# Quantum Theory of Materials: Methods and Applications

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# Outline

- Introduction.
    - Quantum theory of materials.
    - Methods for calculating material properties.
- Defects in materials.
    - Defects in high-$\kappa$ dielectrics.
    - Defects for quantum computing.

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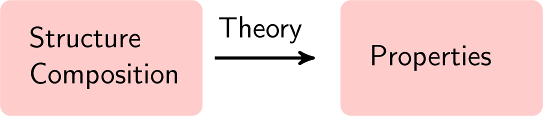
# Quantum Theory of Solids



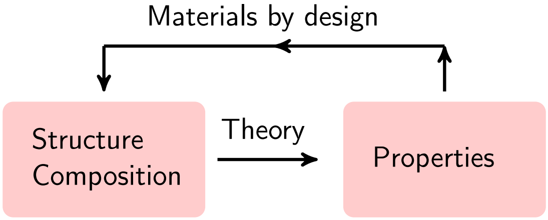
Structure
Composition

Theory

Properties

- Detailed microscopic study – understand relationships between structure, composition and properties.
- Predict and interpret experiment – structural, dynamical, electronic and optical properties of materials.

# Quantum Theory of Solids



Materials by design

Structure
Composition

Theory

Properties

- Detailed microscopic study – understand relationships between structure, composition and properties.
- Predict and interpret experiment – structural, dynamical, electronic and optical properties of materials.
- Assist in designing new materials.

# First-principles theoretical methods

Pros:

- No adjustable parameters.
- Reliable: Well-justified and tested approximations.
- Predictive: Can be used to design and understand properties of new materials.

# First-principles theoretical methods

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- Reliable: Well-justified and tested approximations.
- Predictive: Can be used to design and understand properties of new materials.

Cons:

- Computationally expensive.

# Material properties using *ab initio* methods

Structural properties:

– Lattice parameters, phase transitions, structure factors, pair correlation functions, elastic constants etc.

Dynamical properties:

– Lattice polarizabilities, dielectric constants, Born effective charges, heat capacity, infrared spectra, Raman spectra etc.

Electronic properties:

– Conductivity, density of states etc.

Optical properties:

– Reflectivity, absorption, refractive index, dielectric function etc.

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Dynamical properties:

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Electron

– C

Electronic structure

Optical properties:

– Reflectivity, absorption, refractive index, dielectric function etc.

# Methods

Solve the Schrödinger's equation for a solid:

$$\hat{\mathrm{H}}\Psi = \mathrm{E}\Psi$$

where

$$\hat{\mathrm{H}} = \hat{\mathrm{T}}_e + \hat{\mathrm{T}}_z + \hat{\mathrm{U}}_e + \hat{\mathrm{U}}_z + \hat{\mathrm{U}}_{ez} + \hat{\mathrm{V}}_{ext}$$

where

$\hat{\mathrm{T}}_e, \hat{\mathrm{T}}_z$ :Kinetic energy of electrons and nuclei

$\hat{\mathrm{U}}_e, \hat{\mathrm{U}}_z, \hat{\mathrm{U}}_{ez}$ :Potential energy of electron, nuclei and electron-nuclei interactions

$\hat{\mathrm{V}}_{ext}$ :External potential

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Equation contains 3*Z*N + 3*N variables where Z is the atomic number and N is the number of atoms.

# Methods

> "The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved."
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> — P. A. M. Dirac[1]

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> "It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed ..."
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# Methods – Born-Oppenheimer Approximation

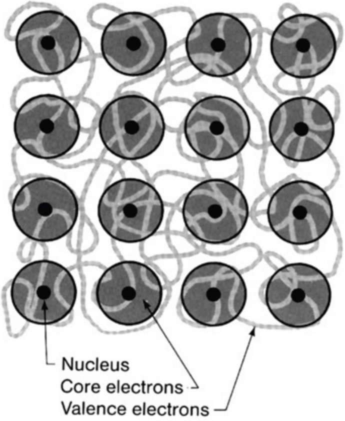
- Electrons move “fast” while nuclei are “slow”.
- Total wavefunction is approximated as:

$$\Psi(\{\vec{\mathrm{r}}\},\{\vec{\mathrm{R}}\}) = \Phi(\{\vec{\mathrm{r}}\};\{\vec{\mathrm{R}}\})\,\chi(\{\vec{\mathrm{R}}\})$$

- Dependence of potential on $\{\vec{\mathrm{R}}\}$ parametric – electrons move in a field created by static ions.

# Pseudopotential Approximation

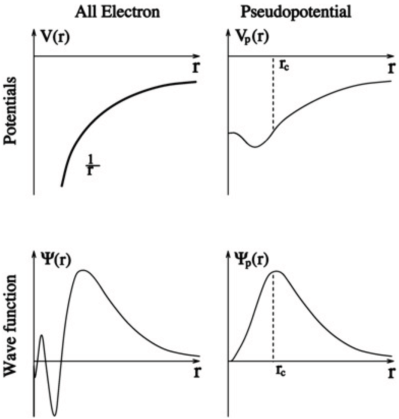
Outer valence electrons determine properties of materials – core electrons do not participate in chemical bonding.



Captures the physical content of the periodic table.

# Pseudopotential Approximation

Valence electrons experience a repulsive potential near core due to orthogonalization to core states.



Energy and length scales set by the valence states.

# Methods – Ground-state properties

Properties that are intrinsic to a system with all its electrons in equilibrium.

- Density functional theory is the “standard model” for understanding ground-state properties.

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# Methods – Ground-state properties

Properties that are intrinsic to a system with all its electrons in equilibrium.

- Density functional theory is the "standard model" for understanding ground-state properties.
- Total energy is a functional of the charge density.
- Ground-state properties depend on the total energy of the system.

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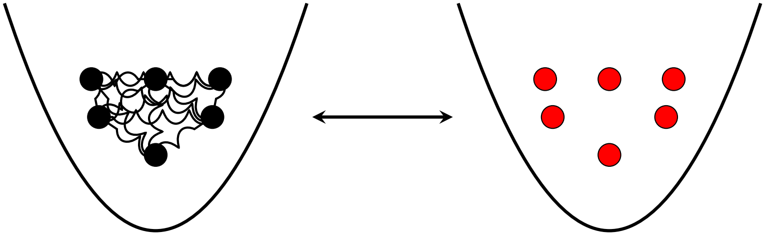
# Methods – Ground-state properties

- Kohn-Sham formulation: Map the interacting many-electron problem to non-interacting electrons moving in a self-consistent field.



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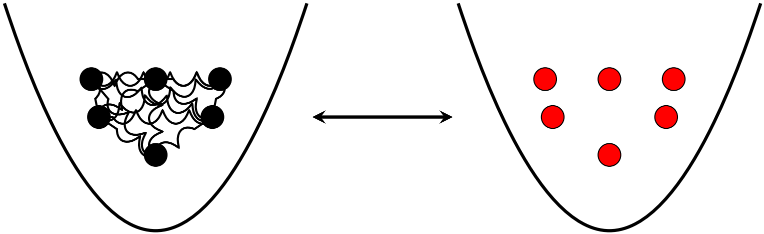

- Not known exactly – local density approximation (LDA) and generalized gradient approximation etc.

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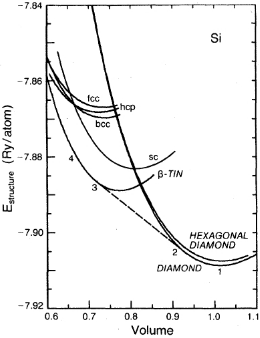
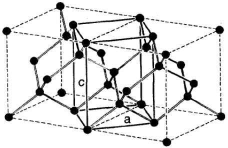
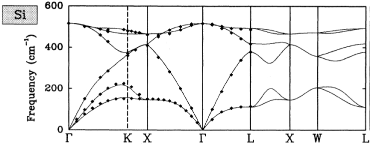


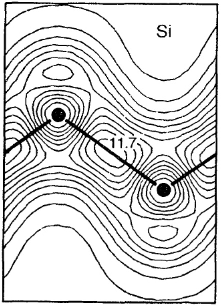
Phase transitions[1]



Crystal Structure[1]



Phonons[2]



Charge density[1]

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[1] M. T. Yin and M. L. Cohen, Phys. Rev. B **26**, 5668 (1982).
[2] P. Giannozzi, S. de Gironcoli, P. Pavone, and S. Baroni, Phys. Rev. B, **43**, 7231 (1991).

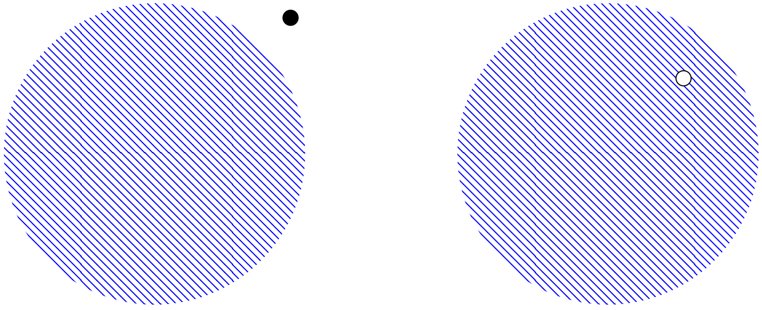
# Methods – Excited-state properties

Spectroscopic properties that involve experiments creating an excited particle above the ground state.

Concept and formalism of the interacting particle Green's function.

# Methods – Excited-state properties

- N±1 particle problem.
- Photoemission, tunneling.
- Quasiparticle approach.



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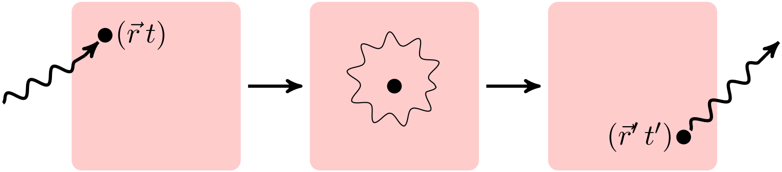
$$\mathrm{G}(\vec{r}\,t, \vec{r}'\,t') = -i\,\langle \mathrm{N}\,|\,\mathrm{T}[\hat{\psi}(\vec{r}\,t)\,\hat{\psi}^{\dagger}(\vec{r}'\,t')]\,|\,\mathrm{N}\rangle$$



# Methods – Excited-state properties

- N±1 particle problem.
- Photoemission, tunneling.
- Quasiparticle approach.

$$\mathrm{G}(\vec{r},\vec{r}',\omega)=\sum_s \frac{f_s(\vec{r})f_s^*(\vec{r}')}{\omega-\omega_s}$$

$$\begin{array}{lll} \omega_s=\mathrm{E}_{\mathrm{N}}-\mathrm{E}_{\mathrm{N}-1,s} & f_s(\vec{r})=\langle \mathrm{N}-1,s\,|\,\hat{\psi}(\vec{r})|\,\mathrm{N}\rangle & \qquad \omega_s<\mu \\ \omega_s=\mathrm{E}_{\mathrm{N}+1,s}-\mathrm{E}_{\mathrm{N}} & f_s(\vec{r})=\langle \mathrm{N}|\,\hat{\psi}(\vec{r})|\,\mathrm{N}+1,s\rangle & \qquad \omega_s\geq\mu \end{array}$$

# Methods – Excited-state properties

- Many-body perturbation theory is the “standard model” for understanding excited-state properties.

$$G^{-1} = G_0^{-1} + \Sigma$$

---

[1] L. Hedin and S. Lundqvist, in Advances in Research and Applications, edited by F. Seiz, D. Turnbull, and H. Ehrenreich, Solid State Physics Vol. 23 (Academic Press, New York, 1969) pp. 1-181.

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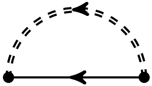
$$G^{-1} = G_0^{-1} + \Sigma$$

- GW approximation to the self-energy ($\Sigma$).

$\Sigma =$



$= iGW$

$$W = \varepsilon^{-1} v$$

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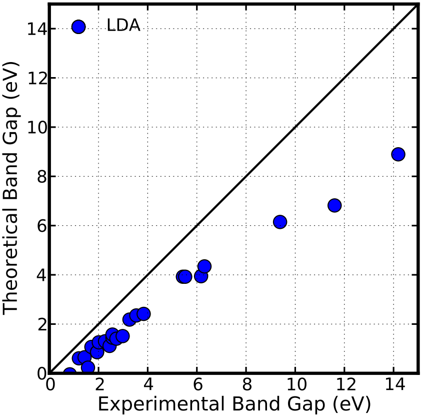
# Methods – Excited-state properties

Materials: InSb, InAs,
Ge,
GaSb, Si, InP,
GaAs, CdS,
AlSb, AlAs,
CdSe, CdTe,
BP, SiC, $C_{60}$,
GaP, AlP,
ZnTe, ZnSe,
c-GaN, w-GaN,
InS, w-BN,
c-BN,
diamond, w-AlN,
LiCl,
Fluorite, LiF



Quasiparticle Gap[1]

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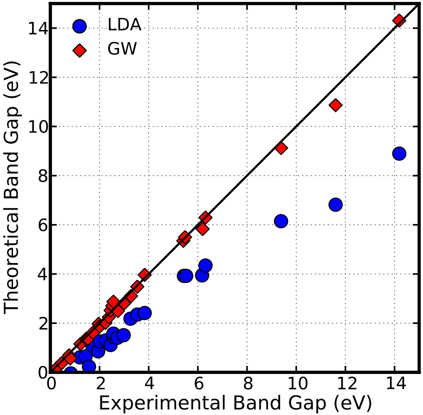

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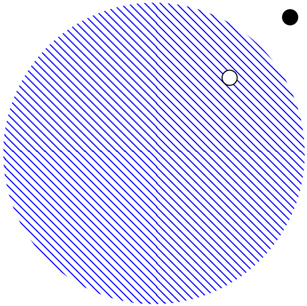
# Methods – Excited-state properties

- N+2 particle problem.
- Optical properties – absorption etc.
- Electron-hole interaction (excitons).



Fermi sea

# Methods – Excited-state properties

- Coupled electron-hole excitations:

$$|\mathrm{S}\rangle = \sum_{v}^{elec} \sum_{c}^{hole} \mathrm{A}^{\mathrm{S}}_{vc}\, \hat{a}^{\dagger}_{v} \hat{b}^{\dagger}_{c} |0\rangle$$

where $|0\rangle$ ground-state of many electron system.
$\hat{a}^{\dagger}_{v}$ and $\hat{b}^{\dagger}_{c}$ create quasi-particles and quasi-holes.
$\mathrm{A}^{\mathrm{S}}_{vc}$ are coupling constants.

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- Solve Bethe-Salpeter equation for two particle Green's function.

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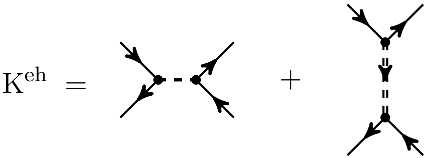
- Solve Bethe-Salpeter equation for two particle Green's function.
- Electron-hole interaction kernel:



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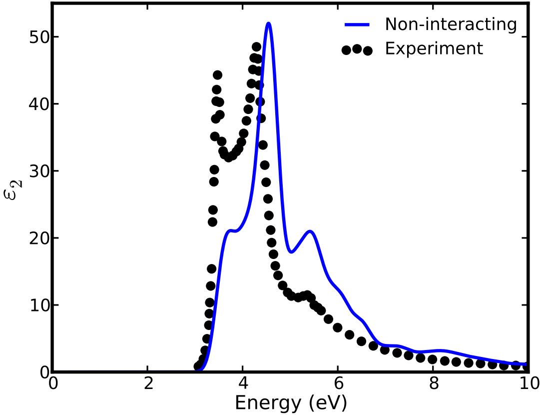

Si Optical absorption[1]

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[1] J. Deslippe, G. Samsonidze, D. A. Strubbe, M. Jain, M. L. Cohen, and S. G. Louie, Comput. Phys. Commun. **183**, 1269 (2012).

[2] P. Lautenschlager, M. Garriga, L. Vina, and M. Cardona, Phys. Rev. B **36**, 4821 (1987).

[3] G. G. Macfarlane and V. Roberts, Phys. Rev. **98**, 1865 (1955).

[4] H. R. Philipp, J. Appl. Phys. **43**, 2835 (1972).

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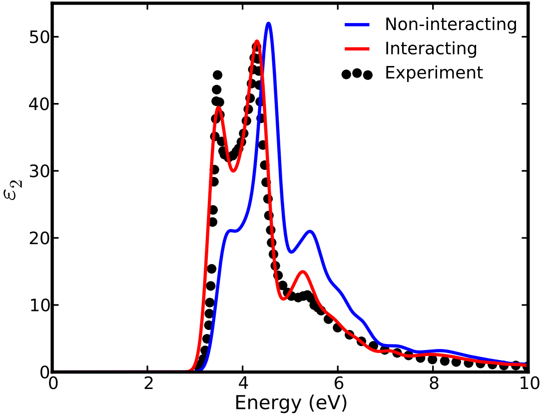

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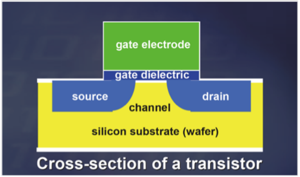
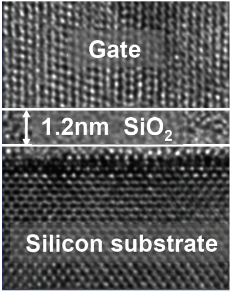
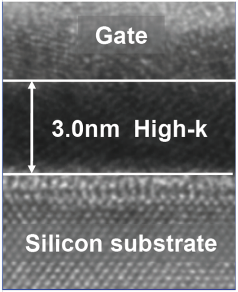
- Defects in materials.
    - Defects in high-$\kappa$ dielectrics.
    - Defects for quantum computing.

# High-$\kappa$ dielectric materials – Motivation

- Moore's law about size of transistor.
- $HfO_2$ has replaced $SiO_2$ in todays MOSFET devices.







$$\kappa_{\mathsf{SiO_2}} \approx 3.9$$

$$\kappa_{\mathsf{HfO_2}} \approx 16 - 17$$

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[1] http://www.intel.com/technology/45nm/index.htm

# High-$\kappa$ dielectric materials – Motivation

- High defect density.
- Charge trapping by defects in the interfacial layer or oxide – threshold voltage instability[1].
- Oxygen-related defects – vacancy[2] ($V_O$) or interstitials ($I_O$) major cause.
- Study the stability of point defects – $V_O$ and $I_O$.

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[1] G. Ribes et. al., IEEE Trans. Device Mater. Reliab. **5**, 5 (2005).

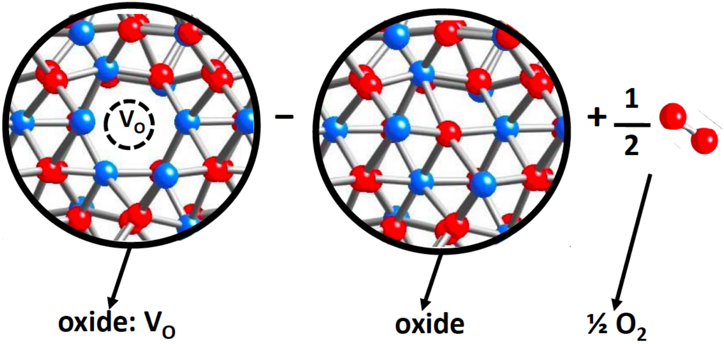
[2] K. Shiraishi et. al., Jpn. J. Appl. Phys., Part 2 **43** L1413 (2004); H. Park et. al., IEEE Electron Device Lett. **29**, 54 (2008).

# High-$\kappa$ dielectric materials – Definitions

Formation energy of an oxygen-vacancy:

$$\mathrm{E}^f[\vec{\mathrm{R}}] = \mathrm{E}[\vec{\mathrm{R}}] - \mathrm{E}_{\mathrm{ref}} + \frac{1}{2}\mathrm{E}_{\mathrm{O}_2}$$

**Example: $V_O$**

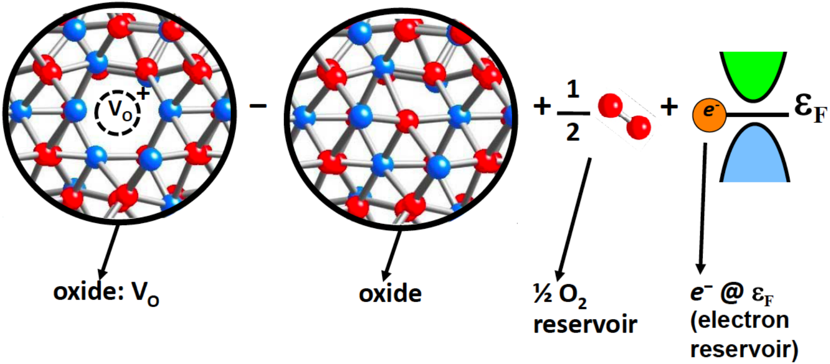


# High-$\kappa$ dielectric materials – Definitions

Formation energy of an oxygen-vacancy:

$$\mathrm{E}_{\mathrm{q}}^{f}[\vec{\mathrm{R}}_{\mathrm{q}}](\mathrm{E}_{\mathrm{F}}) = \mathrm{E}_{\mathrm{q}}[\vec{\mathrm{R}}_{\mathrm{q}}] - \mathrm{E}_{\mathrm{ref}} + \frac{1}{2}\mathrm{E}_{\mathrm{O}_2} + \mathrm{q}(\mathrm{E}_{\mathrm{F}} + \mathrm{E}_{\mathrm{v}})$$

**Example: $V_O$**



# High-$\kappa$ dielectric materials – Definitions

Formation energy of an oxygen-related defect in hafnia :

$$\mathrm{E}_{\mathrm{q}}^{f}[\vec{\mathrm{R}}_{\mathrm{q}}](\mathrm{E}_{\mathrm{F}}) = \mathrm{E}_{\mathrm{q}}[\vec{\mathrm{R}}_{\mathrm{q}}] - \mathrm{E}_{\mathrm{HfO_2}} - \mathrm{n}_{\mathrm{O}}\mu_{\mathrm{O}} + \mathrm{q}(\mathrm{E}_{\mathrm{F}} + \mathrm{E}_{\mathrm{v}})$$

where $\mu_{\mathsf{O}}$ is the oxygen chemical potential.

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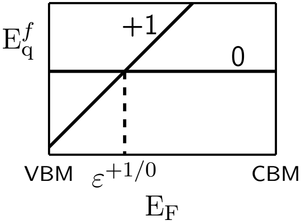
where $\mu_{\mathsf{O}}$ is the oxygen chemical potential.

Charge transition level : $\varepsilon^{\mathrm{q/q\text{-}1}}$ = Fermi energy where defect $\mathrm{q} \rightarrow \mathrm{q} - 1$.



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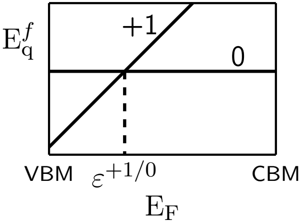
where $\mu_{\mathsf{O}}$ is the oxygen chemical potential.

Charge transition level : $\varepsilon^{\mathrm{q/q\text{-}1}}$ = Fermi energy where defect $\mathrm{q} \rightarrow \mathrm{q}-1$.

$$= \mathrm{E}^{f}_{\mathrm{q\text{-}1}}[\vec{\mathrm{R}}_{\mathrm{q\text{-}1}}](\mathrm{E_F}=0) - \mathrm{E}^{f}_{\mathrm{q}}[\vec{\mathrm{R}}_{\mathrm{q}}](\mathrm{E_F}=0)$$

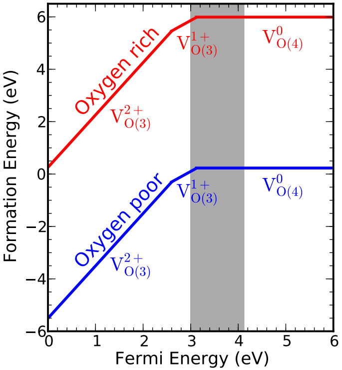


# High-$\kappa$ dielectric materials – Computational details

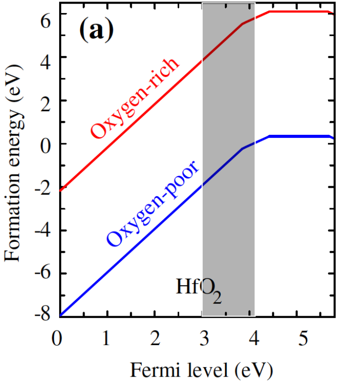
- Three fold coordinated ($V_{O(3)}$) and four fold coordinated ($V_{O(4)}$) vacancies in charge states {0, +1, +2}
- Three fold coordinated ($I_{O(3)}$) and four fold coordinated ($I_{O(4)}$) interstitials in charge states {0, -1, -2}
- 96 atom super cells.
- Bulk structural parameters and band gap (6.00 eV) in good agreement with experiment.

# High-$\kappa$ dielectric materials – Formation energy of vacancies

DFT+GW[1]



HSE[2]



- Qualitative agreement with PBE0[3], HSE[2].
- Quantitatively, charge transition levels are different and which defects are stable when placed next to Si[1].

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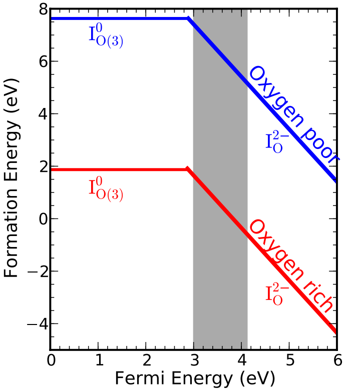
[1] M. Jain, J. R. Chelikowsky and S. G. Louie, Phys. Rev. Lett. **107**, 216803 (2011).

[2] J.L. Lyons, A. Janotti and C.G. Van de Walle, Microelectronic Engineering **88**, 1452 (2011).

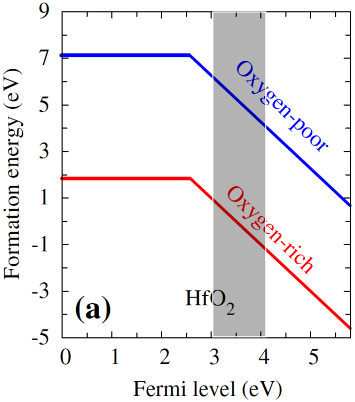
[3] P. Broqvist and A. Pasquarello, Appl. Phys. Lett. **89**, 262904 (2006).

# High-$\kappa$ dielectric materials – Formation energy of interstitials

DFT+GW



HSE[1]



- Qualitative agreement with recent HSE[1] calculations.

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[1] J.L. Lyons, A. Janotti and C.G. Van de Walle, Microelectronic Engineering **88**, 1452 (2011).

# High-$\kappa$ dielectric materials – Conclusions

- DFT+GW method for calculating the stability of oxygen vacancies and interstitals.
- *Qualitative* agreement with previous hybrid functional calculations on the vacancies and interstitials.
- *Quantitative* disagreement with previous hybrid functional calculations - vacancies near a Si/$HfO_2$ interface.

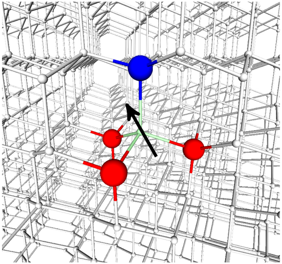
| | DFT+GW | HSE |
|---|---|---|
| $V_O$ | +1,0 | +2,+1 |
| $I_O$ | +2 | +2 |

# Outline

- Introduction.
    - Quantum theory of solids.
    - Methods for calculating material properties.
- Defects in materials.
    - Defects in high-$\kappa$ dielectrics.
    - Defects for quantum computing.

# Defects for spin-qubit applications

- Room temperature individually addressable spin systems in the solid-state for quantum computing.
- $NV^-$ center in diamond is the leading candidate.



- Possible room-temperature qubit with long coherence time ($\sim$1ms) for quantum computing.
- High sensitivity, high-spatial resolution magnetometry.

# NV$^-$ center in diamond – Motivation

Optical initialization at room-temperature provides initial spin pure state for spin-qubit operation.

Notation :$^{2S+1}\ \Lambda$

$\Lambda$ : Irreducible representation of the orbital symmetry

$S$ : Total Spin

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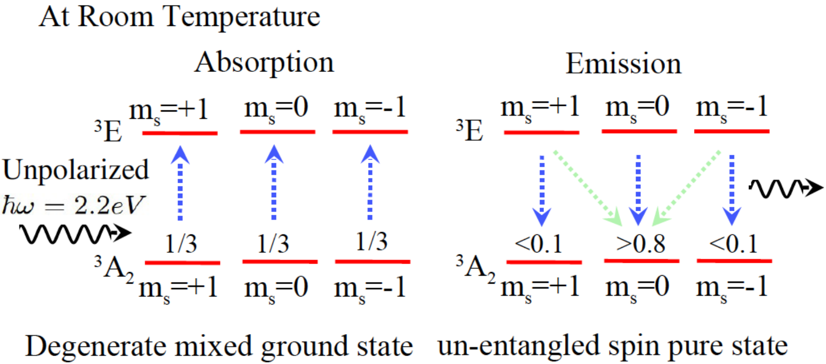
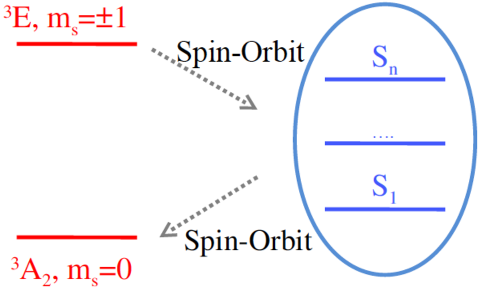


# NV$^-$ center in diamond – Unsolved problem



- Identification of singlet-level structure.
- Effective optical initialization path between the two triplet levels.

# $NV^-$ center in diamond – Unsolved problem

$NV^-$ is a deep level center in a band gap of diamond
with multiple localized, interacting electrons.

- Strong electron-electron correlation
  – Not appropriate for mean-field type calculation
- Screening from diamond
  – mimicking this system by a small isolated-diamond cluster with a $NV^-$ defect without additional input incorrect.
- Large structural relaxation in the excited state.

# NV$^-$ center in diamond – Extended Hubbard model

$$\hat{\mathrm{H}} = \sum_{i,\sigma} \mathrm{E}_i n_{i\sigma} + \sum_{i \neq j,\sigma} t_{i,j} c^{\dagger}_{i,\sigma} c_{j,\sigma} + \sum_{i} \mathrm{U} n_{i,\uparrow} n_{j,\downarrow} + \sum_{i \neq j,\sigma,\sigma'} \mathrm{V} n_{i,\sigma} n_{j,\sigma'}$$

$i, j$ :Atomic sites (C or N)

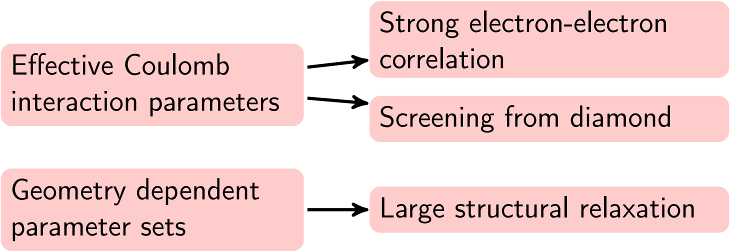
$\sigma, \sigma'$ :Spin direction

$\mathrm{E}_i$ :On-site energy

$t_{i,j}$ :Hopping integral

U :On-site Coulomb repulsion

V :Nearest neighbor Coulomb repulsion



Effective Coulomb interaction parameters → Strong electron-electron correlation

Effective Coulomb interaction parameters → Screening from diamond

Geometry dependent parameter sets → Large structural relaxation

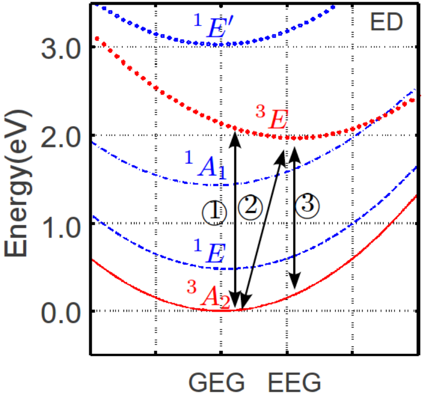
Hindered by the difficulty in getting physically grounded model parameters.

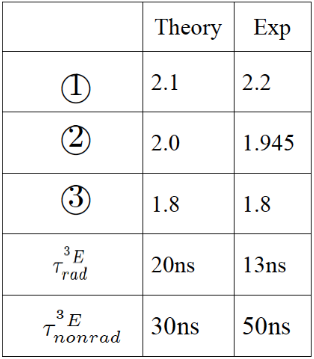
# NV$^-$ center in diamond – Level diagram

Use *ab initio* GW to get model parameters, incorporating realistic electron-electron interactions.

Level diagram[1] from exact diagonalization of model Hamiltonian

All energies in eV.





| | Theory | Exp |
|---|---|---|
| ① | 2.1 | 2.2 |
| ② | 2.0 | 1.945 |
| ③ | 1.8 | 1.8 |
| $\tau_{rad}^{^3E}$ | 20ns | 13ns |
| $\tau_{nonrad}^{^3E}$ | 30ns | 50ns |

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[1] S. Choi, M. Jain and S. G. Louie, submitted to Phys. Rev. Lett.

# $NV^-$ center in diamond – Conclusion

- Constructed extended Hubbard Hamiltonian from *ab initio* GW calculations.
- Through exact diagonalization, many-electron effects strongly affect the energy level diagram qualitatively and quantitatively.
- Computed ground- and excited-state energy surfaces and transition rates between them provided a consistent picture with experiments.
- Proposed an optical initialization pathway in which inter-sytstem crossing plays a crucial role.

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S. Choi, M. Jain and S. G. Louie, submitted to Phys. Rev. Lett.

# Conclusion

- *Ab initio* methods to understand and predict properties of materials.
- Methods – accurate, reliable and applicable to *real* materials.
- Oxygen-related defects in high-$\kappa$ material – HfO$_2$.
- NV$^-$ center in diamond for quantum computing application.

# Improvement of methods

- Using many-body perturbation theory, systematically improve approximations via the linearized Sham-Schlüter equation which would lead to an optimized effective potential:

$$\iiint d\epsilon d\mathbf{r}' d\mathbf{r}'' G_{KS}(\mathbf{r},\mathbf{r}';\epsilon)[\Sigma_{xc}[G_{KS}](\mathbf{r}',\mathbf{r}'';\epsilon) - v_{xc}(\mathbf{r})\delta(\mathbf{r}'-\mathbf{r}'')]G_{KS}(\mathbf{r}'',\mathbf{r};\epsilon) = 0$$

- Finite temperature calculations within the GW approximation including electron-phonon interactions.
- Extending GW approximation to calculate quasiparticle and optical properties of open-shell systems.
- Use higher order Feynman diagrams in the self energy (systematically) to go beyond the GW approximation.

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Y. M. Niquet, M. Fuchs, and X. Gonze, Phys. Rev. A **68**, 032507 (2003).
F. Giustino, S. G. Louie, and M. L. Cohen, Phys. Rev. Lett. **105**, 265501 (2010).
J. Lischner, J. Deslippe, M. Jain, and S. G. Louie, submitted to Phys. Rev. Lett.

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  - D. Strubbe
  - S. Choi
  - J. Lischner
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  - Chelikowsky group at UT Austin
  - Kronik group at Weizmann
  - Materials Modelling group at 3M