

Excited States by Quantum Monte Carlo

QMC in the Apuan Alps 2017

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Outline

Introduction: Ground States

What Changes in Excited States?

- Variational Principles

- Our safety net: the fixed-node approximation

Excited State VMC

- Excited State Trial Wave Functions

Excited State DMC

- Time Step Bias

- Nodal Errors

- Finite Size Effects

Examples

- Atoms and Molecules

- Solids

Wisdom for Excited State DMC Calculations

Ground State (GS) Properties

- ▶ Studying “GS Properties” is sufficient for a large class of important and interesting problems:
 - ▶ Defect studies (e.g. formation energies).
 - ▶ Binding energy calculations (e.g. atoms on surfaces).
 - ▶ Structural energetics (e.g. which structure is the GS).
 - ▶ Phase diagrams.
 - ▶ Born-Oppenheimer potential energy surfaces.
 - ▶ Ground state portions of QMC studies of excited states & many more ...
- ▶ However, **spectroscopy exists**, and (rumour has it) some interesting problems require the study of **excited electronic states**.¹

$$\hat{\mathcal{H}}|\Phi_\lambda\rangle = E_\lambda|\Phi_\lambda\rangle. \quad (1)$$

¹ Here $E_{\text{GS}} = E_{\lambda=0} < E_{\lambda=1} < \dots$

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Variational Principles

- ▶ In a ground state calculation, we always (even in FN-DMC²) have the **variational principle**:

$$E_0 \leq \frac{\langle \Psi_T | \hat{\mathcal{H}} | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle}, \quad (2)$$

where $|\Psi_T\rangle$ is our **trial wavefunction**. Equality is realised only if $|\Psi_T\rangle = |\Phi_0\rangle$.

- ▶ Depending on the nature of the “excited” state, we **may or may not** have a similar situation for an excited trial wavefunction, $|\tilde{\Psi}_T\rangle$.

² P. J. Reynolds et al., The Journal of Chemical Physics **77** (1982).

Variational Principles (II)

- ▶ Let's consider the easy case first. Some classes of excited states are not genuine excited states.
- ▶ Consider calculating the **ionization potential** of an N -electron atom or molecule:

$$\text{IP} \equiv E_{N-1} - E_N, \quad (3)$$

here, E_N is the ground state energy of the atom or molecule, and E_{N-1} is the ground state energy of the **ionized** atom or molecule.

- ▶ In both calculations, we are considering ground states, and the same ground state variational principles **apply to both energies**.³

³ Again, this is true in VMC and in FN-DMC.

Variational Principles (III)

- ▶ Now the second, not so easy, case. Consider the **promotion** of an electron in a system to a higher state.⁴
- ▶ Suppose the true excited state energy is E_λ , and our calculated result is \tilde{E}_T .
- ▶ **Question:** Is the following true?

$$E_\lambda \leq \tilde{E}_T = \frac{\langle \tilde{\Psi}_T | \hat{\mathcal{H}} | \tilde{\Psi}_T \rangle}{\langle \tilde{\Psi}_T | \tilde{\Psi}_T \rangle}. \quad (4)$$

- ▶ **Answer:** In general, **no**.
- ▶ This has been known for a long time. An interesting question to ask is: When does equation 4 hold, if ever?

⁴ In the single-particle picture, one can imagine simply moving one electron to a higher orbital.

Variational Principles (IV) - VMC

- Consider a general trial wave function

$$|\tilde{\Psi}_T\rangle = \sum_{\lambda \neq 0} c_\lambda |\Phi_\lambda\rangle, \quad (5)$$

which has no ground state ($\lambda = 0$) component. Then, $\langle \Phi_0 | \tilde{\Psi}_T \rangle = 0$, and we have

$$E_{\lambda=1} \leq \tilde{E}_T = \frac{\langle \tilde{\Psi}_T | \hat{\mathcal{H}} | \tilde{\Psi}_T \rangle}{\langle \tilde{\Psi}_T | \tilde{\Psi}_T \rangle}, \quad (6)$$

i.e. a variational principle on the excited state energy \tilde{E}_T .

- A similar principle is realised for the n^{th} excited state, if the trial wavefunction is orthogonal to the first $n - 1$ eigenstates of $\hat{\mathcal{H}}$.

Variational Principles (V) - FN-DMC

- ▶ In VMC, an excited state may be orthogonal to the ground state **because of symmetry**.
- ▶ This symmetry might be maintained by particular choices of variational parameters, or because the form of the trial wave function itself is **limited in form**.⁵
- ▶ In FN-DMC, however, the trial wave function only defines the trial nodal surface - this is **not enough** to fix the symmetry of the state produced in the FN-DMC algorithm.

⁵ Consider VMC for a 1D potential well problem. One might “guess” (there’s no way to do *know* this, usually) the position of a node. If the VMC wave function fixes the position of this node, and it is the exact node, then one can imagine having a variational principle on the excited state energy assoc. with it.

FN-DMC (II)

- ▶ If the excited state trial wave function transforms as a 1D irreducible representation of the full symmetry group of $\hat{\mathcal{H}}$ - then an excited state variational principle exists for the FN-DMC energy obtained from that trial wave function.⁶ I.e.

$$E_{\lambda=1} \leq \tilde{E}_{\text{FN-DMC}} \quad (7)$$

- ▶ The details are interesting, and interested parties should read the paper!

⁶ W. M. C. Foulkes et al., Physical Review B **60** (1999).

FNA (III) - Solids

- ▶ Real trial wavefunctions with definite crystal momentum \mathbf{k} satisfy the many-electron Bloch condition (& therefore transform as a 1D irrep. of $\hat{\mathcal{H}}\dots$).⁷
- ▶ Complex wavefunctions (or real linear combinations of these with their conjugates) often *don't* transform this way - and so their use is not always safe.
 - ▶ Reasonable use case: doing an excited state QMC calculation on a \mathbf{k} -point grid that lacks inversion symmetry.

⁷ G. Rajagopal et al., Physical Review B 51 (1995).

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Excited State Trial Wave Functions

- ▶ As we all know, ground state trial wavefunctions typically have Slater-Jastrow-Backflow form:

$$\Psi_{\text{SJB}}(\tilde{\mathbf{x}}) = \exp [\mathcal{J}_{\{\alpha\}}(\tilde{\mathbf{x}})] \cdot \mathcal{D}(\tilde{\mathbf{x}}), \quad (8)$$

where I've used $\tilde{\mathbf{x}}$ as some generic set of backflow-displaced coordinates, and $\{\alpha\}$ are a set of (optimizable) Jastrow parameters.

- ▶ For now, not much will change. As far as excited states are concerned, the important part is the **Slater determinant**.

Excited State VMC (II)

- ▶ By choosing to occupy **empty** states in the Slater determinant, our trial wavefunction describes (approximately) an excited state.
- ▶ For example, consider the formation of an **exciton** in a semiconductor. By switching conduction and valence state occupancies in the determinant, we have formed an approximate **excitonic wave function**:

$$\psi_{\text{SJB}}^{\text{Ex}}(\tilde{\mathbf{x}}) = \exp [\mathcal{J}_{\{\alpha\}}(\tilde{\mathbf{x}})] \cdot \mathcal{D}_{-}^{+}(\tilde{\mathbf{x}}). \quad (9)$$

Excited State VMC (III) - \mathcal{D}_{-}^{+}

- Suppose we have done a Hartree-Fock calculation for a molecule (N electrons), and have obtained a set of occupied single-particle molecular orbitals $\{\phi_i\}$, and empty states $\{\phi_i^*\}$.

$$\mathcal{D}_{\text{HF}}(\tilde{\mathbf{x}}) = \frac{1}{\sqrt{N_e}} \begin{vmatrix} \phi_1(\tilde{\mathbf{x}}_1) & \phi_2(\tilde{\mathbf{x}}_1) & \cdots & \phi_N(\tilde{\mathbf{x}}_1) \\ \phi_1(\tilde{\mathbf{x}}_2) & \phi_2(\tilde{\mathbf{x}}_2) & \cdots & \phi_N(\tilde{\mathbf{x}}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\tilde{\mathbf{x}}_N) & \phi_2(\tilde{\mathbf{x}}_N) & \cdots & \phi_N(\tilde{\mathbf{x}}_N) \end{vmatrix}. \quad (10)$$

Excited State VMC (IV) - \mathcal{D}_{-}^{+} cont.

- ▶ A possible \mathcal{D}_{-}^{+} configuration is:

$$\mathcal{D}_{-, \text{HF}}^{+}(\tilde{\mathbf{x}}) = \frac{1}{\sqrt{N_e}} \begin{vmatrix} \phi_1(\tilde{\mathbf{x}}_1) & \phi^*(\tilde{\mathbf{x}}_1) & \cdots & \phi_N(\tilde{\mathbf{x}}_1) \\ \phi_1(\tilde{\mathbf{x}}_2) & \phi^*(\tilde{\mathbf{x}}_2) & \cdots & \phi_N(\tilde{\mathbf{x}}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\tilde{\mathbf{x}}_N) & \phi^*(\tilde{\mathbf{x}}_N) & \cdots & \phi_N(\tilde{\mathbf{x}}_N) \end{vmatrix}, \quad (11)$$

where we have replaced the orbital ϕ_2 with a previously unoccupied orbital, ϕ^* .⁸

- ▶ This class of trial function has been used in the past to study excited states in Silicon.⁹

⁸ Leaving behind a hole, in the process - hence why I called this an “excitonic” trial wave function.

⁹ A. J. Williamson et al., Physical Review B 57 (1998).

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Excited State DMC

- ▶ Excited state FN-DMC calculations are carried out similar to ground state ones. There are some important excited-state specific extras to be aware of:
 - ▶ Time step bias typically **cancels quite well** in energy gaps.¹⁰
 - ▶ One should **be careful** when optimising parameters that affect the nodal surface in excited-state DMC.
 - ▶ Finite size errors are the **dominant source of error** in excited-state calculations.

¹⁰ Presumably other biases also cancel well, population bias is an example.

Time Step Bias

- ▶ Time step bias is linear in τ for small enough values of τ (TN PPs: sane choice $\sim 0.01 - 0.04$ au).
- ▶ One might expect that, when considering energy *differences*, this cancels to some degree.

$$E(\tau) = E(0) + \lambda(N_e)\tau + \mathcal{O}(\tau^2) \quad (12)$$

$\lambda(N_e)$ is some parameter which varies **slowly** with small changes in N_e :
 $\lambda(N_e + 1) \sim \lambda(N_e)$.

- ▶ Most electrons in an excited state calculation **continue to behave as they previously did**, only a few electrons behave qualitatively differently.

Time Step Bias (II)

Bulk hexagonal boron nitride

Time step bias in test calculations on a $(3 \times 3 \times 1)$ supercell of hBN.

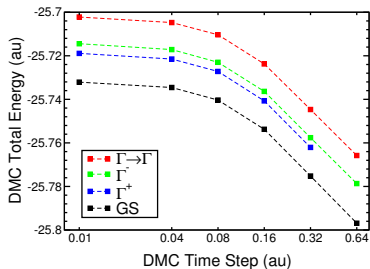


Figure 1: DMC total energies. These curves are non-linear, and plotted on a log axis.

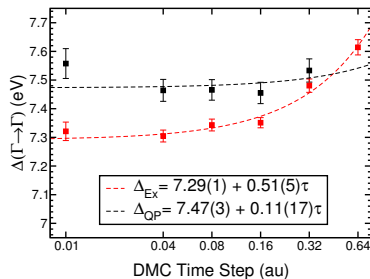


Figure 2: DMC $\Gamma \rightarrow \Gamma$ energy gap. Note: the fits are linear, but the scale is logarithmic.

Nodal Errors

- ▶ In ground state calculations, nodal errors can be controlled: the variational principle **keeps us safe**.
- ▶ There is the chance that the lack of a variational principle in excited states **causes us problems**. Consider as a toy model the (modified) Hydrogen 2S orbital.

$$\psi_{2S}^\gamma = C_\gamma \cdot (2\gamma - r) \cdot \exp\left(-\frac{r}{2}\right), \quad (13)$$

which is exact when $\gamma = 1$, otherwise, the node is wrong and the wave function is not exact.¹¹

¹¹ This is a 1-electron problem, so the nodal surface is $(3 \times 1) - 1 = 2$ dimensional. It is a sphere!

Nodal Errors (II) - the H atom

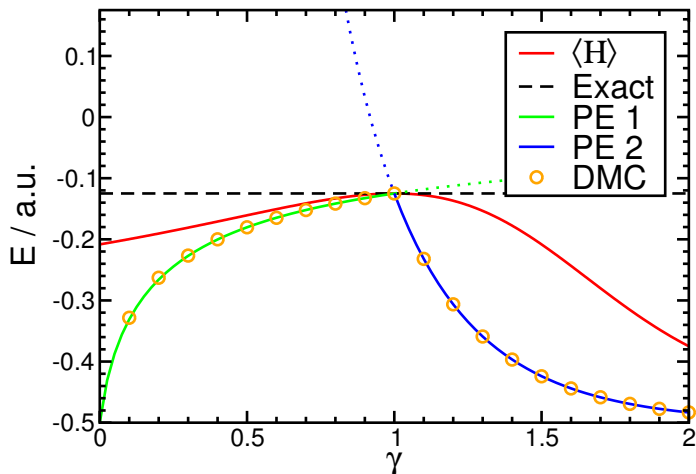


Figure 3: Energies of ψ_{2s}^γ by various means ($E_{\text{Exact}} = -\frac{1}{8} \text{ a.u.}$)

Nodal Errors (III)

- ▶ How else can we affect the nodal surface? Consider

$$\psi_{2S}^{\alpha,\gamma} = D_{\alpha,\gamma} \cdot [2\gamma(1 + \alpha\mathcal{Y}_{\ell,m_\ell=0}(\theta)) - r] \cdot \exp\left(-\frac{r}{2}\right), \quad (14)$$

now γ is chosen to **fix the volume** of the nodal surface.¹²

- ▶ There is a node at $r_n(\theta) = 2\gamma(1 + \alpha\mathcal{Y}_{\ell,m_\ell=0}(\theta))$

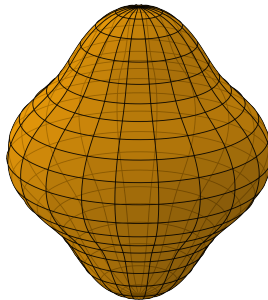


Figure 4: Our new nodal surface.

Nodal Errors (IV)

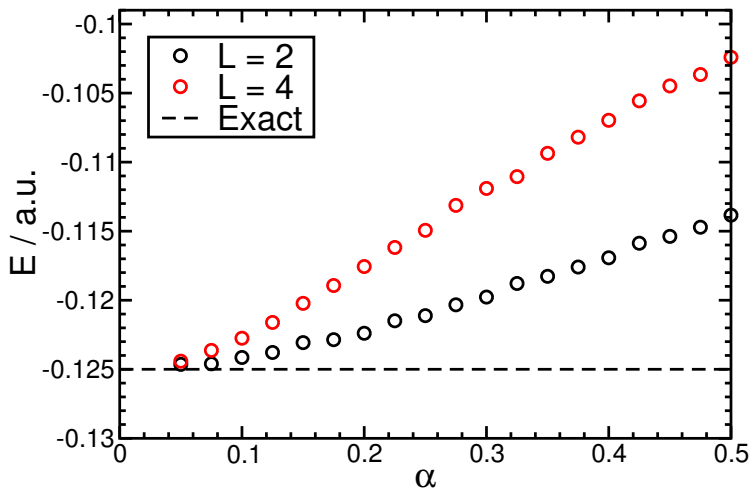


Figure 5: DMC energies of $\psi_{2S}^{\alpha,\gamma}$.

Nodal Errors (V) - The Point

- ▶ Nobody should pretend that the nodal errors we have discussed here are **realistic** or general in any way.
- ▶ This has been a toy model which illustrates something very important.
- ▶ **Never** optimise parameters that affect the nodal surface in a trial excited state - **unless** you are certain that the trial wave function has the important symmetry properties.

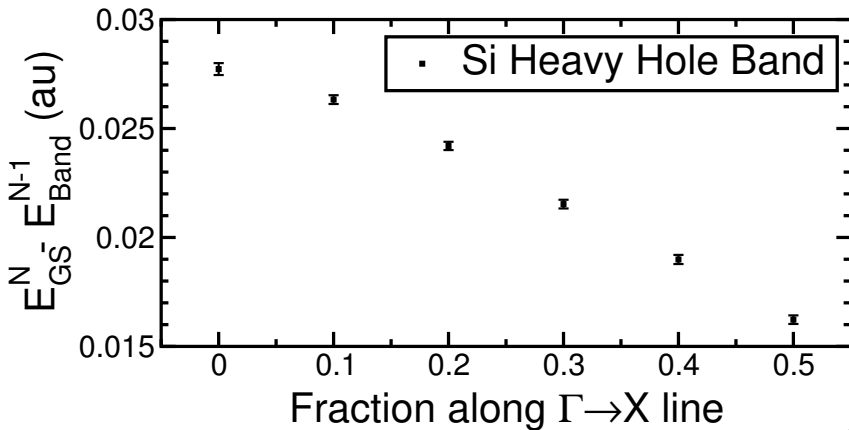
Single-particle Finite Size Effects

- ▶ In common with GS calculations, finite size (FS) effects are often **very important** in excited state calculations.
- ▶ “Single-particle FS effects” are those related to momentum quantisation: the things that we would usually want to twist average over.
- ▶ **Question:** Do SPFSE affect excited-state calculations?

SPFSE (II)

- **Answer:** Apparently not much...we have tested this in InSe (2D) and bulk silicon (3D), finding that energy gaps and quasiparticle energy bands are rather flat for different values of \mathbf{k} .

Figure 6: The heavy hole band in Si, calculated along the line $\Gamma \rightarrow X$



“Twist averaging” Energy Gaps

Credit NDD

- ▶ Choose a point of interest, \mathbf{k}_e , and a twist, \mathbf{k}_s .¹³
- ▶ Calculate GS energy, $E_0(\mathbf{k}_e + \mathbf{k}_s)$.
- ▶ Calculate addition energy, $E^+(\mathbf{k}_e + \mathbf{k}_s)$.
- ▶ Calculate electron-like band,

$$\mathcal{E}(\mathbf{k}_e + \mathbf{k}_s) = E^+(\mathbf{k}_e + \mathbf{k}_s) - E_0(\mathbf{k}_e + \mathbf{k}_s),$$

- ▶ Repeat for desired number of twists. Fit data,

$$\mathcal{E}(\mathbf{k}_e + \mathbf{k}_s) = \mathcal{E}_{\text{TA}}(\mathbf{k}_e) + \mathbf{k}_s \cdot (A\mathbf{k}_s),$$

- ▶ Ultimately, this yields a (TA) **QMC energy band value**, and a **QMC effective mass**.¹⁴

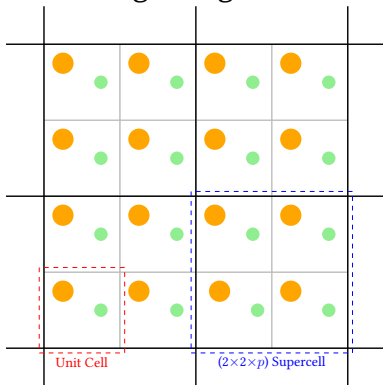
¹³ The point \mathbf{k}_e is supposed to be a band minimum in this case.

¹⁴ This effective mass can be extracted from the matrix A , which is an effective “band curvature tensor”.

Many-body FS Effects (MBFSE)

Specific to solids...

- ▶ Excited state calculations carry more a **far more potent** class of finite size errors.
- ▶ Consider adding an electron to a simulation supercell. $N_e \rightarrow N_e + 1$, and a neutralising background is added to maintain charge neutrality.

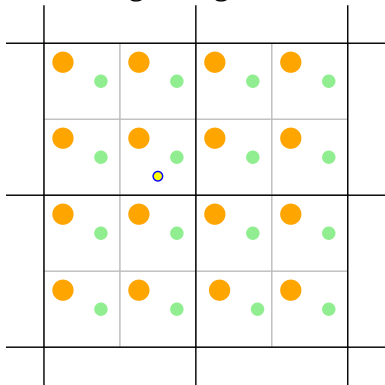


- ▶ UC = 1 square, SC = $2 \times 2 \times p$ grid.

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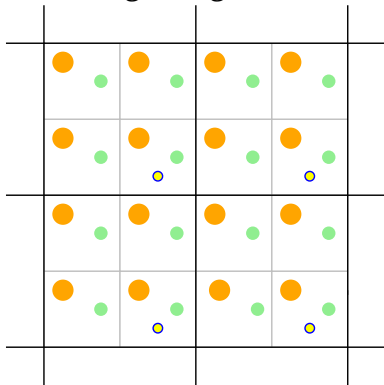


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- ▶ Added a quasiparticle to one unit cell.

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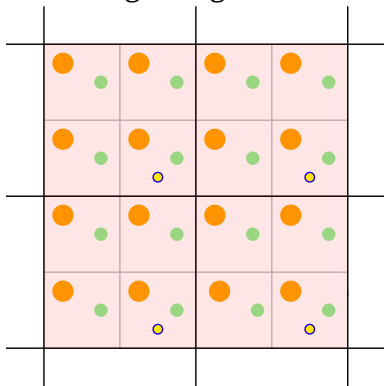


- ▶ UC = 1 square, SC = $2 \times 2 \times p$ grid.
- ▶ Added a quasiparticle to one unit cell.
- ▶ By translational invariance, there are others!

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- ▶ UC = 1 square, SC = $2 \times 2 \times p$ grid.
- ▶ Added a quasiparticle to one unit cell.
- ▶ By translational invariance, there are others!
- ▶ Neutralising background added.

MBFSE (II)

- ▶ These charges interact with the system (as we want them to...), **but** they also interact with themselves.
- ▶ This happens in the ground state case, and such “self-terms” are subtracted in the **Madelung constant**.
- ▶ Here, the leading order correction to the excited state energy is the Madelung constant for particles in neighbouring supercells, interacting **in the effective medium supplied by the rest of the system**.¹⁵
- ▶ This has been studied before, in the context of DFT defect energetics.¹⁶

¹⁵ The interactions between added/removed quasiparticles are **screened** by the rest of the system.

¹⁶ S. T. Murphy and N. D. M. Hine, Physical Review B **87** (2013).

MBFSE (III)

- ▶ I recently found that screened Madelung constants can be evaluated **as they are in the unscreened case**, if you transform variables.¹⁷
- ▶ The Madelung constant for a set of charges in a material with “background” dielectric tensor $\tilde{\epsilon}$ is

$$v_M^{\text{Scr.}}(\mathbf{R}) \rightarrow \frac{1}{\sqrt{\det[\tilde{\epsilon}]}} v_M^{\text{Unscr.}}(\sqrt{\tilde{\epsilon}^{-1}}\mathbf{R}), \quad (15)$$

where \mathbf{R} represents the matrix of supercell lattice vectors.

¹⁷ The idea is to move to the principal axis of the dielectric tensor, and to then scale it to the identity matrix. These transformations manifest in a Jacobian, and can be undone to yield a screened v_M .

MBFSE (IV)

- ▶ This looks **sketchy**¹⁸ but in actual fact the restrictions on $\tilde{\epsilon}$ mean this is a well defined operation.
- ▶ The ability to use anisotropically screened Coulomb interactions in CASINO is a **planned feature**.
- ▶ What use would this have?
 - ▶ Study model systems of electrons and holes in an anisotropically screened environment.
 - ▶ “On-the-fly” **corrections** for QMC gap calculations.
 - ▶ Qualitative study of FS effects in calculations of real materials - e.g. how are FS effects **qualitatively different** (scaling-wise) in cubic vs. hexagonal systems?

¹⁸ For example, which square root do I take?

Example: electronic addition calculation

- ▶ The relevant quantity here is the “quasiparticle band energy”

$$E_{\text{e-QP}} = E_{N+1}^0 - E_N^0, \quad (16)$$

which ought to be corrected. We need to **remove** the energy of a lattice of quasi-electrons interacting in a medium determined by the “rest of the system”.

$$E_{\text{e-QP}}^{\text{corr.}} = E_{\text{e-QP}} - \frac{v_M^{\text{Scr.}}}{2}. \quad (17)$$

MBFSE (VI) - Excitonic FS Effects

- ▶ In the case of a promotion calculation, the FS effects **are not** due to interacting (single) quasiparticles and their compensating background.
- ▶ These FS effects can scale **differently** with system size.
- ▶ There seems to be no general statement to be made here (we are still working!), however, corrections are usually **extrapolated**, with $\mathcal{O}(N_e^{-p})$ corrections accounted for in fitting.
- ▶ The exponent p **changes on a study-by-study basis**, depending on dimensionality, the nature of the excitation ((de)-localised?), the size of the simulation cell, ...

Finite Size Effects: A Brief Summary

- ▶ FS effects **alter the numbers** we get out of excited state calculations at different (fixed) system sizes.
- ▶ We should try to remove them (e.g. with $v_M^{\text{Scr.}}$), but **usually also need to extrapolate** in order to reach the thermodynamic limit.
- ▶ FS effects are the **dominant source of error** in excited state QMC calculations of solids.
- ▶ **None of the nasty FS effects we're currently having trouble with affect calculations on aperiodic (truly finite) systems.**¹⁹

¹⁹ In this case, “FS effects” correspond to *physical phenomena*, e.g. quantum confinement.

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Examples: Atoms and Molecules

Let's talk about aperiodic systems!

- ▶ Obviously, we have **no problem** with FS effects here.
- ▶ We do, however, **potentially** have other problems:
 - ▶ Nodal error
 - ▶ Vibrational effects (I'll include static Jahn-Teller²⁰ effects here)
 - ▶ Pseudopotential-induced error
- ▶ It would be nice to have a handle on these issues, and to know whether or not excited state QMC is any good for these kinds of systems.

²⁰ One can imagine that excited states may suffer a JT distortion - which means we should, in principle, consider the ground and excited state molecular geometries when doing QMC calculations.

The Ne atom

- ▶ The Neon atom and its first ionization potential have been studied before (by some people in the room).²¹
- ▶ There's other work which seems to uncover a general fact about nodal errors in atomic systems: they scale \sim linearly with electron density.²²
- ▶ **Question:** Do nodal errors build up in the n^{th} ionization potentials, as well as the energies?²³

²¹ N. D. Drummond et al., The Journal of Chemical Physics **124** (2006).

²² K. M. Rasch and L. Mitàš, Chemical Physics Letters **528** (2012).

²³ I.e. does the strength of this growth in nodal error matter on the scale of an IP?

The Ne atom: results

- By successively removing electrons from the Ne atom, we obtain the following table of results,

n	Exact NR IP	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)
Avg. MAE		0.83%	0.67%	0.38%	0.34%

Table 1: QMC vs. a set of “Exact NR IP” values, in eV.^a

Miscellaneous Molecules

- ▶ Molecules are one step up from atoms: structural/vibrational effects can be important.²⁴
- ▶ As a test of QMC, we have studied the ionization potentials / electron affinities of various small molecules.

- ▶ Tetracyanoethylene

$$\text{IP} = E_{N-1} - E_N$$

- ▶ Boron trifluoride

$$\text{EA} = E_N - E_{N+1}$$

- ▶ H₂/O₂

- ▶ Benzothiazole

- ▶ 3 energies to be calculated. All obey “ground-state” variational principles.

- ▶ Anthracene

²⁴ E. Mostaani et al., Physical Chemistry Chemical Physics **18** (2016).

Misc. Molecules (II)

- ▶ These calculations are so cheap, we can do them with a PW basis and at various levels of QMC expense: SJ-VMC, SJB-VMC, SJ-DMC, SJB-DMC.
- ▶ Testing multi-determinant wave functions is also probably feasible. But this is tricky/distasteful. Why?
- ▶ We would like our wave function parametrisation to be **compact**, and to have the property that it retrieves correlation energy **efficiently**.
- ▶ Excited state multi-determinant expansions **require care** in preparation. Variational principles become (again) **more complicated**.²⁵

²⁵ Granted, this is not the case for IP/EA calculations.

Tetracyanoethylene (TCNE)

- ▶ TCNE is an electron acceptor, with an EA of 3.16(2) eV.²⁶
- ▶ (Aged) experiments determine IP \sim 11.67-11.79 eV.

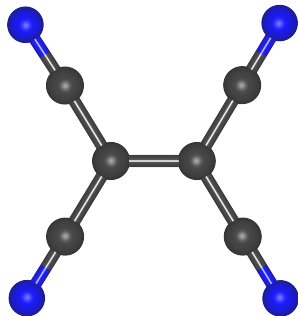


Figure 7: TCNE

Method	IP / eV	EA / eV
SJD	11.87(1)	3.23(1)
SJD-JT	11.85(1)	3.25(1)
SJBD	11.88(1)	3.20(1)
SJBD-JT	11.86(1)	3.23(1)
CCSD (T)	11.99	3.05
<i>GW</i>	??	??
SCQPGW	??	??

Table 2: EA/IP values of TCNE.

- ▶ Errors: PP & dynamical vibrational effects.

²⁶ D. Khuseynov et al., Chemical Physics Letters **550** (2012).

Other Misc. Molecules: A Quick Slide

- How do we generally do, for small molecules and compared to *GW*, etc?

Method	BF ₃		Anthracene		Benzothiazole	
	IP	EA	IP	EA	IP	EA
SJD	16.226(6)	–	7.35(3)	0.33(3)	8.94(2)	0.67(2)
SJD-JT	16.227(6)	–	7.31(3)	0.45(3)	8.80(2)	0.54(2)
<i>GW</i>	–	–	7.06	0.32	8.48	–
SCQPGW	–	–	–	–	8.83	–
CCSD (T)	–	–	7.52	0.33	8.70	–
Expt.	15.7(3)	–	7.439(6)	0.53(2)	8.8	–

Table 3: EA/IP values (in eV) of some more molecules.

Recap of references

Because I'm a good boy

- ▶ I haven't listed all of the references for my comparison data on the relevant slides because there are **too many**.
- ▶ In the interest of being **good** their numbers (see References slides) are:
 - ▶ CCSD (T) reference data.²⁷
 - ▶ GW for anthracene, benzothiazole.²⁸²⁹
 - ▶ SCQPGW benzothiazole.³⁰
 - ▶ Experiments: mostly from NIST web pages.³¹ The value with a tilde is an average of the available (fairly varied) experimental IP data.

²⁷ R. M. Richard et al., Journal of Chemical Theory and Computation **12** (2016).

²⁸ X. Blase et al., Physical Review B **83** (2011).

²⁹ EA not quoted, but IP and HOMO-LUMO gap are. Do the maths.

³⁰ F. Kaplan et al., Journal of Chemical Theory and Computation **12** (2016).

³¹ P. J. Linstrom and W. G. Mallard, eds., (National Institute of Standards and Technology, Gaithersburg MD, 20899, June 2005).

Solids

- ▶ I'll give two brief examples here. The first two projects have been very illuminating for us - I'll aim to **share some wisdom** here.
 - ▶ Silicon: old and new
 - ▶ Boron Nitride: from bulk to monolayer
 - ▶ Fermi Liquid Theory: what can QMC say?

Solids: A Quickfire How-To

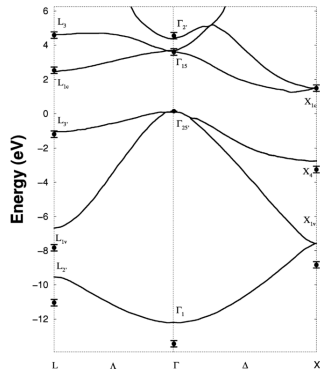
1. Select supercell sizes / supercell matrices (this determines, by the many-body Bloch conditions, the \mathbf{k} -point grid). In symmetrical cases, one probably wants to specify less \mathbf{k} -points (file sizes).
 - ▶ Can you study the excitations you want with the \mathbf{k} -points you are now forced to use? This is not always the case.
 - ▶ Check your pseudopotentials (TM ions are the worst).³²
2. Obtain single-particle orbitals - PW DFT or Gaussian basis DFT. Plane waves if HEG.
3. Check time step biases in some trial excited states - possible to make savings here! (we haven't exploited this fully yet!)
4. Run calculations, reconvene to worry about FS effects some time later...

³² N. D. Drummond et al., Physical Review B **94** (2016).

Silicon: the 90s

- ▶ In the 90s, an early set of QMC calculations for silicon did something interesting...
- ▶ Using excitonic SJ wave functions (as introduced earlier), Williamson *et al.*³³ mapped out the band structure of silicon at high symmetry points.

Figure 8: Band structure at HS points (dots) in silicon, ca. 1998. Solid lines are PP calculations. This was calculated for a $2 \times 2 \times 2$ supercell of silicon.



Silicon: Now

- ▶ Owing to the heightened availability of computational resources, various aspects of the previous work can be improved on.
 - ▶ Lower statistical errors.
 - ▶ **Finite size effects.**
 - ▶ BS away from HS points (see earlier hole band!).
- ▶ Our ongoing work considers the quasiparticle and excitonic gaps in silicon, at various system sizes.

$$\begin{aligned}\Delta_{\text{QP}} &= E_{N+1} + E_{N-1} - 2E_N, \\ \Delta_{\text{EX}} &= E_N^* - E_N.\end{aligned}\tag{18}$$

- ▶ If DMC were not pathological (& it isn't!), we'd expect to be able to take both to the thermodynamic limit and obtain $\Delta_{\text{QP}} \sim \Delta_{\text{EX}}$.

Silicon: Maybe next time

- ▶ We don't actually know if this is true yet ($2 \times 2 \times 2$ & $3 \times 3 \times 3$ results are encouraging).
- ▶ Stay tuned.

What do we know?

- ▶ Single-particle FS effects **don't play much of a role**.
- ▶ QP gap has **more severe** FS effects. (has ramifications for other cases where excitonic effects are **weak**).
- ▶ We are probably **limited** to an error bar of ~ 0.1 eV, thanks to PPs.³⁴
- ▶ **Question:** How do we know all of this?

³⁴ Even if we had a perfect theory of FS effects. In this (cubic) system, this might be less of a pain.

Hexagonal Boron Nitride

- ▶ We have spent far more time on a related project, where our goal is to calculate the excitonic and quasiparticle gaps of hBN.
 - ▶ **Large** gap insulator (bulk and monolayer).
 - ▶ Anisotropic dielectric properties (non-diagonal $\tilde{\epsilon}$).
 - ▶ **Extremely** interesting to experimentalists.
 - ▶ We know almost **nothing**³⁵ about the electronic properties of the monolayer.

³⁵ Nothing correct, that is. Sorry DFT.

HBN: What have we done?

- ▶ We've studied a series of bulk and monolayer system sizes (“square” supercells in the monolayer, “spherical” in the bulk - **maximal WS radius**).
- ▶ We have calculated the QP and EX gaps at various high symmetry points, with a goal of extracting **exciton binding energies** from first principles

$$E_B^X = \Delta_{\text{QP}} - \Delta_{\text{EX}}. \quad (19)$$

- ▶ This would offer a QMC alternative to *GW*-BSE approaches.³⁶

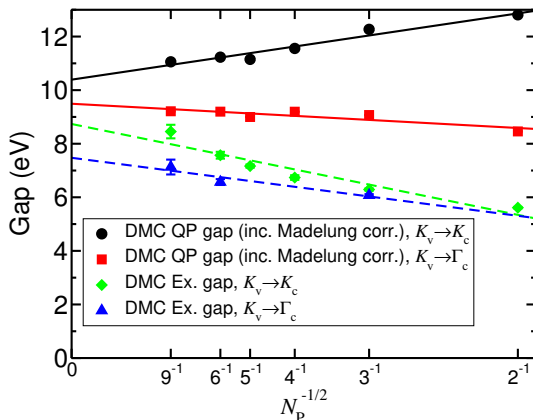
³⁶ This is the only competitor method, and has its own problems.

HBN: Results

Monolayer

- The monolayer results appear quite well-behaved, but feature quasi-random FS errors of order 0.1 eV.

Figure 9: Energy gaps in monolayer hBN as a function of system size



HBN: Results

Monolayer cont.

- ▶ We predict a *vacuum* exciton binding of 2.0(4) eV, which is comparable to GW-BSE (2.1 eV).³⁷ Both of these ought to be modulated by the particular dielectric environment.
- ▶ Experimental comparison (when possible) must be done taking into account the fact that we have *vacuum* results. Our results are **renormalised strongly** if $\epsilon \neq 1$.

³⁷ L. Wirtz et al., Physical Review Letters **96** (2006).

HBN: Results

Bulk

- After correction ($v_M^{\text{Scr.}}$), some gaps OK. Have the same $\mathcal{O}(0.1 \text{ eV})$ quasi-random FS errors as the monolayer.³⁸

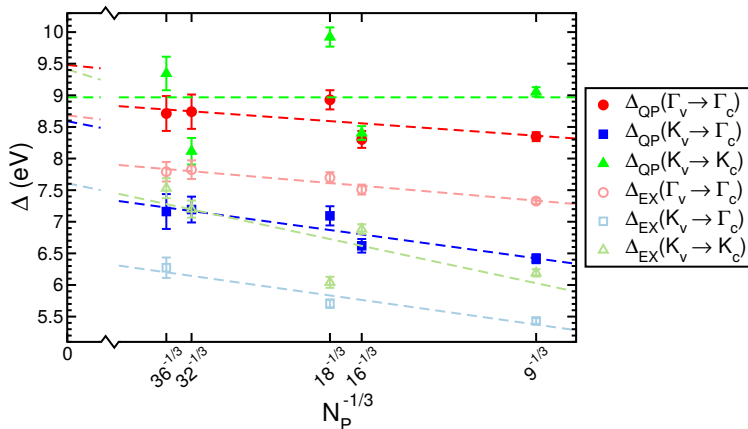


Figure 10: Energy gaps in bulk hBN as a function of system size.

HBN: Loose Ends

- ▶ We are investigating the sources of this quasi-random error, which seems also to affect InSe (monolayer), and phosphorene.

Things that apparently don't matter [at $\mathcal{O}(0.1\text{eV})$]

- ▶ SPFS effects (energy gap landscape as fn. of \mathbf{k}_s is flat)
- ▶ (DFT) Dielectric tensors at “fixed cell sizes” vs. expt. ones.
- ▶ Variational principles: this is common to QP and EX gaps, and the only candidates³⁹ for broken VPs are data points where an increase in the gap would seem to make the situation worse.

³⁹ We use complex wave functions for some of our gaps at K, and take care to re-calculate ground state energies with the shifted grids.

Excited States in Metals: Fermi Liquid Theory

- ▶ A normal metal can (generically) be described by **Fermi liquid theory**.
- ▶ The excitations of such a system can be considered to be “almost free” quasiparticles⁴⁰ - they are quasielectrons with a *renormalised* effective mass, and whose interactions are characterised by a set of numbers (Landau’s interaction parameters).
- ▶ QMC has been used to say something quantitative about this description.
- ▶ (Of course, these kinds of excitations only dominate at low temperature, at higher temperature, others can interfere. Collective modes may exist, for example.)

⁴⁰ This follows from the idea that the interacting ground state is *adiabatically connected* to the non-interacting one.

Fermi Liquid Theory (II) - The Language and Ideas of FLT

- ▶ What is the deviation from the non-interacting ground-state energy, δE , due to the presence of quasiparticles?
- ▶ Let $\delta n_{\mathbf{k},\sigma} = n_{\mathbf{k},\sigma} - n_{\mathbf{k},\sigma}^0$, and work on the assumption that δn is small. The energy can be expanded

$$E[\delta n] = E^0 + \underbrace{\sum_{\mathbf{k},\sigma} \epsilon_{\mathbf{k},\sigma} \delta n_{\mathbf{k},\sigma}}_{\text{QP KE}} + \underbrace{\sum_{\mathbf{k},\sigma} \mathcal{F}_{\mathbf{k}\mathbf{q},\sigma\tau} \delta n_{\mathbf{k},\sigma} \delta n_{\mathbf{q},\tau}}_{\text{QP Int. E.}} + \mathcal{O}[(\delta n_{\mathbf{k}\sigma})^3]. \quad (20)$$

- ▶ In practice, the \mathcal{F} 's are restricted by isotropy and **symmetry** arguments, but I won't focus on them here. Instead I'll focus on the **quasiparticle kinetic energies**.
- ▶ This term describes the kinetic energy of the quasiparticles of the interacting system, whose effective mass is *renormalised* by e-e interactions.

Fermi Liquid Theory (III) - Effective Masses

- ▶ The dispersion relation of quasiparticles close to the Fermi energy (ϵ_F) can be taken to be

$$\epsilon_{\mathbf{k},\sigma} = \epsilon_F + \frac{k_F}{m^*}(k - k_F), \quad (21)$$

where m^* is the *quasiparticle effective mass*.⁴¹

- ▶ I'll now move on to the QMC calculations!
- ▶ Before I do, let's mention that FLT has the ability to **predict its own death**. If some physics lowers the energy of a competing phase, the liquid may be unstable, and this usually signals the dominance of the **new phase**.
 - ▶ Magnetic instabilities.
 - ▶ Density wave / Pomeranchuk instabilities.

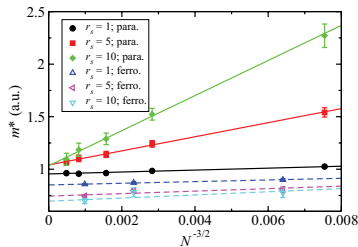
⁴¹ This can be of order m_e , however, it can also exceed $10^3 m_e$ (in so-called “heavy fermion” materials).

Fermi Liquid Theory - What Can QMC Say?

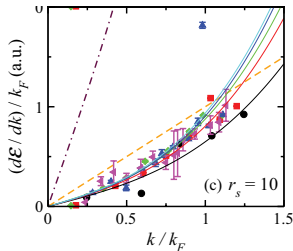
- ▶ QMC for the HEG can be used to explicitly calculate $\epsilon_{\mathbf{k},\sigma}$ in the (para- and ferr-)magnetic case. I.e. we can extract the leading term of the Landau functional, $E[\delta n]$.
- ▶ Using SJB wave functions, Neil Drummond and Richard Needs have studied the HEG, and extracted quasiparticle effective masses.⁴²
 - ▶ Optimize GS wave function.
 - ▶ Add or remove electrons.
 - ▶ Calculate energy band $\epsilon_{\mathbf{k}}$.
 - ▶ Rinse and repeat for systems of varying density and size.

⁴² N. D. Drummond and R. J. Needs, Physical Review B **87** (2013).

Fermi Liquid Theory - What Can QMC Say? (II)



(a) m^* versus system size.



(b) [crop] $\epsilon_{\mathbf{k}}$ versus system size.

Figure 11: Both from earlier referenced study.

- This is another example where the biting point for QMC calculations of excited state is made clear: **Finite Size Effects!**⁴³

⁴³ At high r_s , at least.

Outline

- Introduction: Ground States

- What Changes in Excited States?

 - Variational Principles

 - Our safety net: the fixed-node approximation

- Excited State VMC

 - Excited State Trial Wave Functions

- Excited State DMC

 - Time Step Bias

 - Nodal Errors

 - Finite Size Effects

- Examples

 - Atoms and Molecules

 - Solids

- Wisdom for Excited State DMC Calculations







Wisdom for Excited State DMC Calculations

- ▶ **Do** investigate systematic biases, and try to exploit them.
- ▶ **Do** assess project feasibility before starting: some gap calculations are forbidden by supercell size/shape. Some materials have large unit cells.
- ▶ **Do** be careful when carrying out calculations: check band occupancies, regenerate blip binaries, ...
- ▶ **Do** respect GS wisdom!
- ▶ **Don't** optimize parameters that affect the nodal surface in trial excited states.⁴⁴
- ▶ **Don't** waste time lowering statistical error bars beyond the limits of accuracy (set by FS effects, in solids).







⁴⁴Unless you are **sure**. In our limited tests, we find that backflow has little effect on excited state energy gaps anyway.

Thank you all for listening!






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