Quantum Monte Carlo calculations of energy gaps from first-principles

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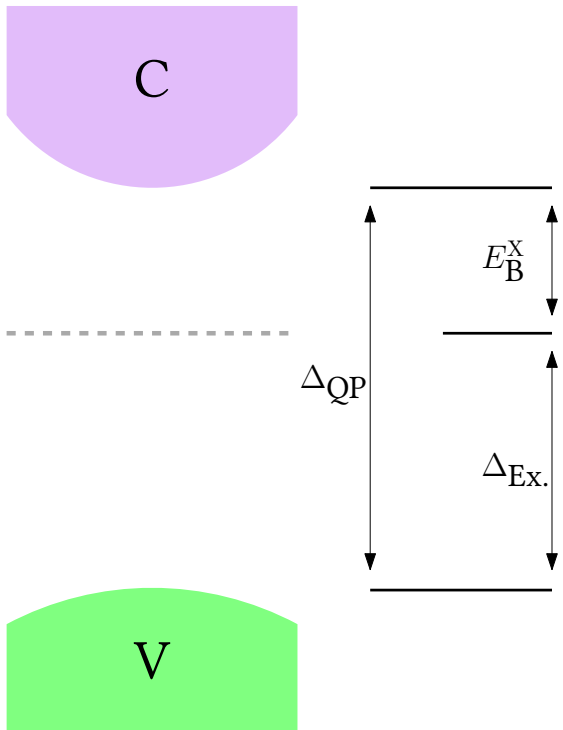
What's the problem?

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] FYI work discussed here is in: **Hunt *et al.***, Phys. Rev. B **98(7)** (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**.[2]

[2] The interaction energy of a quasielectron at $\mathbf{k}_{\mathrm{t}}$ and a quasihole at $\mathbf{k}_{\mathrm{f}}$.

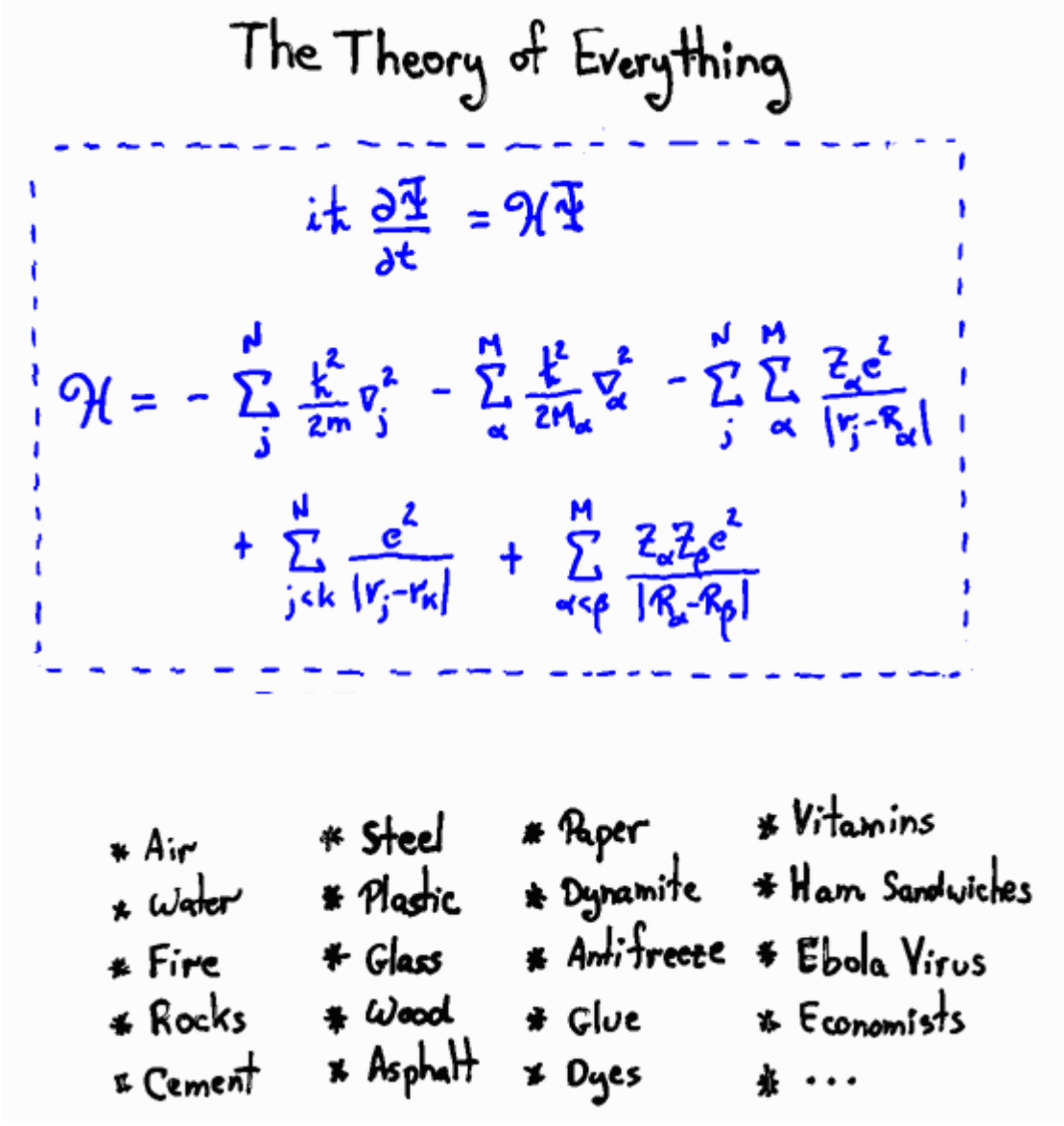


Figure 1: Introductory slide from Laughlin's Nobel lecture.

Why Quantum Monte Carlo (QMC)?

What else?

- Density functional theory (or HF | hybrids)
  - Take differences in Kohn-Sham (Hartree-Fock) SP eigenvalues.
- Many-body perturbation theory (GW | GW-BSE | MPn)
  - QP energies from QP equation (feat. self-energy, $\Sigma(\mathbf{k}, \omega)$).
- Quantum chemistry (post HF | CC | CI | FCI)
  - Most similar to present: direct calculation of total energies.

Either too crude, too scattered, or too expensive.

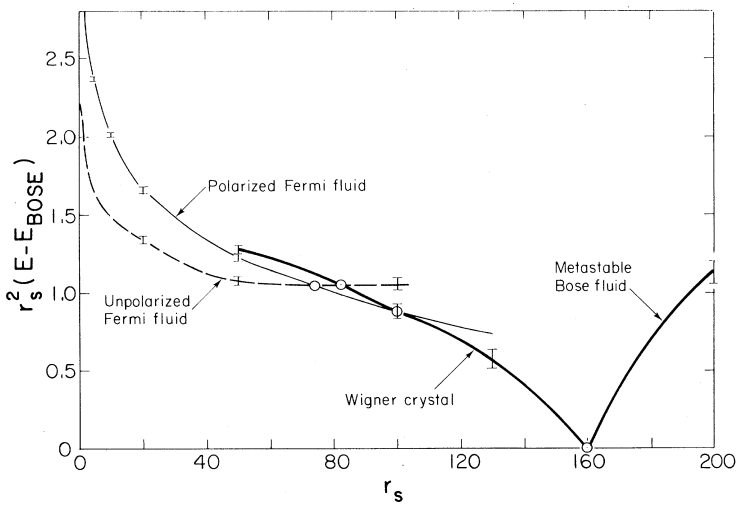
Why QMC - cont.

QMC methods:

- ✓ Are highly accurate, and systematically improvable.
- ✓ Are non-perturbative, and treat correlation effects exactly.
- ✓ Have $\mathcal{O}(N_e{}^3)$ cost, not much worse in "abnormal" cases.

Proof? Lots available, see reviews,[3] or below.[4]

Figure 2: The basis of much modern (computational) electronic structure theory.



[3] W. M. C. Foulkes et al., Rev. Mod. Phys. **73** (2001), R. J. Needs et al., J. Phys. Condens. Matter **22** (2009).

[4] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45** (1980).

QMC Methods[5]

Variational Monte Carlo

- Endow a *trial* wavefunction with variational freedom:

$$\Psi(\mathbf{R}) = \underbrace{\exp\left[\,\mathcal{J}_{\{\alpha\}}(\mathbf{R})\,\right]}_{\text{Our additions}} \times \underbrace{\mathcal{D}(\mathbf{R})}_{\text{DFT, HF, ...}}, \tag{3}$$

  and pick $\{\alpha\}$.

- MC integration used, for example, to evaluate

$$\langle\Psi|\hat{\mathcal{H}}|\Psi\rangle = \int \mathrm{d}\mathbf{R}\,|\Psi(\mathbf{R})|^2 \left[\frac{\hat{\mathcal{H}}\Psi(\mathbf{R})}{\Psi(\mathbf{R})}\right] \approx \sum_i \frac{\mathcal{H}(\mathbf{R}_i)\Psi(\mathbf{R}_i)}{\Psi(\mathbf{R}_i)}, \tag{4}$$

  ($\{\mathbf{R}_i\}$ distributed as $|\Psi(\mathbf{R})|^2$).

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

Diffusion Monte Carlo

- DMC is a stochastic projector-based method for solving

$$\hat{\mathcal{H}}\,\Psi(\mathbf{R},\tau) = (E_T - \partial_\tau)\Psi(\mathbf{R},\tau), \tag{5}$$

or, if you like

$$\Psi(\mathbf{R},\tau+\Delta\tau) = \int G(\mathbf{R}\leftarrow\mathbf{R}',\Delta\tau)\Psi(\mathbf{R}',\tau)\mathrm{d}\mathbf{R}'. \tag{6}$$

- **Separable** $(\partial_\tau\hat{\mathcal{H}} = 0)$ [6]

$$\Psi(0) = \sum_n c_n\Phi_n \implies \Psi(\tau) = \sum_n c_n\Phi_n \exp\left[-(\mathcal{E}_n - E_T)\tau\right] \tag{7}$$

[6] $\{\Phi_i\} \rightarrow$ complete basis of eigenstates of the interacting problem.

DMC - cont.

Effectively we take:

$$\lim_{\tau \to \infty} \Psi(\tau) \sim \Phi_0, \tag{8}$$

by having the DMC Green's function take configurations $\mathbf{R}' \to \mathbf{R}$, with caveats:

- **Time steps**: know $G(\mathbf{R} \leftarrow \mathbf{R}', \Delta\tau)$ in limit of small $\Delta\tau$.
- **Population control**: number of walkers in DMC fluctuates. Control mechanism introduces a bias.
- **Finite-size (FS) effects**: extrapolation to TD limit a necessity.
- **Fixed-node approximation**: (non-local) antisymmetry enforced by (local) boundary condition ($\Psi = 0$ surface is fixed).

Gaps: expect some of these to matter less!

Excited States

Briefly:

- QP gap $\rightarrow$ $E_{\mathrm{N},\mathrm{N}\pm1}$ (VP on each *ground* state).
- Ex. gap $\rightarrow$ *may* have VP on E^{+}. *May* only have at VMC level. FN-DMC VP obtained in special circumstances.[7]
- (FN constraint means effective VP)

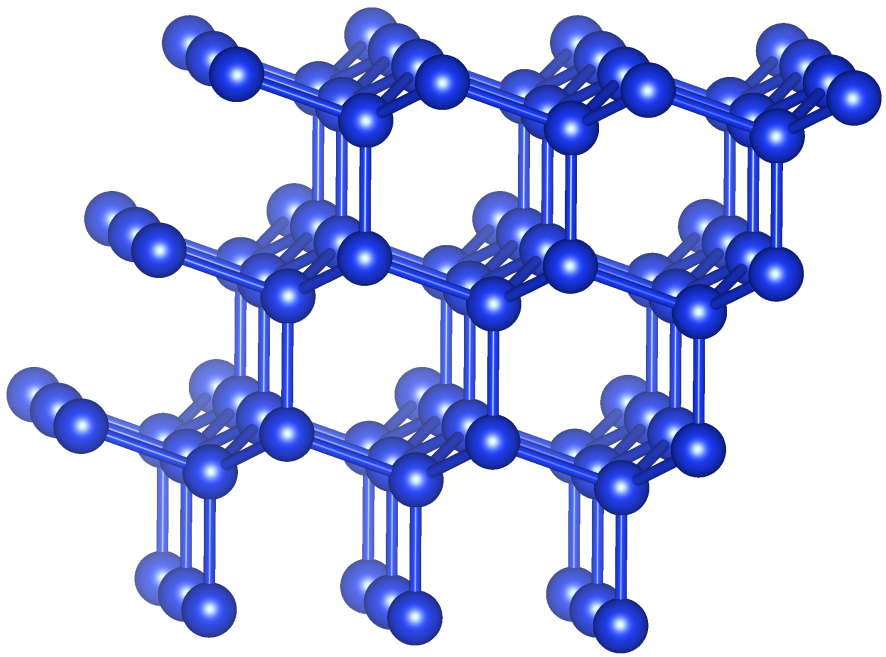
[7] W. M. C. Foulkes et al., Phys. Rev. B **60** (1999).

Bulk solids

We've studied Si, α-SiO_2, and cubic BN in the current work. Previous QMC studies had claimed success in evaluation of "QMC band structures",[8] minus discussions of:

- Finite-size errors.
- Fixed-nodal errors.
- Δ_{QP} vs. $\Delta_{Ex.}$.

Will concentrate on Si here, exploring the above.



[8] P. R. C. Kent et al., Phys. Rev. B **57** (1998), A. J. Williamson et al., Phys. Rev. B **57** (1998).

Bulk solids: FS errors

- Able only to simluate a finite *chunk* of material (supercell), under PBCs. Excitations "1/N" effects. Need statistical accuracy + careful FS treatment.

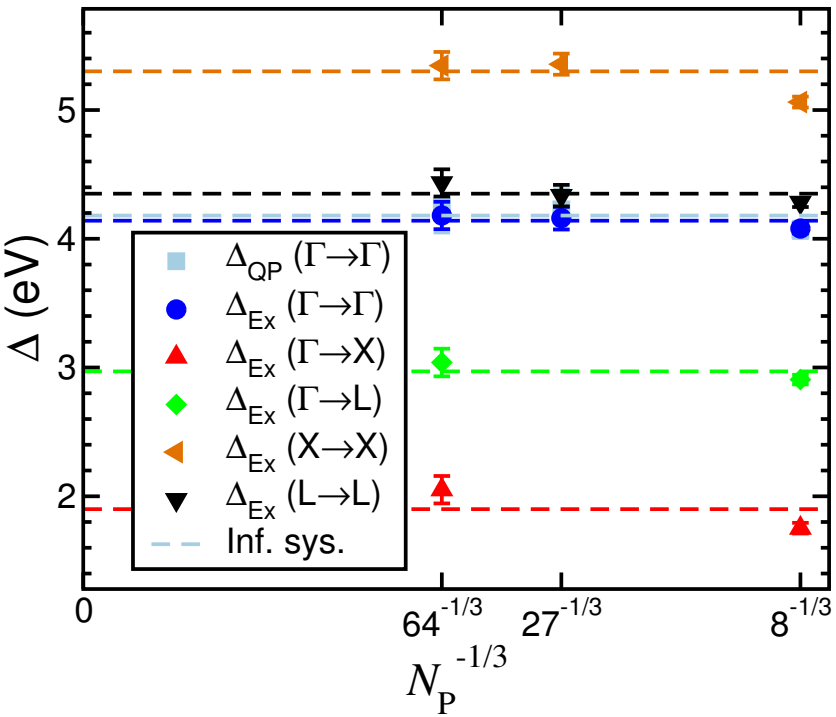


Figure 3: Uncorrected SJ-DMC gaps of Si. FS effect characteristic and quantifiable, largely from image-interactions.

- Then why do Δ_{QP} & $\Delta_{Ex.}$ behave same?

Bulk solids: Fixed-nodal error

- Probe with Backflow transformation:

$$\mathbf{r}_i \to \mathbf{x}_i = \mathbf{r}_i + \boldsymbol{\xi}_i(\mathbf{R}) \tag{9}$$

  which can change nodal surface.[9]

- Tested $\Delta_{\mathrm{QP/Ex}}(\Gamma_{\mathrm{v}} \to \Gamma_{\mathrm{c}})$ and $\Delta_{\mathrm{QP}}(\Gamma_{\mathrm{v}} \xrightarrow{\sim} \mathrm{CBM})$, in $2 \times 2 \times 2$ supercell.
- We find that backflow leads to a reduction in gaps, of at least 0.2 eV, but upto 0.3–0.4 eV when one re-optimises $\boldsymbol{\xi}_i$.[10]

[9] P. Lopez Rios et al., Phys. Rev. E **74** (2006).

[10] C.f. controllable uncertainty: $\mathcal{O}(0.1\ \mathrm{eV})$ for each of pseudopotentials, statistics, NLO FS effects (?).

Phosphorene

A direct gap 2D semiconductor, with large exciton binding energy.[11]

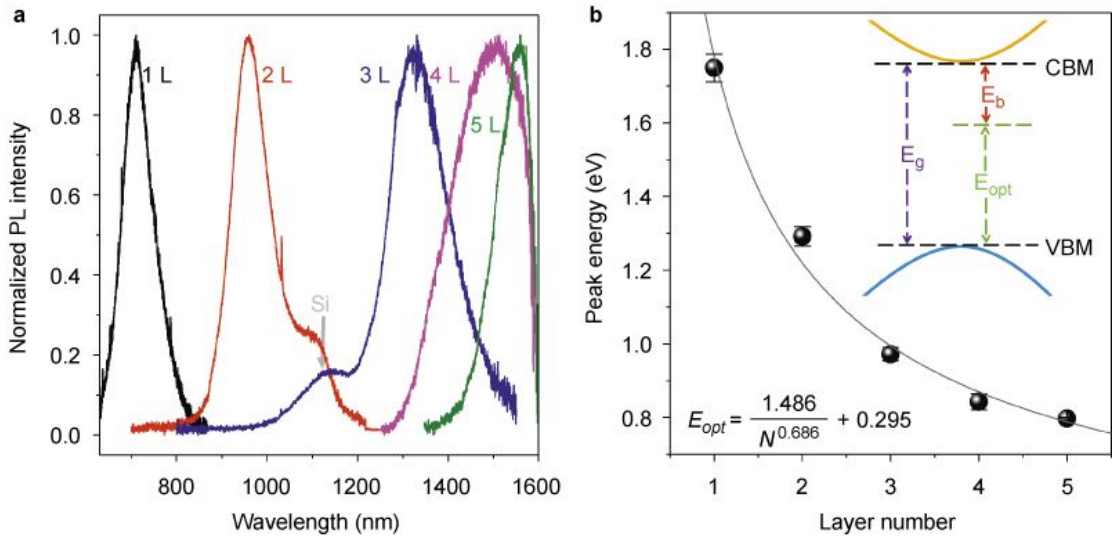
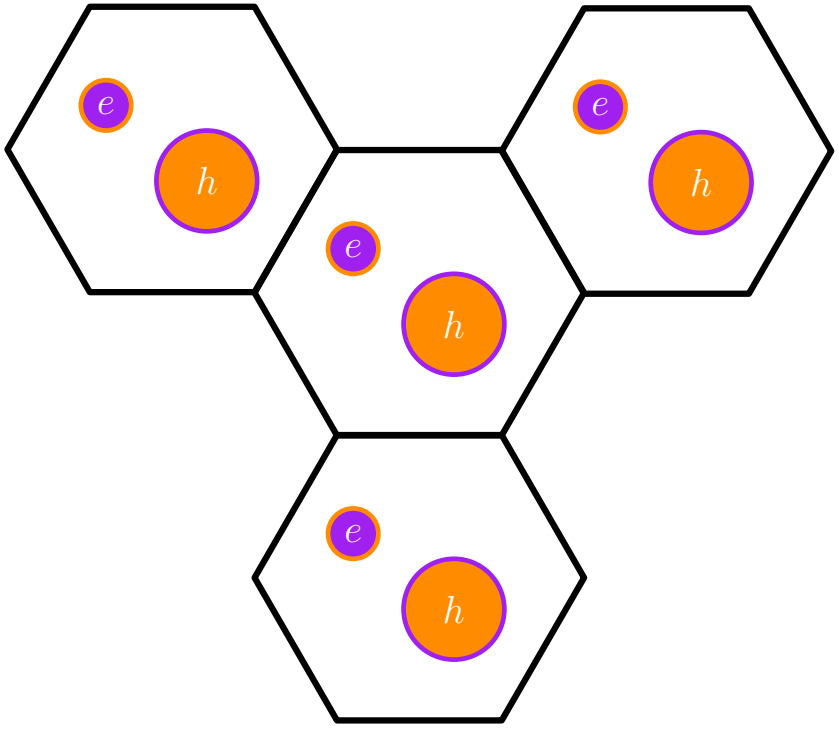


Figure 4: PL measurements of Phosphorene *n*-layers.

- Do **not** expect $\Delta_{QP} \sim \Delta_{Ex.}$
- FS effects in $\Delta_{QP/Ex.}$ much more important.

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

Physics of FS effects in 2D



- We want to model a *free* excitonic complex
- Perform supercell calculation (SC characteristic size L), subject to periodic BCs
- Hence incurr an unphysical image-interaction

- Need to remove E_{int}. **How does it scale?**

Physics of FS effects in 2D (cont.)

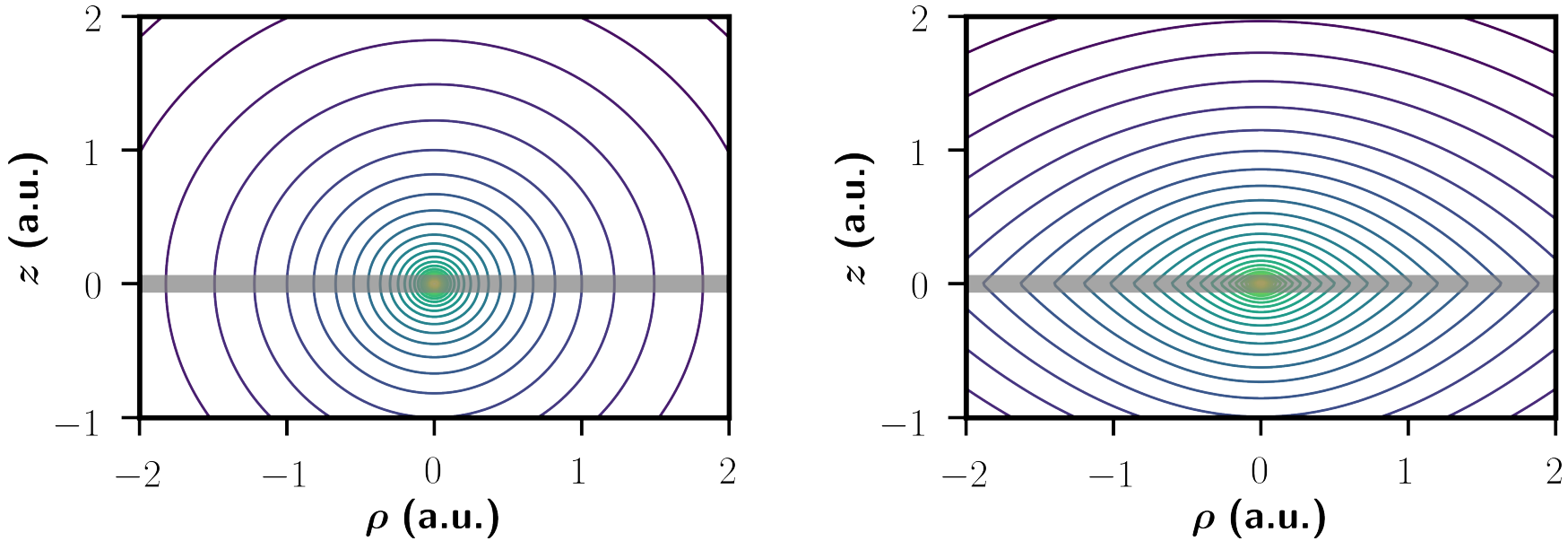


Figure 5: Unscreened (left) and screened (right) field lines from point charges at $\rho = z = 0$.

- With 2D screening (Keldysh interaction), charge-quadrupole interaction[12] leads to expected scaling which is $\mathcal{O}(L^{-2})$.

[12] Note no dipole in inversion symmetric system!

Physics of FS effects in 2D (cont.)

Δ_{QP}

- Similar image effects, easier to manage.
- Subtract single-particle v_{M} ($\mathcal{O}(L^{-1})$).
- From regularized lattice sum over screened interaction ($\sim$ Ewald sum).

$$\sum_{\mathbf{R}} W(\mathbf{r}-\mathbf{R}) \to \overbrace{\sum_{\mathbf{R}} V(\mathbf{r}-\mathbf{R})}^{\textbf{Ewald}} + \underbrace{\sum_{\mathbf{R}} \delta V(\mathbf{r}-\mathbf{R})}_{\textit{safe}}\,. \tag{10}$$

- "*Safety*": $\lim_{r\to\infty} \delta V(r) = 0$.

Physics of FS effects in 2D (cont.)

- FSE appear to scale as argued.
- Big gaps (ϵ!),[13] but good agreement w/ Gaufrès *et al.*[14]
- Phonon renormalisation $\sim$ 0.17 eV @ 300K.[15]

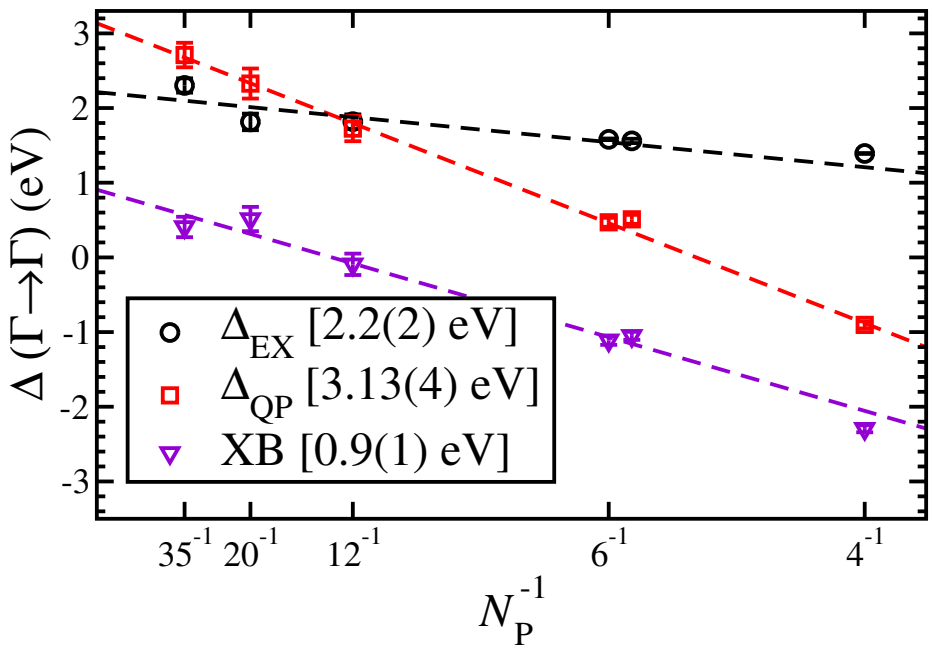


Figure 6: QMC energy gaps in phosphorene vs. system size.

[13] Also, this is not due to FN error! Backflow has $\mathcal{O}(0.05\text{ eV})$ effect here.

[14] This result is unpublished, so far, but was presented at GW 2018 by A. Loiseau. $\Delta_{\text{Ex}} = 1.95$ eV.

[15] Via Tomeu Monserrat, also as yet unpublished.

Physics of FS effects (cont.)

Another approach is to consider passivated (finite) clusters. Here FS effect is kinetic in origin (confinement).[16]

- FS converge faster (QP gap $\mathcal{O}(L^{-2})$ by default), **but**…
- State under study may not be relevant[17]…

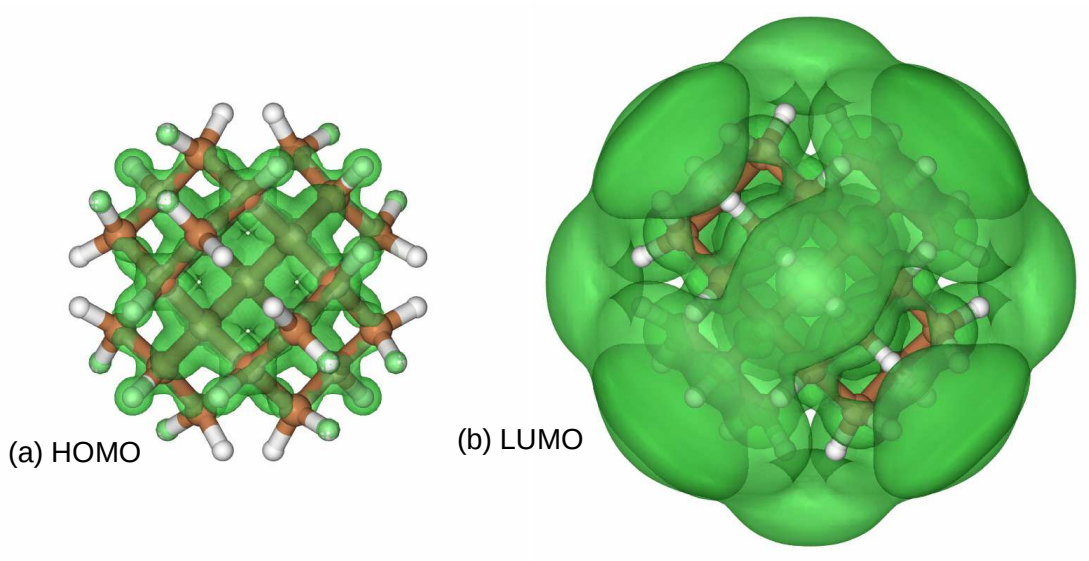


Figure 7: Band charge densities in $C_{29}H_{36}$.

[16] T. Frank et al., arXiv:1805.10823 (2018).

[17] N. D. Drummond et al., Phys. Rev. Lett. **95** (2005).

Another QMC study of Phosphorene

Frank *et al.* have also studied phosphorene. We're dissatisfied with their approach. Why?

- Used cluster calculations to argue scaling in bulk calculations.
- Calculated the *wrong gap*:

Figure 8: Excerpt from preprint.

by QMC methods within the error bars[28]. The gap Δ_f was extracted as the singlet-singlet vertical excitation energy. Here $\Delta_f \approx E_v^{ss} = E_1^s - E_0^s$, with E_0 and E_1 being, respectively, the ground- and the first excited-states obtained by fixed-node QMC[38] not allowing any

- Our excitonic gap (2.2(2) eV) agrees with their "quasiparticle" gap (2.4 eV) ☺.[18]

[18] Guessed wrong scaling exponent (1/N) for QP gap, but this isn't a QP gap! Just so happen to have calculated and taken TD limit for an excitonic gap. Assuming they've done the calculations correctly, a good test of our result!

Conclusion

- QMC methods offer a direct, real-space approach to the many-body problem.
- They allow for accurate determination of energy gaps from first-principles in one, two and three-dimensional systems.
- They can be systematically extended, and treat various important pieces of physics **exactly**.

Acknowledgements

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