

# Quantum Monte Carlo calculations of energy gaps from first-principles

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# Outline

## Motivation

What's the problem?

Why Quantum Monte Carlo (QMC)?

## QMC Methods

VMC and DMC

Excited-state QMC

## Case studies

Atoms and molecules

Bulk solids

Phosphorene

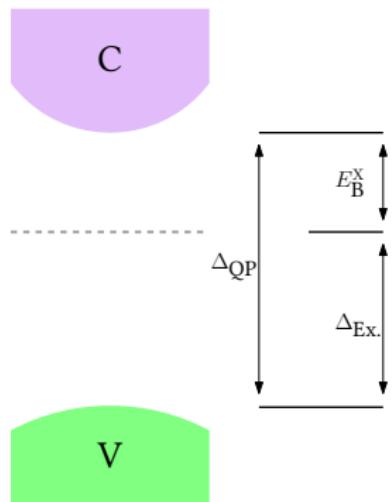
## Conclusion

# What's the problem?

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

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



# Energy gaps: definitions

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

$$\begin{aligned}\Delta_{QP}(\mathbf{k}_f, \mathbf{k}_t) &= \mathcal{E}_{CBM}(\mathbf{k}_t) - \mathcal{E}_{VBM}(\mathbf{k}_f) \\ &= [E_{N+1}(\mathbf{k}_t) - E_N(\mathbf{k}_t)] - [E_N(\mathbf{k}_f) - E_{N-1}(\mathbf{k}_f)] \\ &= E_{N+1}(\mathbf{k}_t) + E_{N-1}(\mathbf{k}_f) - E_N(\mathbf{k}_t) - E_N(\mathbf{k}_f),\end{aligned}\quad (1)$$

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

$$\Delta_{Ex.}(\mathbf{k}_f, \mathbf{k}_t) = E_N^+(\mathbf{k}_f, \mathbf{k}_t) - E_N,\quad (2)$$

Their difference is the **exciton binding**.<sup>1</sup>

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<sup>1</sup> The interaction energy of a quasielectron at  $\mathbf{k}_t$  and a quasihole at  $\mathbf{k}_f$ .

# The Theory of Everything

$$it \frac{\partial \tilde{\Psi}}{\partial t} = \mathcal{H}\tilde{\Psi}$$

$$\begin{aligned} \mathcal{H} = & - \sum_j^N \frac{k^2}{2m} \nabla_j^2 - \sum_\alpha^M \frac{k^2}{2M_\alpha} \nabla_\alpha^2 - \sum_j^N \sum_\alpha^M \frac{Z_\alpha e^2}{|r_j - R_\alpha|} \\ & + \sum_{j < k}^N \frac{e^2}{|r_j - r_k|} + \sum_{\alpha < p}^M \frac{Z_\alpha Z_p e^2}{|R_\alpha - R_p|} \end{aligned}$$

- \* Air      \* Steel      \* Paper      \* Vitamins
- \* Water      \* Plastic      \* Dynamite      \* Ham Sandwiches
- \* Fire      \* Glass      \* Antifreeze      \* Ebola Virus
- \* Rocks      \* Wood      \* Glue      \* Economists
- \* Cement      \* Asphalt      \* Dyes      \* ...

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

# Why Quantum Monte Carlo (QMC)?

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What else?

- ▶ Density functional theory (or HF | hybrids)
  - ▶ Take differences in Kohn-Sham (Hartree-Fock) SP eigenvalues.
- ▶ Many-body perturbation theory ( $GW$  |  $GW$ -BSE | MP $n$ )
  - ▶ 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.

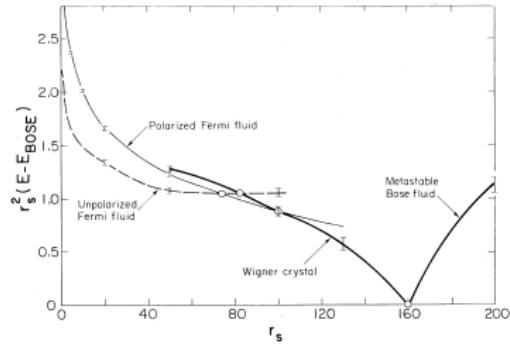
# Why QMC - cont.

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,<sup>2</sup> or below.<sup>3</sup>

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



<sup>2</sup> W. M. C. Foulkes et al., Rev. Mod. Phys. **73** (2001), R. J. Needs et al., J. Phys. Condens. Matter **22** (2009).

<sup>3</sup> D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45** (1980).

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## Variational Monte Carlo

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

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

and pick  $\{\alpha\}$ .

- ▶ MC integration used, for example, to evaluate

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

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

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<sup>4</sup> W. M. C. Foulkes et al., Rev. Mod. Phys. 73 (2001).

## Picking $\{\alpha\}$ : a super-simple example

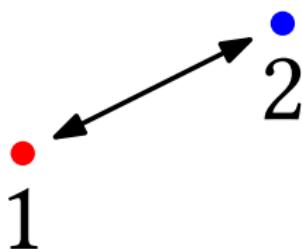
For example, a “guessed” H atom trial wave function might look like:

$$\Psi_H(\mathbf{r}_e) = \exp \left[ \underbrace{(r_e - L)^C \Theta(L - r_e)}_{\text{Smooth cutoff}} \sum_{i=0} \alpha_i r_e^i \right]. \quad (5)$$

We use robust optimization algorithms to vary the  $\{\alpha\}$  such that our guess looks more like an eigenstate.

- ▶ Minimise  $E$ ,  $\sigma_E^2$ , or another measure of spread, ...

- ▶ Jastrow factor ( $\exp[\mathcal{J}]$ ) describes  $n$ -body correlations **explicitly** in real-space, and allows  $\Psi$  to satisfy properties of the **exact** many-electron wavefunction.<sup>5</sup>
- ▶ E.g. the Kato<sup>6</sup> cusp conditions:



- ▶ As (1,2) coalesce, if  $V(r_{12})$  diverges,  $T$  must also ( $\hat{\mathcal{H}} = \hat{T} + \hat{V}$ ).
- ▶ Kinetic energy  $\Rightarrow$  derivatives of  $\Psi$   $\Rightarrow$  derivatives of  $\mathcal{J}$ .
- ▶ Fixes some of the  $\{\alpha\}$ .

<sup>5</sup> Also critical for efficiently describing *dispersion* interactions.

<sup>6</sup> T. Kato, Comms. on Pure and Appl. Math. **10** (1957).

## Diffusion Monte Carlo

- DMC is a stochastic projector-based method for solving

$$\hat{\mathcal{H}} \Psi(\mathbf{R}, \tau) = (E_T - \partial_\tau) \Psi(\mathbf{R}, \tau), \quad (6)$$

or, if you like

$$\Psi(\mathbf{R}, \tau + \Delta\tau) = \int G(\mathbf{R} \leftarrow \mathbf{R}', \Delta\tau) \Psi(\mathbf{R}', \tau) d\mathbf{R}'. \quad (7)$$

- **Separable** ( $\partial_\tau \hat{\mathcal{H}} = 0$ )<sup>7</sup>

$$\Psi(0) = \sum_n c_n \Phi_n \implies \Psi(\tau) = \sum_n c_n \Phi_n \exp [-(\mathcal{E}_n - E_T)\tau] \quad (8)$$

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<sup>7</sup>  $\{\Phi_i\}$  → complete basis of eigenstates of the interacting problem.

Effectively we take:

$$\lim_{\tau \rightarrow \infty} \Psi(\tau) \sim \Phi_0, \quad (9)$$

by having the DMC Green's function take configurations  $\mathbf{R}' \rightarrow \mathbf{R}$ ,  
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!

In special circumstances, what I have just said also applies to the ground state *of a given symmetry*.<sup>8</sup> Key idea concerns excited-states and generalised variational principles

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- ▶ **Jargon:** If trial wfn. transforms as a 1D irrep. of the symmetry group of the Hamiltonian, have a variational principle on states of that symmetry (could be excited state).<sup>9</sup>

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<sup>8</sup> Actually, the variational principle on ground states in fixed-node DMC is an excited state one, fermion GS transforms as 1D irrep. of permutation group.

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- ▶ **Jargon:** If trial wfn. transforms as a 1D irrep. of the symmetry group of the Hamiltonian, have a variational principle on states of that symmetry (could be excited state).<sup>9</sup>
- ▶ **Simple practical upshot:** the many-body Bloch conditions for periodic calculations mean that states with definite crystal momentum belong to a 1D irrep. (of the translation group).

There are *many* other means of obtaining variational bounds.<sup>10</sup>

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<sup>9</sup> W. M. C. Foulkes et al., Phys. Rev. B **60** (1999).

<sup>10</sup> L. Zhao and E. Neuscamman, J. Chem. Theory Comput. **12** (2016), J. K. L. MacDonald, Phys. Rev. **43** (1933), P. G. Hipes, Phys. Rev. B **83** (2011).

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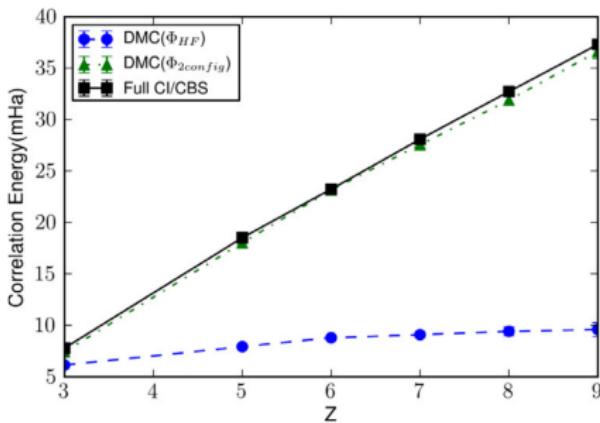
# Intrinsic accuracy: Ne atom

The neon atom ground state is (famously) closed shell. None of the cations are, and there's a potential for build-up of nodal<sup>11</sup> error in IP.<sup>12</sup>

$$\text{IP}(n) = E(n) - E(n-1), \quad (10)$$

Q: Does this happen?

Figure 3: DMC and FCI correlation energies of atoms versus atomic number (from Rasch *et al.*). NB  $30\text{mHa} \sim 0.8\text{ eV}$ .



<sup>11</sup> FN-error  $\equiv$  error arising from (local) B.C. on  $\Psi$  ( $\Psi = 0$  “surface” fixed to please Pauli).

<sup>12</sup> K. M. Rasch *et al.*, J. Chem. Phys. **140** (2014), A. H. Kulahlioglu *et al.*, Chem. Phys. Lett. **591**

“Exact”  $\implies$  expt. minus best est. relativistic correction.<sup>13</sup>

$n$	IP( $n$ ) (eV)				
	Exact	SJ-VMC	SJB-VMC	SJ-DMC	SJB-DMC
1	21.61333	22.08(2)	21.96(2)	21.72(1)	21.72(1)
2	40.99110	41.48(2)	41.39(2)	41.10(1)	41.06(1)
3	63.39913	63.44(2)	63.23(1)	63.35(2)	63.39(1)
4	97.29312	97.91(2)	97.78(1)	97.75(2)	97.72(1)
5	126.28846	126.85(2)	126.72(2)	126.85(1)	126.79(1)
6	157.80001	158.43(2)	158.30(1)	158.25(2)	158.34(1)
7	207.04137	204.48(2)	204.56(1)	205.04(2)	205.26(1)
8	238.78949	238.10(1)	238.49(1)	238.70(2)	238.79(1)
MAE	0%	0.83%	0.67%	0.38%	0.34%

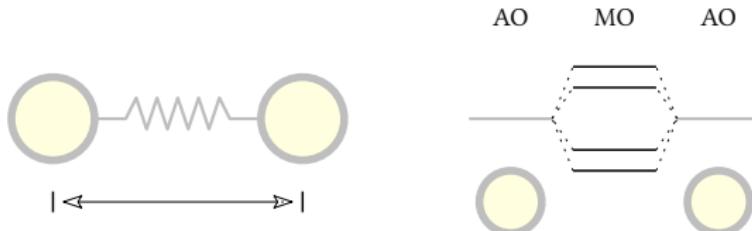
So? IPs related to QP energies. More later!

<sup>13</sup> S. J. Chakravorty et al., Phys. Rev. A 47 (1993).

# Molecules - dimers

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- ▶ O<sub>2</sub>: singlet/triplet, (near)degeneracy, multideterminants.



- ▶ H<sub>2</sub>: vibrations, quantum protons.



$$\Psi(\mathbf{r}_{e1}, \mathbf{r}_{e2}, \mathbf{r}_{p1}, \mathbf{r}_{p2})$$

# Dimers (cont.)<sup>14</sup>

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Figure 4: O<sub>2</sub> and H<sub>2</sub> dimer results.

Method	Ionization potential (eV)	
	H <sub>2</sub>	O <sub>2</sub>
SJ-DMC (AE-PW)	16.465(3)	—
SJ-DMC (AE-G)	16.462(6)	13.12(7)
SJ-DMC (PP-PW)	16.377(1)	12.84(2)
SJ-DMC (PP-PW-ER)	15.582(1)	12.33(2)
J-DMC (p <sup>+</sup> p <sup>+</sup> e <sup>-</sup> e <sup>-</sup> )	15.4253(7)	—
QSGW	16.04, <sup>[120]</sup> 16.45 <sup>[121]</sup>	—
CC-EPT	—	12.34,12.43 <sup>[122]</sup>
MP2	—	11.72 <sup>[123]</sup>
CCSD	—	11.76,12.13 <sup>[124]</sup>
CCSD(T)	—	11.95 <sup>[125]</sup>
QCISD(T)	—	12.18 <sup>[123]</sup>
JCE	15.42580 <sup>[125]</sup>	—
Experiment	15.4258068(5) <sup>[126]</sup>	12.0697(2) <sup>[127]</sup>

- ▶ For O<sub>2</sub>, also determined singlet-triplet splitting of 1.62(2) [0.20(3)] eV, c.f. 0.9773 eV.
- ▶  $\mathcal{D}/\sum_i \mathcal{D}_i$  and ability of QMC to treat on equal footing is key!

<sup>14</sup> R. J. Hunt et al., Phys. Rev. B 98 (2018).

In terms of computational cost, QMC for small molecules ( $N_e \sim 100$ ) is roughly on par with  $GW$ (-BSE). Recently, a slew of such studies have focussed on studying small molecules.

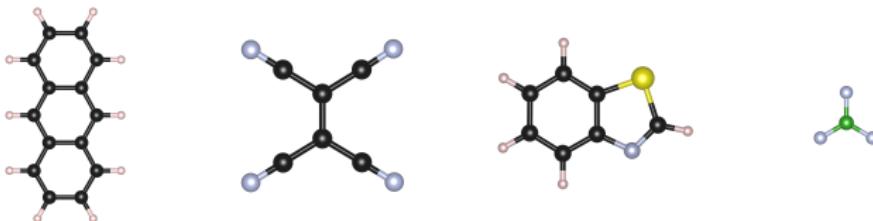


Figure 5:  $C_{14}H_{10} \rightarrow C_6N_4 \rightarrow C_7H_5NS \rightarrow BF_3$ .

- ▶ Results vary significantly, and are  $G_0$ ,  $W_0$ ,  $v_{xc}$  ... dependent.
- ▶ Is QMC a worthy competitor in the realm of small molecules?

Example use:  $T(E)$  in molecular electronics, for example.  
Determines  $I$ - $V$  characteristics of a molecular junction.

# Nondimers (cont.)

Anthracene ( $C_{14}H_{10}$ ):

- ▶  $\Delta_{Ex}^{S=0,1} = 3.07(3), 2.36(3)$  eV. (PAH & **Hund!**).
- ▶ Expt. says 3.38-3.433, 1.84-1.85<sup>\*</sup> eV.
- ▶ No comparable *GW*.<sup>15</sup>



Benzothiazole ( $C_7H_5NS$ ):

- ▶ IP =  $\underbrace{8.92(2)}_V \rightarrow \underbrace{8.80(2)}_A$  eV
- ▶ Expt. says 8.72(5) eV [A].
- ▶ *GW* says 8.2-8.5 eV [V].

- ✓ QMC as tool for probing **molecular excitons**. Relevant in materials screening for biological imaging, for example. (FRET).
- ✗ Relevant quantities are (really) resonance timescales.

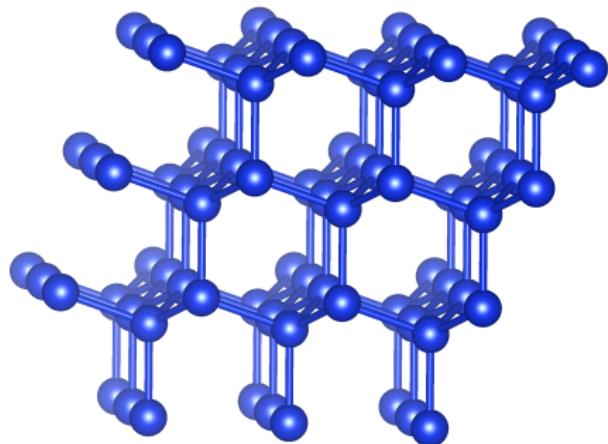
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<sup>15</sup> Hummer *et al.* studied mol. cry. anthracene: PRL 92(14), (2004). Unreferenced numbers found (w/ refs) in our article, excluded for space.

We've studied Si,  $\alpha\text{-SiO}_2$ , and cubic BN in the current work. Previous QMC studies had claimed success in evaluation of "QMC band structures",<sup>16</sup> minus discussions of:

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

Will concentrate on Si here, exploring the above.



<sup>16</sup> 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

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- ▶ Able only to simulate a finite *chunk* of material (supercell), under PBCs.
- ▶ Excitation energies are “ $1/N$ ” effects. Need statistical accuracy + careful FS treatment.

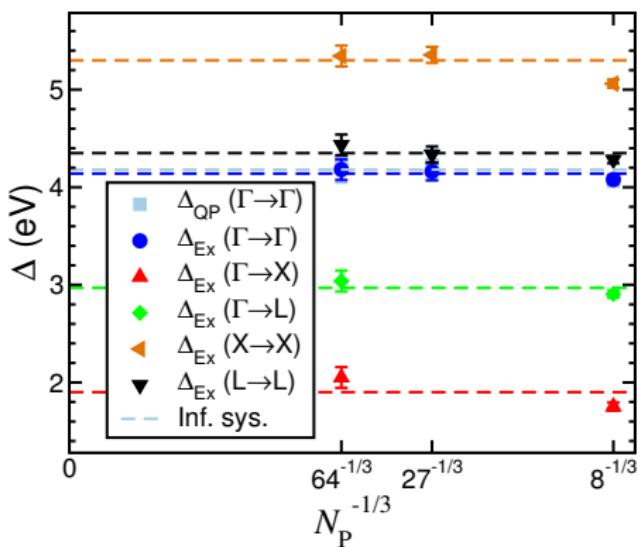


Figure 6: Uncorrected SJ-DMC gaps of Si vs. system size. Answer is, basically, **no**. But...error is quantifiable. Largely from image-interactions (Madelung energy of QP).

- ▶ Probe with Backflow transformation:

$$\mathbf{r}_i \rightarrow \mathbf{x}_i = \mathbf{r}_i + \boldsymbol{\xi}_i(\mathbf{R}) \quad (11)$$

which can change nodal surface.<sup>17</sup>

- ▶ Tested  $\Delta_{\text{QP/Ex}}(\Gamma_v \rightarrow \Gamma_c)$  and  $\Delta_{\text{QP}}(\Gamma_v \xrightarrow{\sim} \text{CBM})$ , in  $2 \times 2 \times 2$  supercell.

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<sup>17</sup> P. Lopez Rios et al., Phys. Rev. E 74 (2006).

We find:

- ▶ Inclusion of backflow correlations:
  - ▶ Lowers  $\Delta_{QP}(\Gamma_v \rightarrow \Gamma_c)$  by 0.13 eV.
  - ▶ Lowers  $\Delta_{Ex.}(\Gamma_v \rightarrow \Gamma_c)$  by 0.12 eV.
- ▶ Re-optimisation of excited-state backflow functions ( $\xi_i(\mathbf{R})$ ) further lowers:
  - ▶  $\Delta_{QP}(\Gamma_v \rightarrow \Gamma_c)$  by 0.18 eV.
  - ▶  $\Delta_{QP}(\Gamma_v \xrightarrow{\sim} CBM)$  by 0.20 eV.

**Point:** FN errors **not** insignificant ( $\gtrsim 0.2$  eV), but can be remedied<sup>18</sup> w/ backflow.

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<sup>18</sup> Always safe for QP gaps. Sometimes safe for Ex. gaps.

In bulk Si  $E_B^X \sim 15 \text{ meV}$ .

- ▶ Expect  $\Delta_{\text{QP}} \sim \Delta_{\text{Ex.}}$  (in TD limit).
- ▶ (potentially) qualitatively different FS effects, however.
- ▶ ...but already seen that this doesn't happen in Si.

## Explanation:

Confine an exciton too tightly,  $E_K$  dominates, no binding, behave effectively uncorrelated. Balance of supercell length scale and exciton length scale important.

⇒  $a_B^*$  in Si is **huge**. Cell never big enough to accomodate X.

# Bulk solids: the old calculations (briefly) < 27 | 43 >

No  $q_k \Rightarrow \Delta \uparrow$       Bad wfn.  $\Rightarrow \Delta \uparrow$       FS effects  $\Rightarrow \Delta \downarrow$

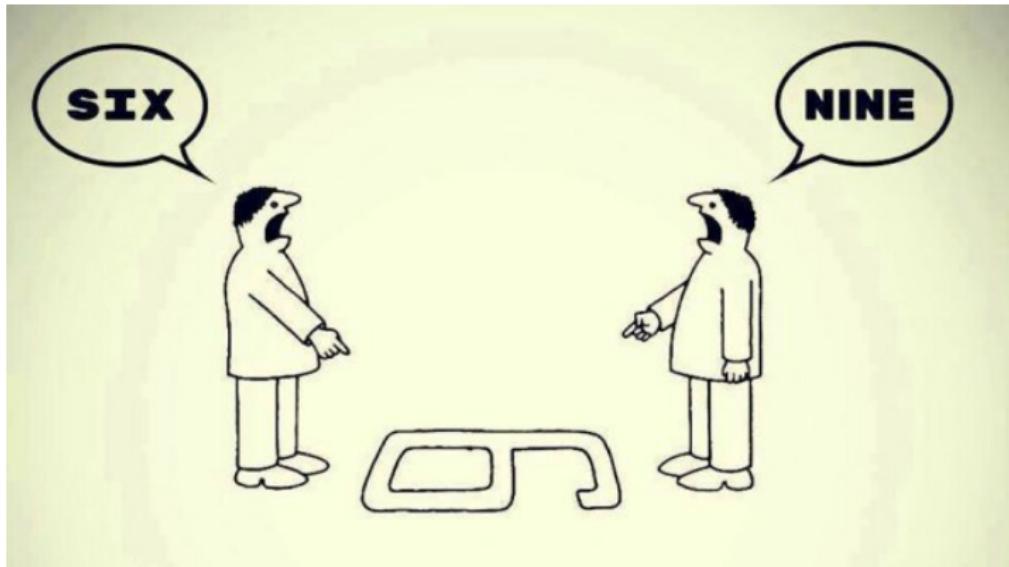


Figure 7: Perspective.

...and if you're trying to justify the need for many-body theory, you'd best not connect  $\Delta_{QP}$  and  $\Delta_{Ex}$  by means of a M.-W. model!

# Phosphorene

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A direct gap 2D semiconductor, with large exciton binding energy.<sup>19</sup>

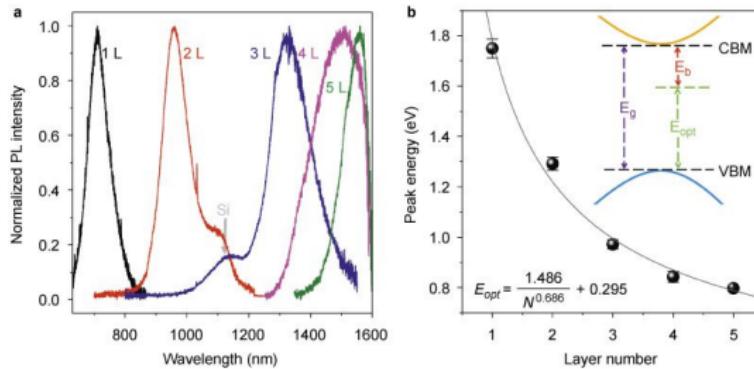


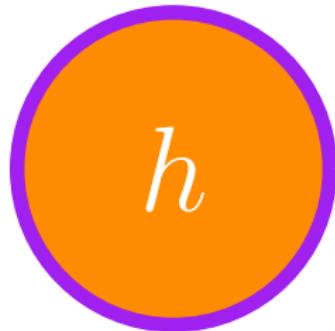
Figure 8: PL measurements of Phosphorene  $n$ -layers.

- Do **not** expect  $\Delta_{\text{QP}} \sim \Delta_{\text{Ex}}$ .
- Potential non-triviality of FS effects in  $\Delta_{\text{QP}/\text{Ex}}$ .

<sup>19</sup> J. Yang et al., Light Sci. Appl. 4 (2015).

# Physics of FS effects in 2D

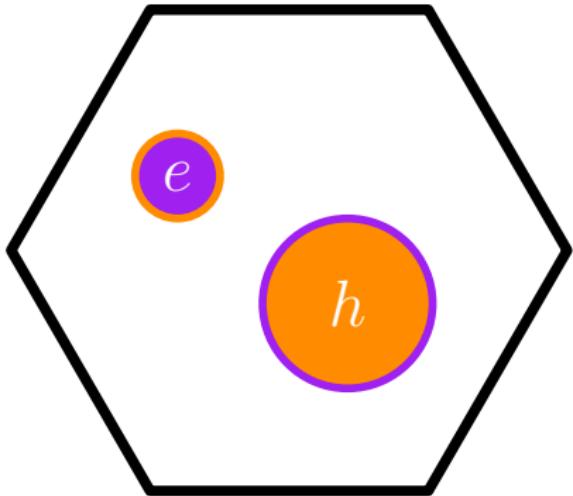
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- ▶ Want to model a free excitonic complex

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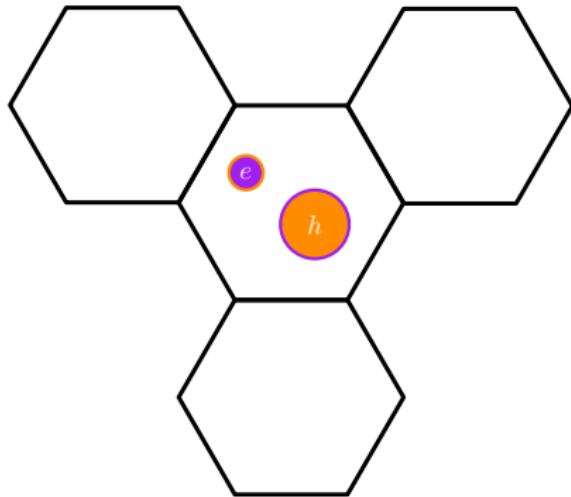
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- ▶ Want to model a free excitonic complex
- ▶ Supercell calculation (characteristic size  $L$ )

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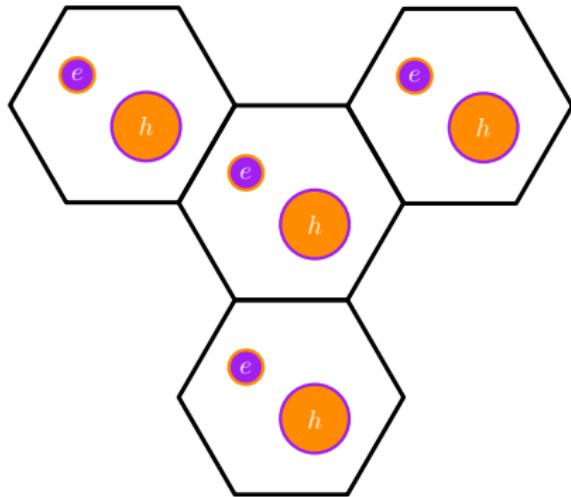
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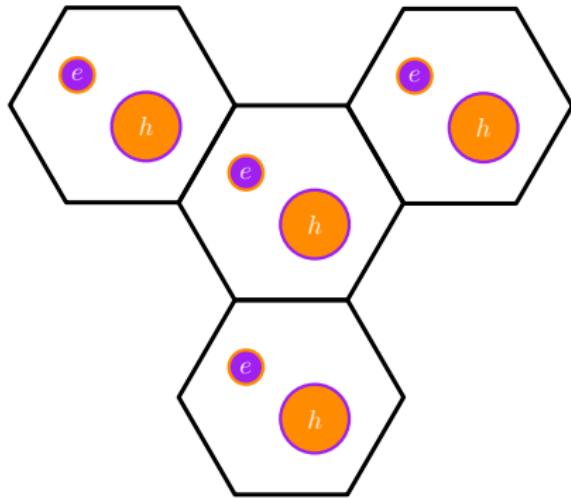
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- ▶ Hence incur an unphysical image-interaction

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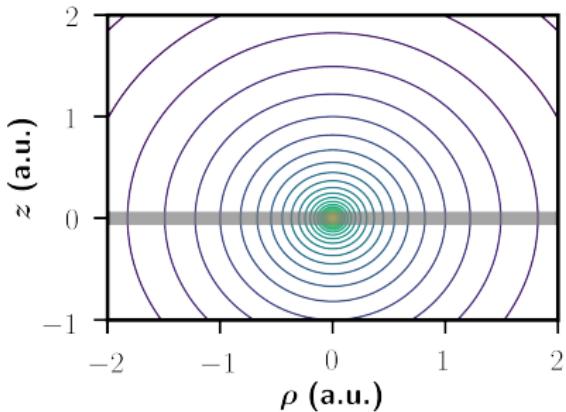


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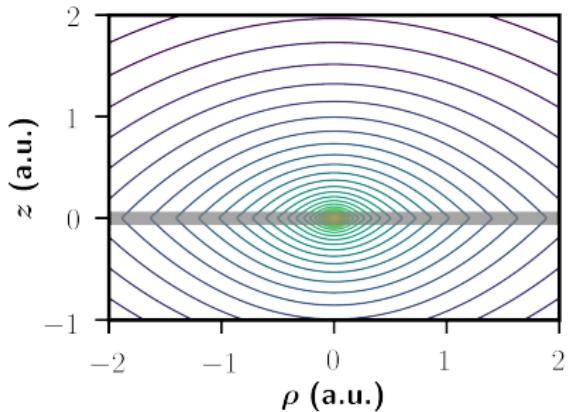
- ▶ Need to remove  $E_{\text{int.}}$ .
- ▶ Scaling arguments, or model calculations?

# Physics of FS effects in 2D (cont.)

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(a)  $r_* = 0$  (Coulomb).



(b)  $r_* = 50$  a.u. (Keldysh).

Figure 9: Field lines from point charges at  $\rho = z = 0$ .

- ▶ With 2D screening (Keldysh interaction), charge-quadrupole interaction<sup>20</sup> leads to expected scaling which is  $\mathcal{O}(L^{-2})$ .<sup>21</sup>
- ▶ Model calculation: study periodic excitons directly (lattice sums over screened interaction). **In progress.**<sup>22</sup>

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<sup>20</sup> Note no dipole in inversion symmetric system!

<sup>21</sup> (from taking sum to be an integral - really only valid at large distances).

<sup>22</sup> At last check, the data I had were best fit by a model  $\Delta(a) = \Delta(\infty) + Ca^{-p}$ , with exponent  $p$  of 2.0073...

## $\Delta_{\text{QP}}$

- ▶ 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).

$$\sum_{\mathbf{R}} W(\mathbf{r} - \mathbf{R}) \rightarrow \underbrace{\sum_{\mathbf{R}} V(\mathbf{r} - \mathbf{R})}_{\text{Ewald}} + \underbrace{\sum_{\mathbf{R}} \delta V(\mathbf{r} - \mathbf{R})}_{\text{safe}}. \quad (12)$$

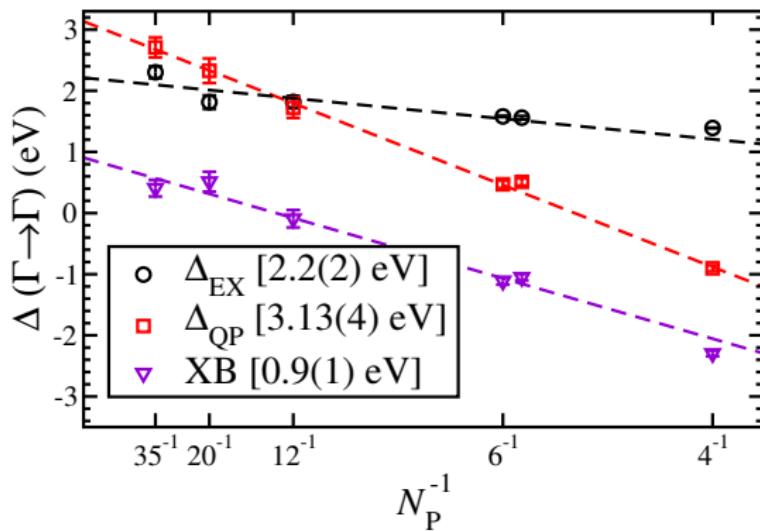
- ▶ “*Safe*” is safe so long as screening becomes irrelevant at long-range in real-space.

# Physics of FS effects in 2D (cont.)

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- ▶ FSE appear to scale as argued.
- ▶ Big gaps ( $\epsilon!$ ), but good agreement w/ Gaufrès *et al.*<sup>23</sup>
- ▶ Phonon renormalisation  $\sim 0.17$  eV @ 300K.<sup>24</sup>

Figure 10: QMC energy gaps in phosphorene vs. system size.



<sup>23</sup> This result is unpublished, so far, but was presented at GW 2018 by A. Loiseau.  $\Delta_{\text{Ex}} = 1.95$  eV.

<sup>24</sup> Via Bartomeu Monserrat, also as yet unpublished.

# Physics of FS effects in 2D (cont.)

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Another approach is to consider passivated (finite) clusters. Here FS effect is kinetic in origin (confinement).<sup>25</sup>

- ▶ FS converge faster (QP gap  $\mathcal{O}(L^{-2})$  by default), **but...**
- ▶ State under study may not be relevant<sup>26</sup>...

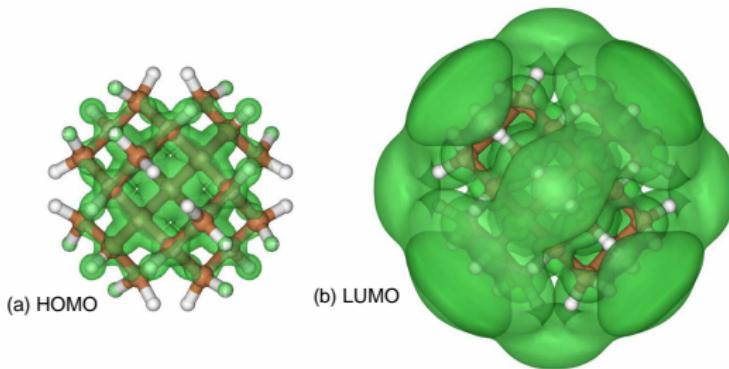


Figure 11: Band charge densities in  $C_{29}H_{36}$ .

<sup>25</sup> T. Frank et al., arXiv:1805.10823 (2018).

<sup>26</sup> N. D. Drummond et al., Phys. Rev. Lett. **95** (2005).

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 12: Excerpt from preprint.

by QMC methods within the error bars<sup>28</sup>. The gap  $\Delta_f$  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<sup>28</sup> not allowing any

- ▶ Our excitonic gap (2.2(2) eV) agrees with their “quasiparticle” gap (2.4 eV) ☺.<sup>27</sup>

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<sup>27</sup> 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!

# Nodal errors in Phosphorene

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We've tested the inclusion of backflow functions in a small Phosphorene test system.

- ▶  $\Delta_{QP}$  lowered by 0.03(9) eV.
- ▶  $\Delta_{Ex.}$  lowered by 0.04(5) eV.

Q Why is backflow seemingly irrelevant here, when it was critical in Si? When, generally, do nodal errors tend to matter?



Backflow QMC has  $\mathcal{O}(N_e^4)$  cost scaling. Further “computational exploration” unlikely to provide answer.

# Outline

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## Motivation

What's the problem?

Why Quantum Monte Carlo (QMC)?

## QMC Methods

VMC and DMC

Excited-state QMC

## Case studies

Atoms and molecules

Bulk solids

Phosphorene

## 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**. **But...**

QMC might benefit from improvements in:

- ▶ Trial wave function technology: size-consistent determinant selection? (further) compact parametrisation of correlations?
- ▶ Algorithms: cubic scaling isn't bad, can we get prefactor down?  
Can we cut more corners with energy differences?
- ▶ FS treatment: extensive literature on ground states, can we do better for excitations? Are  $\rho$ -based electrostatics methods better?

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⟨ 40 | 43 ⟩

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⟨ 40 | 43 ⟩

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Thanks for your attention!

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# Backup I : The Keldysh interaction

$\langle 1 | 3 \rangle$

Consider a planar sheet of (polarisable, 2D susc.  $\kappa$ ) charge, at  $z = 0$ , within a medium of dielectric constant  $\epsilon$

$$\rho(\mathbf{r}) = \rho_2(x, y)\delta(z), \quad (13)$$

Electric displacement field associated with sheet is

$$\begin{aligned} \mathbf{D}(x, y, z) &= -\epsilon \nabla \phi(x, y, z) + \mathbf{P}_\perp(x, y)\delta(z), \\ &= -\epsilon \nabla \phi(x, y, z) + \kappa(\nabla \phi(x, y, 0))\delta(z), \end{aligned} \quad (14)$$

and Gauss' Law says  $\nabla \cdot \mathbf{D}(x, y, z) = \rho(x, y, z)$ .

# Backup I : The Keldysh interaction (cont.)

⟨ 2 | 3 ⟩

After FT and with some algebraic re-arrangement, leads to

$$\phi(\mathbf{q}, z = 0) = \frac{\rho_2(\mathbf{q})}{q(2\epsilon + \kappa q)}. \quad (15)$$

with  $\mathbf{q}$  the 2D momentum. Looks like

$$V(r) = \text{expression}, \quad (16)$$

in real-space. The “Keldysh” interaction,<sup>28</sup> but which was known to Rytova<sup>29</sup> some time earlier...

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<sup>28</sup> L. V. Keldysh, J. Exp. Theor. Phys. **29** (1979).

<sup>29</sup> N. S. Rytova, Dokl. Akad. Nauk. SSSR **163** (1965), N. S. Rytova, Vestn. Mosk. Univ. Fiz. Astron. **3** (1967).

## Backup II: Variational Bounds

⟨ 3 | 3 ⟩

Excitonic promotion calculations: electron number fixed. Where states of definite crystal momentum can be chosen to populate the Slater determinant, trial state transforms (trivially) as 1D irrep. of group of translations (in a way that is basically as complicated as for 1D Bloch waves).

Quasiparticle addition/removal: electron number varies. Key is that these are **not** bona fide excited states. QP energies formed from *ground state* total energies of  $N, N \pm 1$ -electron systems.