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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• Defects in materials.
  • Defects in high-\(\kappa\) dielectrics.
  • Defects for quantum computing.
- 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

- 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.
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

Pros:

- **No** adjustable parameters.
- **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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Electronic properties:
- Conductivity, density of states etc.

Optical properties:
- Reflectivity, absorption, refractive index, dielectric function etc.
Solve the Schrödinger’s equation for a solid:

\[ \hat{H} \Psi = E \Psi \]

where

\[ \hat{H} = \hat{T}_e + \hat{T}_z + \hat{U}_e + \hat{U}_z + \hat{U}_{ez} + \hat{V}_{ext} \]

where

\[ \hat{T}_e, \hat{T}_z \] : Kinetic energy of electrons and nuclei
\[ \hat{U}_e, \hat{U}_z, \hat{U}_{ez} \] : Potential energy of electron, nuclei and electron-nuclei interactions
\[ \hat{V}_{ext} \] : External potential
Methods

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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.
“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.”

— P. A. M. Dirac

\[^{1}\text{P. A. M. Dirac, Proc. R. Soc. Lond. A 123, 714 (1929).}\]
“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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“It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed ...”

— P. A. M. Dirac

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Electrons move “fast” while nuclei are “slow”.

Total wavefunction is approximated as:

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

Dependence of potential on \(\{\vec{R}\}\) 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.
Valence electrons experience a repulsive potential near core due to orthogonalization to core states.

Energy and length scales set by the valence states.
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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- Total energy is a functional of the charge density.

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

\[ W. \text{Kohn and L. Sham, } \text{Phys. Rev. } 140, \text{ A1133 (1965).} \]
Kohn-Sham formulation: Map the interacting many-electron problem to non-interacting electrons moving in a self-consistent field.

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

Methods – Ground-state properties

Phase transitions\(^1\)

Crystal Structure\(^1\)

Charge density\(^1\)

Phonons\(^2\)

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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.

Fermi sea

Fermi sea
Methods – Excited-state properties

- $N \pm 1$ particle problem.
- Photoemission, tunneling.
- Quasiparticle approach.

\[
G(\vec{r}t, \vec{r}'t') = -i \langle N | T[\hat{\psi}(\vec{r}t) \hat{\psi}^{\dagger}(\vec{r}'t')] | N \rangle
\]
N±1 particle problem.
- Photoemission, tunneling.
- Quasiparticle approach.

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

\[
\omega_s = E_N - E_{N-1,s} \quad f_s(\vec{r}) = \langle N - 1, s | \hat{\psi}(\vec{r}) | N \rangle \quad \omega_s < \mu
\]

\[
\omega_s = E_{N+1,s} - E_N \quad f_s(\vec{r}) = \langle N | \hat{\psi}(\vec{r}) | N + 1, s \rangle \quad \omega_s \geq \mu
\]
Many-body perturbation theory is the “standard model” for understanding excited-state properties.

\[ G^{-1} = G_0^{-1} + \Sigma \]

Methods – Excited-state properties

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

\[ G^{-1} = G_0^{-1} + \Sigma \]

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

\[ \Sigma = \text{Diagram} = iGW \]

\[ W = \varepsilon^{-1} v \]

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Methods – Excited-state properties

Materials: InSb, InAs, Ge, GaSb, Si, InP, GaAs, CdS, AlSb, AlAs, CdSe, CdTe, BP, SiC, C₆₀, GaP, AlP, ZnTe, ZnSe, c-GaN, w-GaN, InS, w-BN, c-BN, diamond, w-AlN, LiCl, Fluorite, LiF

Quasiparticle Gap

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

Methods – Excited-state properties

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

\[ |S\rangle = \sum_{v} \sum_{c} A^{S}_{vc} \hat{a}_{v}^{\dagger} \hat{b}_{c}^{\dagger} |0\rangle \]

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

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

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\[ ^1 \text{M. Rohlfing and S. G. Louie, Phys. Rev. B 62, 4927 (2000).} \]
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Solve Bethe-Salpeter equation for two particle Green’s function.

Electron-hole interaction kernel:

\[K^{eh} = \begin{array}{c}
\begin{array}{c}
\bullet \\
\_ \\
\_ \\
\end{array}
\end{array} + \begin{array}{c}
\begin{array}{c}
\_ \\
\bullet \\
\_ \\
\end{array}
\end{array}\]

Methods – Excited-state properties

Si Optical absorption

Methods – Excited-state properties

Si Optical absorption

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High-$\kappa$ dielectric materials – Motivation

- Moore’s law about size of transistor.
- HfO$_2$ has replaced SiO$_2$ in today's MOSFET devices.

$\kappa_{\text{SiO}_2} \approx 3.9$

$\kappa_{\text{HfO}_2} \approx 16 - 17$

1 http://www.intel.com/technology/45nm/index.htm
High-κ 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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High-κ dielectric materials – Definitions

Formation energy of an oxygen-vacancy:

\[ E^f[\vec{R}] = E[\vec{R}] - E_{\text{ref}} + \frac{1}{2}E_{O_2} \]
High-κ dielectric materials – Definitions

Formation energy of an oxygen-vacancy:

\[ E^f_q[\vec{R}_q](E_F) = E_q[\vec{R}_q] - E_{\text{ref}} + \frac{1}{2} E_{\text{O}_2} + q(E_F + E_v) \]
Formation energy of an oxygen-related defect in hafnia:

$$E^f_q[\vec{R}_q](E_F) = E_q[\vec{R}_q] - E_{HfO_2} - n_O \mu_O + q(E_F + E_V)$$

where $\mu_O$ is the oxygen chemical potential.
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Charge transition level: $\varepsilon^{q/q-1} = \text{Fermi energy where defect } q \rightarrow q - 1$. 
High-$\kappa$ dielectric materials – Definitions

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

$$= E^f_{q-1}[\vec{R}_{q-1}](E_F = 0) - E^f_q[\vec{R}_q](E_F = 0)$$

![Diagram](image-url)
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$^1$

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

Qualitative agreement with recent HSE\textsuperscript{1} calculations.

\textsuperscript{1}J.L. Lyons, A. Janotti and C.G. Van de Walle, Microelectronic Engineering 88, 1452 (2011).
■ DFT+GW method for calculating the stability of oxygen vacancies and interstitials.

■ *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.

<table>
<thead>
<tr>
<th></th>
<th>DFT+GW</th>
<th>HSE</th>
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</thead>
<tbody>
<tr>
<td>$V_O$</td>
<td>+1,0</td>
<td>+2,+1</td>
</tr>
<tr>
<td>$I_O$</td>
<td>+2</td>
<td>+2</td>
</tr>
</tbody>
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Defects for spin-qubit applications

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

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

**At Room Temperature**

**Absorption**

\[
\begin{array}{ccc}
3^E & m_s=+1 & m_s=0 & m_s=-1 \\
\text{Unpolarized} & \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \\
\hbar \omega = 2.2 eV \\
\text{Depolarized} & \text{mixed ground state}
\end{array}
\]

**Emission**

\[
\begin{array}{ccc}
3^E & m_s=+1 & m_s=0 & m_s=-1 \\
<0.1 & >0.8 & <0.1 \\
\text{un-entangled spin pure state}
\end{array}
\]
Identification of singlet-level structure.

Effective optical initialization path between the two triplet levels.
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.
$\hat{H} = \sum_{i,\sigma} E_i n_{i\sigma} + \sum_{i \neq j, \sigma} t_{i,j} c_{i,\sigma}^\dagger c_{j,\sigma}^{} + \sum_{i} U n_{i,\uparrow} n_{i,\downarrow} + \sum_{i \neq j, \sigma, \sigma'} V n_{i,\sigma} n_{j,\sigma'}$

$i, j$ : Atomic sites (C or N)
$\sigma, \sigma'$ : Spin direction
$E_i$ : 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

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.

<table>
<thead>
<tr>
<th></th>
<th>Theory</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.1</td>
<td>2.2</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>1.945</td>
</tr>
<tr>
<td>3</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>$\tau_{rad}$</td>
<td>20ns</td>
<td>13ns</td>
</tr>
<tr>
<td>$\tau_{nonrad}$</td>
<td>30ns</td>
<td>50ns</td>
</tr>
</tbody>
</table>

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-system crossing plays a crucial role.

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:

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

- 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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  - Prof. S. G. Louie
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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