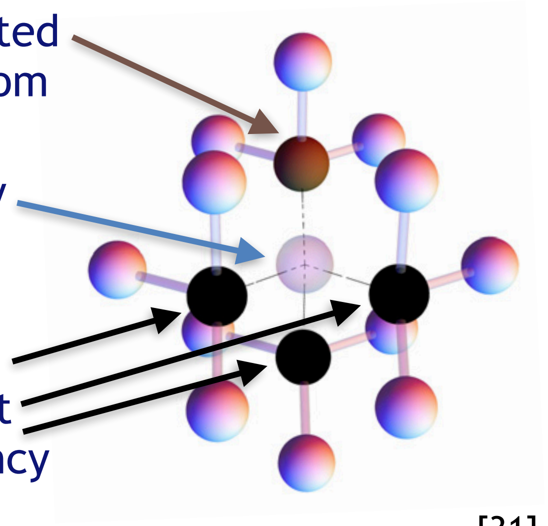
Calculations:

- 511 atoms in the supercell, (results for 215 atom calcs. are within 5 meV)
- plane wave basis set,
- PAW for inner electrons,
- 600 eV kinetic energy cutoff,
- compare results obtained with LDA, PBE, TPSS and r2SCAN functionals.

Calculated band gap 4.2 eV using PBE,
4.7 eV using r2SCAN
5.4 eV using PBE-SIC/2 and HSE06
Experimental value 5.5 eV.

3 orbitals within the band gap are occupied by 4 electrons near the three C atoms by the vacancy





N atom substituted for C atom

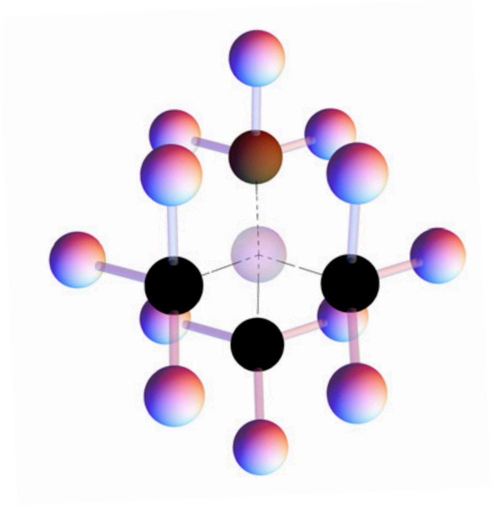
vacancy

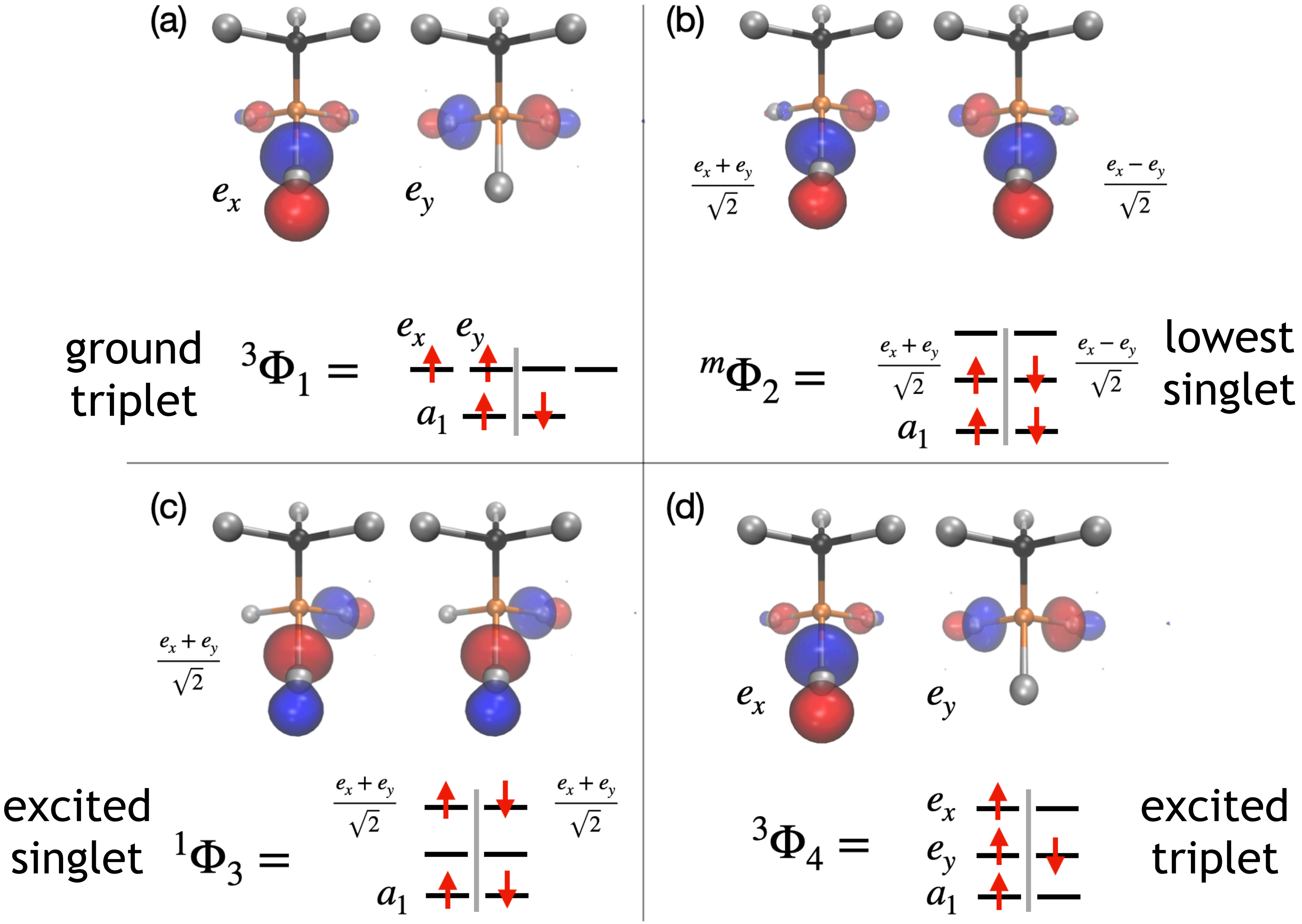
C atoms adjacent to vacancy

[31]

Negatively charged nitrogen-vacancy defect in diamond

A single density functional calculation gives one of the following Slater determinants that place 4 electrons in localized orbitals, within the band gap:

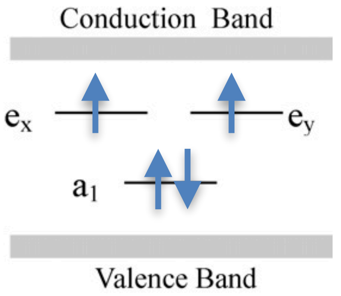




[32]

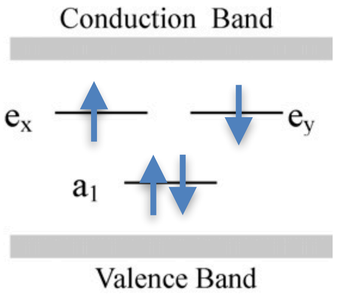
Negatively charged nitrogen-vacancy defect in diamond

Single Slater determinant (SD) calculations give



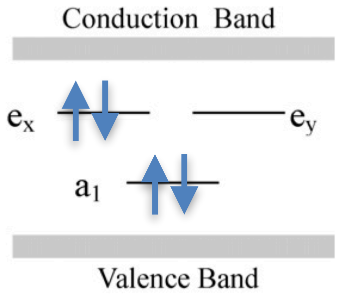
$|e_y e_x\rangle$

triplet ground state



$|e_x \overline{e_y}\rangle$

singlet ground state



$|e_x \overline{e_x}\rangle$

singlet excited state,
second order SP (spin polarized)

Use the C_{3V} symmetry and the character table from group theory to write the SDs for the singlet states in terms of symmetry adapted wave functions, $\Psi\left({}^1E\right)$ and $\Psi\left({}^1A_1\right)$,

$$
\begin{aligned}
{}^m\Phi_2 = |e_-\overline{e_+}\rangle &= \left(|e_x\overline{e_x}\rangle - |e_y\overline{e_y}\rangle\right)/2 + \left(|e_x\overline{e_y}\rangle - |e_y\overline{e_x}\rangle\right)/2 \\
&= \frac{1}{\sqrt{2}}\left(\Psi\left({}^1E\right) + \Psi\left({}^3A_2\right)\right),
\end{aligned}
$$

$$
\begin{aligned}
{}^1\Phi_3 = |e_+\overline{e_+}\rangle &= \left(|e_x\overline{e_x}\rangle + |e_y\overline{e_y}\rangle\right)/2 + \left(|e_x\overline{e_y}\rangle + |e_y\overline{e_x}\rangle\right)/2 \\
&= \frac{1}{\sqrt{2}}\left(\Psi\left({}^1A_1\right) + \Psi\left({}^1E\right)\right),
\end{aligned}
$$

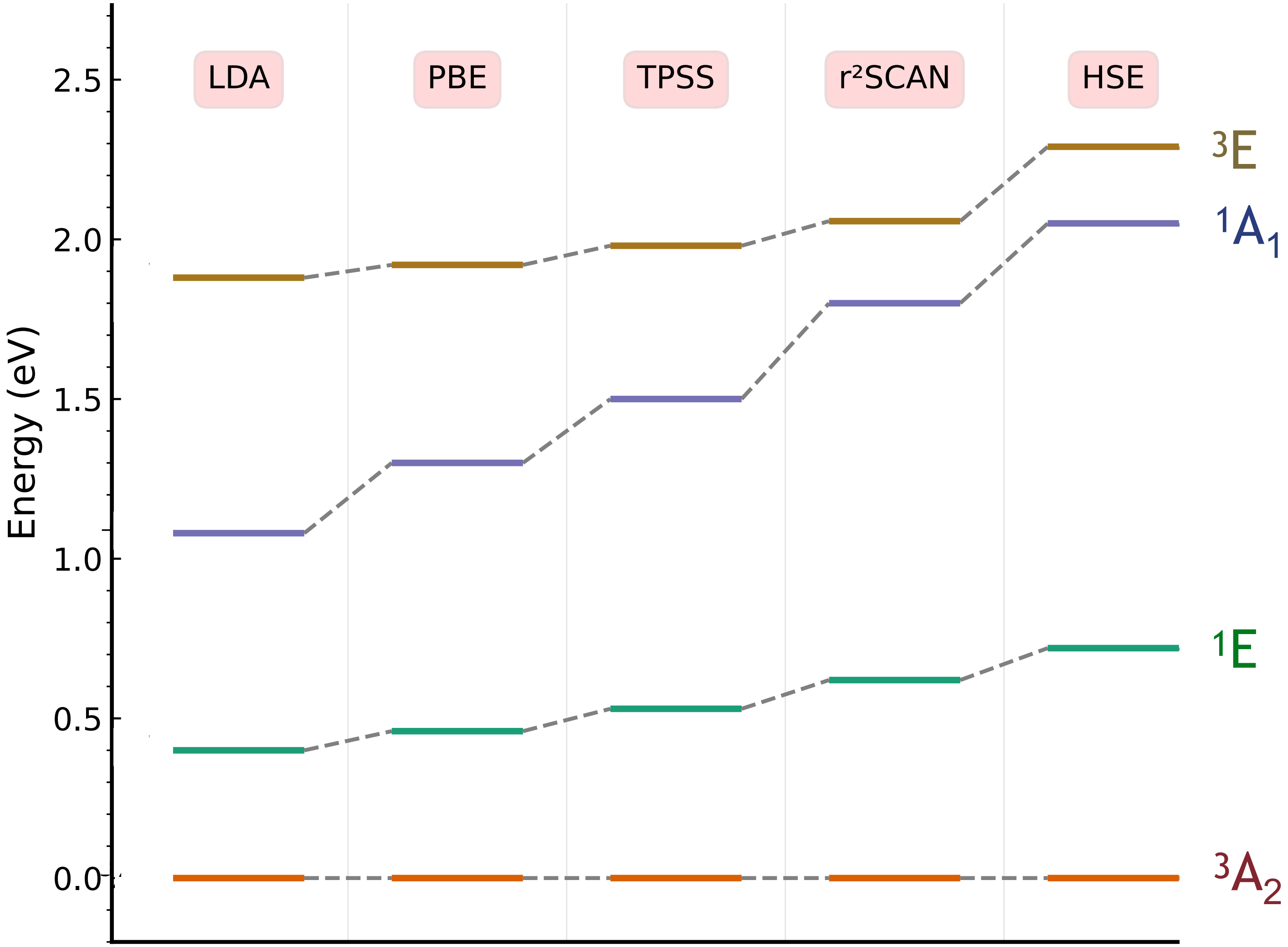
The energy of the states can be obtained from the energy of the single SDs as

$$
\begin{aligned}
\mathcal{E}[{}^1E] &= 2\mathcal{E}[{}^m\Phi_2] - \mathcal{E}[{}^3\Phi_1], \\
\mathcal{E}[{}^1A_1] &= \mathcal{E}[{}^3\Phi_1] + 2(\mathcal{E}[{}^1\Phi_3] - \mathcal{E}[{}^m\Phi_2])
\end{aligned}
$$

[33]

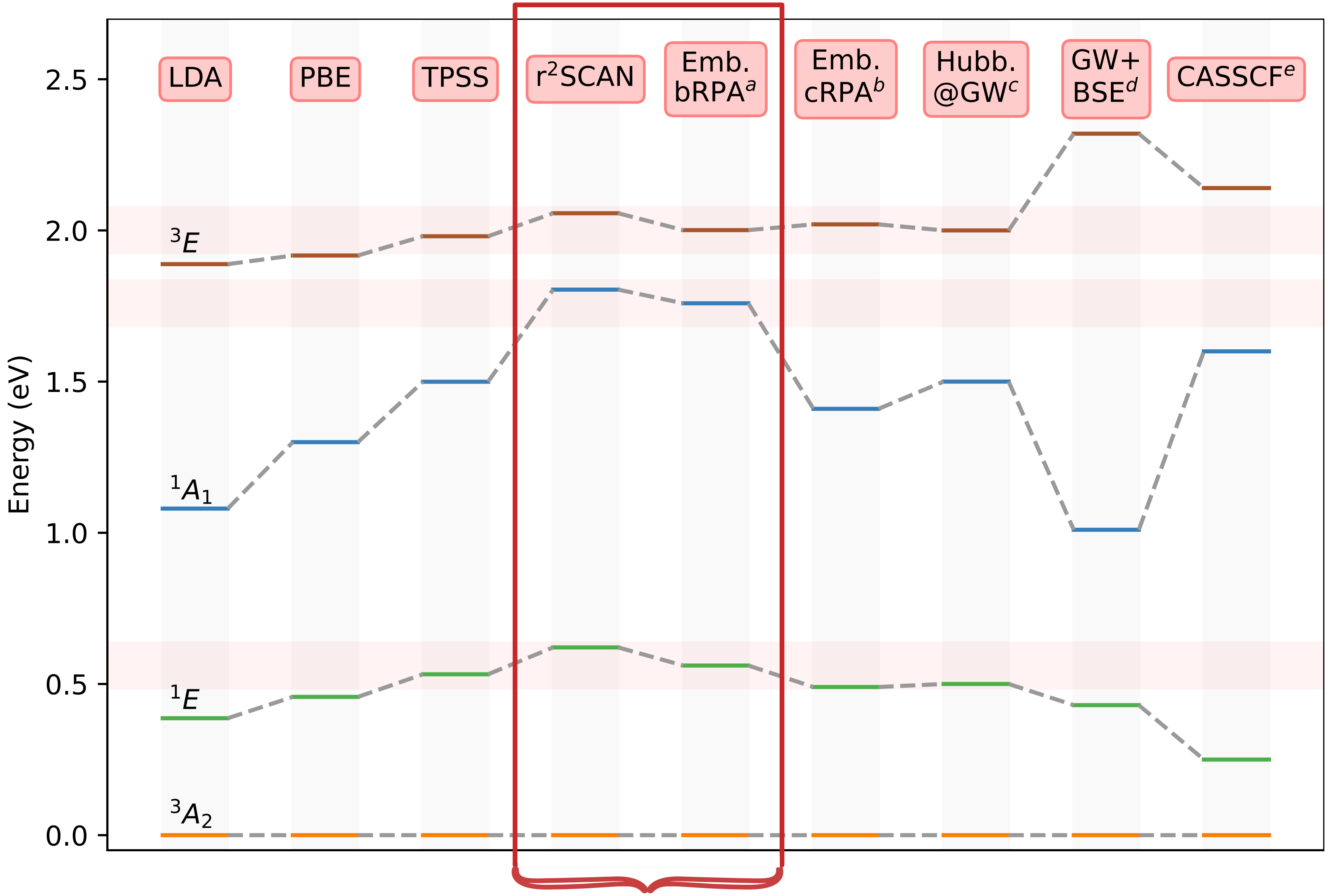
Negatively charged nitrogen-vacancy defect in diamond

Results obtained here with various density functionals



The excited singlet state is especially sensitive to the level of functional used

Negatively charged nitrogen-vacancy defect in diamond



r2SCAN gives similar results as ‘embedded beyond RPA' calculations of
H. Ma, M. Govoni & G. Galli, *npj Computational Materials* **6**, 85 (2020).

Structural relaxation lowers the excited triplet state by 0.24 eV,
in agreement with experimental estimate to within 0.04 eV.

A. Ivanov, Y.L.A. Schmerwitz, G. Levi, H. Jónsson, SciPost Physics **15**, 009 (2023).

[35]

Summary

Methodology:

Saddle point searches can be used to calculate excited electronic states
in a time *in*dependent density functional approach,
variational calculations with orbitals optimised for the excited state.

Generalized mode following **(GMF)**
gives convergence to an *n*-th order saddle point on the energy surface.
Gives robust convergence on excited states, also when symmetry breaks.
Need to follow a saddle point of a given order to stay on a given state.

Applications:

For ethylene, the conical intersection between ground and first excited state involving rotation around the C=C bond and pyramidalization, as well as avoided crossing between ground and second excited state.

Rydberg excited states of molecules.

Charge transfer excitation in n-phenylpyrrole: 1*st* order SP → 6*th* order SP.

Energy levels of negatively charged NV-defect in diamond well reproduced, even multi-configurational singlet excited states.