Quantum Monte Carlo calculations of energy gaps from first-principles

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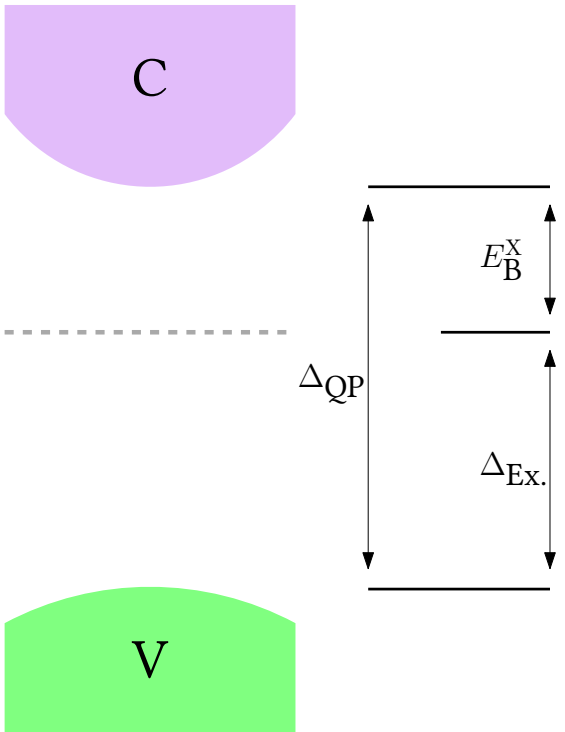
What's the problem?

We'd like to be able to predictively model the (opto)electronic behaviour of materials. Because this could be *useful*.

- Specifically, $\Delta_{\text{Ex.}}$, Δ_{QP}, and E_{B}^{X} in semiconductors.[1]
- Don't define "material heaven", but are a start.
- (The blue LED is blue for a reason.)



[1] R. J. Hunt et al., Phys. Rev. B **98** (2018)

Energy gaps: definitions

The **quasiparticle gap**, Δ_{QP}, is defined as the difference between the CBM and the VBM:

$$\begin{aligned}\Delta_{\mathrm{QP}}(\mathbf{k}_\mathrm{f},\mathbf{k}_\mathrm{t}) &= \mathcal{E}_{\mathrm{CBM}}(\mathbf{k}_\mathrm{t}) - \mathcal{E}_{\mathrm{VBM}}(\mathbf{k}_\mathrm{f}) \\ &= [E_{\mathrm{N}+1}(\mathbf{k}_\mathrm{t}) - E_{\mathrm{N}}(\mathbf{k}_\mathrm{t})] - [E_{\mathrm{N}}(\mathbf{k}_\mathrm{f}) - E_{\mathrm{N}-1}(\mathbf{k}_\mathrm{f})] \\ &= E_{\mathrm{N}+1}(\mathbf{k}_\mathrm{t}) + E_{\mathrm{N}-1}(\mathbf{k}_\mathrm{f}) - E_{\mathrm{N}}(\mathbf{k}_\mathrm{t}) - E_{\mathrm{N}}(\mathbf{k}_\mathrm{f}),\end{aligned} \tag{1}$$

The **excitonic gap**, $\Delta_{\mathrm{Ex.}}$, is defined as the energy difference between an excited N-electron state and the ground N-electron state:

$$\Delta_{\mathrm{Ex.}}(\mathbf{k}_\mathrm{f},\mathbf{k}_\mathrm{t}) = E^{+}_{\mathrm{N}}(\mathbf{k}_\mathrm{f},\mathbf{k}_\mathrm{t}) - E_{\mathrm{N}}, \tag{2}$$

Their difference is the **exciton binding** ($\Delta_{\mathrm{QP}} \geq \Delta_{\mathrm{Ex.}}$, in TD limit).[2]

[2] The interaction energy of a quasielectron at $\mathbf{k}_\mathrm{t}$ and a quasihole at $\mathbf{k}_\mathrm{f}$. Many-body Bloch conditions restrict us!

Variational Principles

Excitonic gaps:

- In VMC, if $\psi_{\mathrm{T}}(\mathbf{R}; \{\alpha\})$ has some symmetry $\forall\{\alpha\}$, have VP w.r.t. lowest energy state of given symmetry.
- In FN-DMC, such symmetry may be **broken** (nodes are not enough!).[3]

Implications: the practical upshot

- Δ_{QP}: all ground states. **Effective VP** on QP gap.
- $\Delta_{\mathrm{Ex.}}$: vulnerable to variational collapse unless symmetry constraint met. **Beware**.[4]

[3] W. M. C. Foulkes et al., Phys. Rev. B **60** (1999).

[4] Safe if one *constructs* determinantal expansion with target symmetry class.

Finite-size effects

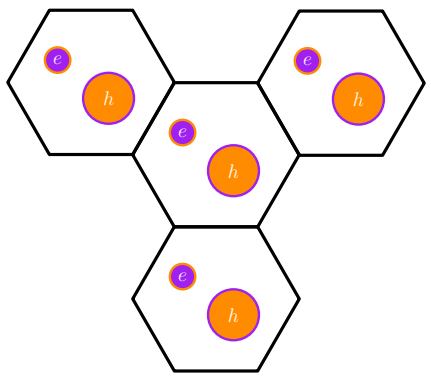
Semiconductors

- Single-particle FS negligible, Coulomb or many-body FS dominant.

Gaps

- Δ_{QP}: a difference in QP energies…
  - Leading-order FS error in each calc. $\sim v_M$ assoc. with the *quasiparticles* in their host *environment*.[5]
  - Remainder negligible in solids, but appears systematic (charge-quadrupole) in 2D materials (expect from Makov-Payne…[6]).
- $\Delta_{\mathrm{Ex.}}$: energy needed to create exciton

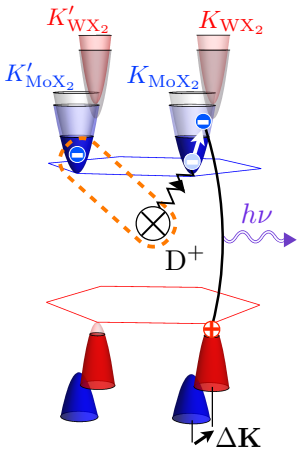
If cell big enough
$\Longrightarrow$ FSE $\sim$ lattice of image-excitons.
Else
$\Longrightarrow$ FSE $\sim$ uncorrelated QPs (exciton *squeezed*).

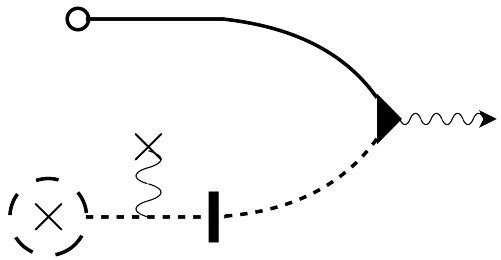


[5] Not the "bare" v_M which goes into the Ewald interaction…
[6] G. Makov and M. C. Payne, Phys. Rev. B **51** (1995).

Miscellany

- "Excited state QMC" isn't just gaps. Lifetimes, dip. mom., etc.[7]





$$\Gamma \sim \left| \overbrace{\int \mathrm{d}^2 r \, \mathrm{e}^{i\Delta\mathbf{K}\cdot\mathbf{r}} \chi(\mathbf{r})}^{\text{QMC!}} \right|^2$$

- Won't say anything about "intraband" excitations. Excitations in metals (HEG, parameterising FLT) studied elsewhere.[8]

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[7] M. Danovich et al., Phys. Rev. B **97** (2018), R. N. Barnett et al., Int. J. Quantum Chem. **42** (1992).

[8] Y. Kwon et al., Phys. Rev. B **50** (1994), N. D. Drummond and R. J. Needs, Phys. Rev. B **87** (2013), N. D. Drummond and R. J. Needs, Phys. Rev. B **88** (2013).

Some Results: Atoms and Molecules

Neon

Is single-determinant only inherently bad? $1^{\text{st}} \ldots 8^{\text{th}}$ IP of Ne (MAE):

$$\underbrace{0.83\%}_{\text{SJ-VMC}} \rightarrow \underbrace{0.67\%}_{\text{SJB-VMC}} \rightarrow \underbrace{0.38\%}_{\text{SJ-DMC}} \rightarrow \underbrace{0.34\%}_{\text{SJB-DMC}} \tag{3}$$

no real trend amongst the individual IPs, save for larger-than-typical error on 7th IP (3-e^-!).

O_2 dimer

Electronic ground state triplet: $({}^3\Sigma_g^-)$. Singlet-triplet splitting around 0.9773 eV.

- SD SJ-DMC: 1.62(2) eV, MD-Δ SJ-DMC: 0.20(3) eV.
- Other little tests;
  - PP ($\mathcal{O}(0.3$ eV$)$ in IP).
  - Geometry ($\mathcal{O}(0.5$ eV$)$ in IP).

H_2 dimer

- Full-quantum electron/proton DMC calculation. See paper. More to come…?

Some Results: Bulk Solids

Silicon

Previous studies looked at Si. SD SJ calculations, claimed good agreement with expt.[9]

- Revisit suggests FS effects hinder prior study ($\mathcal{O}(0.2\,\text{eV})$).
- Inclusion of backflow ($\mathcal{O}(0.1\,\text{eV})$) (& re-opt. – further $\mathcal{O}(0.1\text{eV})$) crucial for good QP energies.

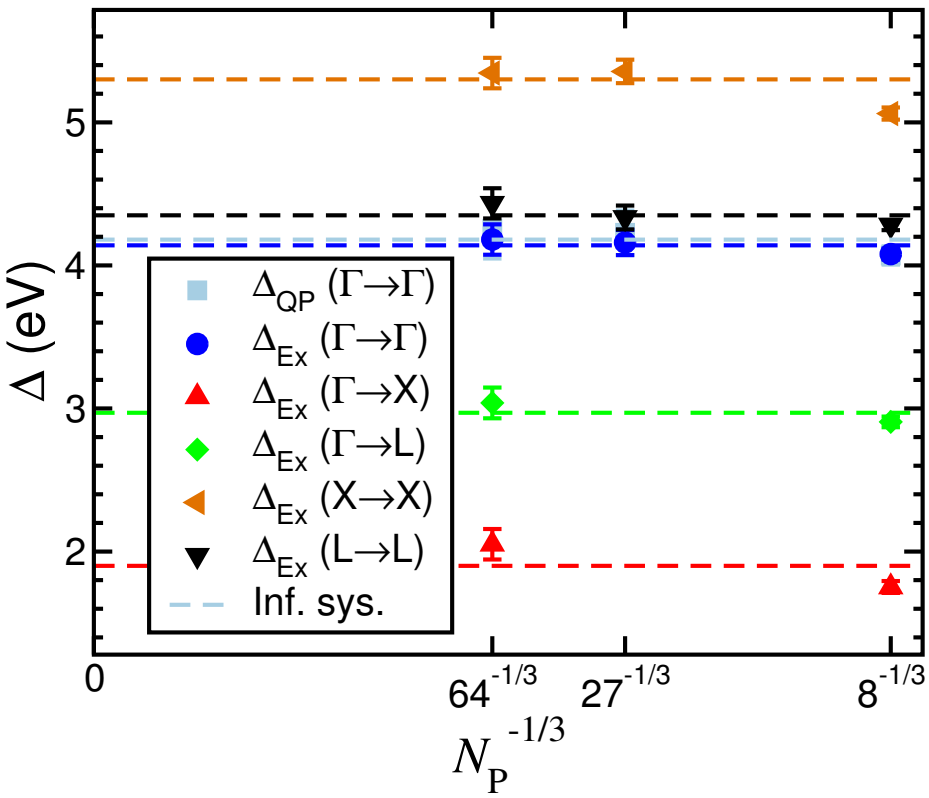
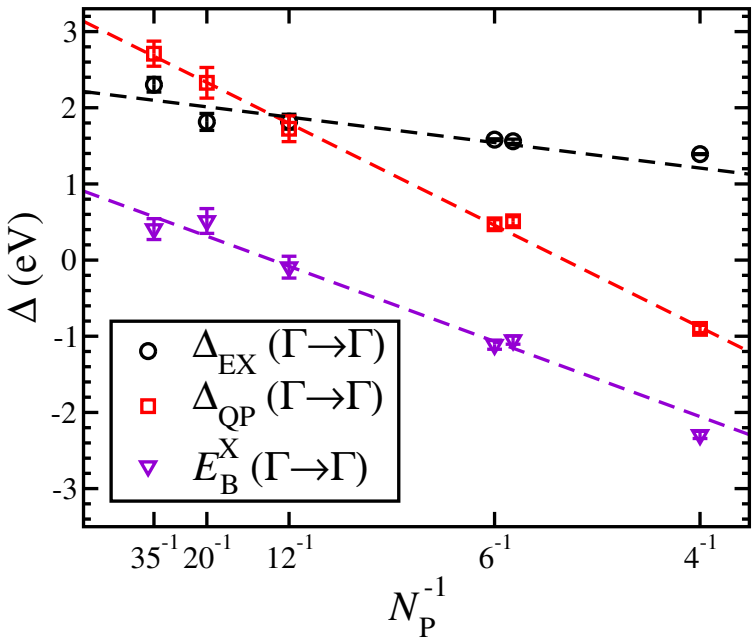


Figure 1: Uncorrected SJ-DMC gaps in Si.

- $\Delta_{\text{Ex.}}$ studied before, **but** cannot directly study $\Gamma \rightarrow 0.85\text{X}$ excitation.

[9] A. J. Williamson et al., Phys. Rev. B **57** (1998)

Some Results: Phosphorene



- FS treatment: Keldysh-screened v_M necessary for QP. Keldysh-exponent charge-quadrupole necessary for Ex.[10]
- Backflow doesn't lower gaps (QP or Ex.) by statistically significant amt.
- Prelim. vibrational corrections: ZP ($\geq$)-0.07 eV, 300K -0.17 eV.

NB another QMC study on phosphorene exists. Authors there also considered HW BCs (make dominant FS error kinetic, $\mathcal{O}(L^{-2})$).[11] Generally, need to be careful doing this.[12]

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10 L. V. Keldysh, J. Exp. Theor. Phys. **29** (1979)

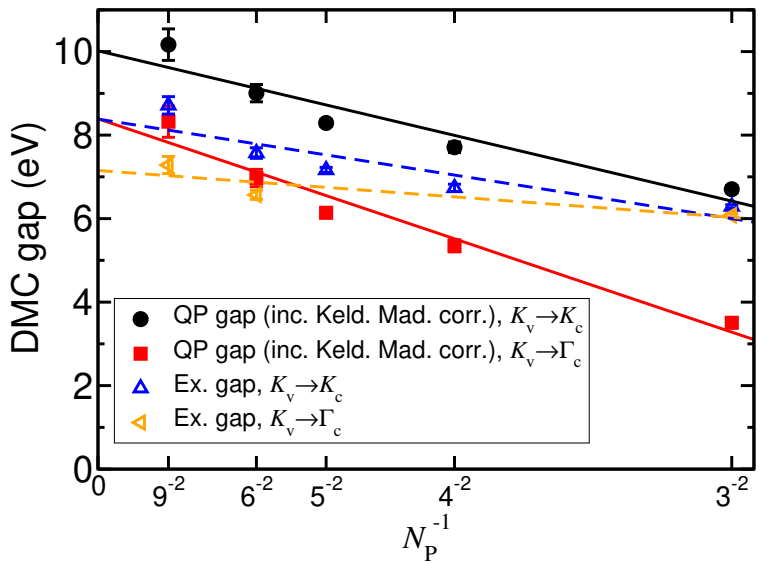
11 T. Frank et al., Phys. Rev. X **9** (2019).

12 N. D. Drummond et al., Phys. Rev. Lett. **95** (2005).

Some Results: Monolayer hBN

A few of you know of these calculations, Neil (Drummond) performed years ago.

- FS treatment: as in phosphorene.
- Vibrations: ZP correction -0.54 eV (-0.73 eV @ 300K) (similar for K $\rightarrow$ K or Γ).



- Systematic $1/N$ FS effect recovered after subtraction of $\tilde{v}_M$ from Δ_{QP}. $\Delta_{Ex.}$, and corrected Δ_{QP} same systematic FS.
- $E_B^X(K \rightarrow \Gamma)$=1.9(4) eV
- $E_B^X(K \rightarrow K)$=1.8(4) eV
- (Wirtz *et al.* *GW*-BSE: 2.1 eV)

Conclusions

QMC Specifics

- Non-negligible comp. savings possible: time step bias in a gap is almost imperceptible (definitely is at $\mathcal{O}(0.1\,\mathrm{eV})$).[13]
- FS effects accuracy limiting.
- Best possible QP energies (safely) rely on best possible individual wfns.
- FN error from excitonic gaps cannot be too high: all else accounted for, we've never done too badly. We have been **super-conservative**.

Gap Generalities

- Vibrations: for gaps, an electronic theory alone is not enough.

[13] Potential further savings are in localization of low-lying states.

Acknowledgements

Lancaster:

- Neil Drummond
- Marcin Szyniszewski

Japan (JAIST):

- Ryo Maezono
- Genki Prayogo

Manchester:

- Vladimir I. Fal'ko
- Viktor Zólyomi

Cambridge:

- Tomeu Monserrat

Thanks for your attention!