Quantum Defects from First Principles

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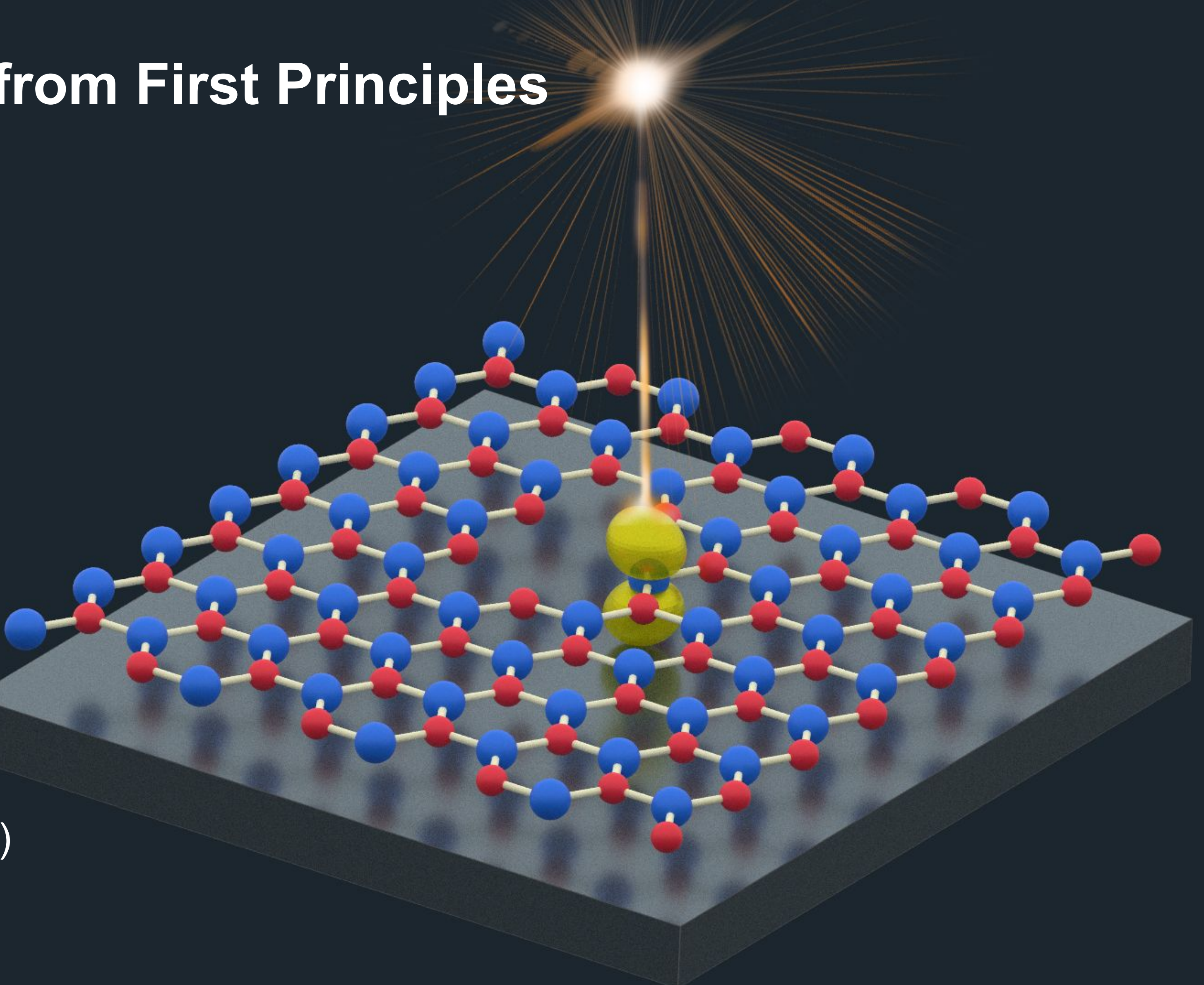
University of California, Santa Barbara



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NSF

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Harnessing Quantum Mechanics

NSF QuBBE

- Second quantum revolution
  - tes
  - n Flagship: $1.2b
  - China Nat

CIQM CENTER for INTEGRATED QUANTUM MATERIALS
Quantum Information Science and Technology

EPiQC

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STAQ SOFTWARE-TAILORED ARCHITECTURES for QUANTUM CODESIGN

IMOD

CUA MIT-Harvard Center for Ultracold Atoms
a National Science Foundation Physics Frontier Center

C^{2}QA

SQMS

JQI JOINT QUANTUM INSTITUTE

Q-NEXT NEXT GENERATION QUANTUM SCIENCE AND ENGINEERING

QUANTUM SYSTEMS ACCELERATOR
Catalyzing the Quantum Ecosystem

LQC

HQAN Hybrid Quantum Architectures and Networks

CIQC Challenge Institute for Quantum Computation

QUANTUM SCIENCE CENTER℠

QNM | QUANTUM NEW MEXICO
New Mexico is a Quantum State

IQIM

Institute for Robust Quantum Simulation

Q-SEnSE
An NSF Quantum Leap Challenge Institute

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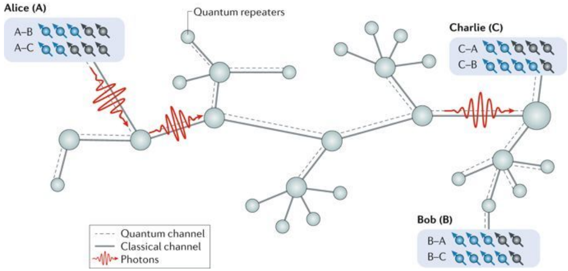
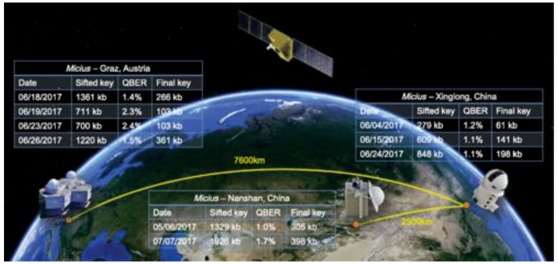
Quantum Information Science

Quantum Computing



M. Atatüre *et al.*,
Nat. Rev. Mater. **3**, 38 (2018)

Quantum Cryptography



Micius – Graz, Austria

Date	Sifted key	QBER	Final key
06/18/2017	1361 kb	1.4%	266 kb
06/19/2017	711 kb	2.3%	103 kb
06/23/2017	700 kb	2.4%	103 kb
06/26/2017	1220 kb	1.5%	361 kb

Micius – Xinglong, China

Date	Sifted key	QBER	Final key
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06/15/2017	609 kb	1.1%	141 kb
06/24/2017	848 kb	1.1%	198 kb

Micius – Nanshan, China

Date	Sifted key	QBER	Final key
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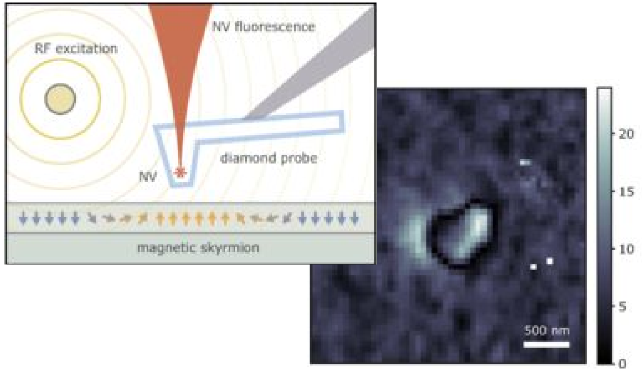
07/07/2017	1926 kb	1.7%	398 kb

S.-K. Liao *et al.*,
Phys. Rev. Lett. **120**, 030501 (2018)

Quantum Metrology



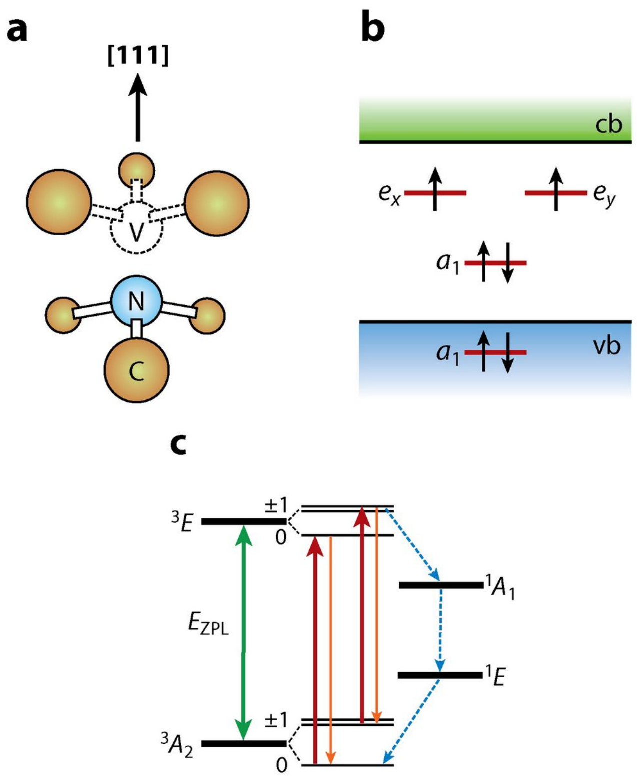
Jenkins et al.,
Phys. Rev. Materials **3**, 083801 (2019)

- Potential platforms
  - Superconducting junctions
  - Trapped ions
  - Topologically protected states
  - Quantum dots
  - ...
  - **Defects in semiconductors**

Quantum Defects

- Scope
  - Defects + impurities
  - Deep not shallow
  - Two types
    - Quantum emitters & spin centers
- Deep-level defects
  - Record coherence
    - T_1 ~ 8 h for NV^- in diamond
      T. Astner *et al*., Nat. Mater. **17**, 313 (2018).
    - T_2 ~ 1.8 ms for NV^- in diamond *at room T*
      G. Balasubramanian *et al*., Nat. Mater. **8**, 383 (2009).
  - Many options for control
  - Scalability - benefits from mature semiconductor industry

NV- in diamond

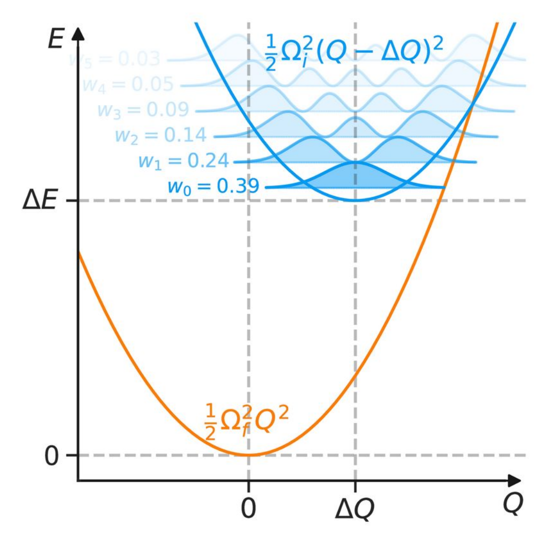


Dreyer *et al*., Annu. Rev. Mater. Res. **48**, 1 (2018).

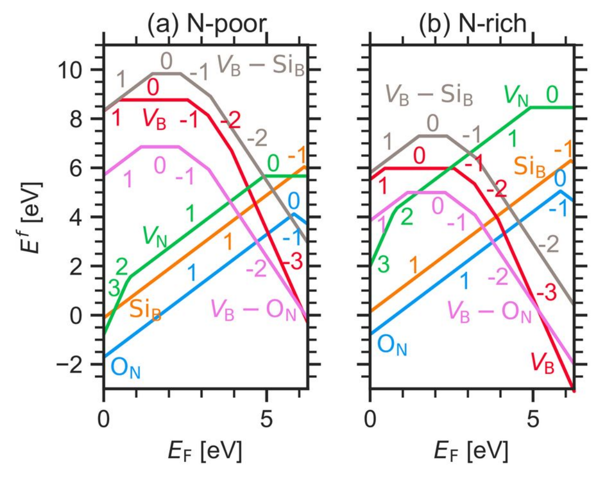
Outstanding Challenges

1) Develop first-principles methodologies to describe quantum defects.
2) Predict novel quantum defects with superior properties.

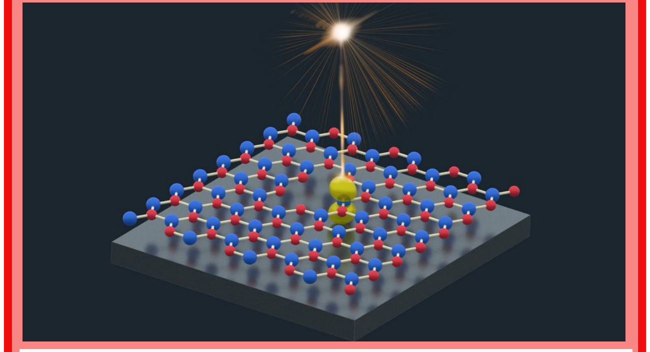
Theory

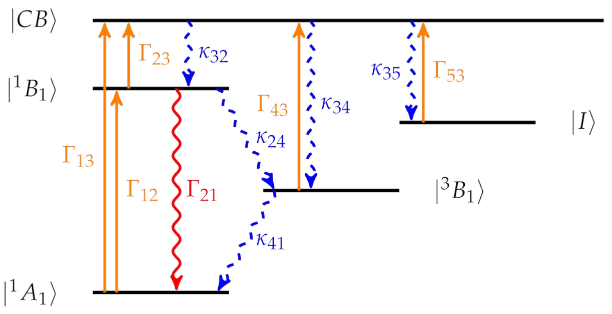


Cubic Boron Nitride



Hexagonal Boron Nitride





Density Functional Theory

- Many-body wavefunction

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_{N_e}) \sim (N_G)^{3N_e}$$

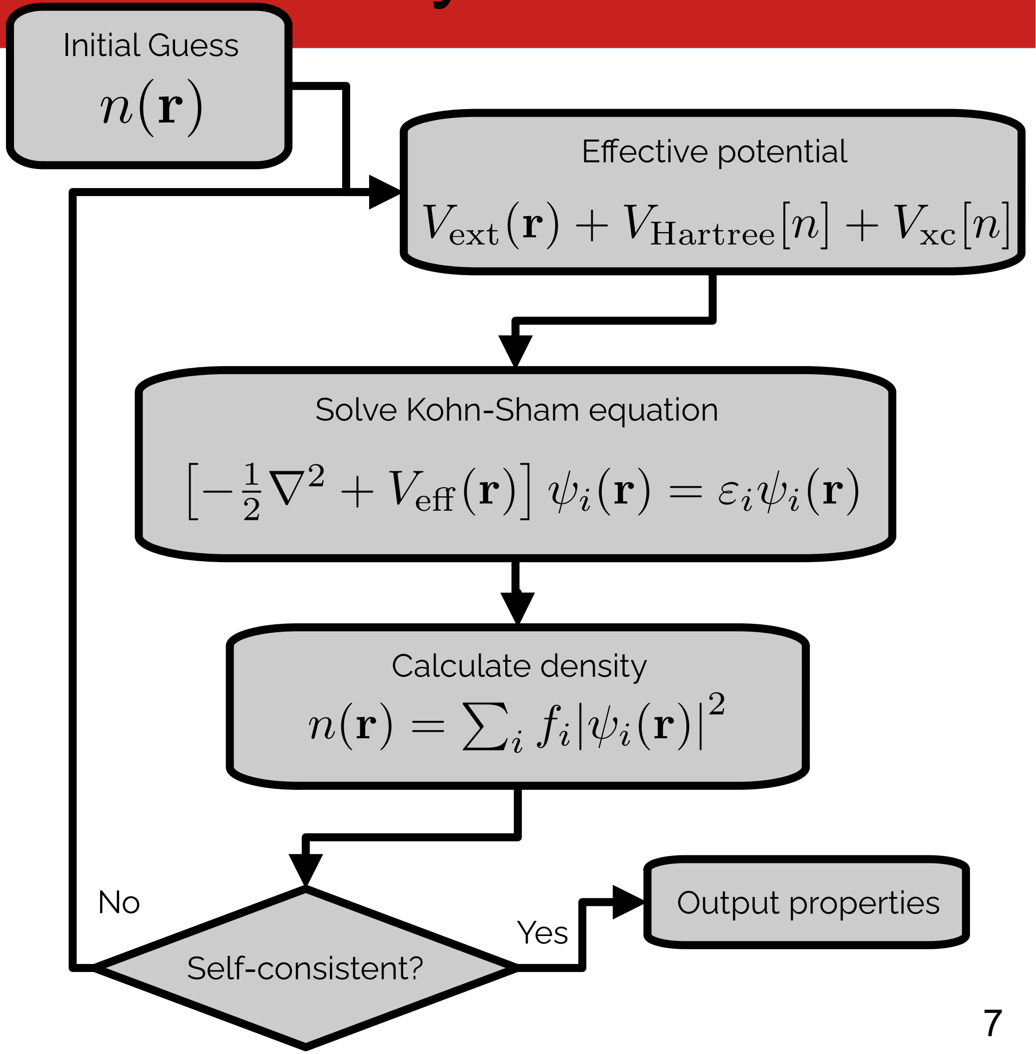
- P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

$$V_{\text{ext}} \Leftrightarrow n_0$$

- W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
  - Mean-field approx.

$$n_0^{\text{int}} \Leftrightarrow n_0^{\text{non-int}}$$

$$V_{\text{xc}}[n] = \langle \hat{T} \rangle - T_s[n] + \langle \hat{V}_{\text{int}} \rangle - E_{\text{Hartree}}[n]$$



Initial Guess

$n(\mathbf{r})$

Effective potential

$V_{\text{ext}}(\mathbf{r}) + V_{\text{Hartree}}[n] + V_{\text{xc}}[n]$

Solve Kohn-Sham equation

$\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$

Calculate density

$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2$

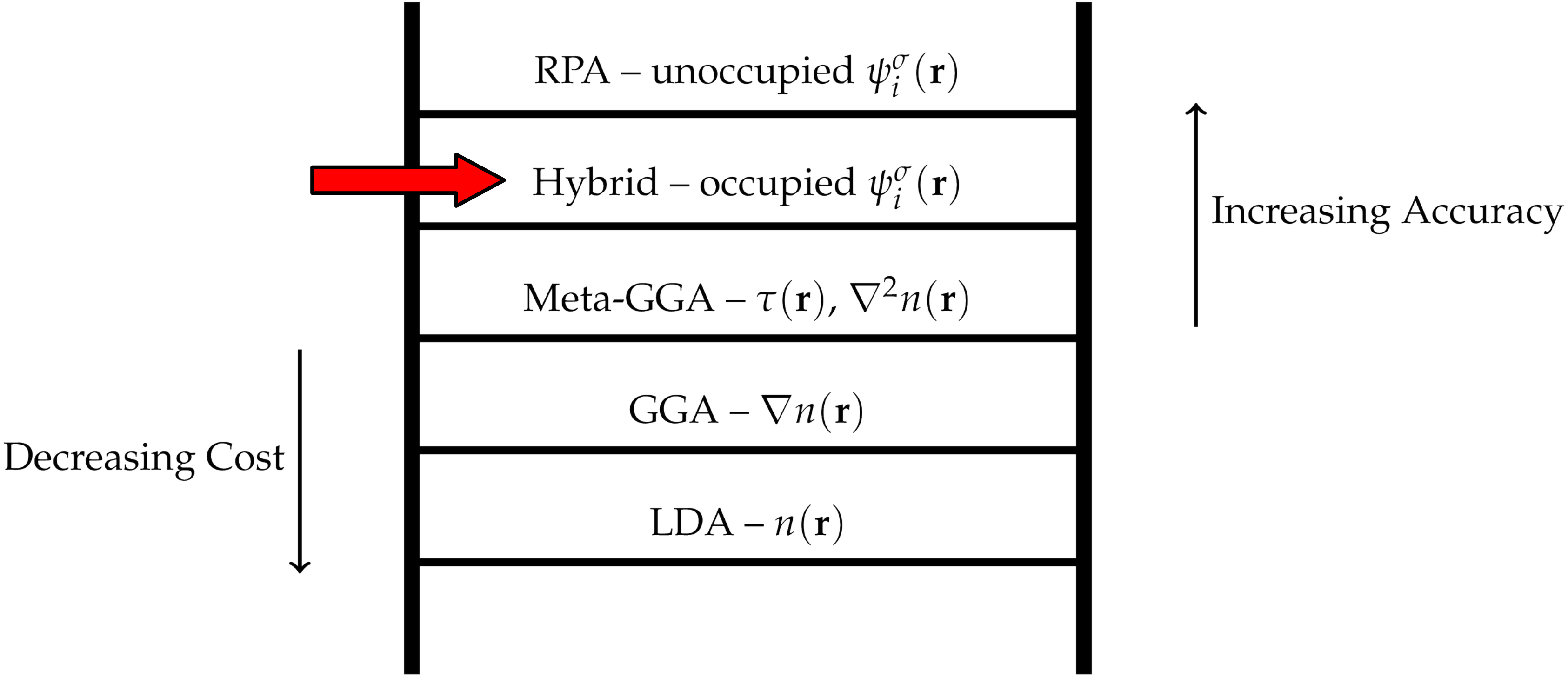
Self-consistent?

No

Yes

Output properties

Exchange-Correlation Functionals



RPA – unoccupied $\psi_i^\sigma(\mathbf{r})$

Hybrid – occupied $\psi_i^\sigma(\mathbf{r})$

Meta-GGA – $\tau(\mathbf{r})$, $\nabla^2 n(\mathbf{r})$

GGA – $\nabla n(\mathbf{r})$

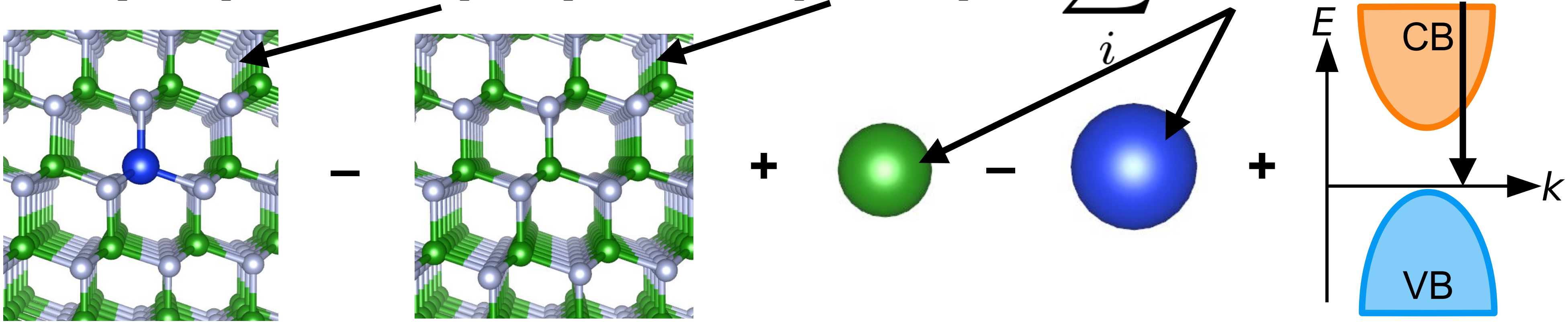
LDA – $n(\mathbf{r})$

- HSE hybrid functional implemented in VASP
  - Heyd *et al*., J. Chem. Phys. **124**, 219906 (2006)
  - Kresse and Furthmüller, Phys. Rev. B **54**, 11169 (1996)

Computational Details

- Nudged elastic band method to investigate migration
  - G. Henkelman *et al*., J. Chem. Phys. **113**, 9901 (2000)
- Constrained-occupation ΔSCF to address excited states
  - R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989)
- First-principles approach for defects
  - Freysoldt *et al*., Rev. Mod. Phys. **86**, 253 (2014)

$$E^f[X^q] = E_{\mathrm{tot}}[X^q] - E_{\mathrm{tot}}[\text{c-BN}] - \sum_i n_i \mu_i + q E_{\mathrm{F}}$$



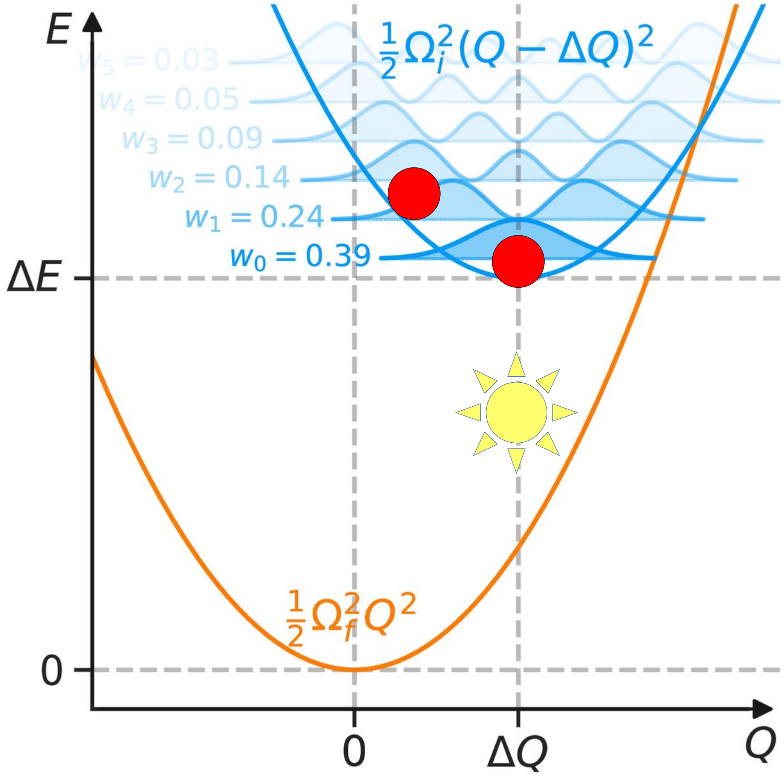
Configuration Coordinate Diagram

- Electron-phonon coupling
  - Huang-Rhys factor

$$S = \frac{1}{2\hbar}\Omega(\Delta Q)^2$$

- Semi-classical picture
  - Nonradiative
  - Radiative

- Used as the basis for a full quantum-mechanical treatment

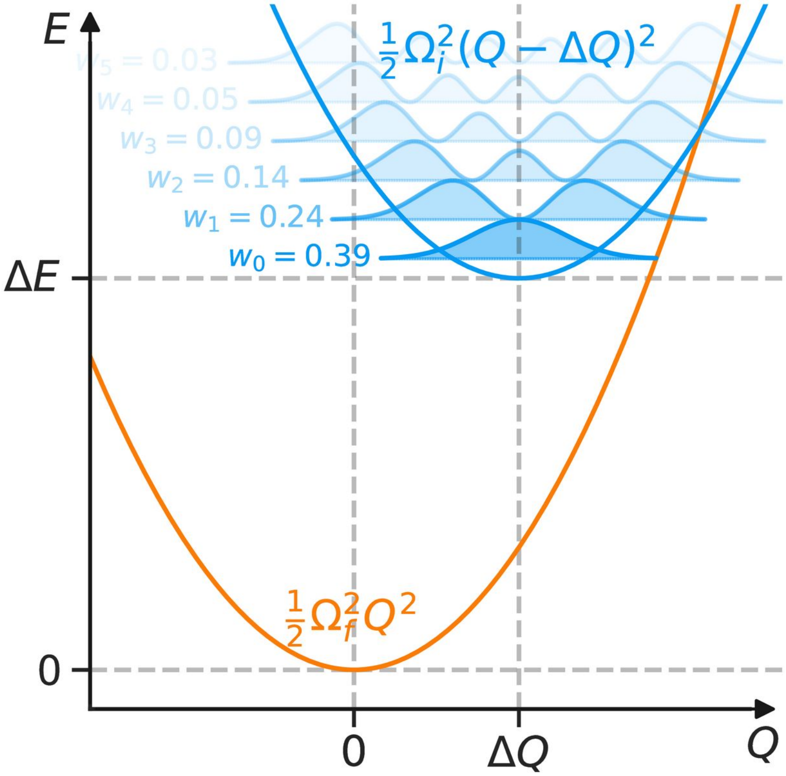


Nonradiative Capture

- First-principles formulation
  - A. Alkauskas *et al.*, Phys. Rev. B **90**, 075202 (2014).
  - Single, special mode approximation

$$C = f \frac{2\pi}{\hbar} g V W_{if}^2 \sum_m w_m \times$$

$$\sum_n \left|\langle \chi_{im} | \hat{Q} - Q_0 | \chi_{fn} \rangle\right|^2 \delta(\Delta E + m\hbar\Omega_i - n\hbar\Omega_f)$$



- Localized transitions
  - *f* = 1, *V* = 1
- Open-source code
  - https://github.com/mturiansky/nonrad
- Improvements
  - PAW formalism
  - Broadening
  - Sommerfeld parameter

M. E. Turiansky *et al.*, Comput. Phys. Commun. **267**, 108056 (2021).

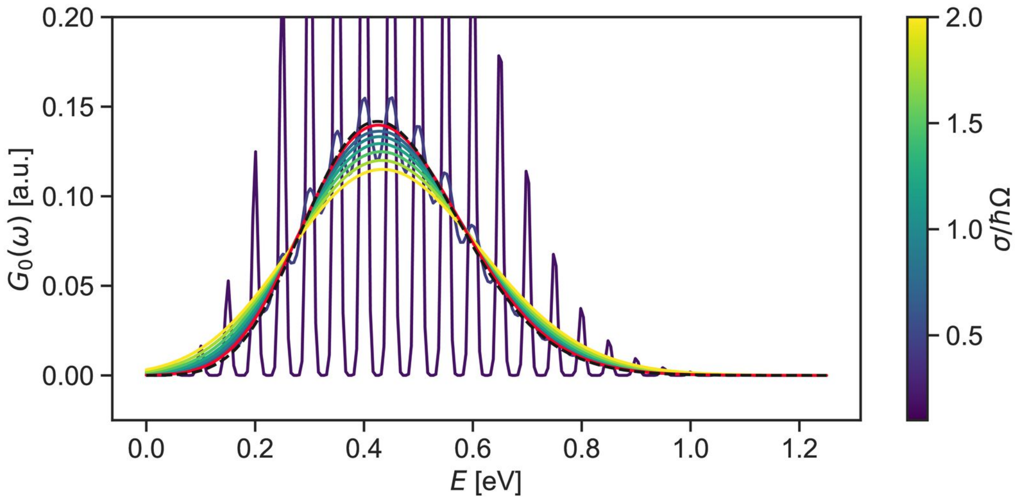
Broadening

$$C = f\frac{2\pi}{\hbar} g V W_{if}^2 \sum_m w_m \times$$

$$\sum_n \left|\langle\chi_{im}|\hat{Q}-Q_0|\chi_{fn}\rangle\right|^2 \boxed{\delta(\Delta E + m\hbar\Omega_i - n\hbar\Omega_f)}$$

- Delta function too restrictive
  - Random internal fields
  - Finite lifetime of states
  - 1D approximation
- Delta → Gaussian
  - Used in a diverse range of first-principles calculations
- Alternate scheme: interpolation
  - Cubic spline
  - Piecewise cubic hermite interpolating polynomial

$$G_0(\omega) = \sum_n \left|\langle\chi_{i0}|\hat{Q}-Q_0|\chi_{fn}\rangle\right|^2 \delta(\Delta E - n\hbar\Omega)$$



Broadening

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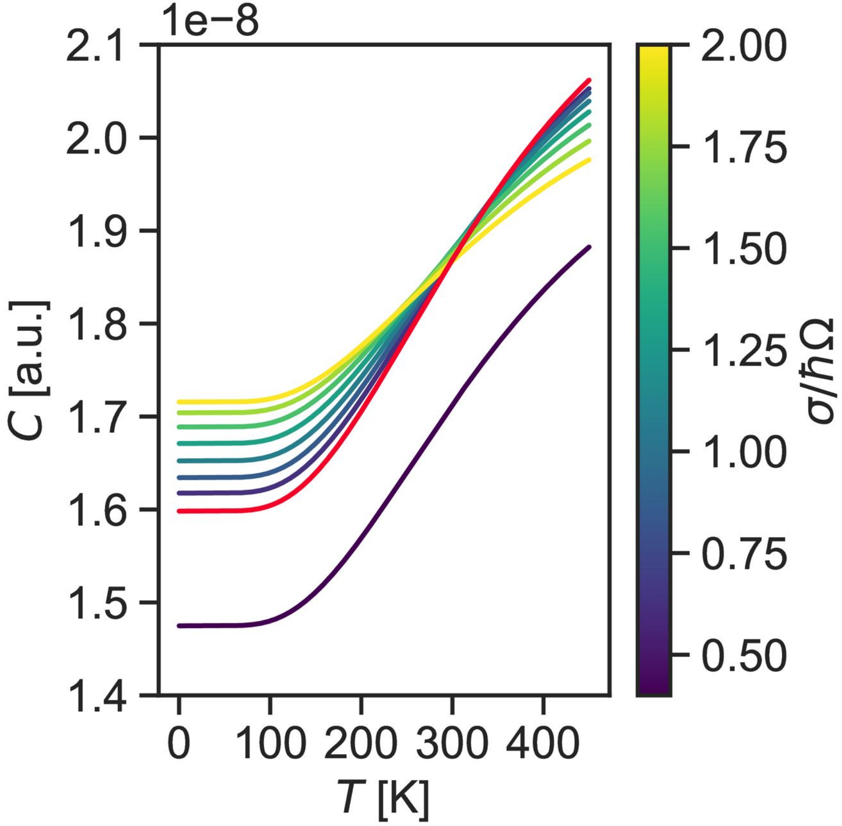


Sommerfeld Parameter

- Enhancement/suppression of carrier wavefunction near charge
- Analytic form $\theta_b = m_b e^4 / 32 k_B \epsilon_0^2 \hbar^2$

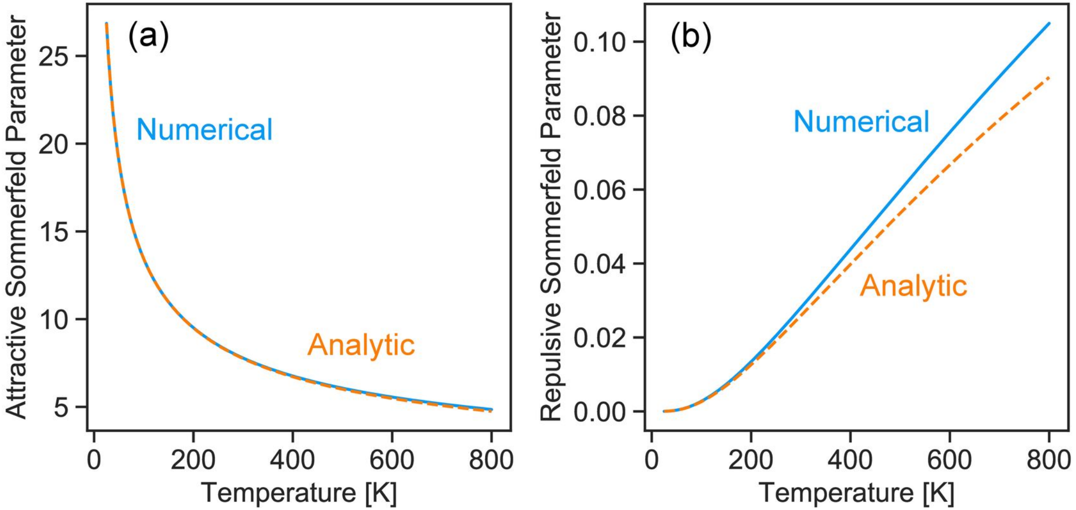
$$s(T) = \begin{cases} \frac{4}{\sqrt{\pi}} \left[\frac{Z^2\theta_b}{T}\right]^{1/2} & Z < 0 \\ \frac{8}{\sqrt{3}} \left[\frac{Z^2\theta_b}{T}\right]^{2/3} \exp\left(-3\left[\frac{Z^2\theta_b}{T}\right]^{1/3}\right) & Z > 0 \end{cases}$$

- Temperature averaging

$$s(\mathbf{k}) = -\frac{2\pi Z}{a_b|\mathbf{k}|} \frac{1}{1 - e^{2\pi Z / a_b |\mathbf{k}|}}$$

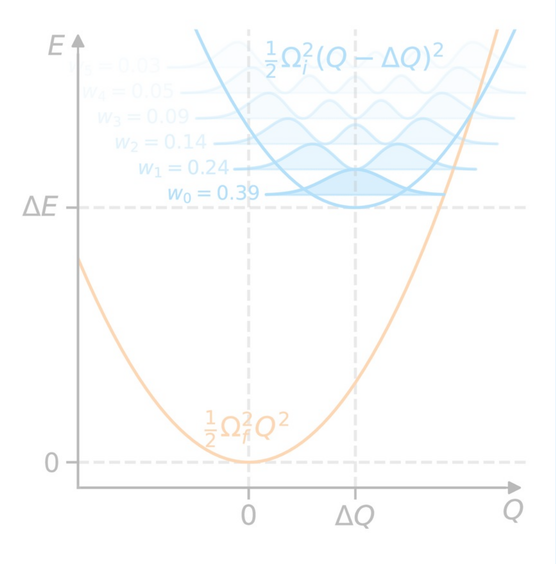
$$s(T) = \frac{\int_0^\infty d|\mathbf{k}|\, 4\pi |\mathbf{k}|^2\, s(\mathbf{k}) e^{-\hbar^2|\mathbf{k}|^2/2m_b k_B T}}{\int_0^\infty d|\mathbf{k}|\, 4\pi |\mathbf{k}|^2\, e^{-\hbar^2|\mathbf{k}|^2/2m_b k_B T}}$$

$|\mathbf{k}| \ll 2\pi|Z|/a_b$ $a_b = 4\pi\epsilon_0\hbar^2/m_b e^2$

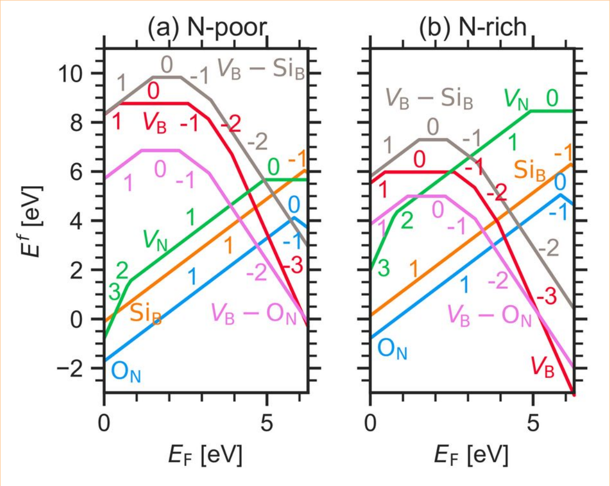


Outline

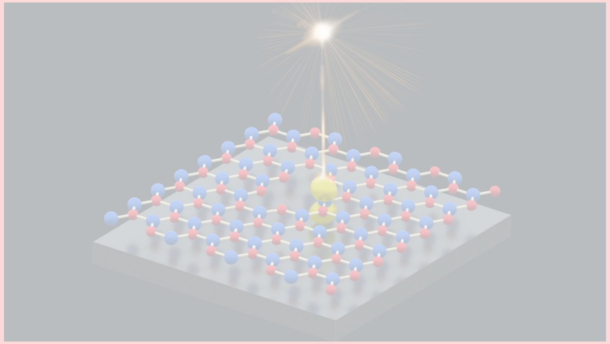
Theory

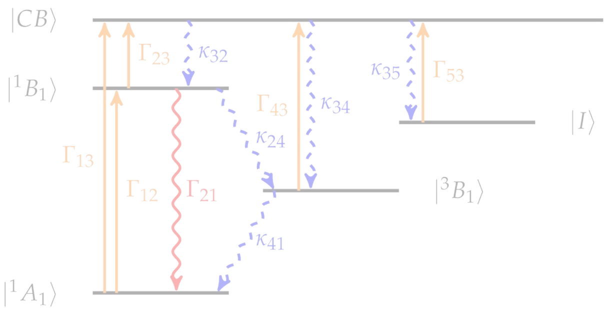


Cubic Boron Nitride



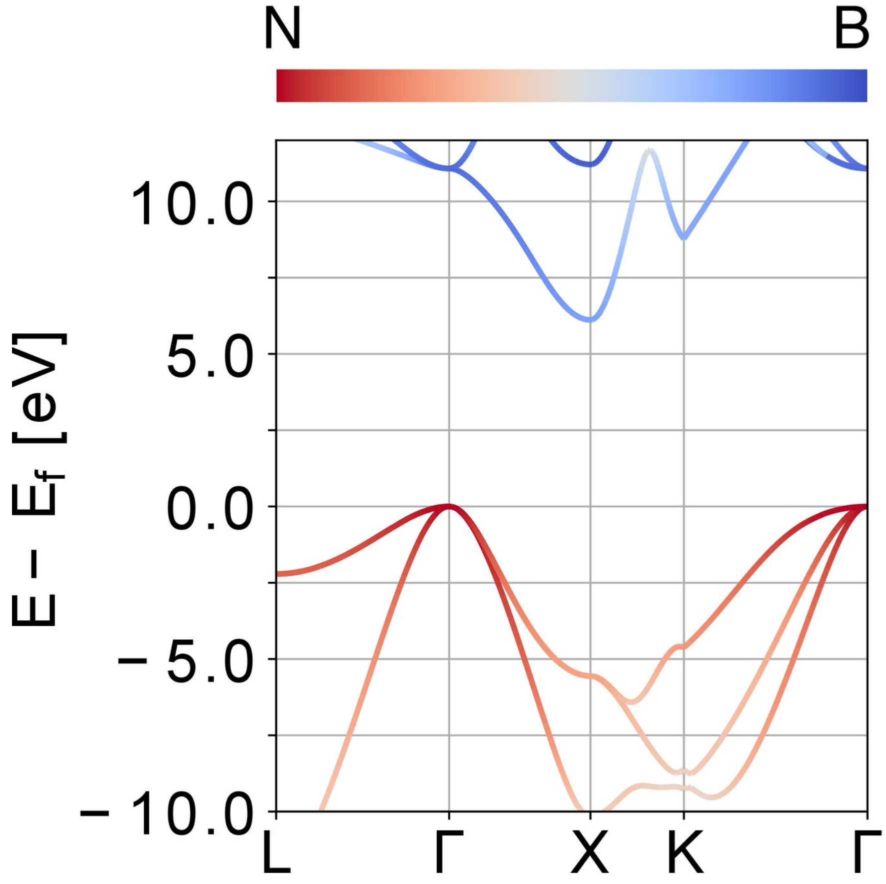
Hexagonal Boron Nitride



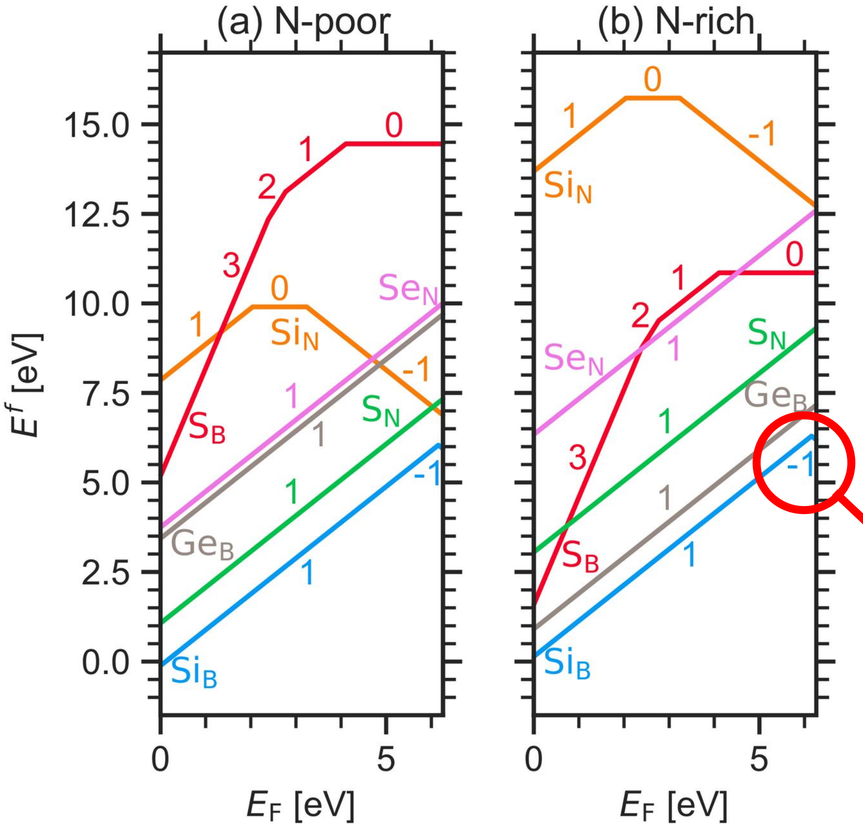


Motivation

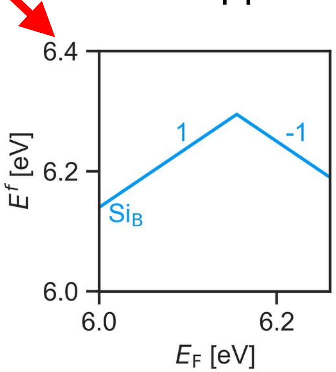
- Cubic boron nitride
  - Wide band gap (6.26 eV)
  - High breakdown field
  - Thermal + chemical stability
  - Claims of *n*- and *p*-type dopability
- Promising applications
  - Power electronics
  - Deep-UV optoelectronics
  - Host for quantum defects
- *Controllable dopability is essential for applications!*
  - L. Weston *et al.*, Phys. Rev. B **96**, 100102 (2017)



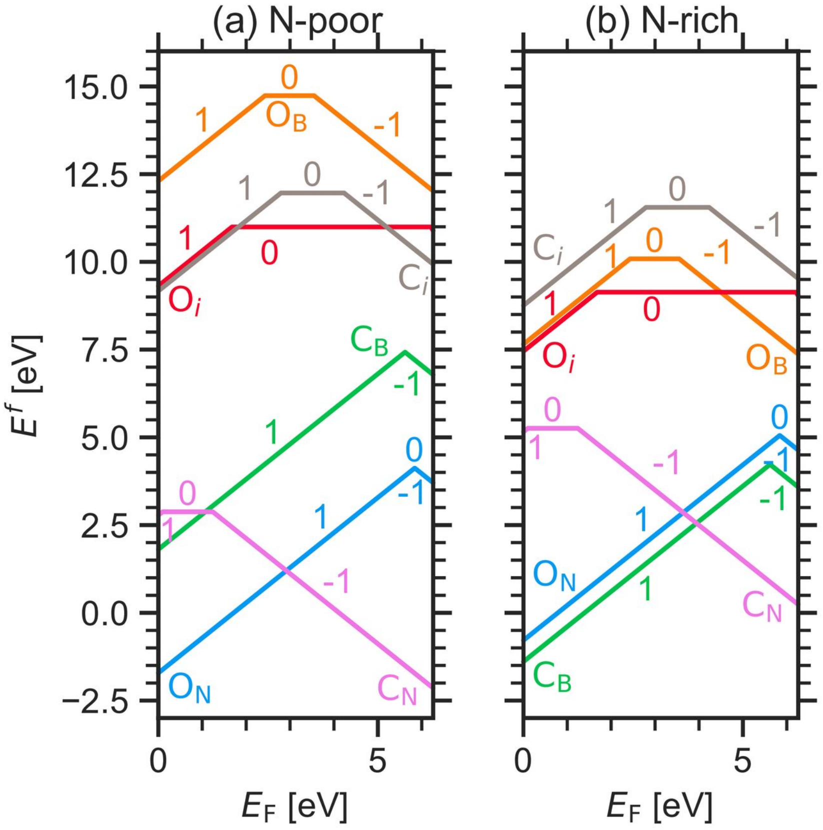
Intentional Dopants



- Considered Si, Ge, S, and Se
- Ge_B and S_N high in formation energy
- Si_B is promising
  - Free from self-compensation
  - *DX* center
  - ε(+/-) = 0.11 eV below conduction band
  - K. Hirama *et al*., Appl. Phys. Lett. **116**, 162104 (2020)



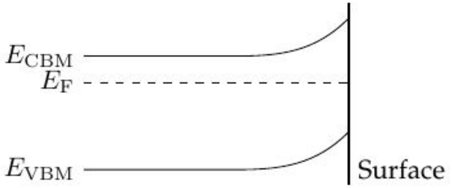
Unintentional Impurities

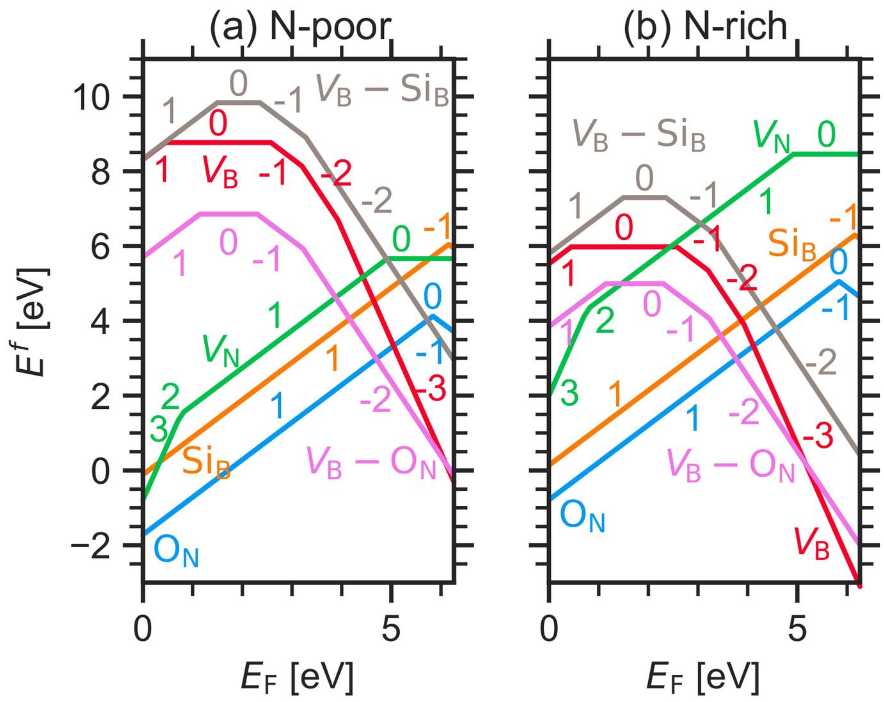


- C, O ubiquitous impurities
- C prone to self-compensation
- O_N is promising
  - Free from self-compensation
  - *DX* center
  - ε(+/-) = 0.42 eV below conduction band
  - At room temperature, 10^{16} cm^{-3} O → 10^{14} cm^{-3} carriers
  - T. Taniguchi *et al*., Jpn. J. Appl. Phys. **41**, L109 (2002).

Compensation by Vacancies

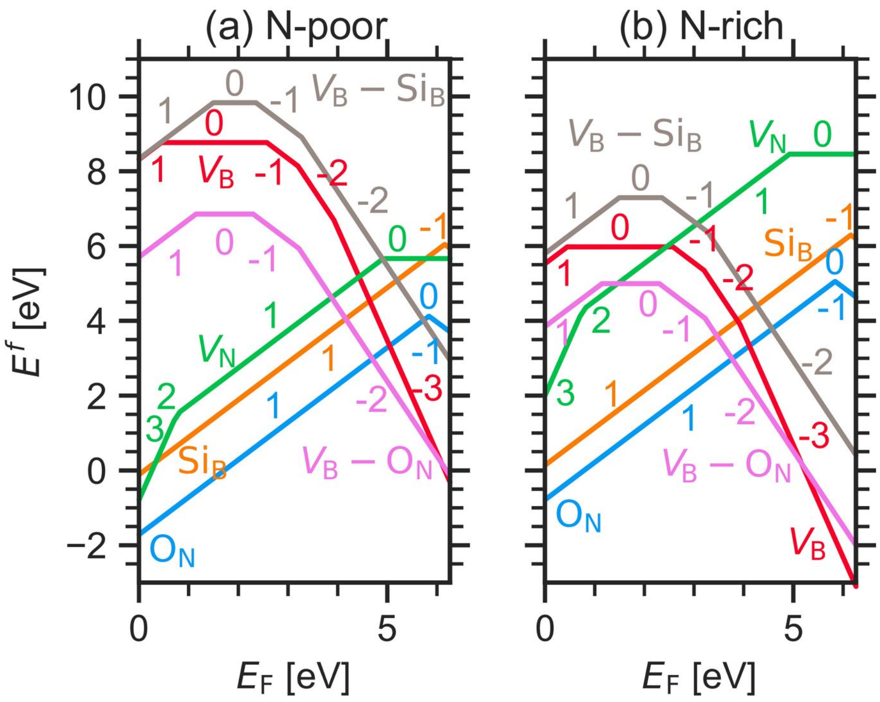
- V_B deep acceptor
    - Compensation
- Complex formation makes things worse!
- V_B immobile below 1300 K
    - Non-equilibrium effects
    - High pressure, high temperature growth > 1300 K
    - Thin film growth < 1300 K
    - Band bending favors incorporation of dopants





Summary

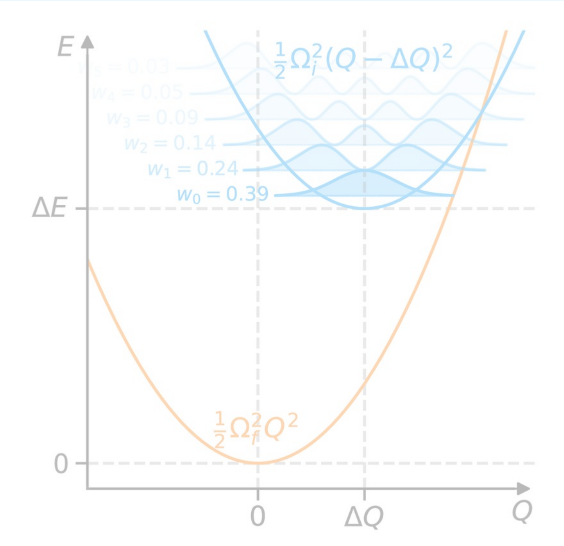
- Si$_B$ and O$_N$ are the most promising *n*-type dopants.
- Compensation by V_B poses a problem for doping efforts.
- Control of growth kinetics is essential to improve doping.



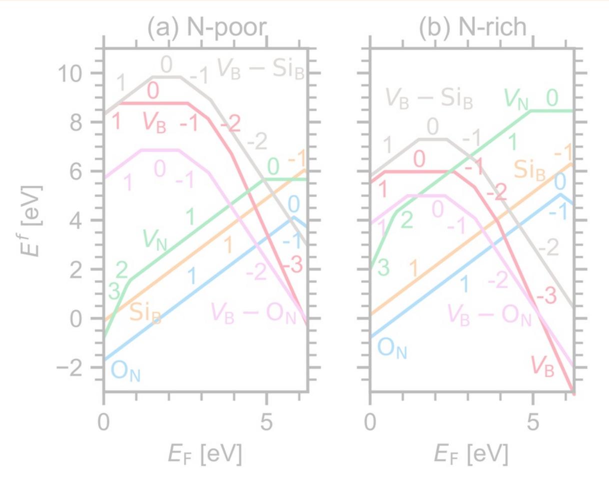
M. E. Turiansky, D. Wickramaratne,
J. L. Lyons, and C. G. Van de Walle,
Appl. Phys. Lett. **119**, 162105 (2021).

Outline

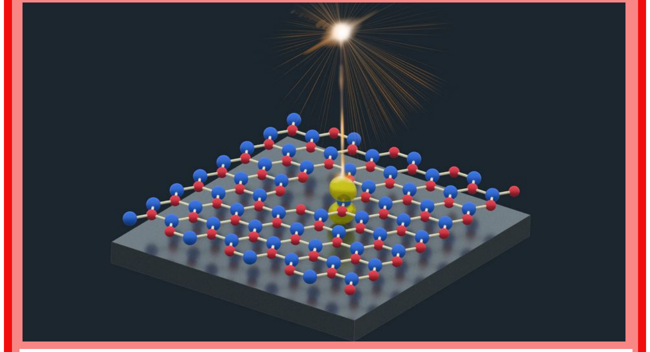
Theory

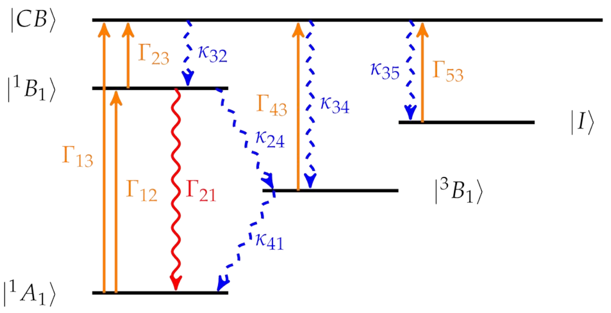


Cubic Boron Nitride



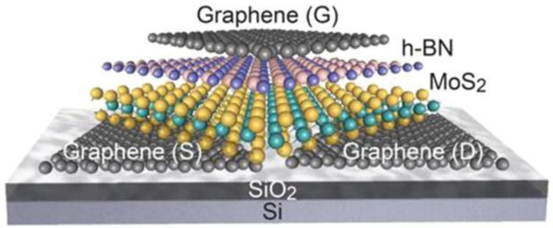
Hexagonal Boron Nitride





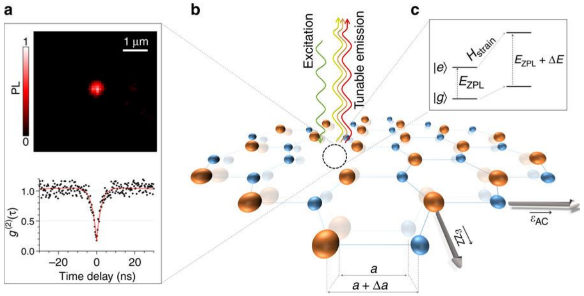
Hexagonal Boron Nitride (h-BN)

Two-dimensional devices



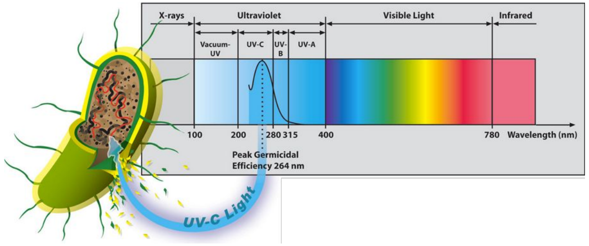
T. Roy *et al.*,
ACS Nano **8**, 6259 (2014).

Single-photon emission



G. Grosso *et al.*,
Nat. Commun. **8**, 705 (2017).

Ultra-wide-bandgap devices

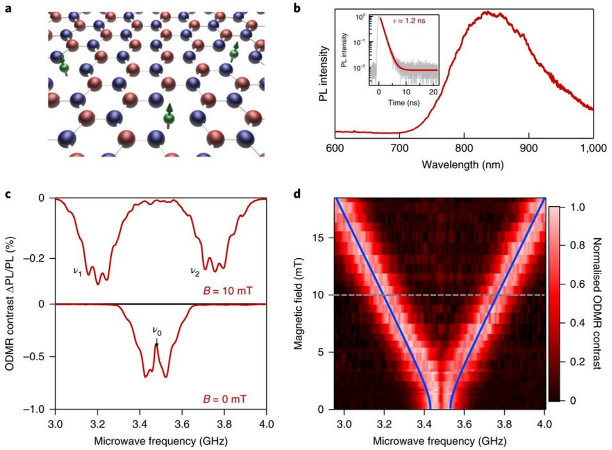


Kowalski, “Mathematical Modeling of Ultraviolet
Germicidal Irradiation for Air Disinfection” (2000).

- Two-dimensional, layered material
- Large, indirect band gap of 6.08 eV
- Promising for electronics + optoelectronics, and as *a host for quantum defects*

Quantum Defects in hBN

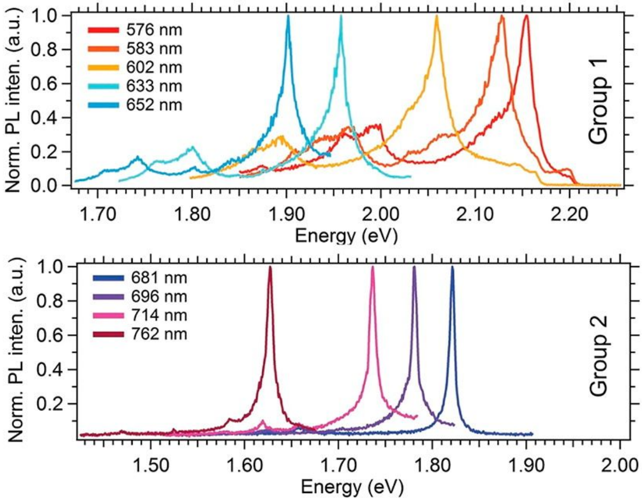
Spin center



V_B^-

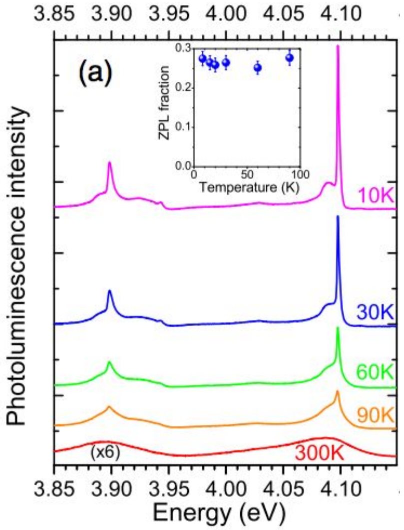
A. Gottscholl *et al.*,
Nat. Mater. **19**, 540 (2020).
M. E. Turiansky *et al.*,
Nat. Mater. **19**, 487 (2020).

Visible emitters



T. Tran *et al.*, ACS Nano **10**, 7331 (2016).

UV emitters

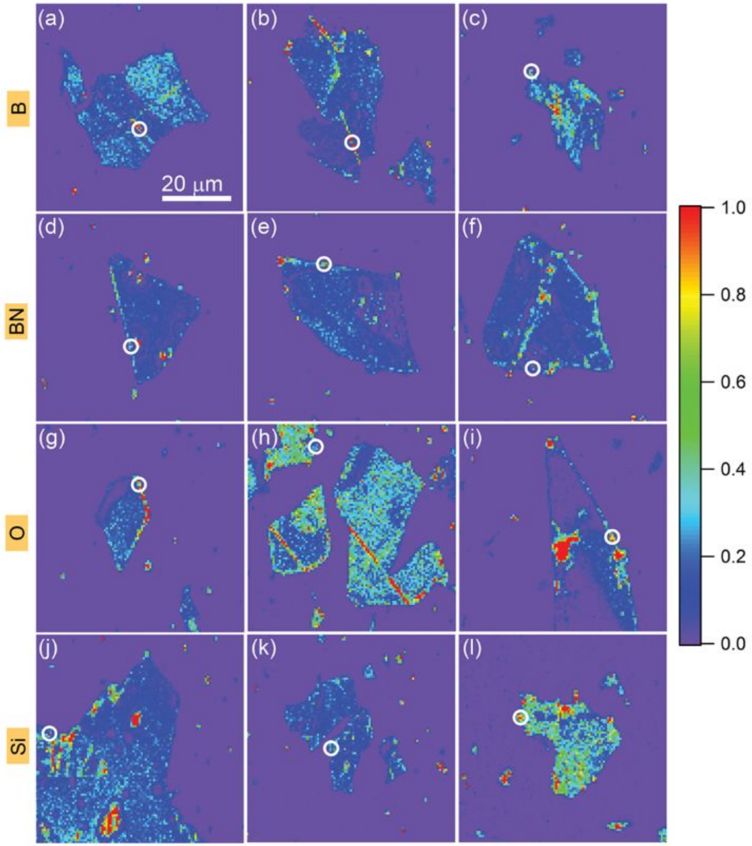


$C_BC_N^0$

T. Vuong *et al.*,
Phys. Rev. Lett. **117**, 097402 (2016).
M. Mackoit-Sinkevičienė *et al.*,
Appl. Phys. Lett. **115**, 212101 (2019).

2 eV Single-Photon Emitters

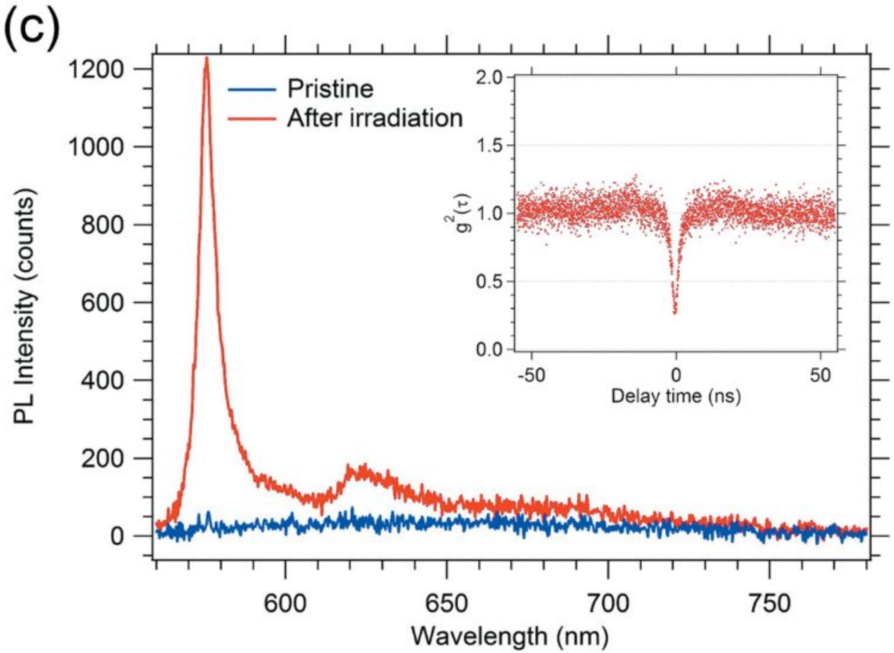
- Rare → low densities
- Present in as-grown samples
- Can be created/activated with irradiation, annealing, nanopillars, ...
- Generally near flake edges or extended defects



S. Choi *et al.*,
ACS Appl. Mater. Interfaces **8**, 29642 (2016).

2 eV Single-Photon Emitters

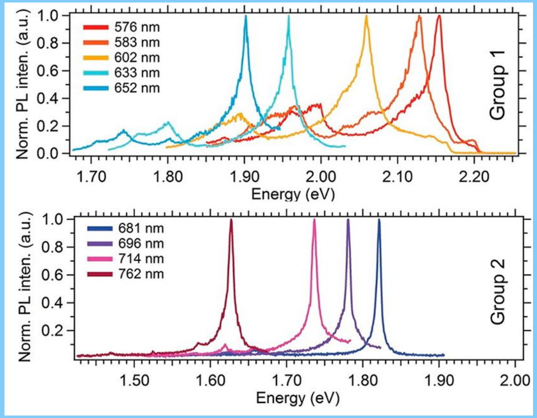
- Zero-phonon line ~ 2 eV
- Linearly polarized emission
- Relatively weak coupling to phonons
  - Huang-Rhys factor S ~ 1-2
  - N. R. Jungwirth *et al*., Nano Lett. **16**, 6052 (2016).
  - Acoustic phonons in 2D → S ~ 2-3



S. Choi *et al*.,
ACS Appl. Mater. Interfaces **8**, 29642 (2016).

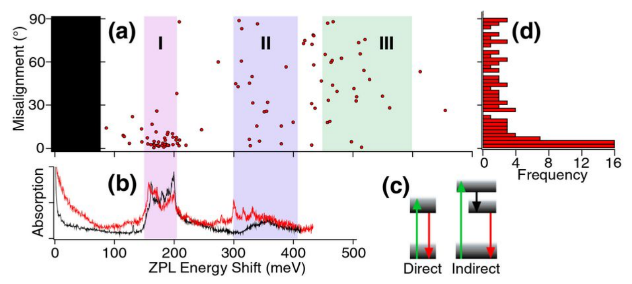
2 eV Single-Photon Emitters

Multicolor emission



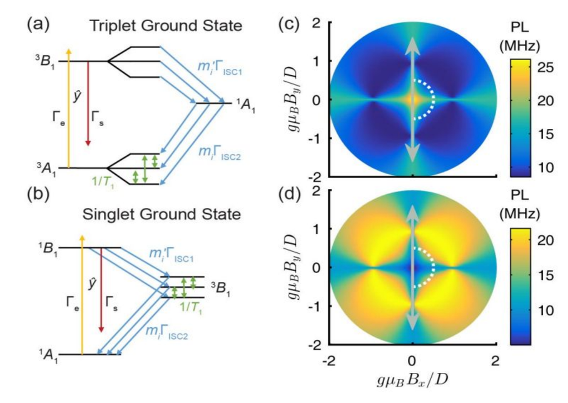
T. Tran *et al.*,
ACS Nano **10**, 7331 (2016).

Optical polarization



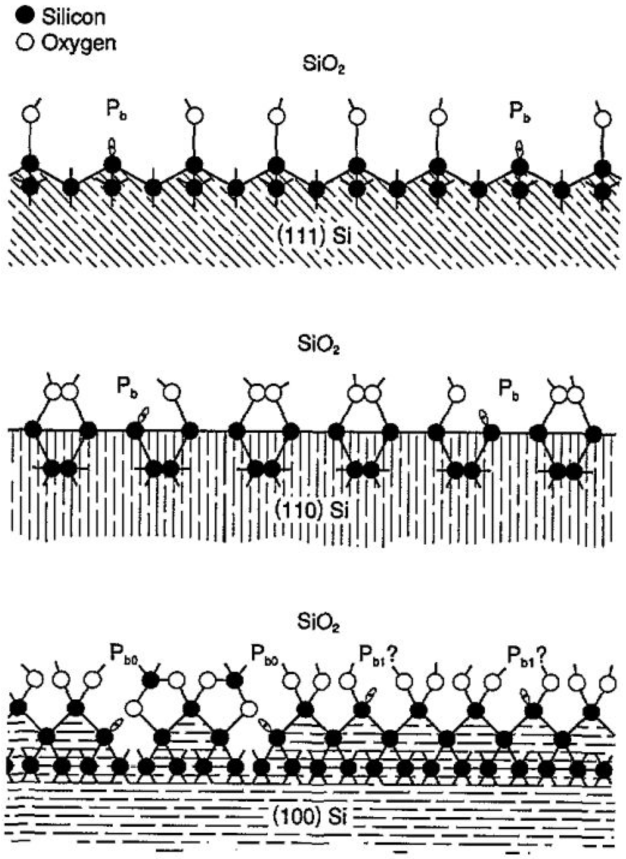
N. Jungwirth and G. Fuchs,
Phys. Rev. Lett. **119**, 057401 (2017).

Magnetic field response



A. Exarhos *et al.*,
Nat. Commun. **10**, 222 (2019).

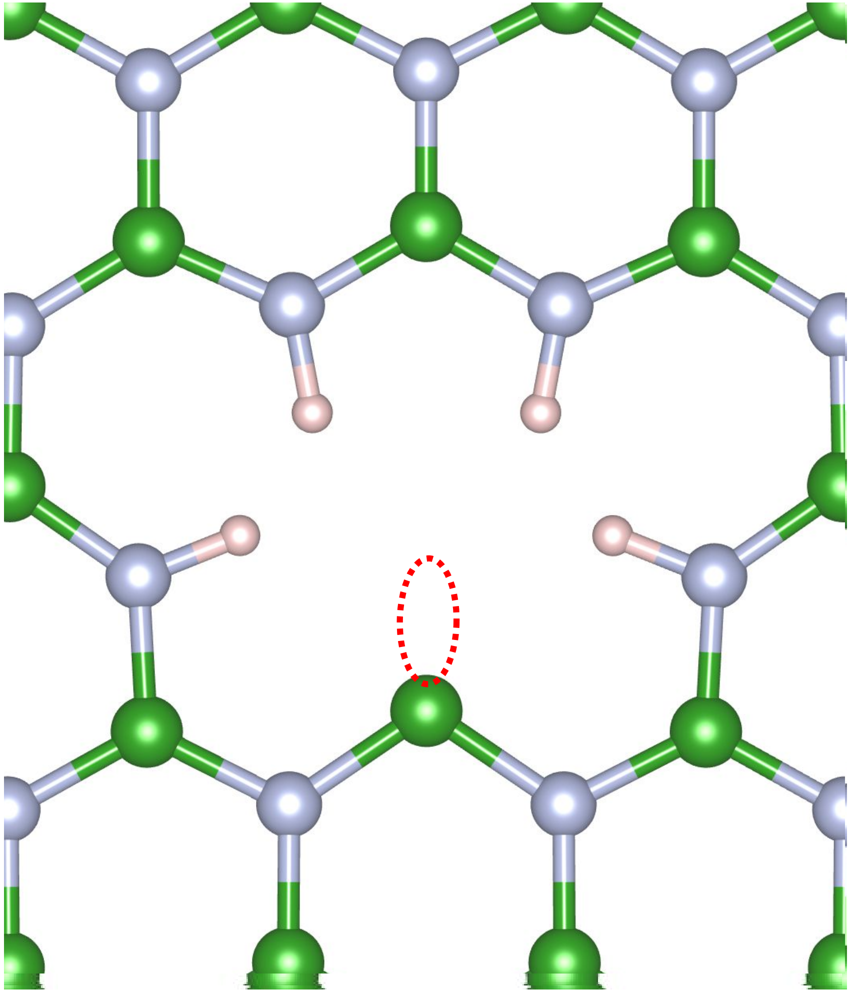
Dangling Bonds?



C. R. Helms and E. H. Poindexter, Rep. Prog. Phys. **57**, 791 (1994).

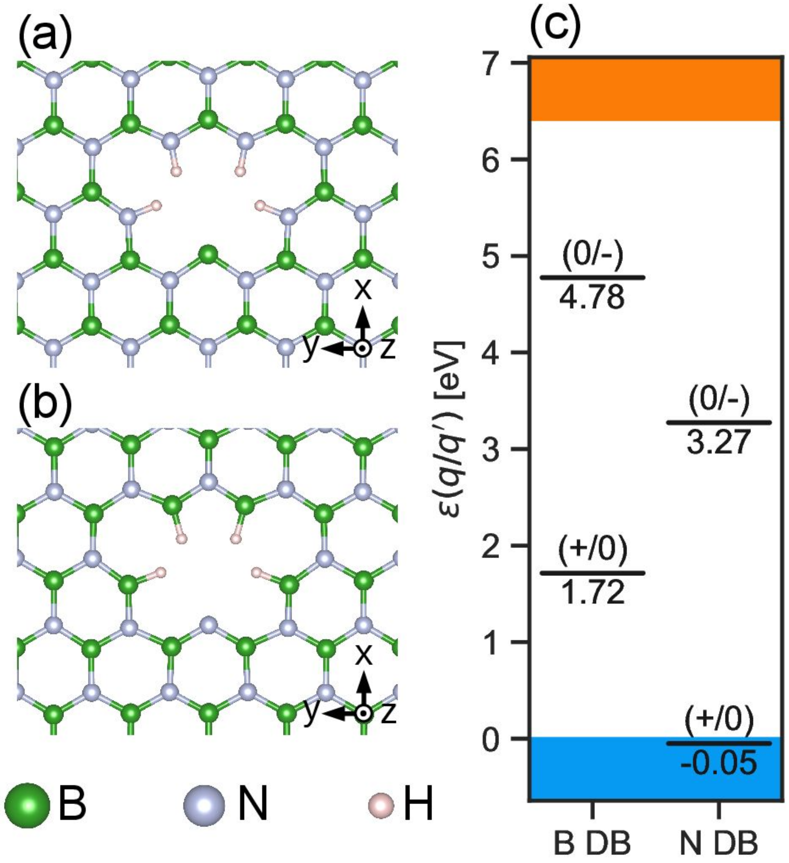
- Ubiquitous defect in Si
- Single broken bond
  - “partial” vacancy
- Found where bonding is disrupted
  - interfaces, grain boundaries, line defects, large voids, ...
- Sensitive to local environment
  - Heterogeneity
  - Could explain multicolor emission
- May be extremely stable

Modeling a Dangling Bond



Transition Levels

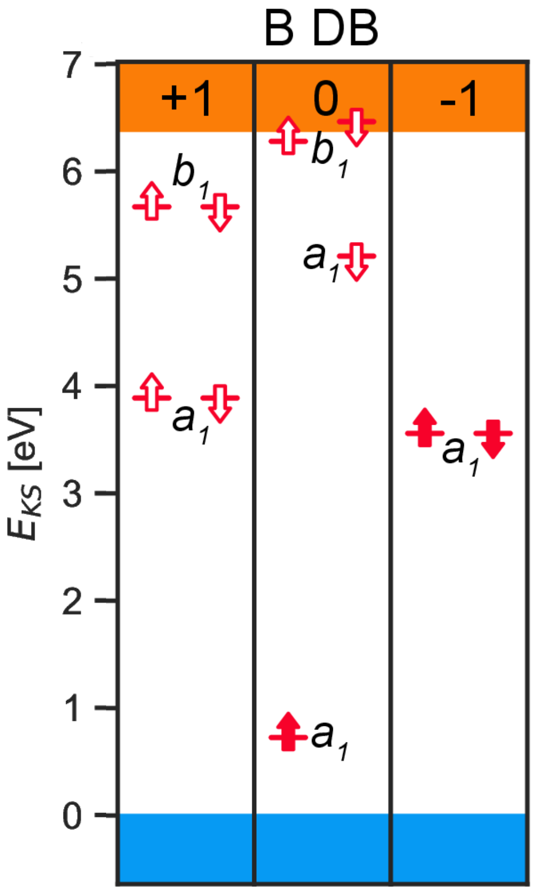
- Considered both B and N dangling bonds
- C_{2v} symmetry
- Rule out N dangling bonds
- Expect transition level in upper half of band gap
  - Z.-Q. Xu *et al.*, 2D Mater. **7**, 031001 (2020).



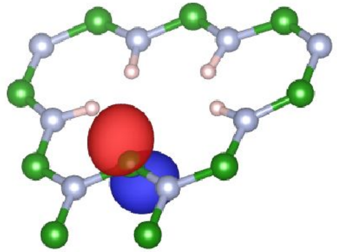
M. E. Turiansky *et al.*, Phys. Rev. Lett. **123**, 127401 (2019).

Single-Particle States

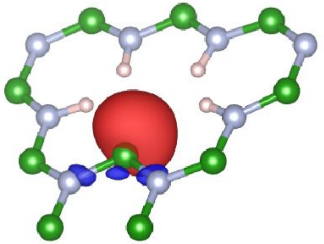
- a_1 → dangling bond
- b_1 → localized p_z state
- Rule out +1 and 0 states
  - 3.27 eV transition in 0
- Focus on -1
  - Doubly occupied dangling bond state
  - Hypothesize that b_1 will become localized



(b) b_1

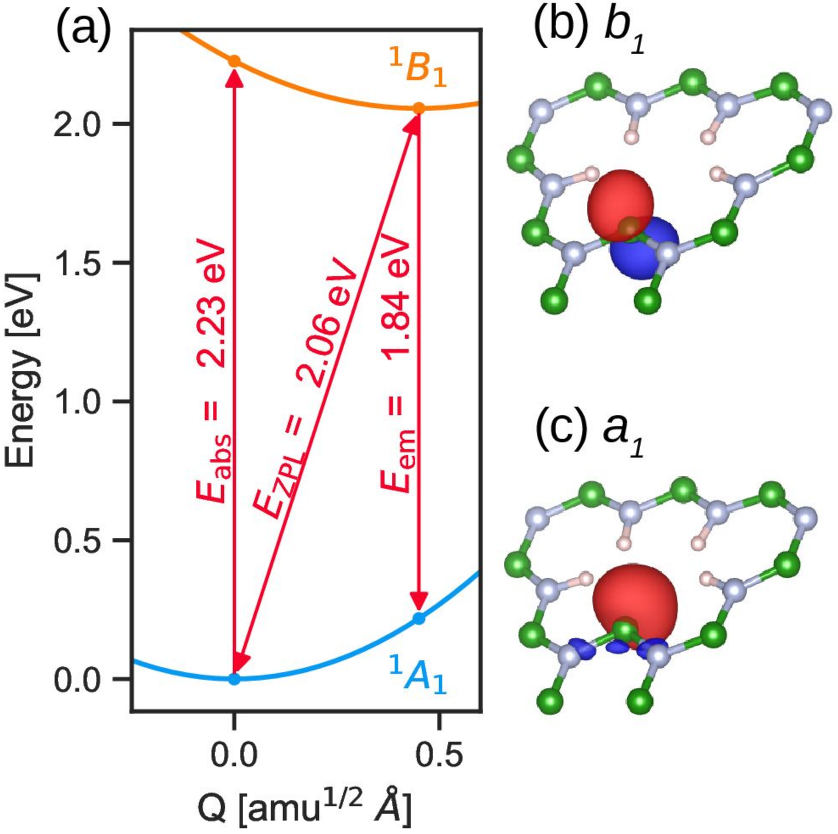


(c) a_1



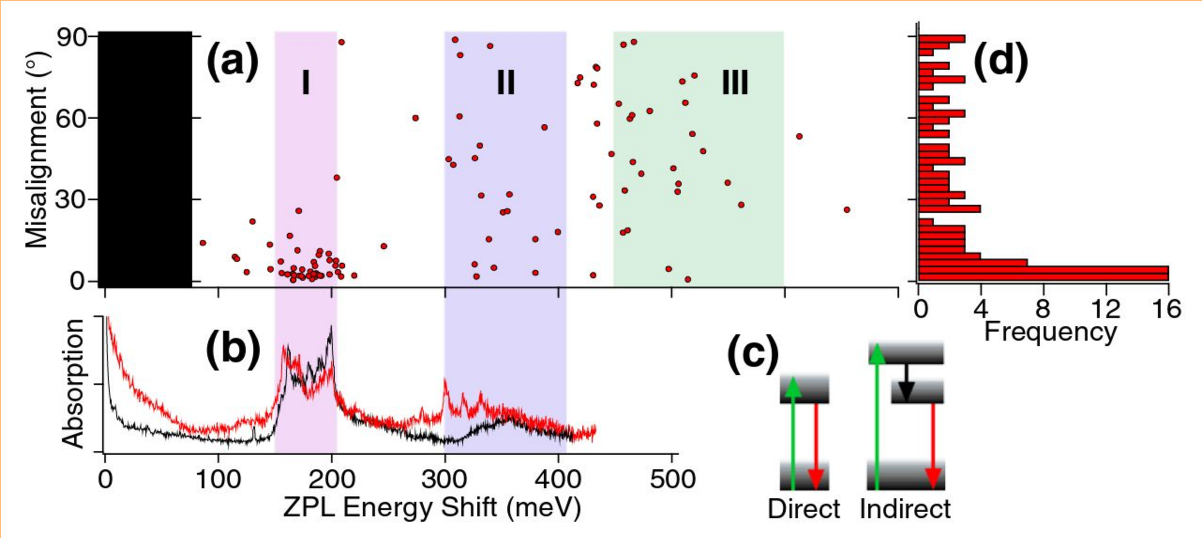
Optical Transition

- Zero-phonon line (ZPL) agrees well with experiment
- Huang-Rhys factor *S* = 2.3
- Linearly polarized
  - Expect lower symmetry

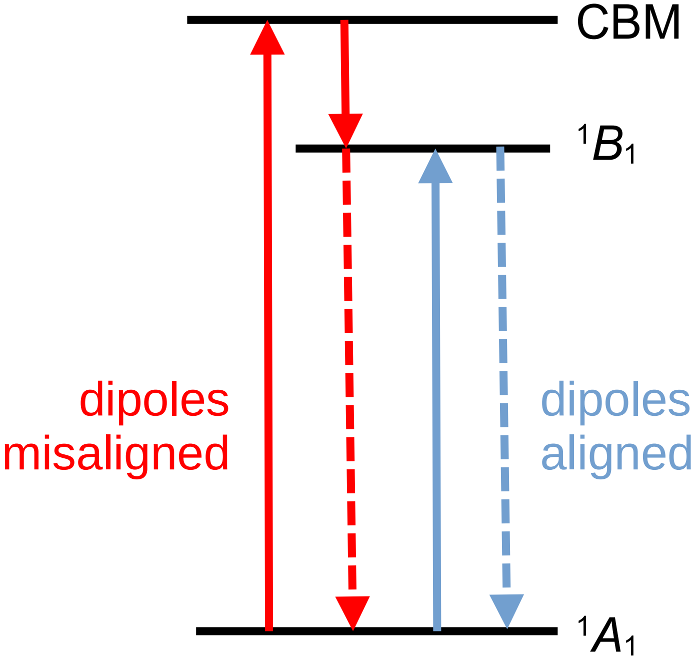


Dipole Misalignment

Optical polarization



N. Jungwirth and G. Fuchs,
Phys. Rev. Lett. **119**, 057401 (2017).

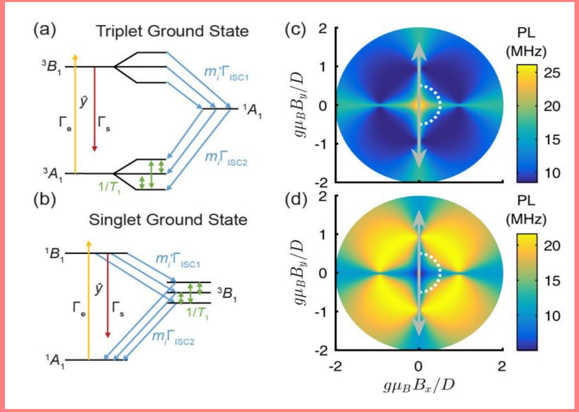


- Photoionization may be important
  - P. Khatri *et al*., Nano Lett. **20**, 4256 (2020).

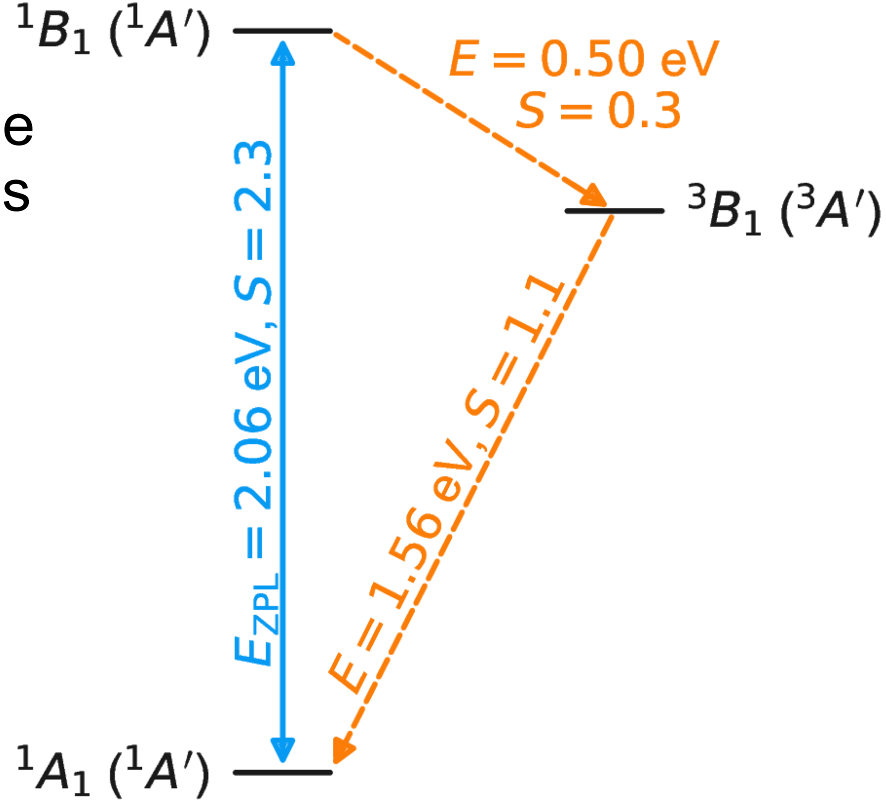
Magnetic-Field Dependence

- High spin configuration
- Magnetic-field dependent optical response
- Consistent with experimental observations after considering C_{1h} symmetry
- Necessary for spin-based sensing

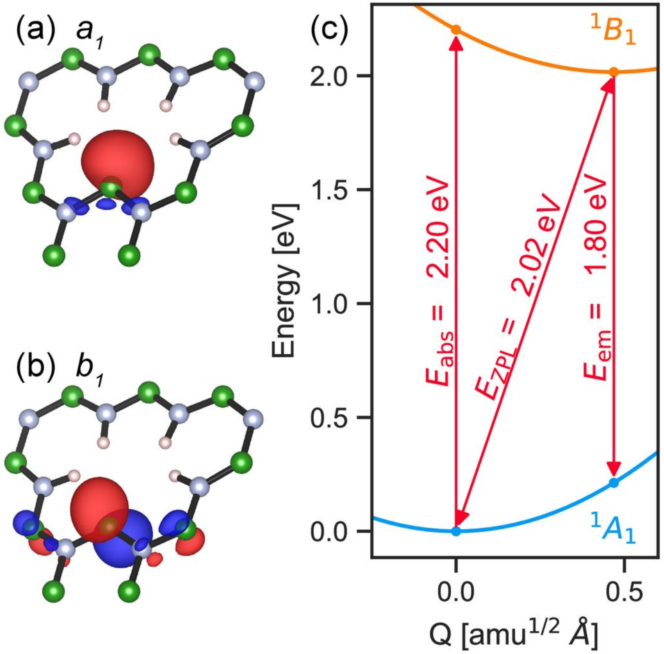
Magnetic field response

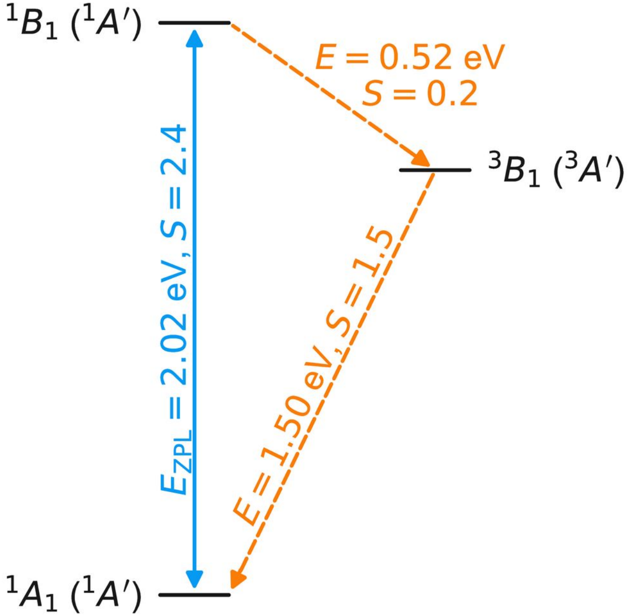


A. Exarhos *et al.*,
Nat. Commun. **10**, 222 (2019).



Dangling Bonds in a Monolayer



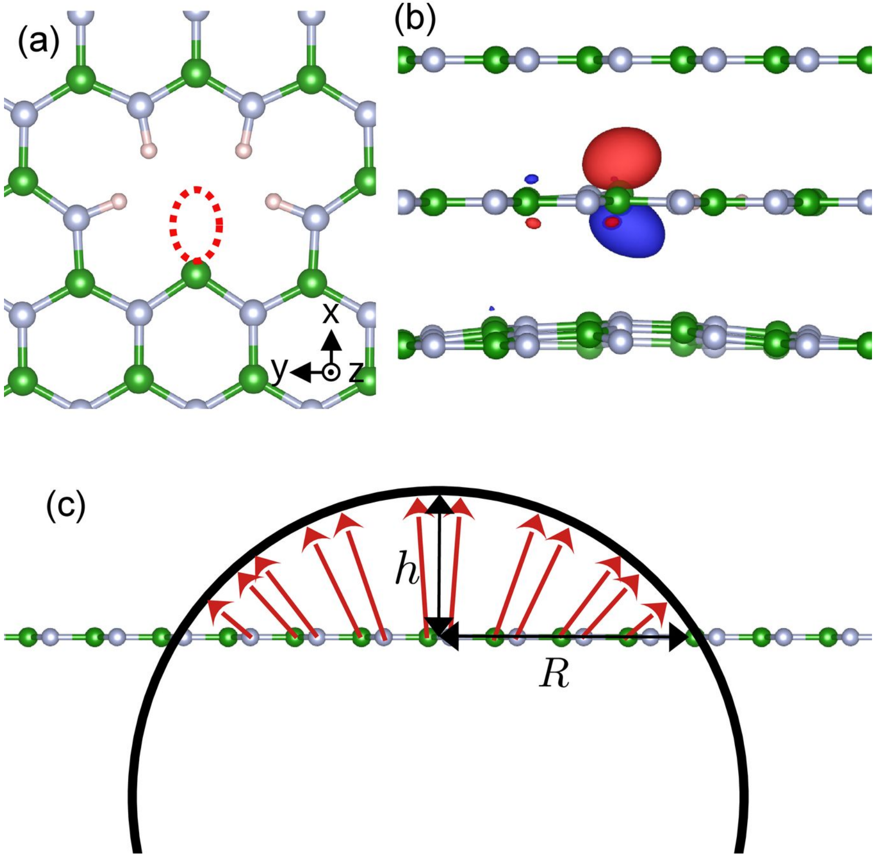


- Optical transition in monolayer is similar to transition in bulk
- Differences in triplet state may affect magnetic-field dependence

M. E. Turiansky and C. G. Van de Walle, J. Appl. Phys. **129**, 064301 (2021).

Out of Plane Distortions

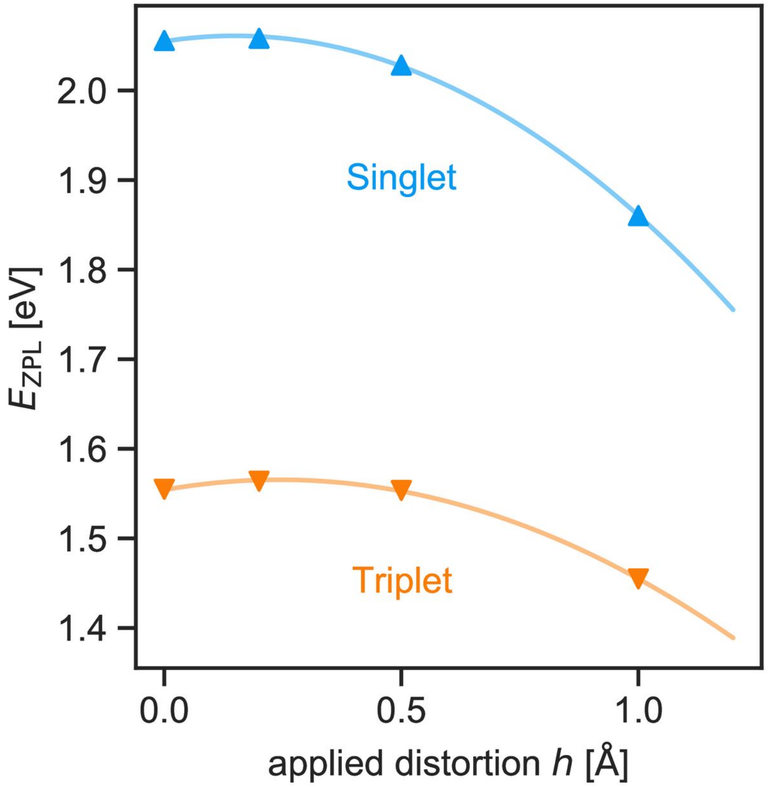
- 2D materials live in 3D
- Symmetry lowering is a consistent theme for dangling bonds
- Emitters found near extended defects and wrinkles
- Nanobubbles to activate emitters
  - W. Liu *et al*., Physica E Low Dimens. Sys. Nanostruct. **124**, 114251 (2020).



M. E. Turiansky and C. G. Van de Walle, 2D Mater. **8**, 024002 (2021).

Zero-Phonon Line

- Distortion reduces zero-phonon line energy
  - Could explain range of energies observed
- Increases coupling to phonons (Huang-Rhys factor)
  - Excited state moves further out of plane
  - N. R. Jungwirth *et al.*, Nano Lett. **16**, 6052 (2016).

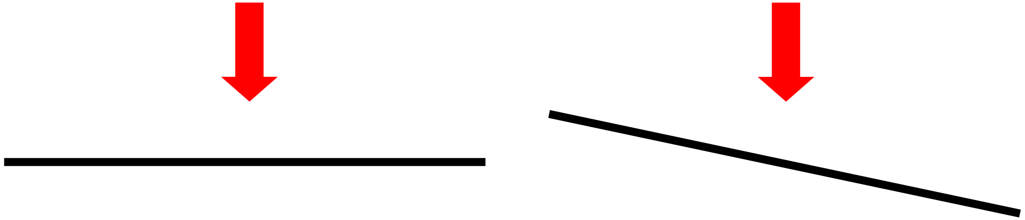


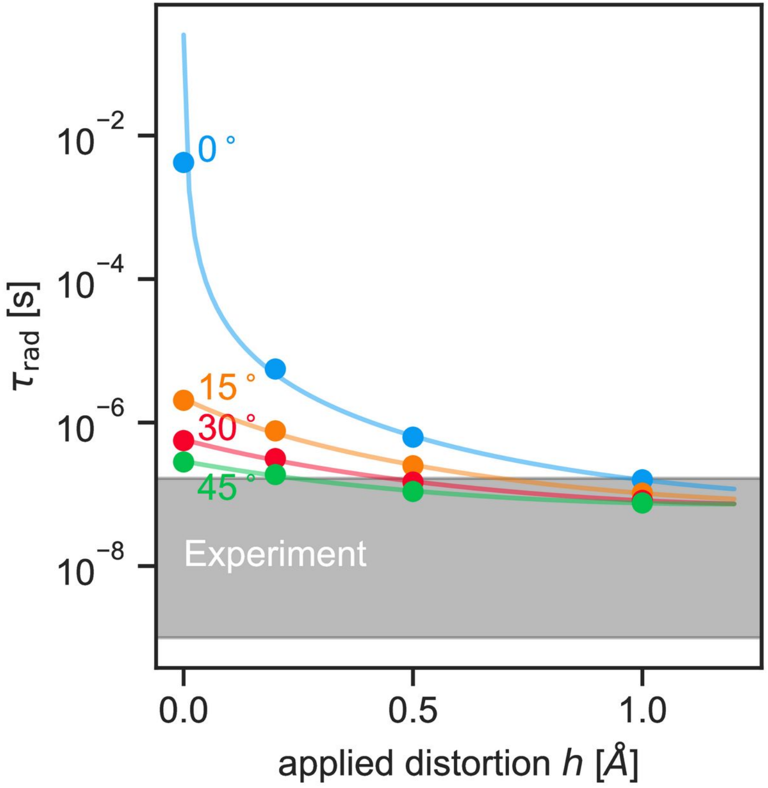
Radiative Lifetime

- Radiative lifetime

$$\Gamma_{\text{rad}} = \tau_{\text{rad}}^{-1} = \frac{n E_{\text{ZPL}}^3 \mu^2}{3\pi\varepsilon_0 c^3 \hbar^4}$$

- Typical anti-bunching lifetime ~1-10 ns
- Quantum efficiency as low as 6%
  - X. Li *et al*., ACS Nano **13**, 6992 (2019).
- Two important effects
  - Distortion
  - Misalignment
    - Is the light really orthogonal to the plane?

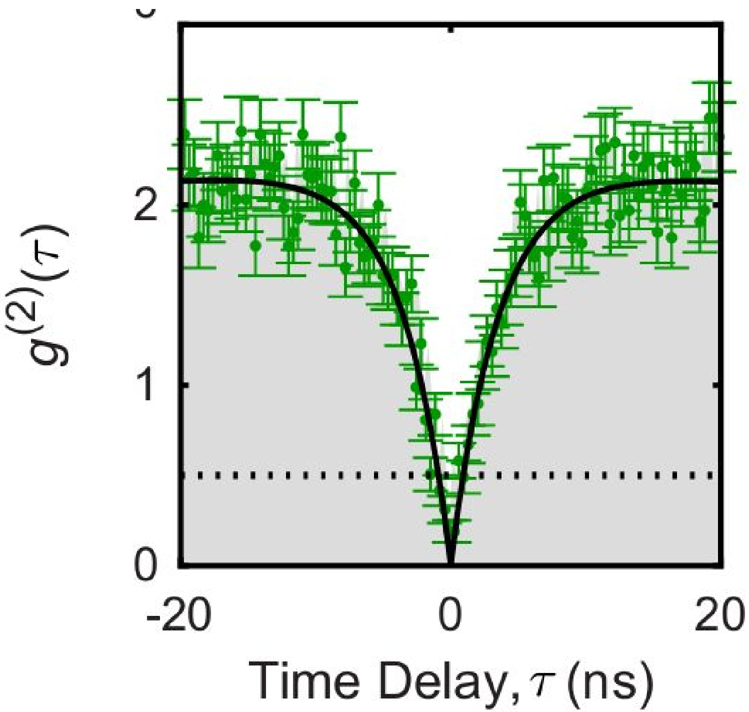




Photon Autocorrelation

- Measurements performed by experimental collaborators at UPenn
- Hanbury Brown-Twiss experimental setup
- Demonstrates single-photon emission

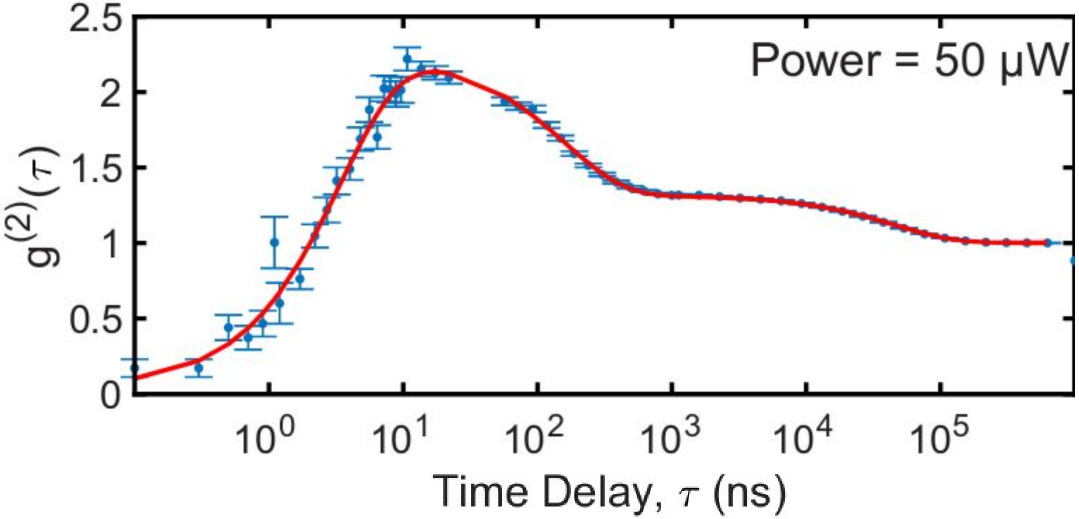
$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2}$$



Photon Emission Correlation Spectroscopy

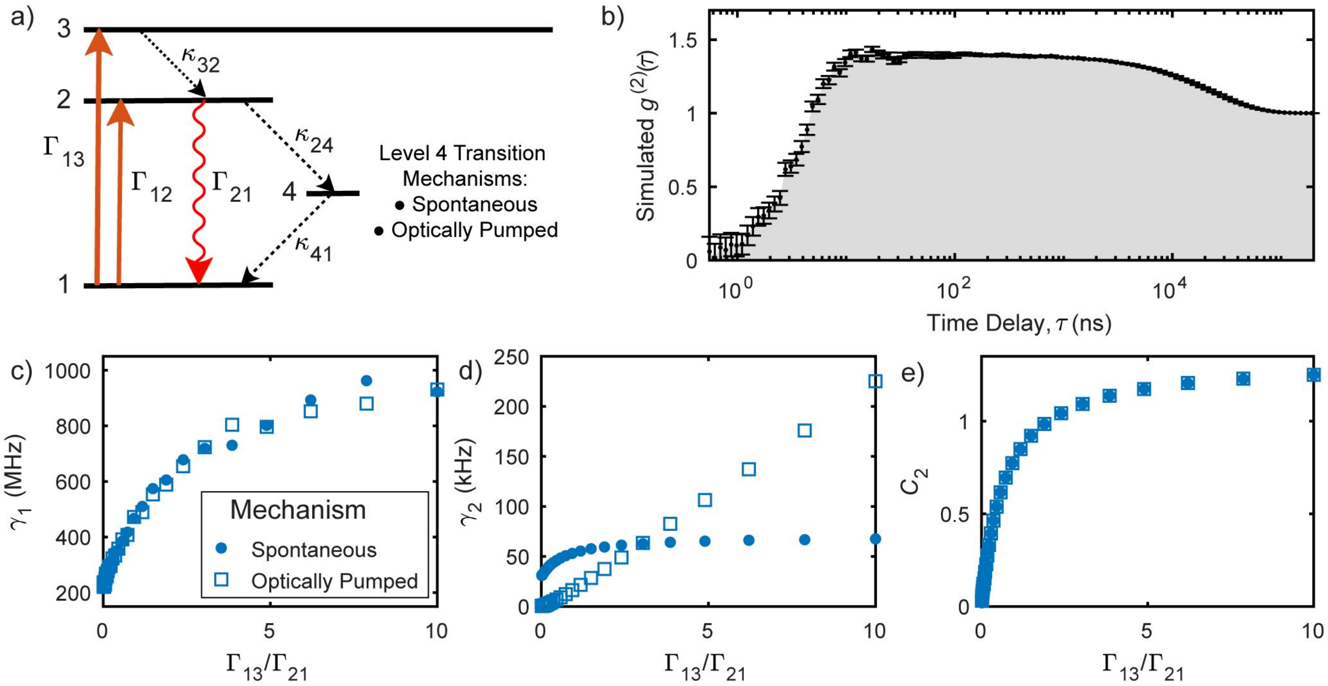
- Long time scales provide insight into level structure
- Fitting function → quantitative insight into the timescales involved
- Compare with simulations

$$g^{(2)}(\tau) = 1 - C_1 e^{-\gamma_1 \tau} + \sum_{i=2}^{N} C_i e^{-\gamma_i \tau}$$



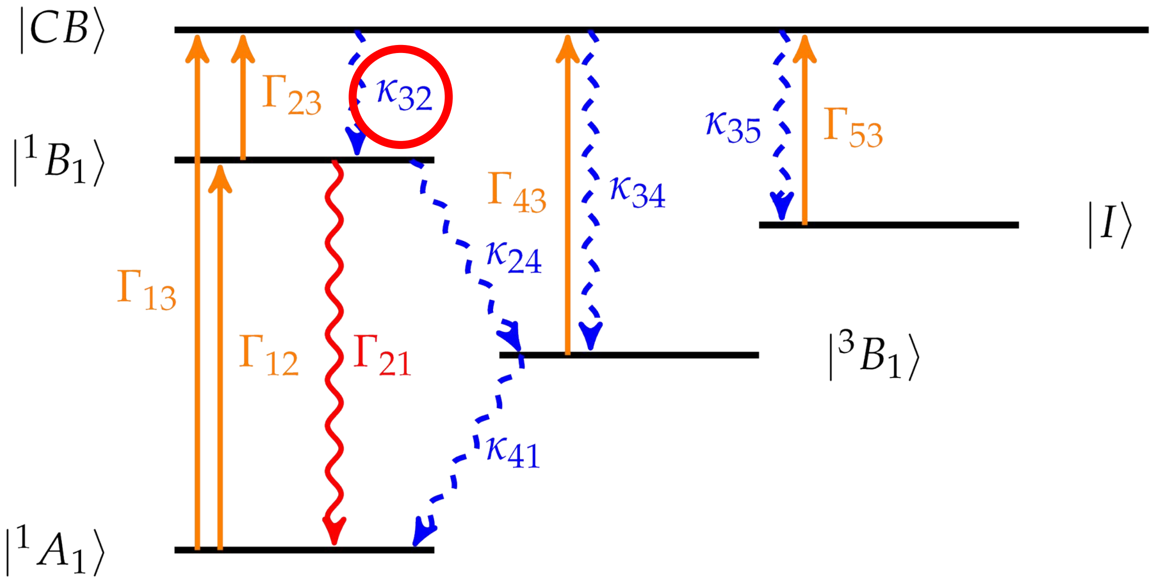
R. N. Patel, …, **M. E. Turiansky** *et al.*, arXiv:2201.08881 (2022).

Optical Dynamics



- Construct level diagram that explains experiments
- Two relevant conclusions:
  - Anti-bunching shows evidence of indirect excitation
  - Different number of bunching levels in each emitter

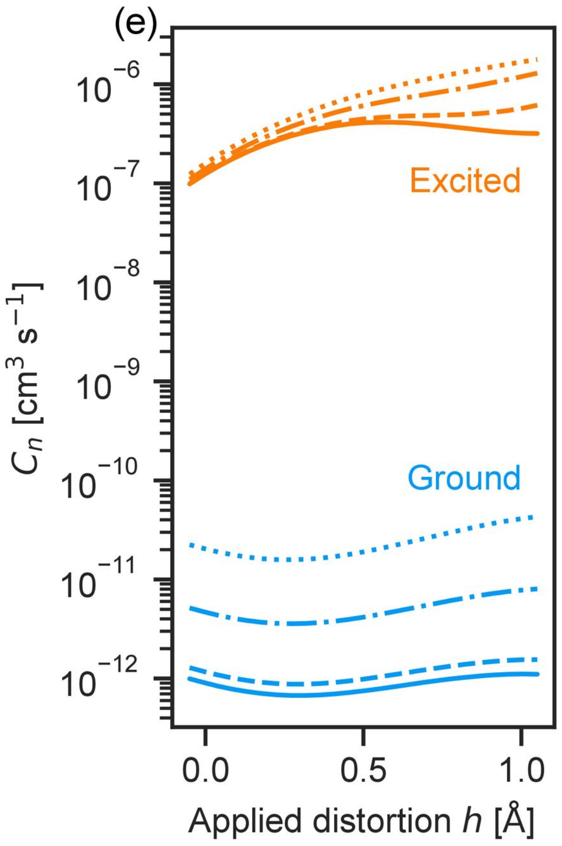
Dangling Bond Level Structure



- Dangling bond → rich level structure
- Explains heterogeneity (e.g. multiple bunching times)
- Consider nonradiative capture of electron

Comparison

- Capture into excited state favored by ~5 orders of magnitude
- C ~ 4 × 10^{-7} cm^3 s^{-1}
- Density of electrons
  - Thermal velocity – 10^5 m s^{-1}
  - Relaxation time – 1 ps
  - Distance – 100 nm
  - Density – 2.4 × 10^{14} cm^{-3}
- Capture rate
  - Calculated ~ 100 MHz
  - Experiment ~ 300-800 MHz
- Supports dangling bond as microscopic model



Summary

- Nonrad code
  - **M. E. Turiansky** *et al.*, Comput. Phys. Commun. **267**, 108056 (2021).
  - https://github.com/mturiansky/nonrad
- O_N and Si_B are promising dopants in c-BN, but control of growth kinetic is necessary
  - **M. E. Turiansky** *et al.*, Appl. Phys. Lett. **119**, 162105 (2021).
- Boron dangling bonds are the likely origin of the 2 eV single-photon emission in h-BN
  - **M. E. Turiansky** *et al.*, Phys. Rev. Lett. **123**, 127401 (2019).
  - **M. E. Turiansky** and C. G. Van de Walle, J. Appl. Phys. **129**, 064301 (2021).
  - **M. E. Turiansky** and C. G. Van de Walle, 2D Mater. **8**, 024002 (2021).
- Optical dynamics of emitters in h-BN support dangling bond as the microscopic origin
  - R. N. Patel, …, **M. E. Turiansky** *et al.*, arXiv:2201.08881 (2022).

Nonradiative Losses in Perovskite Solar Cells

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- X. Zhang, **M. E. Turiansky**, and C. G. Van de Walle, Cell Rep. Phys. Sci. **2**, 100604 (2021).
- X. Zhang, J.-X. Shen, **M. E. Turiansky**, and C. G. Van de Walle, Nat. Mater. **20**, 971 (2021).
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- X. Zhang, **M. E. Turiansky**, and C. G. Van de Walle, J. Phys. Chem. C **124**, 6022 (2020).
- X. Zhang, J.-X. Shen, **M. E. Turiansky**, and C. G. Van de Walle, J. Mater. Chem. A **8**, 12964 (2020).

Recombination

- F. Zhao, **M. E. Turiansky**, and C. G. Van de Walle, *in preparation*.
- **M. E. Turiansky**, A. Alkauskas, and C. G. Van de Walle, *in preparation*.
- **M. E. Turiansky**, X. Zhang, and C. G. Van de Walle, *in preparation*.

Boron-Containing Alloys

- J.-X. Shen, **M. E. Turiansky**, D. Wickramaratne, and C. G. Van de Walle, Phys. Rev. Mater. **5**, L030401 (2021).
- **M. E. Turiansky**, J.-X. Shen, D. Wickramaratne, and C. G. Van de Walle, J. Appl. Phys. **126**, 095706 (2019).

Polarons

- **M. E. Turiansky**, J. B. Varley, A. Alkauskas, and C. G. Van de Walle, *in preparation*.

Unique Defects in a Variety of Materials

- Y. Chen, **M. E. Turiansky**, and C. G. Van de Walle, *in preparation*.
- S. Mu, **M. E. Turiansky**, M. W. Swift, and C. G. Van de Walle, *in preparation*.
- **M. E. Turiansky** and C. G. Van de Walle, *in preparation*.

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  - Audrius Alkauskas, Xie Zhang, Raj N. Patel, Lee C. Bassett, Manuel Engel, Georg Kresse
- Van de Walle group members
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