Excitons in two-dimensional materials from first-principles (by Quantum Monte Carlo!)

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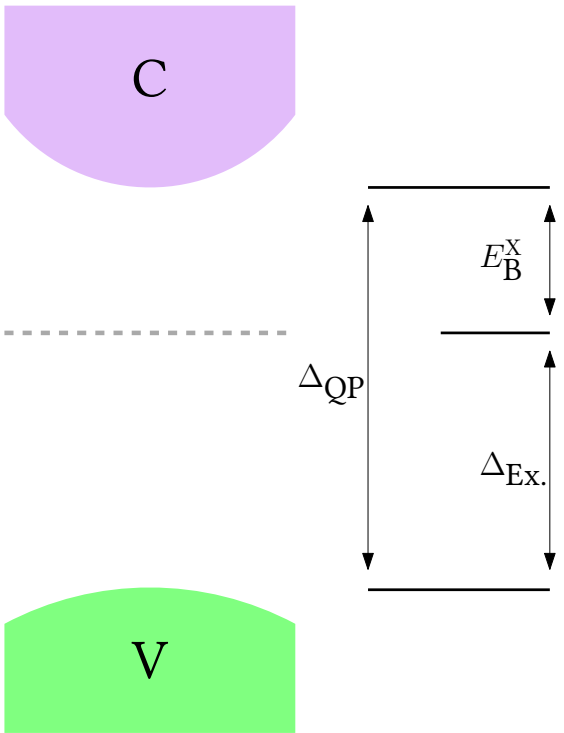
GRAPHENE NOWNANO CDT

Excitons

- Objects are translucent when some of the light incident on them is *absorbed*.
- Absorption is mediated by individual absorbing units (e^-).



- In crystals, e^- live in discrete *energy bands*. In semiconductors, all of the e^- live under a *band gap*.[1]
- The onset of optical absorption is defined by the position of lowest-lying *exciton levels*.
- Band theory + independent e^- approx. $\Longrightarrow$ cannot describe excitonic effects.

[1] Or ϵ_F lies in a *band gap*.

Energy Gaps & Exciton Binding

- How do we define the exciton binding energy in a way that allows for first-principles calculation?
- For excitations between $\mathbf{k}_\mathrm{f}$ and $\mathbf{k}_\mathrm{t}$,

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

Most challenging aspects?

1. Can only calculate these in finite *supercells*.
2. E_N^+ is a genuine many-body excited state energy.

Step back: Mott-Wannier Models

Q: What could we do instead of first-principles modelling?

- Invoke effective mass approximation, try to cook up realistic electron-hole interaction potentials V.[2]

Then, solve

$$\left[-\sum_{\alpha=1}^{n}\frac{\hbar^2}{2m_\alpha}\nabla_\alpha^2+\sum_{\alpha<\beta}\frac{q_i q_j}{4\pi\epsilon_0}V(\mathbf{r}_\alpha,\mathbf{r}_\beta)\right]\Psi(\mathbf{R})=E\Psi(\mathbf{R}),\ \mathbf{R}\equiv(\mathbf{r}_1,\ldots,\mathbf{r}_n) \quad (2)$$

- Neglecting many-particle correlation effects, relying on parameters, and *failing* in physically reasonable cases.[3]
- Have done this numerous times for "reasonable" cases.[4]

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[2] N. S. Rytova, Dokl. Akad. Nauk. SSSR **163** (1965), N. S. Rytova, Vestn. Mosk. Univ. Fiz. Astron. **3** (1967), L. V. Keldysh, J. Exp. Theor. Phys. **29** (1979).

[3] Frenkel excitons, for example, are perfectly reasonable objects.

[4] E. Mostaani et al., Phys. Rev. B **96** (2017), M. Danovich et al., Phys. Rev. B **97** (2018), O. Witham et al., Phys. Rev. B **97** (2018), D. M. Thomas et al., Phys. Rev. B **99** (2019).

Quantum Monte Carlo methods (abridged)[6]

- In Variational Monte Carlo (VMC), we *guess* a many particle wave function, and improve our guess by monitoring observables (whilst tweaking parameters $\{\alpha\}$!).

$$\Psi(\mathbf{R}) = \exp\left[J(\mathbf{R};\{\alpha\})\right] \times D(\mathbf{R}) = \Psi(\mathbf{R},0). \tag{3}$$

- In Diffusion Monte Carlo (DMC), we take our trial wave function and propagate it through imaginary time. Removing excited components, and allowing us to sample an estimate of the true energy.[5]

$$\Psi_{\mathrm{DMC}}(\mathbf{R},\tau) = \exp\left[-\tau(E_{\mathrm{T}} - \mathcal{H})\right]\Psi(\mathbf{R},0) \tag{4}$$

$$\vdots$$

$$\Psi_{\mathrm{Exact}} \sim \lim_{\tau\to\infty} \Psi_{\mathrm{DMC}}(\mathbf{R},\tau) \tag{5}$$

- **People don't generally do this because it requires the use of supercomputers.**

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[5] With various caveats.

[6] W. M. C. Foulkes et al., Rev. Mod. Phys. **73** (2001).

Phosphorene

A direct gap 2D semiconductor, with large exciton binding energy.

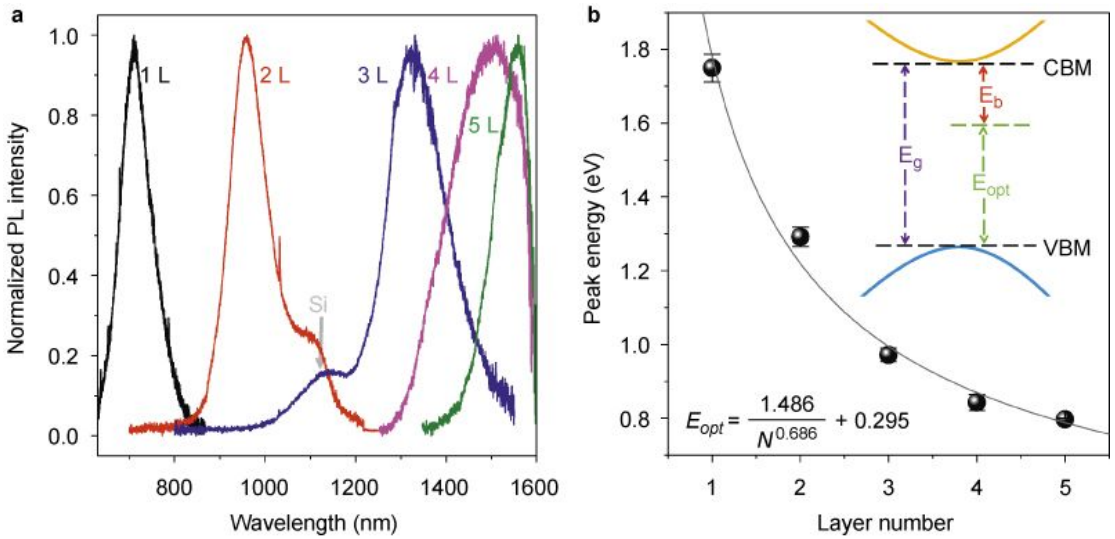


Figure 1: PL measurements of Phosphorene n-layers.[7]

- Can we extract the $n = 1$ exciton binding energy w/ QMC?
- What are the issues that affect such QMC calculations?

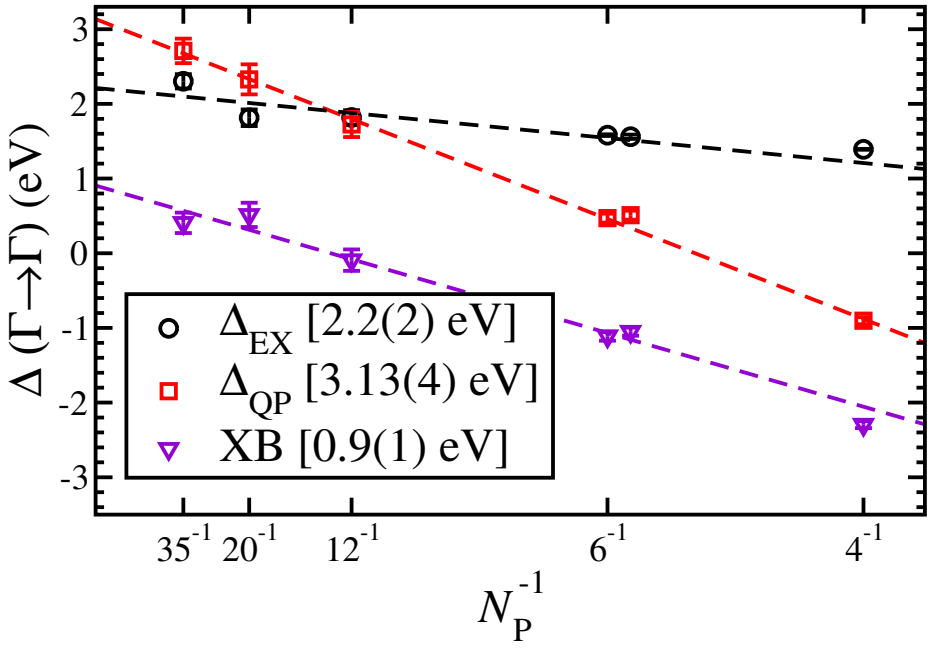
[7] J. Yang et al., Light Sci. Appl. **4** (2015)

Phosphorene (cont.)

Yes, expt. on suspended monolayers give 0.9(1) eV.[8]

We must pay attention to:

- Finite-size errors.
- Vibrational effects.
- Computational efficiency.



- Nuclear vibrations renormalise the QP gap by $\mathcal{O}(-0.09\ \text{eV})$ @ 0K.[9]
- We have tested the relaxation of a serious technical assumption in DMC, finding that it *does not* affect our results.[10]

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[8] X. Wang et al., Nat. Nanotechnol. **10** (2015), A. Carvalho et al., Nat. Rev. Mater. **1** (2016)

[9] B. Monserrat, private communication (2018). Correction roughly doubles at room temperature.

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

Conclusions: Outlook for QMC

- It is possible to model excitons (and band gaps!) in 2D materials using QMC. Results are in **agreement with experiment**, *where reasonable*.
- QMC calculations are still expensive, but perhaps to a **similar degree to alternatives** (e.g. fully converged *GW*-BSE).
- Extraction of more relevant (?) quantities (oscillator strengths, lifetimes, full absorption spectra) in solids still a **pipe dream** for QMC.
- Extraction of the same quantities for more *realistic* cases (defects, finite carrier concentration, under external fields) is **perfectly possible**.[11]

[11] Though maybe in a couple of centuries.

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