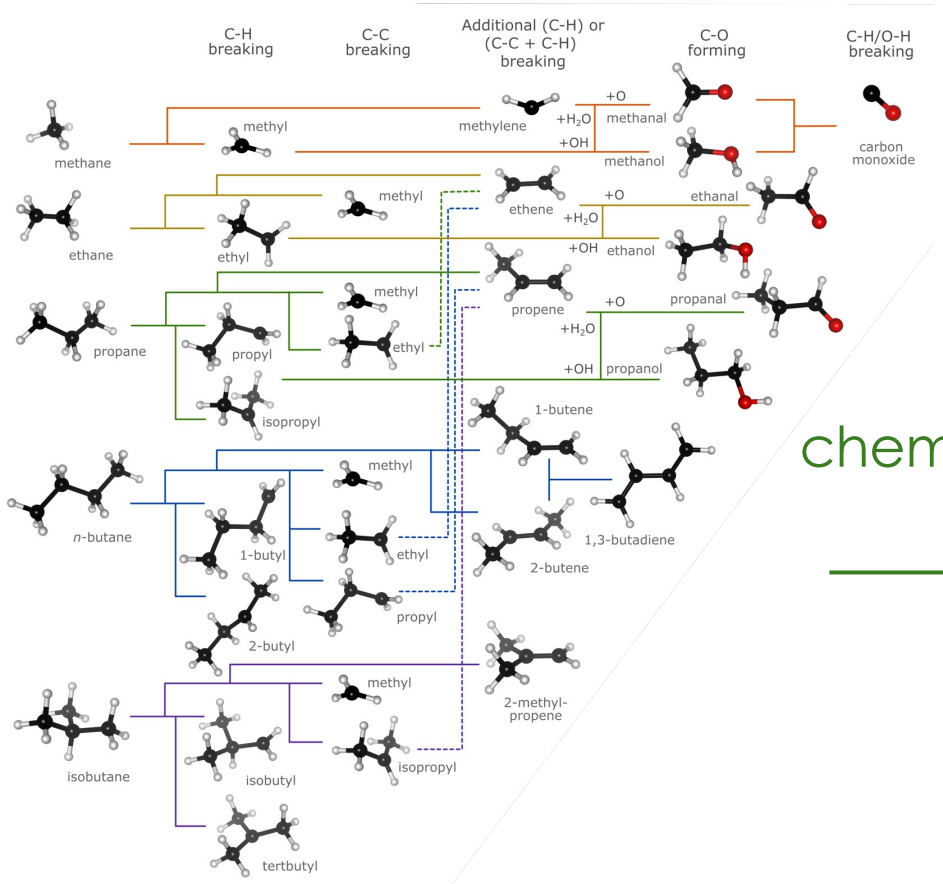


PPPL PRINCETON PLASMA PHYSICS LABORATORY

PRINCETON UNIVERSITY

# Modeling excited-state chemistry and quantum defects via quantum mechanics

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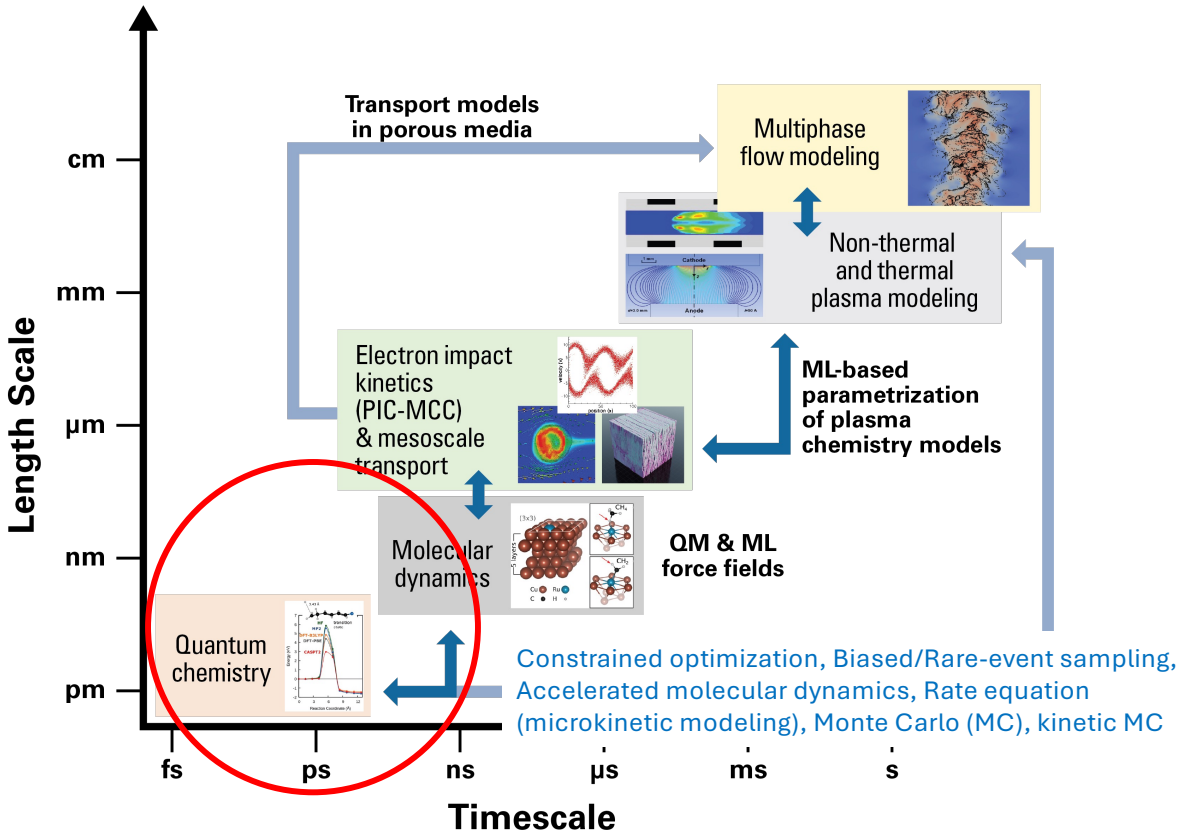
Applied Materials and Sustainability Sciences
Princeton Plasma Physics Laboratory
Princeton University

July 30, 2025

# Temporal and spatial scales of reactions and enabling computational methods




**Multi-level and multi-scale** schemes can facilitate systematic understanding of the elementary processes, from atomic-scale chemistry to continuum physics

Continuum physics-based models for millisecond and micrometer-scale phenomena (longer/larger)

DFT for short MD simulations

DFT-based ML force-fields enable proper sampling of slow/rare events (or even parameterization of continuum models)

Correlated wavefunction theory and Density functional theory (DFT) for elementary chemical reactions in gas/plasma and surfaces

# Hierarchy of Quantum mechanical (QM) methods

**Solve Schrodinger Equation:** $H\psi(\boldsymbol{r},\boldsymbol{R}) = E\psi(\boldsymbol{r},\boldsymbol{R})$

**Approximations** introduced - mostly physically guided/inspired

Ideally, **errors are tractable**, and method is **systematically improvable** (*fortuitous error cancelation occurs*)

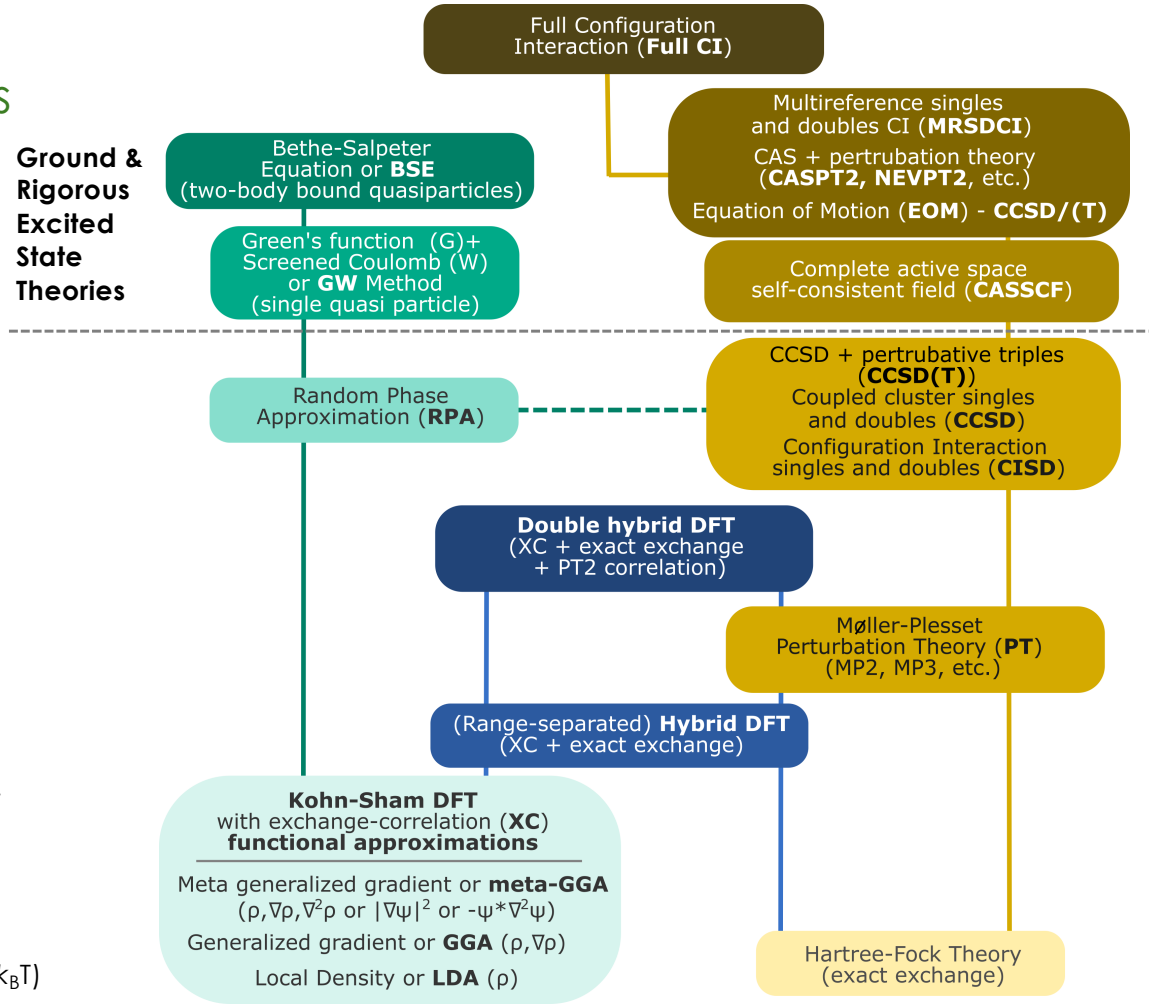
**Not all methods are created equal**

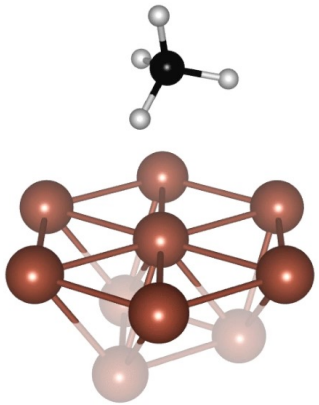
Electron and nuclear degrees of freedom separated (Born-Oppenheimer – "fixed" nuclei); nuclei generally treated classically

In QM, one starts with classical interactions of electrons and nuclei (Coulomb – charged particles) and electrons' kinetic energy (a wave)

Systematically add quantum "world" effects – electron exchange (Pauli exclusion principle) and correlation (correlated electron motion reducing Coulomb repulsion, electron as wave)

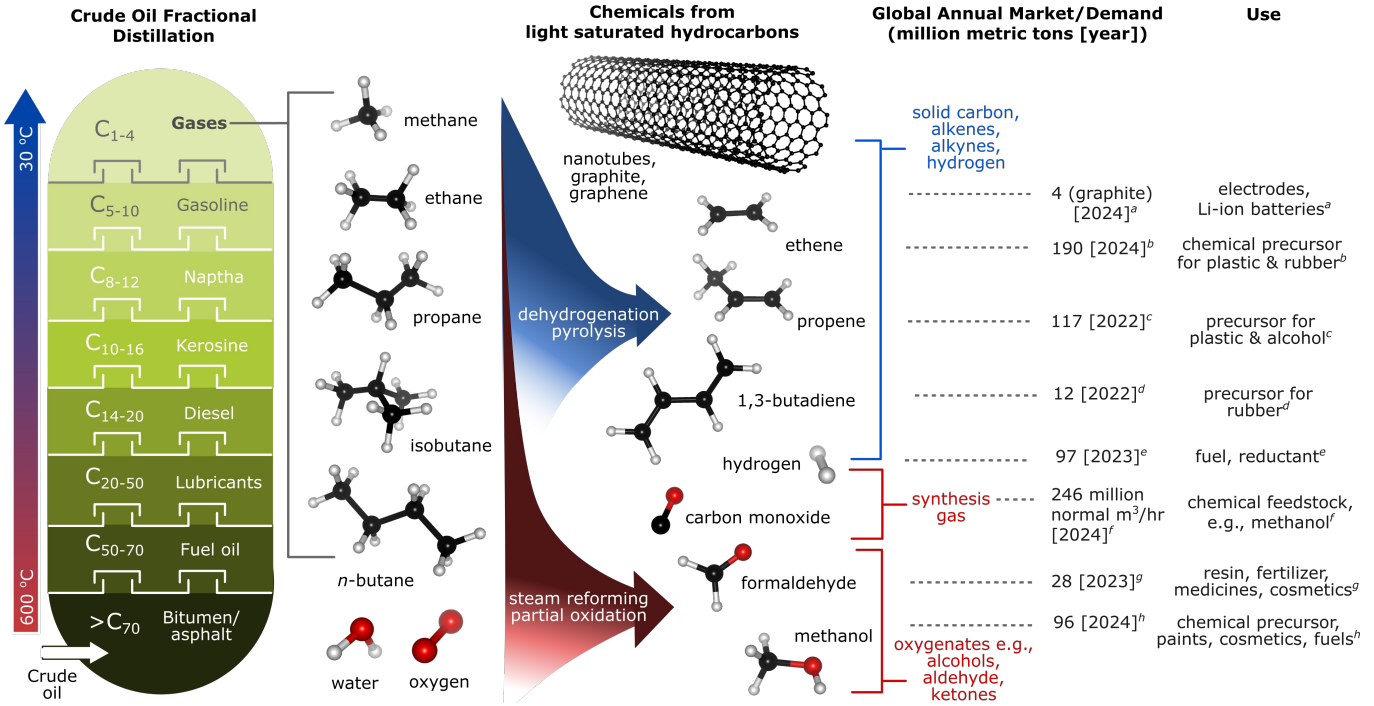
Chemical accuracy ~ 0.043 eV → r ∝ exp(±E/$k_B$T) ~ 6 or 1/6; DFT errors ~ 0.1 – 1.0 eV





# Excited-State Chemistry
## Enabled by Light and Plasma

# Chemical production and manufacturing

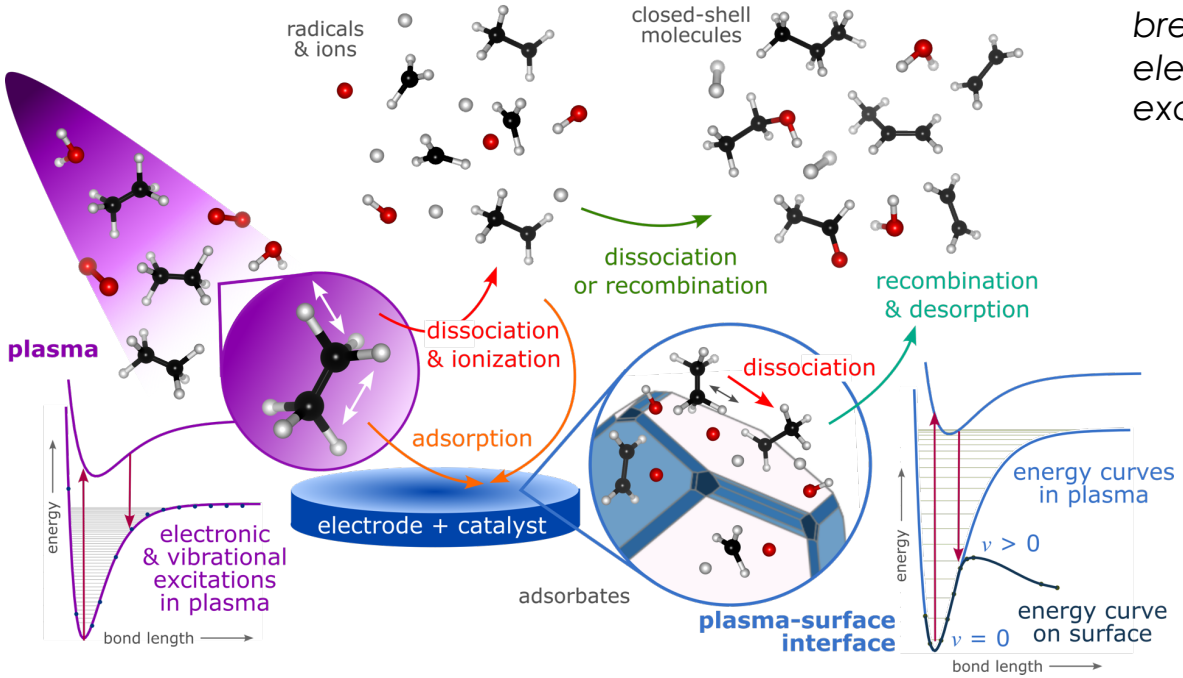



**Light gases from petroleum are important chemical feedstocks** to generate chemical precursors → produce economically important commodities, e.g., plastic, rubber, alcohols, fertilizers, cosmetics, etc.

**Their conversion are typically facilitated by heat (fossil fuel combustion)**

***How can we enable electrification and decentralization? Plasma?***

# Chemical processes in (low-temperature) plasma(and photolysis)



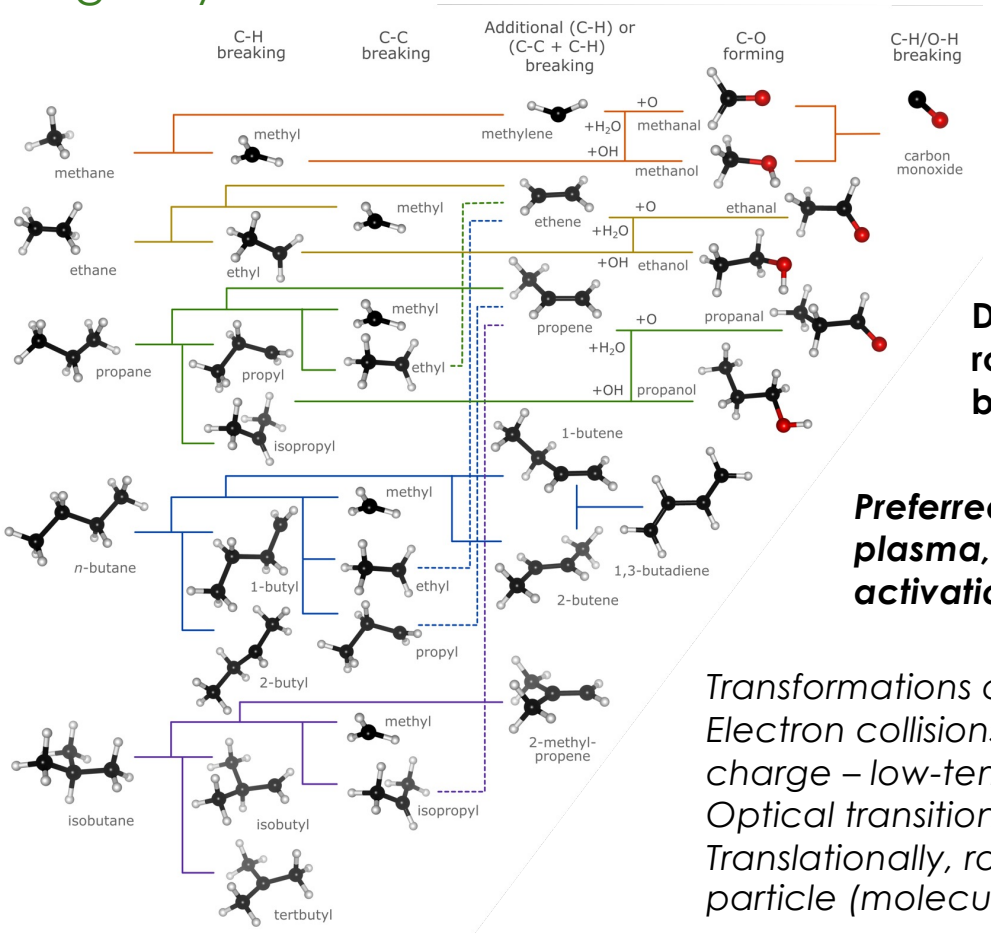

**Energy dissipation channels** of molecules after collision with an energetic electron ($e^-$) in plasmas: *break/form bonds; lose/gain electron(s); electronically/vibronically excited*

**Surfaces may influence preferred channel:** *chemistry-driven*

**Explore role of heterogenous catalysts** e.g., *Cu and Pt* in plasma-assisted partial dehydrogenation of light alkanes

**Excited-state methods for molecules are essential**

# Dehydrogenation and partial oxidation of light hydrocarbons




$C_xH_y$ (+ $O_2$/$H_2O$)

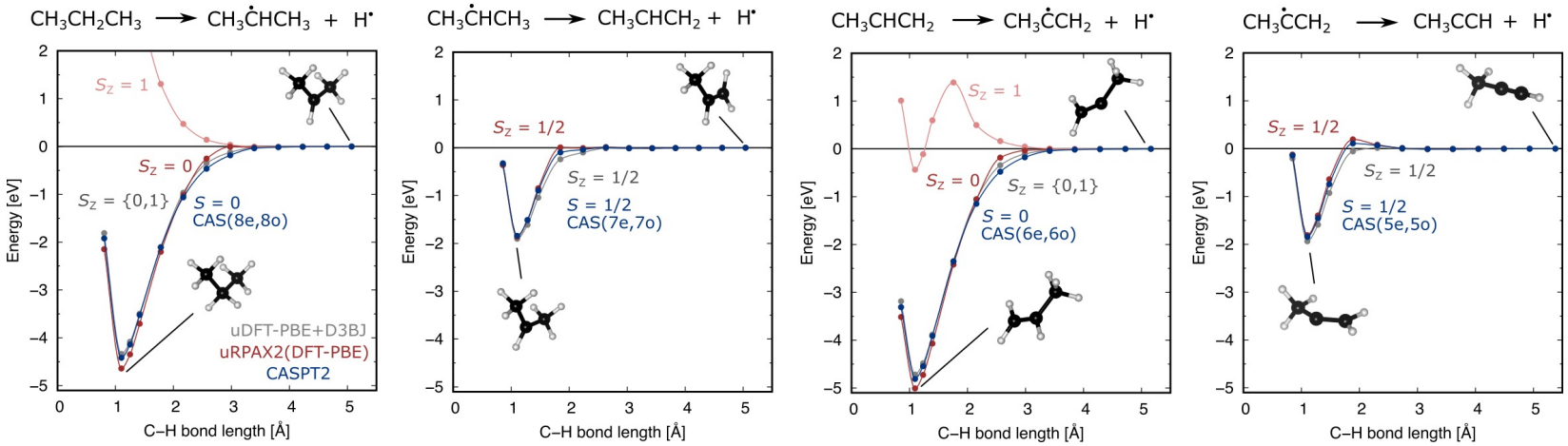
**Chemistry may be (beautifully) complex but can be tractable**

**Dissociation channels are primary routes** (C-H and C-C - easier), but **new bonds may also form** (C-C, C-O, O-H)

***Preferred*** *processes may be* ***different*** *between* ***plasma, photolysis*** *(light-driven)* ***and thermal activation*** *(heat-driven)*

*Transformations are driven by:*
*Electron collisions, imparting energy and sometimes charge – low-temperature plasmas;*
*Optical transition – photolysis;*
*Translationally, rotationally, & vibrationally energized particle (molecules and atoms) collisions – thermal;*

## Comparing QM methods: **propane dehydrogenation** gas-phase energetics




| Reaction \ Reaction Energy (eV) | $\Delta(H_f(0K)\text{-}ZPE)_{exp}$ | uDFT-PBE+D3BJ | uRPAX2 | CASPT2 | NEVPT2 |
|---|---|---|---|---|---|
| $CH_3CH_2CH_3 \rightarrow CH_3HC{=}CH_2 + H_2$ | 1.60 | 1.70 | 1.71 | 1.65 | 1.50 |
| $CH_3HC{=}CH_2 \rightarrow CH_3C{\equiv}CH + H_2$ | 1.99 | 2.12 | 2.02 | 2.05 | 2.02 |

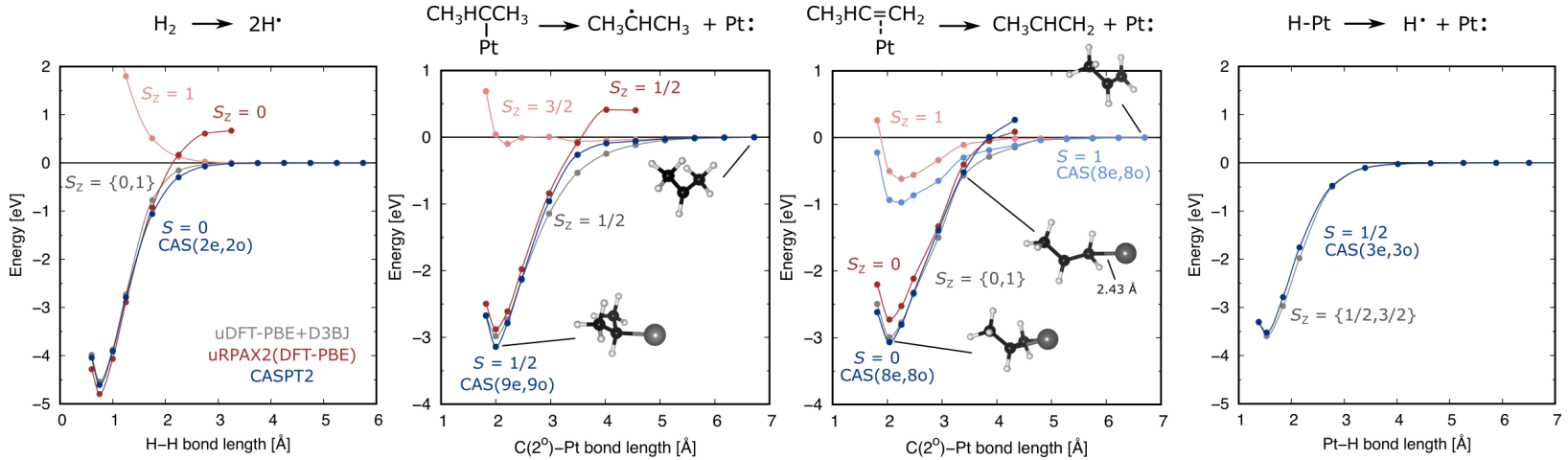
**Accurate predictions across the board**: spin-unrestricted (spin-contaminated) DFT-PBE+D3BJ and RPA(DFT-PBE) vs. spin-restricted multireference CASPT2/NEVPT2

**exp :** Computational Chemistry Comparison and Benchmark Database NIST (https://cccbdb.nist.gov)

**Unrestricted DFT-PBE+D3BJ**
C,H – PAW, planewave, 700 eV kinetic energy cut-off

**RPAX2 :** A. Heβelmann, *Phys. Rev. A*, 85, 012517 (2012)
**CASPT2** : H.-J. Werner, *Mol. Phys.* 89, 645 (1996)
**NEVPT2** : C. Angeli, et al., *J. Chem. Phys.*, 114,10252, (2001)
C,H – All-electron; aug-cc-PVTZ

# Comparing QM methods: **H-H and Pt-C/Pt-H bond dissociation**




| Reaction \ Reaction Energy (eV) | $\Delta(H_f(0K)\text{-}ZPE)_{exp}$ | uDFT-PBE+D3BJ | uRPAX2 | CASPT2 | NEVPT2 |
|---|---|---|---|---|---|
| $H_2 \rightarrow 2H$ | 4.75 | 4.54 | 4.79 | 4.61 | 4.53 |
| $CH_3CH_2CH_3 \rightarrow CH_3HC{=}CH_2 + H_2$ | 1.60 | 1.70 | 1.71 | 1.65 | 1.50 |
| $CH_3HC{=}CH_2 \rightarrow CH_3C{\equiv}CH + H_2$ | 1.99 | 2.12 | 2.02 | 2.05 | 2.02 |

**exp :** G. Herzberg, A. Monfils, *J. Mol. Spectrosc*. 5, 482 (1961); https://cccbdb.nist.gov

**Unrestricted DFT-PBE+D3BJ**
C,H,Pt – PAW, planewave,
700 eV kinetic energy cut-off

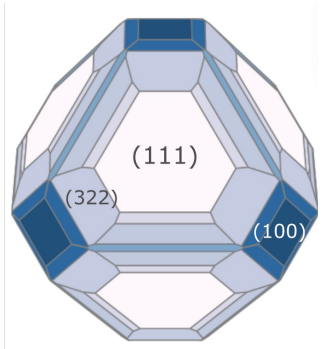
**RPAX2 :** A. Heßelmann, *Phys. Rev. A*, 85, 012517 (2012)
**CASPT2** : H.-J. Werner, *Mol. Phys*. 89, 645 (1996)
**NEVPT2** : C. Angeli, et al., *J. Chem. Phys*., 114,10252, (2001)
C,H – All-electron; aug-cc-PVTZ,
Pt – 80-electron ECP; aug-cc-PVTZ

Spin-unrestricted DFT-PBE+D3BJ comparable to CASPT2

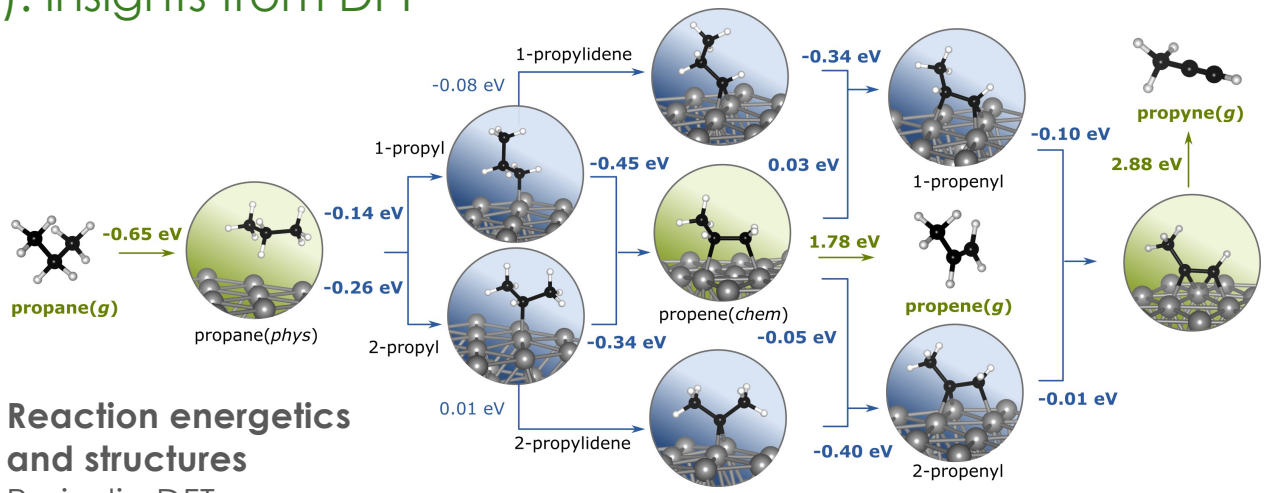
Spin-unrestricted RPAX2(DFT-PBE) : the same as DFT-PBE+D3BJ for $H_2$, **but under-binds Pt-$C_3H_x$ complexes and fails convergence for Pt-H**

# Propane dehydrogenation mechanism on Pt(111): insights from DFT

**Stable surfaces of face-centered cubic platinum (Pt)** *Wulff construction – shape that minimizes the surface energy (equilibrium) given a crystal volume*




Platinum (fcc)




## Reaction energetics and structures

Periodic DFT-PBE+D3BJ

(atomic models: C,H, Pt – black, white, grey spheres)

C,H, Pt – PAW potentials
Planewave 660 eV kinetic energy cut-off
Five-layer (3 x 3) Pt(111) slab, 7x7x1 k-point mesh

- ✓ Dehydrogenation at the 2° carbon preferred
- ✓ Decomposition energetically down hill on Pt(111)
- ✓ Strong Pt-H bond (desorption energy of $H_2$ = 1.09 eV/$H_2$)
- ✓ 1- or 2-propenyl formation favored over propene desorption

X propene and propyne too strongly bound

**How reliable are the calculated energetics?**

## **Divide and Conquer**: Combining DFT and correlated wavefunction methods for surface reactions

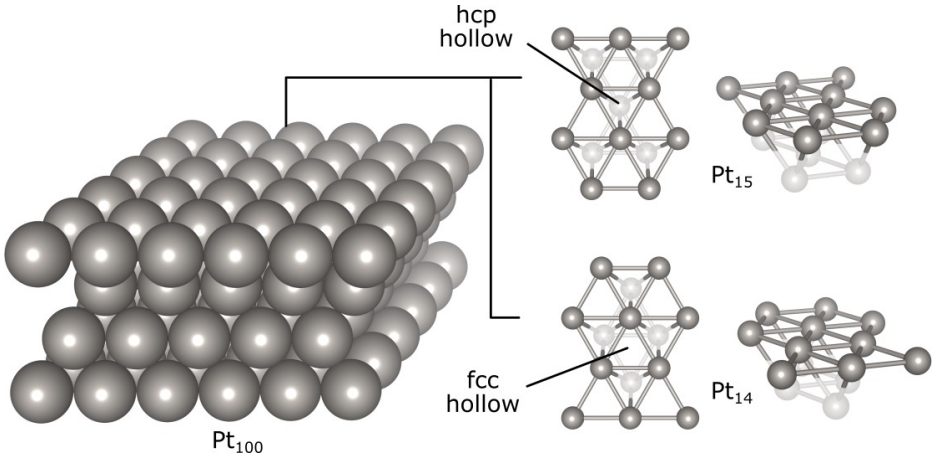
$$\max\left[W = E^{A}_{eDFT}[\rho^{A}, V_{emb}] + E^{B}_{eDFT}[\rho^{B}, V_{emb}] - \left\{\int V_{emb}\,\rho^{A+B}\,dr\right\}\right]$$

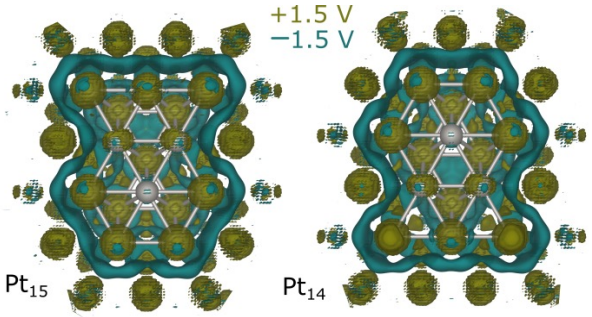
Density Functional Embedding Theory (DFET)

**Embedding scheme:**

Density functional embedding theory +
Embedded correlated wavefunction (CW) theory

$$\frac{\delta W}{\delta V_{emb}(\boldsymbol{r})} = \frac{\delta E^{A}_{eDFT}}{\delta V_{emb}(\boldsymbol{r})} + \frac{\delta E^{B}_{eDFT}}{\delta V_{emb}(\boldsymbol{r})} - \frac{\delta E^{A+B}_{DFT}}{\delta V_{emb}(\boldsymbol{r})}$$
$$\approx \rho^{A}[V_{emb}](\boldsymbol{r}) + \rho^{B}[V_{emb}](\boldsymbol{r}) - \rho^{A+B}(\boldsymbol{r})$$



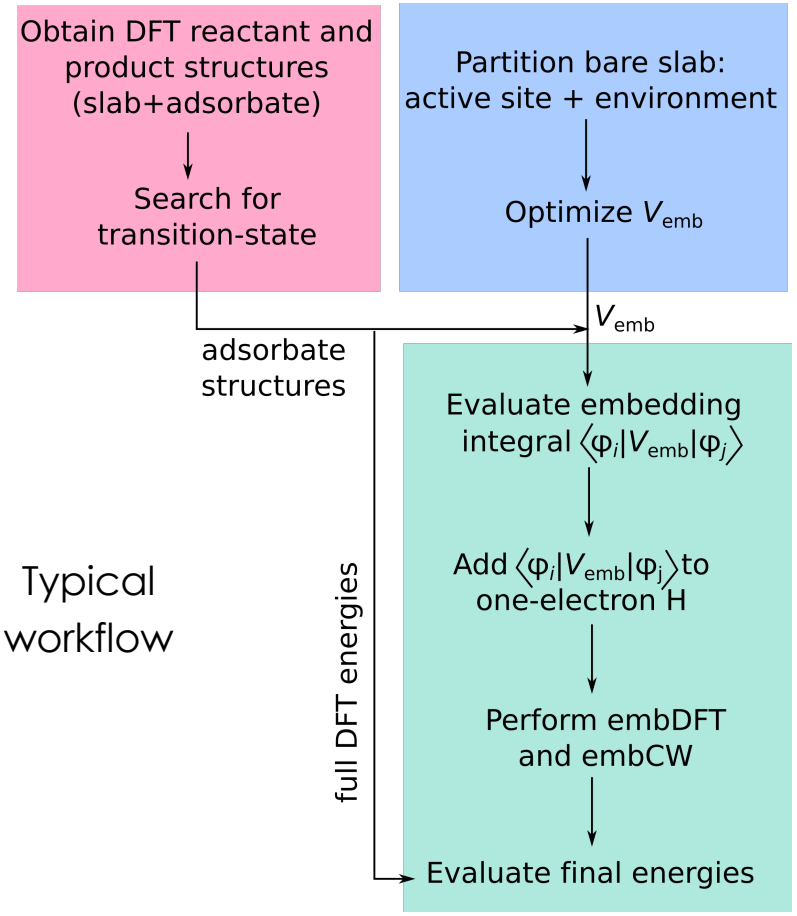




$$E^{DFET} = E^{PW-DFT}_{full} + \left(E^{embGTO-CW}_{cluster}[V_{emb}] - E^{embGTO-DFT}_{cluster}[V_{emb}]\right)$$

**Refinement for ground-state** reaction energy surfaces AND enables **accurate treatment of excited-state** surfaces


C. Huang, M. Pavone, E. A. Carter, *J. Chem. Phys.*, 134, 154110 (2011)
K. Yu, F. Libisch, E. A. Carter, *J. Chem. Phys.*, 143, 102806 (2015)

## **Divide-and-Conquer**: DFET and embedded CW workflow




Perform DFT simulations

Typical workflow

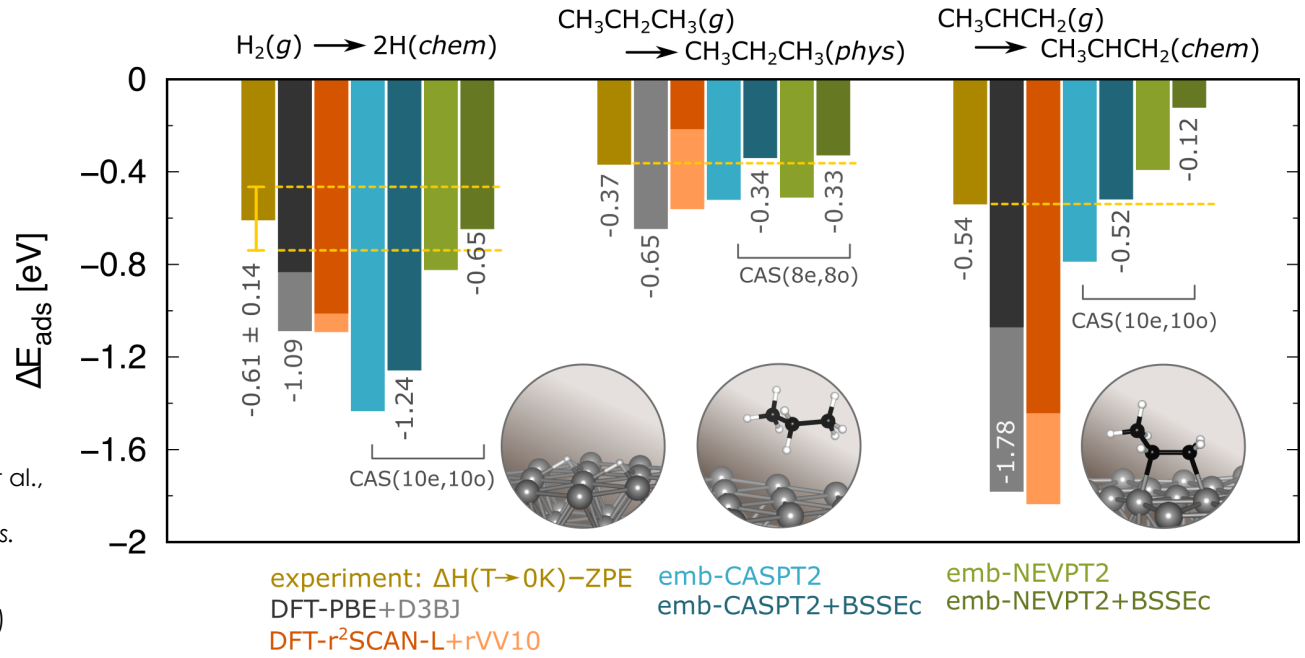
Density functional embedding theory

Modify electronic Hamiltonian

Perform QM simulations

# Select Pt(111) surface reaction energetics from ECW theory

**DFT(PBE)+D3BJ vs. emb-CASPT2/NEVPT2**
(w/ experimental benchmarks)




**Experimental values**
(0K- extrapolated and ZPE removed)
**Propane on Pt(111):** M.C. McMaster, et al., *Chem. Phys.*, 177, *461* (1993)
**H on Pt(111):** B. Poelsema, et al., *J. Phys. Condens. Matter*, 22, *304006* (2010)
**Propene on Pt(111):** M. Salmeron, G.A. Somorjai, *J. Phys. Chem.*, 86, 341 (1982)

**Restricted DFT-PBE+D3BJ**
C,H,Pt – PAW, planewave, 660 eV kinetic energy cut-off

**CASPT2** and **NEVPT2**
C,H – All-electron; aug-cc-PVTZ
Pt – 80-electron ECP; aug-cc-PVTZ

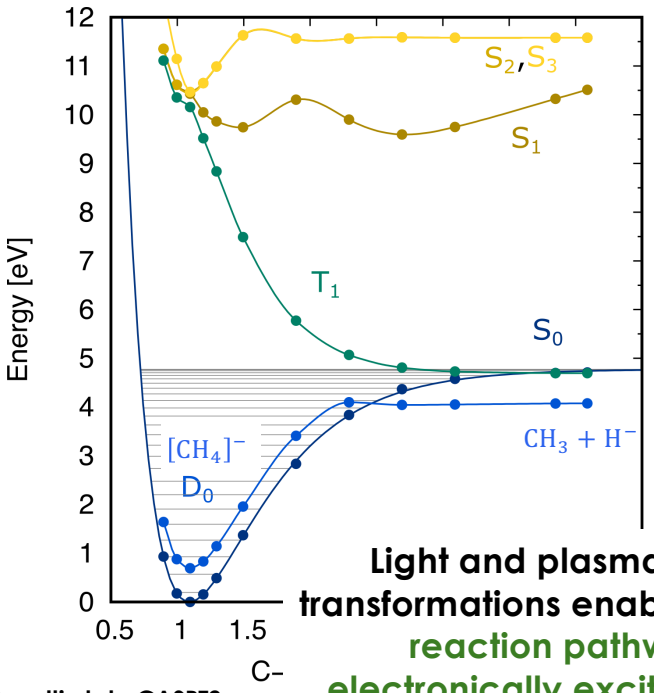
- DFTs and embCASPT2 over-bind *H on Pt(111)
- embNEVPT2 ($\theta_H$ = 0.222 H coverage, 2H* adjacent fcc sites)within experimental range ($\theta_H$ = 0.1 to 1.0)
- **Improvement in prediction accuracy across the board when using correlated wavefunction methods**

# Excited-state decomposition of gaseous methane

**vertical excitation energy** ($V_{ee}$) = 10.4 eV
**vertical ionization energy** = 14.2 eV (exp = 13.6 eV)
**vertical electron affinity** ($V_{EA}$) = -0.72 eV

**Dissociative electron impact excitation**

$$CH_4 + e^-(\varepsilon) \rightarrow [CH_4]^*(V_{ee}) + e^-(\varepsilon - V_{ee}) \rightarrow CH_3 + H$$

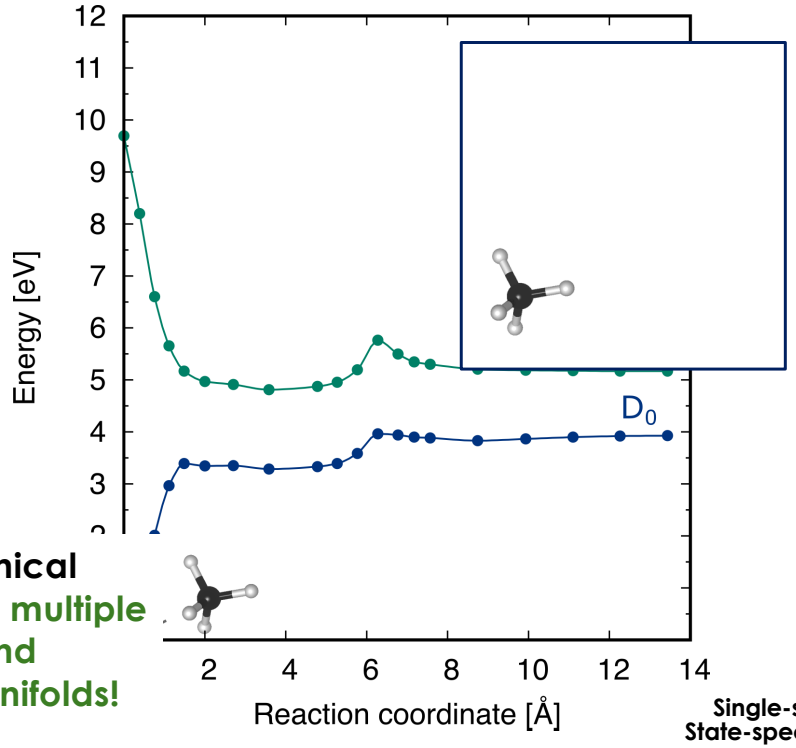



**(Four-state) multi-state CASPT2**
**State-averaged CASSCF**
active space: (8e,8o), basis set: aug-cc-pvtz
**DFT structures**

**Light and plasma: chemical transformations enabled by multiple reaction pathways and electronically excited manifolds!**

**Dissociative electron attachment**

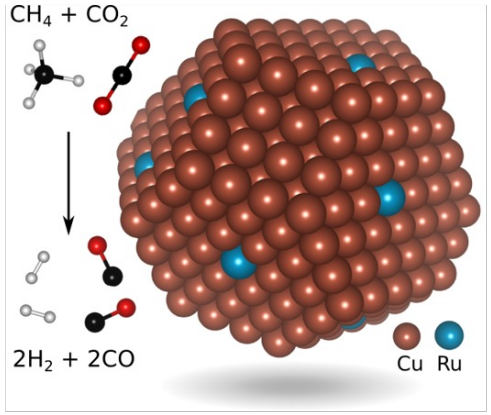
$$CH_4 + e^- \rightarrow [CH_4]^{*-} \rightarrow [CH_2]^- + H_2$$



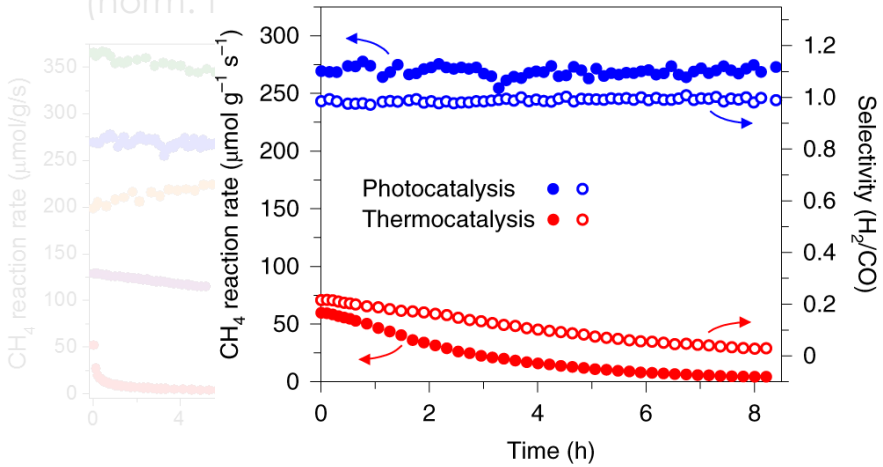

**Single-state CASPT2**
**State-specific CASSCF**
active space: (9e,9o), basis set: aug-cc-pvtz
**DFT structures**

# Light-activated (plasmonic) catalysis: methane dry reforming to syngas (industrially important chemical precursor)

Methane dry reforming on Ru-doped Cu




- $H_2$ + CO (syngas)
- Cu nanoparticles <10 nm (varying low Ru fractions) on $MgO/Al_2O_3$
- white light illumination (19.2 W-cm$^{-2}$, room temp.)




**Conversion of thermal vs. photo (Cu:Ru = 100:1)**

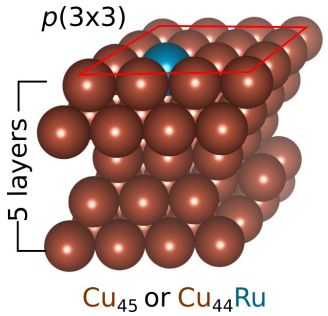
Effective (light) and thermocatalytic (dark) temperatures ~ 1000 K.

Light =19. 2 W/cm$^2$ white light

L. Zhou, et al.; ***Nat. Energy*, *5*,** 61 (2020)

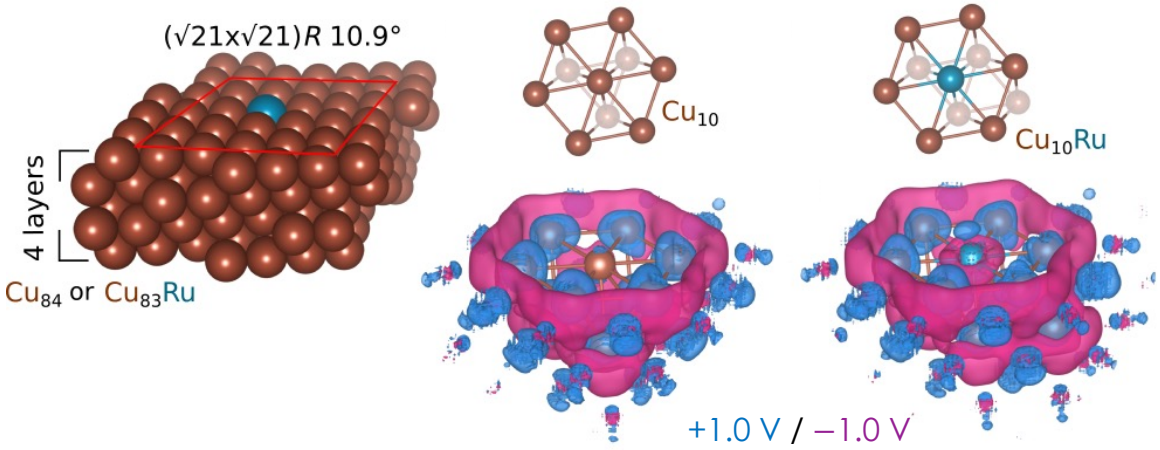
# Slab and cluster models

**C-H bond breaking** (forming $CH_3$, $CH_2$, CH, and C fragments) **slow**




**Periodic DFT (PBE+D3BJ)** with semiempirical van der Waals correction for *reaction pathways*

Embedding potential from **DFET**

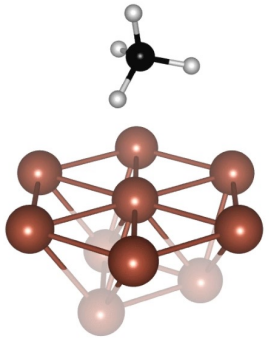



L. Zhou, et al.; ***Nat. Energy*, *5*,** 61 (2020)

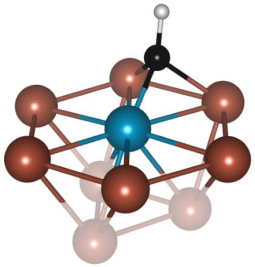
# Excited-state C-H bond activation from embedded NEVPT2

**First C-H** bond breaking **most difficult** on **pure Cu**

**Fourth C-H** bond breaking for **Ru single atom on Cu**



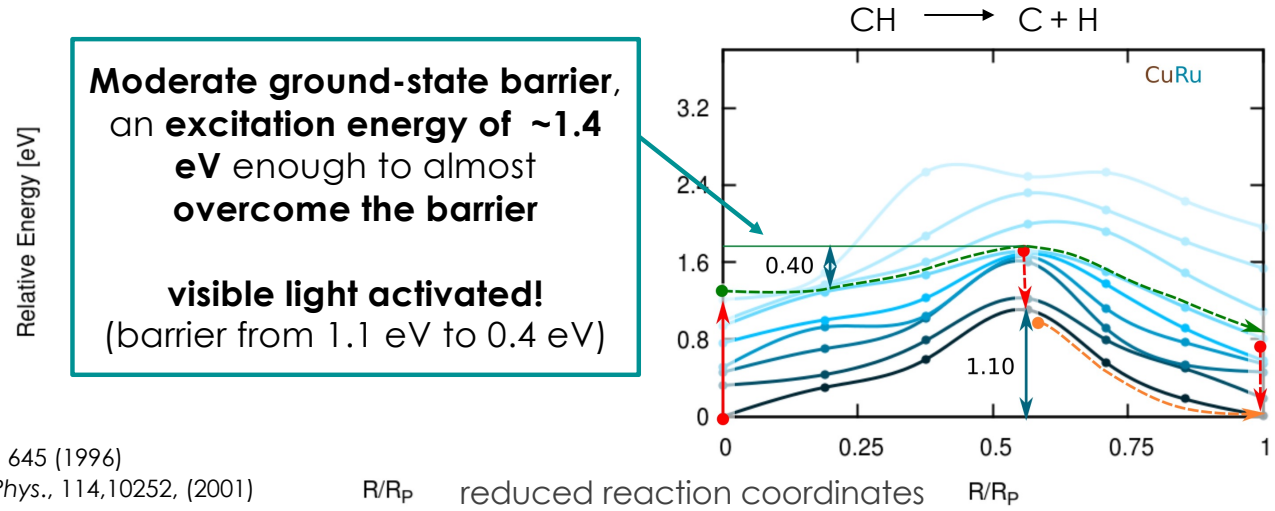
Key:
Cu/Ru/C/H



**NEVPT2** using multiconfigurational **CASSCF** with an active space of (10e,10o) as reference

**Moderate ground-state barrier**, an **excitation energy of ~1.4 eV** enough to almost **overcome the barrier**

**visible light activated!**
(barrier from 1.1 eV to 0.4 eV)





**CASSCF** : H.-J. Werner, *Mol. Phys*. 89, 645 (1996)
**NEVPT2** : C. Angeli, et al., *J. Chem. Phys*., 114,10252, (2001)
L. Zhou, et al.; ***Nat. Energy*, 5,** 61 (2020)

# Summary

**Spin-contaminated DFT** with semi-local (PBE) exchange-correlation functional proved to be **adequate for gas-phase hydrocarbon dehydrogenation** chemistry

**Spin-unrestricted RPA** show similar performance as DFT for gas-phase rxns., although **worse for an open shell transition metal atom (Pt)**

**Newer generation XC functional r$^2$SCAN-L with rVV10** vdW correction predicts similarly as PBE + D3BJ for $H_2$ and $C_3H_x$ adsorption on Pt(111) – does not justify increase computational cost

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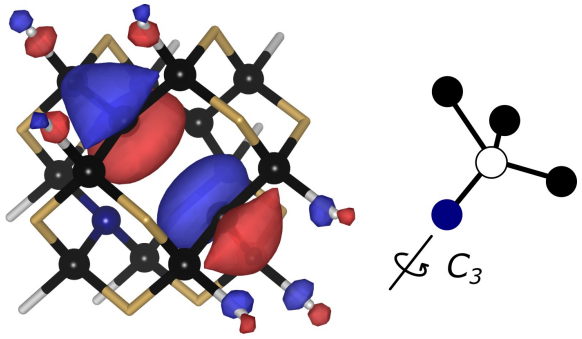
**Multireference perturbation theories (enabled by DFET for surfaces) produce the best result** across the board – gaseous and surface reactions

**Multireference perturbation theories** provide **valuable insight** into **excited-state chemical processes**

**Surfaces may influence conversion pathways** for excited state species harnessed through plasma or light excitations




# Using **Quantum Mechanics** For Designing **Qubits**

# Optical and magnetic properties of diamond "color centers"

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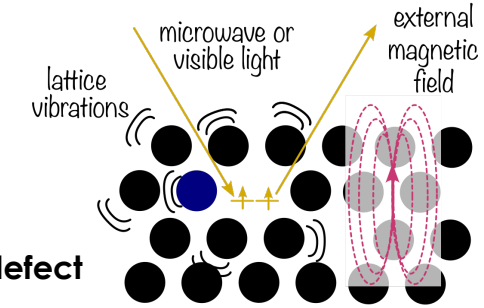
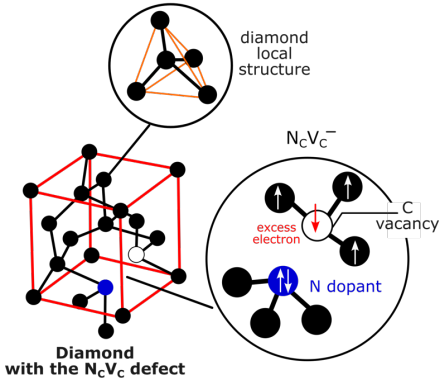
## Qubits (quantum bits)

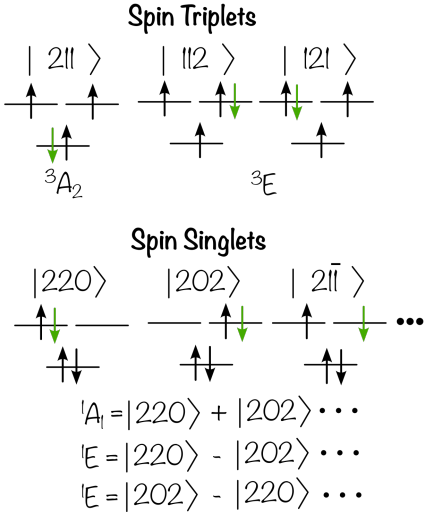
- ***Basic units of information*** *in quantum devices that* ***enable computation, communication, and sensing***
- Takes advantage of ***quantum phenomena***: ***electron and nuclear spins, state superposition, & entanglement***
- **Prepared/manipulated via static magnetic field** (energy splitting **via Zeeman effect**); generate a coherent state (different $m_s$ sublevels) via microwave (zero-field splitting energy)
- **Pumped using visible light excitation**
- **Probed measuring emission (fluorescence)**

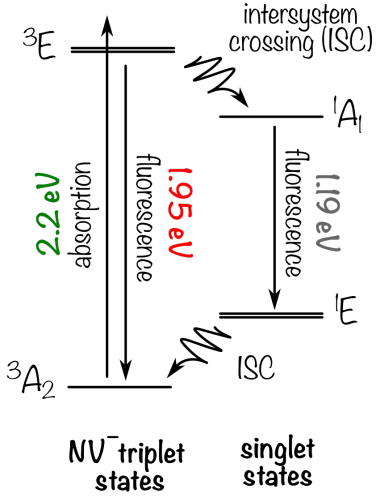
**e.g., diamond defect**




**Example: negatively charged NV center in diamond**



# Exploring novel "quantum" defects in diamond

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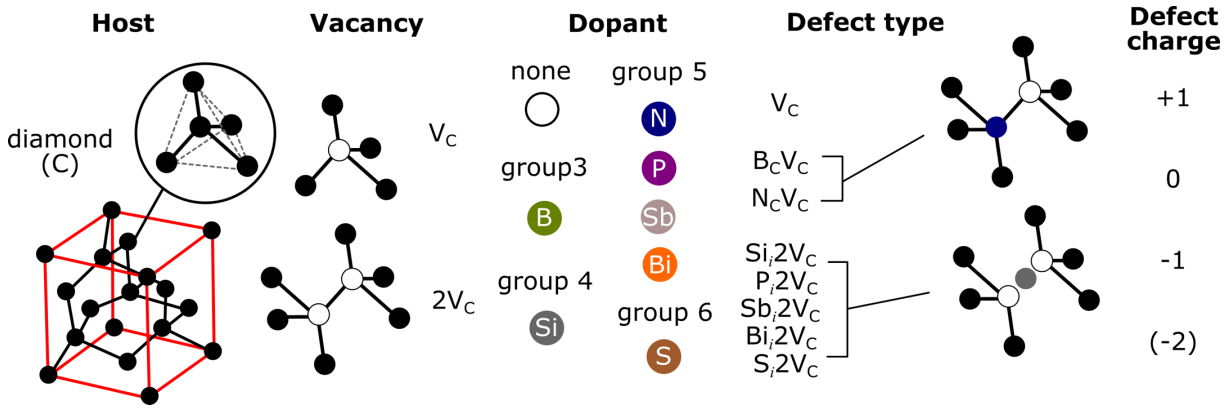
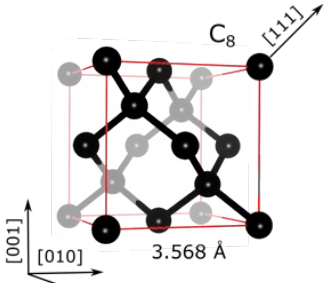
## Diamond

- **Wide-band gap** (5.5 eV) group IV semiconductor
- **Diamagnetic** ("nonmagnetic")
- Can form **magnetic defects**
- High breakdown voltage
- Can be made with **high purity and precisely placed defects**

Ferrenti, A. M., de Leon, N. P., Thompson, J. D. & Cava, R. J., *npj Computational Materials* 6, 126 (2020)



# QM method benchmarking for pure diamond




**Band gap of pure diamond: Different DFT exchange correlation functionals and quasi-particle method vs. experiment**

**Table 1**. Predicted lattice constant and indirect band gap[a] for a pristine diamond ($C_8$ supercell) from different DFT approximations compared to the experimental structure and fundamental band gap.

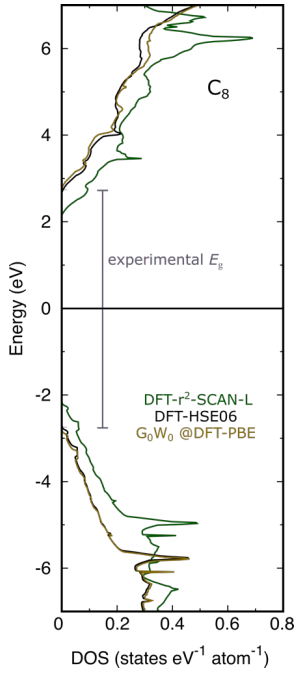
| Method | Cubic *a* (Å) | $E_g$ (eV) |
|---|---|---|
| Experiment | $3.56712 \pm 0.00005$[b] | $5.480 \pm 0.004$[c] |
| DFT-r$^2$-SCAN-L | 3.5677 | $4.22 \pm 0.02$ |
| DFT-HSE06 | - | $5.30 \pm 0.02$ |
| $G_0W_0$ @DFT-PBE | - | $5.50 \pm 0.02$[d] |

[a]Difference between the energies of the **conduction band minimum and valence band maximum**

[b]X-ray diffraction at room temperature, Yamanaka, T. & Morimoto, S. Acta Crystallographica Section B 52, 232 (1996)

[c]photoemission-inverse photoemission, Cheng, L., Zhu, S., Ouyang, X. & Zheng, W., Diamond and Related Materials 132, 109638 (2023)

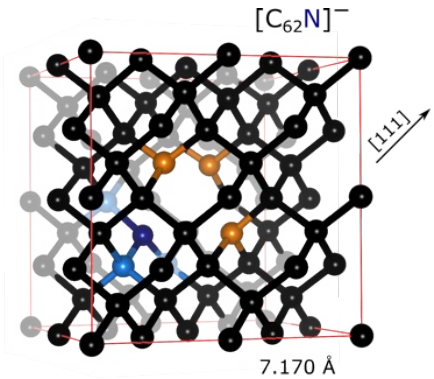
[d]formally corresponds to the fundamental gap

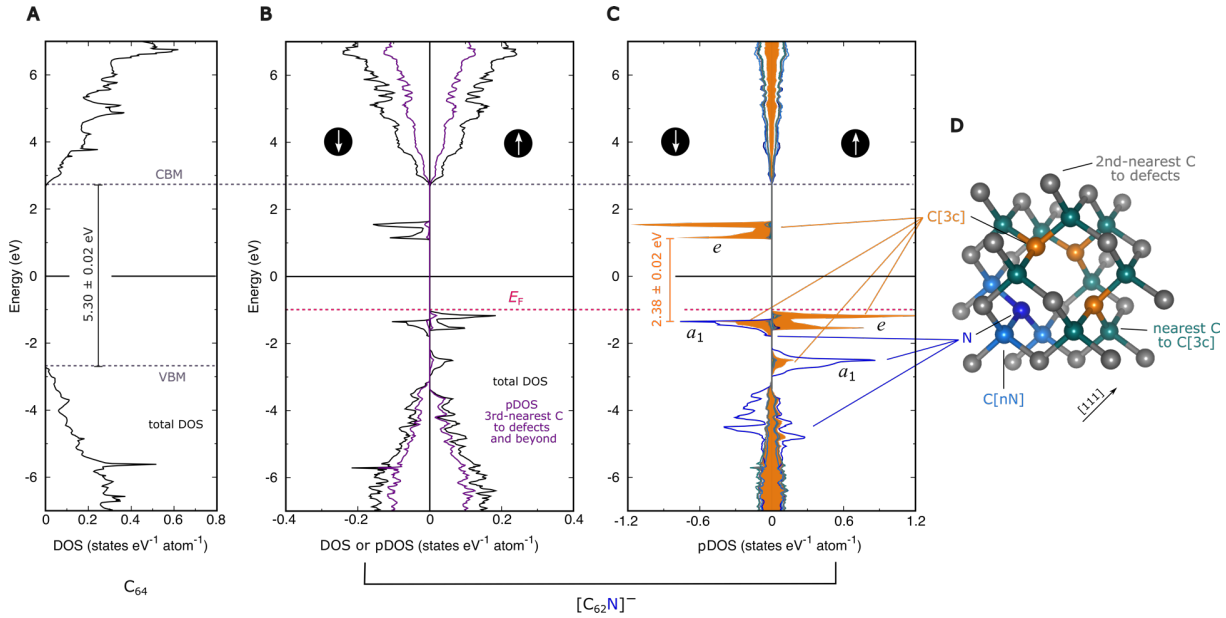



**Pure diamond electronic structures (densities of states)**

Martirez, *arXiv*, 2505.01250 (2025)

# Single-particle picture: DFT-predicted electronic structure of $NV^-$ defect in bulk diamond




N, C except
3-fold coordinated C (C[3c])
C next to N (C[nN])

Gap states from under-coordinated C atoms: C[3c]
*Defect orbital transition: $a_1$ → $e$*
*"Defect gap" (2.38 eV) higher than experimental optical vertical excitation (2.18 eV) and emission (1.95 eV)*

Martirez, *arXiv*, 2505.01250 (2025)


Davies, G., Hamer, M. F. & Price, W. C. *Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences* 348, 285 (1976)
Ma, Y., Rohlfing, M. & Gali, A. Phys. Rev. B 81, 041204 (2010)

# Are the defect states sensitive to defect concentration?

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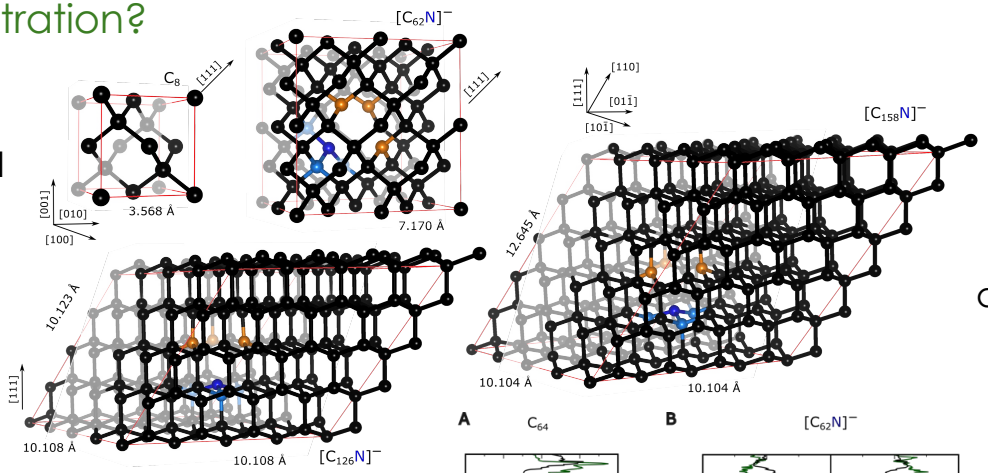
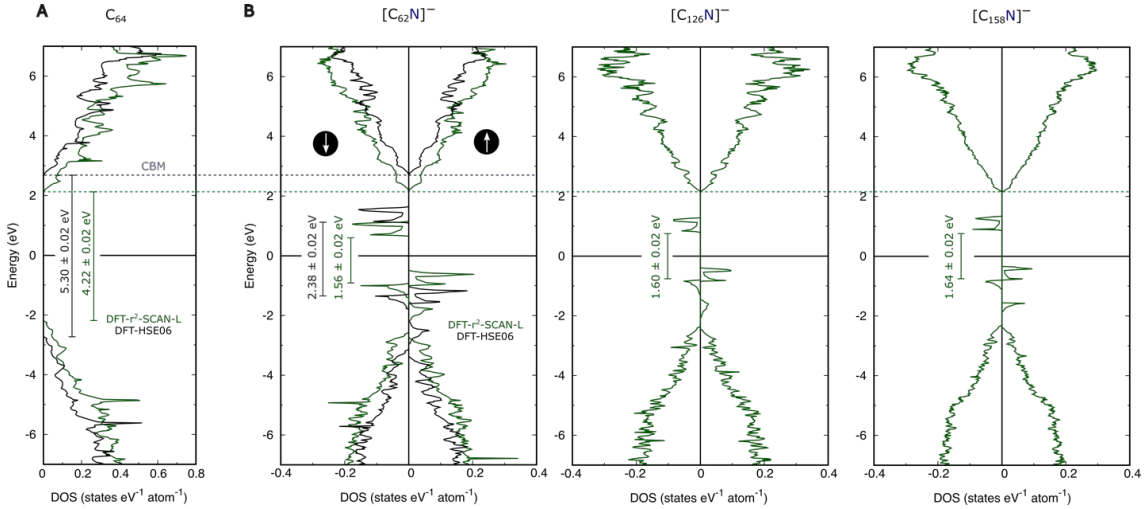
**Supercell sizes**




**Yes,** to some extent, defect "gap" a function of supercell size (~0.1 eV)

**Electronic structure (densities of states)**




pure

w/ $NV^-$ defect

Martirez, *arXiv*, 2505.01250 (2025)

# Excited-state Property Predictions via Capped Density Functional Embedding Theory

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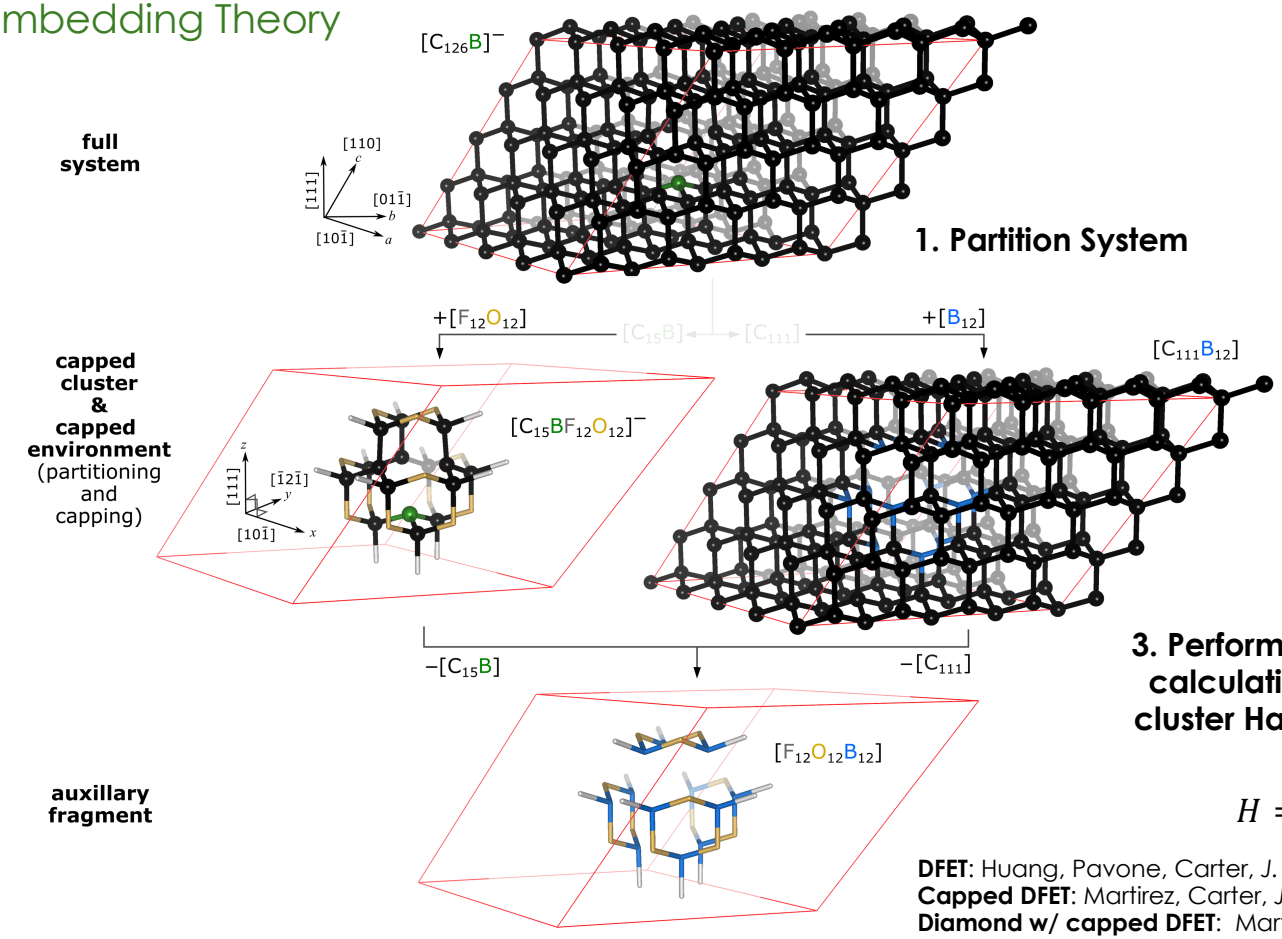



## 2. Optimize an embedding potential

$$W = E_{DFT}^{cl+cap1}[\rho^{cl}, V_{emb}] + E_{DFT}^{env+cap2}[\rho^{env}, V_{emb}] - \int V_{emb}\left(\rho^{full} + \rho^{cap1+cap2}\right) dr$$

$$\frac{\delta W}{\delta V_{emb}(\boldsymbol{r})} = \rho^{cl+cap1}(\boldsymbol{r}) + \rho^{env+cap2}(\boldsymbol{r}) - \left(\rho^{full} + \rho^{cap1+cap2}\right) \rightarrow 0$$

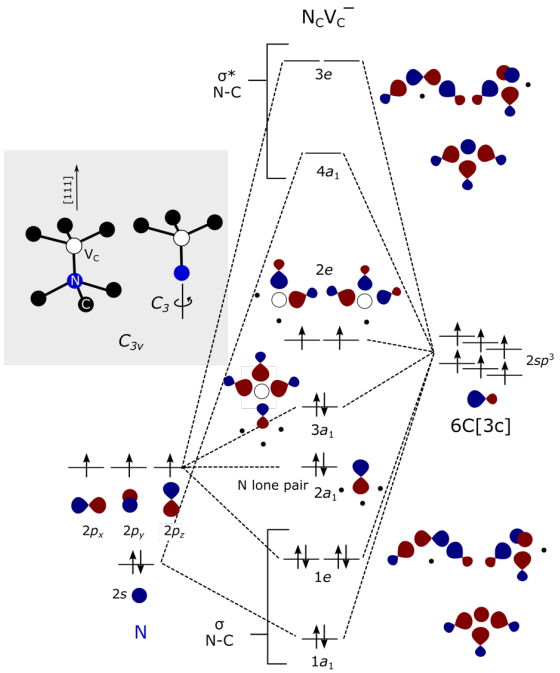
$$\rho^{cl+cap1}(\boldsymbol{r}) + \rho^{env+cap2}(\boldsymbol{r}) - \rho^{cap1+cap2} = \rho^{full}$$

## 3. Perform correlated wavefunction theory calculations with modified non-periodic cluster Hamiltonian (no slowly convergent Coulomb interactions)

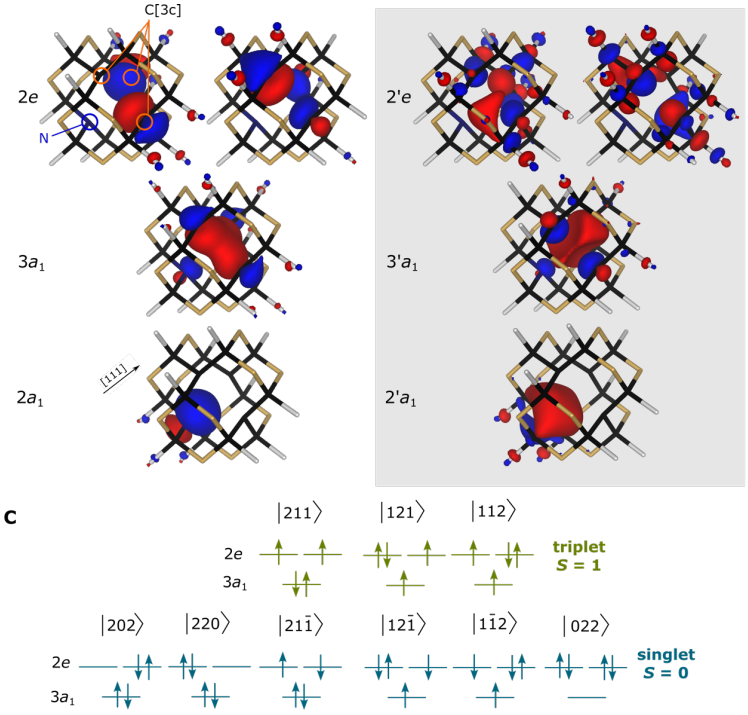
$$H = H^{\circ} + V_{emb}$$ ← *free of defect-defect interaction*


**DFET**: Huang, Pavone, Carter, *J. Chem. Phys.* 134, 154110 (2011)
**Capped DFET**: Martirez, Carter, *J. Chem. Theory. Comput.* 17, 4105 (2021)
**Diamond w/ capped DFET**: Martirez, *arXiv*, 2505.01250 (2025)

# Molecular orbital picture & multiconfigurational picture




**Point Group Symmetry + Molecular Orbital Diagram** (explains spin structure and frontier orbital character) – **molecule-like not atom-like**

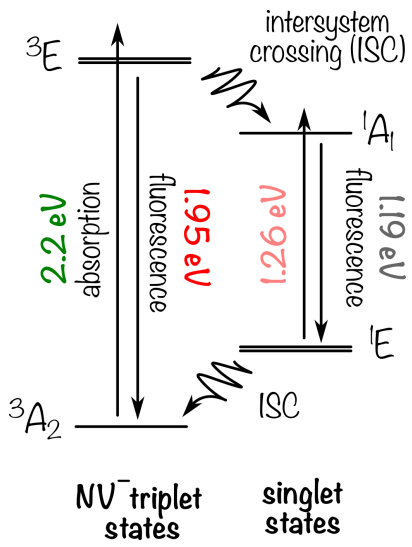


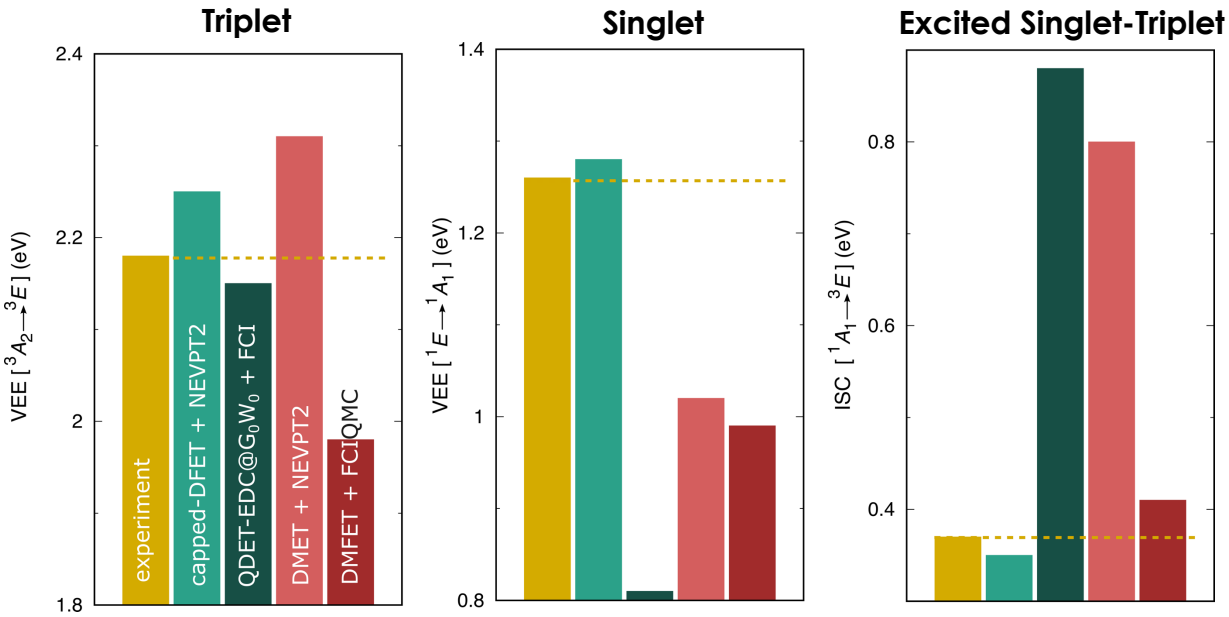

**Calculated Natural Orbitals from multiconfigurational CW** (verifies frontier orbital character and approximate symmetry)

**Relevant electronic configurations** (illustrates multiconfigurational nature of states)

Martirez, *arXiv*, 2505.01250 (2025)

# Vertical Excitation Energy (VEE) Benchmark




Structures : **DFT-r²-SCAN-L**
Optimized embedding potential : **DFT-HSE06**
Excitation energies : **multistate CASSCF + NEVPT2**

Calculated properties:
Excitation energies, transition dipole moments → relative absorption strength and natural lifetimes, spin-orbit coupling → zero-field splitting

Martirez, *arXiv*, 2505.01250 (2025)

**EXP**: G. Davies et al., Proc. R. Soc. Lond. 348, 285 (1976); P. Kehayias, et al. Phys. Rev. B, 88, 165202 (2013); M. Goldman, et al. Phys. Rev. B, 96, 039905 (2017)
**capped DFET + NEVPT2**: embedded $C_{15}NF_{12}O_{12}$; Martirez, arXiv (2025)
**QDET + FCI**: $C_{510}N$; N. Sheng … G. Galli, JCTC, 18, 3512 (2022)
**DMET + NEVPT2**: $C_{214}N$; S. Haldar … L. Gagliardi, J. Phys. Chem. Lett., 14, 4273 (2023)
**DMFET + FCIQMC**: $C_{42}H_{42}N$; Y. Chen … J. Chen, Phys. Rev. B, 108, 045111 (2023)

**Method is accurate and rivals best-in-class!**
**Performs well across the board**

# Summary

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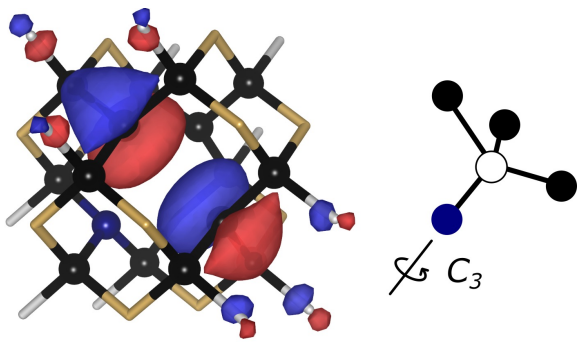
- **Detailed benchmarking of the capped-DFET method** using embedded NEVPT2 using the negatively charged **"NV center" in diamond** as example
- We found **capped-DFET with emb-NEVPT2** reproduces VEEs and the ISC energy for spin triplet and singlet $N_CV_C^-$ with **errors less than 0.1 eV, rivaling more expensive methods**
- **Confirm** and thus **establish an accuracy-retaining method** that will potentially **enable fully ab initio QM characterization** of an array of **localized defects in diamond** that may be **key materials as building blocks for quantum devices**



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***Alkane dehydrogenation on Pt***: U.S. Department of Energy, Office of Science Energy Earthshot Initiative as part of the **Non-equilibrium Energy Transfer for Efficient Reactions (NEETER)** under contract # **DE-AC05-00OR22725**

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