

Quantum Monte Carlo studies of Energy Gaps in Semiconductors

CMT Group Meeting



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Outline

Why QMC?

Firstly, what gaps and why?

Alternatives: Mean-field theories, $G_x W_y$, CC/CI

General Trends

QMC Methods

Variational MC

Diffusion MC

Excited State DMC

Some Applications

Small Molecules

Boron Nitride

Silicon

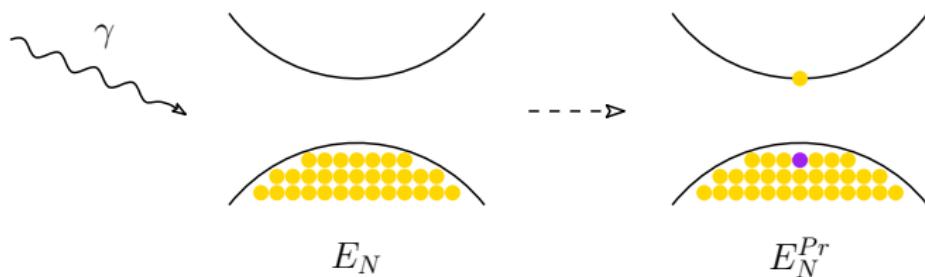
What gaps and why?

- ▶ There are actually **two** bandgaps one could attempt to calculate

1: Excitonic Gap

$$\Delta_{Ex} = E_N^{Pr} - E_N \quad (1)$$

which is the price, in energy, a photon must pay to create a **bound** electron-hole pair in the SC.

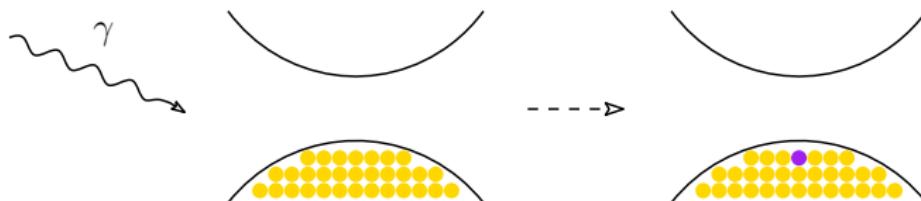


Gaps cont.

2: Quasiparticle Gap

$$\Delta_{QP} = E_{N+1} + E_{N-1} - 2E_N \quad (2)$$

the price a photon pays to create a **free** electron, leaving behind a hole in the SC.



How might we calculate these?

Mean-field theories

- ▶ Hartree-Fock, Density Functional Theory and hybrids thereof solve auxiliary problems

$$\left(-\frac{\nabla^2}{2} + v_{\text{eff}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (3)$$

with v_{eff} an effective potential we do not ¹ know in general.

- ▶ "Determine gaps" from differences in single-particle **Kohn-Sham** or **Hartree-Fock** eigenvalues $\epsilon_i(\mathbf{k})$. Shady.

¹And indeed - may never know.

Why is it *Shady*?

Hartree-Fock Eigenvalues

- ▶ Hartree-Fock eigenvalues can be interpreted as electron addition and removal energies (charged excitation energies).
- ▶ However, HF theory includes **absolutely no** description of electronic correlation (gaps typically 2 times too big).

Kohn-Sham DFT

- ▶ DFT includes *some* treatment of electronic correlation.
- ▶ **BUT** it's locked away in an uncontrolled approximation - the *exchange-correlation functional* - $E_{XC}[n(\mathbf{r})]$.

Quantum Chemistry Methods?

Coupled Cluster

- ▶ Based on the exponential ansatz

$$|\Psi_{CC}\rangle = e^{\hat{T}} |\Psi_{Ref.}\rangle \quad (4)$$

- ▶ Size-extensive, cost scales as n_e^{6-7} depending on particulars

Full Configuration Interaction

- ▶ Rather than circumventing exponential curse, embrace it

$$|\Psi_{FCI}\rangle = \sum_{symm. i} c_i |\Psi_i\rangle \quad (5)$$

The $G_x W_y$ Approximation

- ▶ The **self-energy**, Σ can be approximated by the product of the Green's Function G and the screened Coulomb potential W^2 .
- ▶ If we can do this, we can solve the quasiparticle equation

$$\left(-\frac{\nabla_i^2}{2} + v_{\text{ion}} + v_{\text{H}} \right) \psi_i(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}', E_i^{QP}) \psi_i(\mathbf{r}') = E_i^{QP} \psi_i(\mathbf{r}) \quad (6)$$

- ▶ As before, but with non-local Σ and hope of **systematic extension** (via *vertex corrections*).

² L. Hedin. In: Phys. Rev. 139.3A (1965), F. Aryasetiawan and O. Gunnarsson. In: Rep. Prog. in Phys. 61.3 (1998).

GW vs Perturbation Theory Proper

Hedin's Equations³

These are exact statements of many-body perturbation theory⁴. Don't they look tractable.

$$G(1, 2) = G_0(1, 2) + \int d(34) G_0(1, 3)\Sigma(3, 4)G(4, 2)$$

$$\Sigma(1, 2) = i \int d(34) W(1, 4)G(1, 3)\Lambda(3, 2, 4)$$

$$\Lambda(1, 2, 3) = \delta(1, 2)\delta(1, 3) + \int d(4567) \frac{\delta\Sigma(1, 2)}{\delta G(4, 5)} G(4, 7)\Lambda(7, 6, 3)G(6, 5)$$

$$W(1, 2)^5 = v(1, 2) + \int d(34) W(1, 3)v(2, 4)P(3, 4)$$

$$P(1, 2) = -i \int d(34) G(2, 3)\Lambda(3, 4, 1)G(4, 2^+)$$

³ L. Hedin. In: Phys. Rev. 139.3A (1965).

⁴ $n \equiv (\mathbf{r}_n, t_n)$. All integrals over all of space-time.

⁵ NB : some people split this into two, and define a dielectric matrix separately. This requires more space + makes business of functional derivatives stranger.

Short Summary

Or, why is this presentation primarily about QMC?

Mean-field theories

- ✓ **Antisymmetry** of (approx.) many-body wavefunction
- ✗ No real hope of systematic extension
- ✗ Even in principle, can't extract gaps - $E_{tot}^N, n^N(\mathbf{r})$ only

$G_x W_y$

- ✓ Systematic extension feasible
- Better than MFT on average
- ✗ **Dependance on G_0 , etc.**, full SC not cheap (or desirable)

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QMC Methods⁷

Variational Monte Carlo

- ▶ Endow a **trial wavefunction** with variational freedom:

$$\Psi(\mathbf{R}) = \underbrace{\exp \left[\mathcal{J}_{\{\alpha\}}(\mathbf{R}) \right]}_{\text{Our additions}} \times \underbrace{\mathcal{D}(\mathbf{R})}_{\text{DFT, HF, ...}} \quad (7)$$

and optimise some functional of Ψ by varying $\{\alpha\}$.

- ▶ The Jastrow factor, $\exp [\mathcal{J}]$, allows $\Psi(\mathbf{R})$ to satisfy properties of the **exact** many-electron wavefunction⁶.

⁶ T. Kato. In: Comms. on Pure and Appl. Math. 10.2 (1957).

⁷ W. M. C. Foulkes et al. In: RMP 73.1 (2001).

QMC Methods II

Diffusion Monte Carlo

- DMC is a stochastic projector-based method for solving⁸

$$\hat{\mathcal{H}} \Psi(\mathbf{R}, \tau) = (E_T - \partial_\tau) \Psi(\mathbf{R}, \tau) \quad (8)$$

or, if you like

$$\Psi(\mathbf{R}, \tau + \Delta\tau) = \int G(\mathbf{R} \leftarrow \mathbf{R}', \Delta\tau) \Psi(\mathbf{R}', \tau) d\mathbf{R}' \quad (9)$$

- **Separable** - time dependance is exponential⁹

$$\Psi(0) = \sum_n c_n \Phi_n \implies \Psi(\tau) = \sum_n c_n \Phi_n \exp [-(\mathcal{E}_n - E_T)\tau] \quad (10)$$

⁸ $i\tau = t$ (this is a "Wick rotated" Schrödinger equation).

⁹ $\{\Phi_i(\mathbf{R})\}$ → complete basis of eigenstates of the interacting problem.

DMC - cont.

Key things I won't have enough time to explain properly

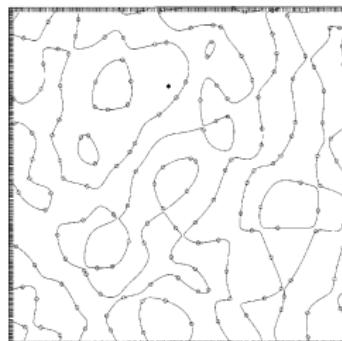
- ▶ **Time steps:** don't know interacting system $G(\mathbf{R} \leftarrow \mathbf{R}')$, but know approximation valid for small $\Delta\tau$.
- ▶ **Population control:** number of walkers in a DMC simulation fluctuates. Control mechanism introduces (small, controllable) bias.
- ▶ **Finite Size effects:** extrapolation to the thermodynamic limit is a necessity, physics of FS critical.
- ▶ **Gaps:** we might expect these problems to matter even less!

Excited State DMC

Wait a second...

- ▶ To make DMC¹⁰ workable, we have to **fix the nodes** of our trial wavefunctions.

Figure 1: 2D slice through 321D nodal surface of a 161-e⁻ system studied by Ceperley in 1991.



- ▶ This is the **only way** we can calculate excitation energies.

¹⁰Even GS DMC.

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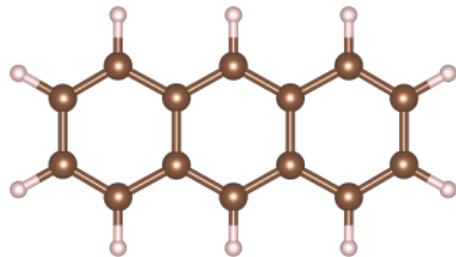
Small Molecules

Boron Nitride

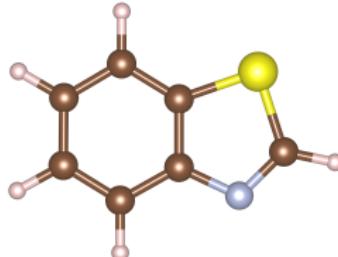
Silicon

Small Molecules

(A)nthracene - $C_{14}H_{10}$



(B)enzothiazole - C_7H_5NS



- ✓ Both have a slew of associated *GW*/expt./QC data
- ✓ Both are small enough for geometry to matter
(Jahn-Teller distortion)
- ✓ Both are desktop-sized DMC jobs ($N_e \sim 50$ or so)

Small Molecules - cont.

What do we find w/ QMC?

Method	Expt.	DMC	DMC-JT
IP^A / eV	7.439(6)	7.34(4)	7.28(5)
IP^B / eV	8.72(5)	8.92(3)	8.81(3)

- ▶ Jahn-Teller effect is important¹¹!
- ▶ (I would say) it's quite astounding that we can do this with a **single determinant**. Quantum chemists would cringe.

¹¹Ok, it isn't clear here. In our tests of dimers / smaller molecules it is easier to make the difference statistically significant.

Hexagonal Boron Nitride

Monolayer

Bulk

- ▶ Gaps **hard to determine.**
 - ▶ Gaps largely **known.**
-

- ▶ Dominant change after shedding dimensionality is the loss of **screening**.
- ▶ DMC can access this physics, and treat both systems **fairly**.
- ▶ If our bulk results stand up to scrutiny, can reason that we have an **equally good** description of the physics in 2D (desirable).

Hexagonal Boron Nitride

Continued...

- ▶ Some of our monolayer and bulk results

System →	Bulk/ Expt.	Monolayer
$\Delta_{Ex}(K_v \rightarrow K_c) / \text{eV}$	5.8(1)/ 5.971 ⁹	8.7(3)
$\Delta_{Ex}(K_v \rightarrow \Gamma_c) / \text{eV}$	5.69(8)	7.5(3)
$\Delta_{Ex}(\Gamma_v \rightarrow \Gamma_c) / \text{eV}$	7.9(1)	-

- ▶ We see that there is a **significant** enhancement of energy gaps on thinning to a monolayer.
- ▶ **In agreement** with the best available value ¹²(but again; phonons).

¹² K. Watanabe, T. Taniguchi, and H. Kanda. In: Nature Materials 3.6 (2004).

Hexagonal Boron Nitride

An interesting test

- Gaps are **energy differences**, do we necessarily need to use computationally demanding sets of time steps?

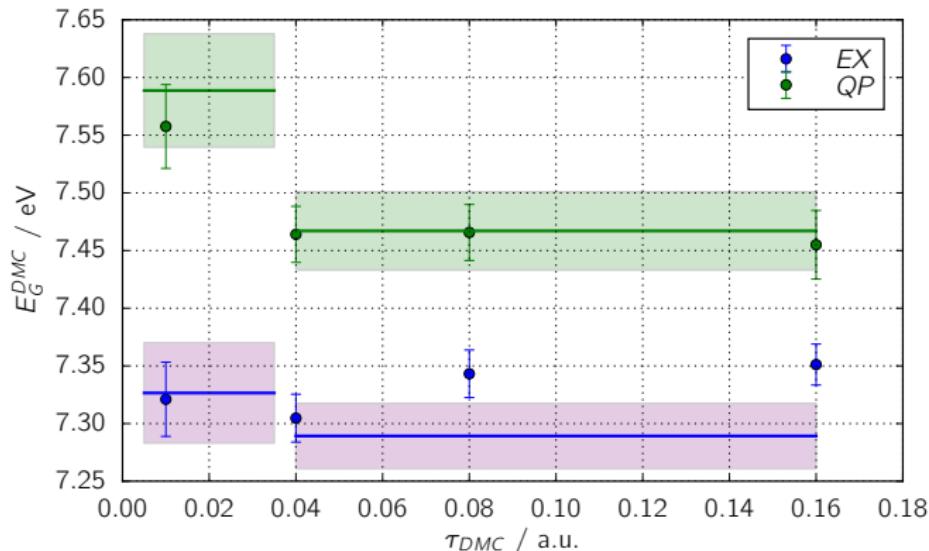
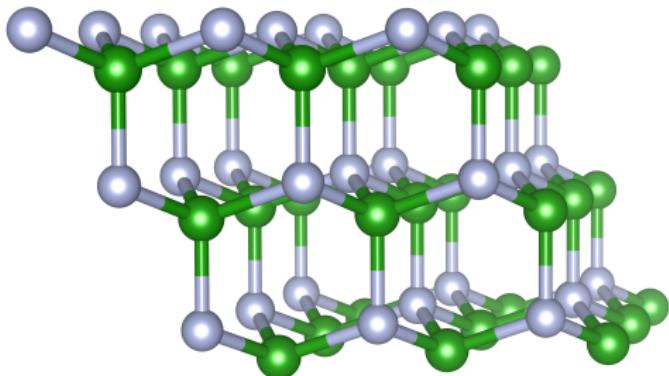


Figure 2: Some gap time step tests, in a (3 3 1) supercell of BhBN.

Cubic Boron Nitride

- ▶ CBN is also a **very good insulator.**
- ▶ **Understudied** w.r.t. hBN.
- ▶ Some ageing *GW* studies to compare with¹³, and is of general interest given recent discoveries involving C/B/N materials¹⁴.



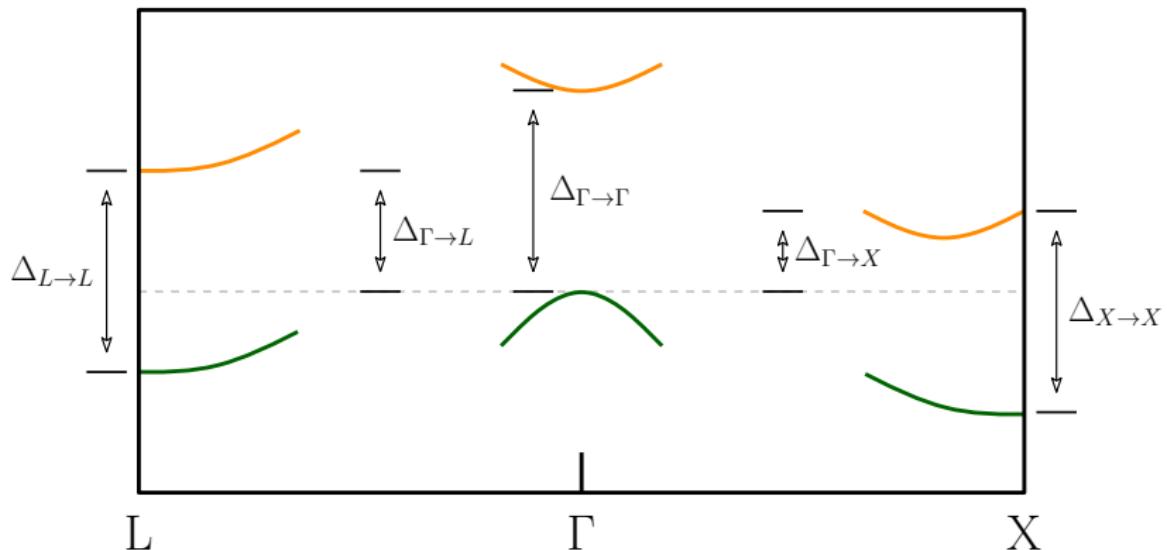
¹³ G. Satta et al. In: Physical Review B 64.3 (2001), G. Satta et al. In: Physical Review B 70.19 (2004).

¹⁴ C. J. Pickard et al. In: Phys. Rev. B 94 (9 2016).

Silicon

...in the diamond structure

Excitonic Gaps



- ▶ Exciton binding tiny - $\mathcal{O}(10^{-2})$ eV $\implies \Delta_{Ex} \sim \Delta_{QP}$.

Silicon cont.

Preliminary results

- ▶ So far, I have some preliminary results which are **without a treatment of FS errors¹⁵**;

Gap / eV \	$L \rightarrow L$	$\Gamma \rightarrow L$	$\Gamma \rightarrow \Gamma$	$\Gamma \rightarrow X$	$X \rightarrow X$
DMC	3.77(4)	2.39(4)	3.57(4)	1.24(4)	4.55(4)
ioffe ¹⁶	-	2.0	3.4	1.2	-

- ▶ Interestingly, Δ_{Ex} **agree nicely with experiment** (w/ deviation well within the realm of phononic effects).
- ▶ **BUT** so do $\Delta_{QP}...$

¹⁵Actually, we are discovering that FS is far less important for excitonic gaps. Don't expect significant change from full FS treatment.

¹⁶At 300K. These are from numerous sources, which I will omit for length reasons. Sorry.

Silicon cont.

A topic of current investigation

- ▶ Our proposed FS treatment scheme for **QP Gaps** is;

$$\begin{aligned}\Delta(N) = & \Delta(\infty) + b v_M(N) \\ & + c (\Delta_{DFT}(N) - \Delta_{DFT}(\infty))\end{aligned}\quad (11)$$

where v_M is the **Madelung** constant evaluated for a given supercell (system size).

- ▶ ∴ for Si, where we know $\Delta_{Ex} \sim \Delta_{QP}$, we don't expect to have the situation we do!

Silicon cont.

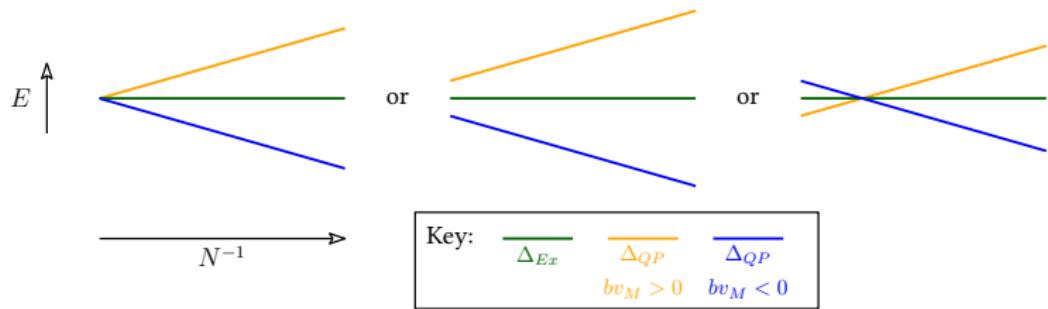


Figure 3: The possible FS behaviours of quasiparticle and excitonic gaps.

- **Take-home point :** We know FS effects are more difficult for charged excitations. We are **open** to the idea that DMC could be **over**/under estimating QP gaps.¹⁷

¹⁷I am currently determining the DMC excitation energies of various small molecules, in order to try to get a handle on this.

Summary

- ▶ FN-DMC is capable of **predictive** determination of energy gaps¹⁸ for **diversely bonded** systems of all dimensionalities.
- ▶ The full extent to which computational savings can be made for DMC energy gap calculations is **unclear** and we will continue to probe!

¹⁸For the pessimists : at least for one important kind of gap (excitonic). Investigations ongoing. Monsters may emerge.

Thank you all for listening!