Wave functions in QMC

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Many-Body Wave Functions

$$\Psi\left(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, \ldots, \mathbf{r}_N\sigma_N\right)$$

$$\hat{H}\Psi = E\Psi$$

Wave functions are not observables .....
but they are very "physical"!

Electronic wave functions

Determinant of single-particle orbitals

$$D = \hat{A}\, \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_N(\mathbf{r}_N)$$

Simplest antisymmetric function
Already gets a lot of chemistry right

Multiply by a Jastrow factor

$$e^{-\frac{B}{r_{ij}}\left[1-\exp\left(-Cr_{ij}\right)\right]}$$

Short-range or dynamical correlation from electron-electron cusps

Multi-determinant expansion

$$\Psi = \sum_i c_i D_i$$

Long-range or static correlation due to near degeneracy

Singlet pairing (BCS) - pair up-spin electrons with down-spin electrons

$$\Psi = \hat{A}\, g(|\mathbf{r}_1 - \mathbf{r}_2|) g(|\mathbf{r}_3 - \mathbf{r}_4|) \cdots g(|\mathbf{r}_{N-1} - \mathbf{r}_N|)$$

Chemist's "geminal-power" (Hurley, Lennard-Jones and Pople, 1954)

$$g(\mathbf{r}_1, \mathbf{r}_2) = \sum_i \alpha_i \phi_i^*(\mathbf{r}_1) \phi_i(\mathbf{r}_2)$$

Equivalent number of determinants $\propto e^{\lambda N}$

Backflow

Classical backflow - related to flow of fluid around a large impurity

Quantum backflow (Feynman, 1954) local current conservation for excitations in ^{4}He

Imaginary-time evolution argument

Replace coordinates in orbitals by "quasiparticle" coordinates

$$\phi(\mathbf{r}_i) \Rightarrow \phi\left(\mathbf{r}_i + \sum_{j \neq i} \eta(\mathbf{r}_i, \mathbf{r}_j)[\mathbf{r}_i - \mathbf{r}_j]\right)$$

Variable parameters in wave functions

$$e^{J_3(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_k)}\, e^{J_2(\mathbf{r}_i,\mathbf{r}_j)}\, e^{J_1(\mathbf{r}_i)}\, \det\left[\phi_\alpha\left(\mathbf{r}_i + \sum_{j\neq i}\eta(\mathbf{r}_i,\mathbf{r}_j)[\mathbf{r}_i - \mathbf{r}_j]\right)\right]$$

importance $\longrightarrow$

Parameterise: ϕ_α, J_1 and J_2, η and J_3

We don't have J_3 *yet*
We also have multi-dets and some pairing functions

Our forms for J_1, J_2, η appear to be rather general
ϕ_α are the most important objects $\Rightarrow$ shouldn't we optimise these as well?

Atoms: we are trying

$$\begin{aligned}\phi_{nlm}(r,\theta,\phi) &= r^l \rho_{nl}(r) Y_{lm}(\theta,\phi)\\ \rho_{nl}(r) &= \rho_{nl}^{\mathrm{HF}}(r) + \Delta\rho_{nl}(r)\end{aligned}$$

I am quite optimistic about this!

Variable parameters in orbitals

How do we parameterise orbitals in molecules and solids?

N orbitals expanded in $\mathcal{O}(N)$ basis functions $\Rightarrow \mathcal{O}(N^2)$ parameters
Wannier functions?

Filippi and Fahy parameterised orbitals in terms of the potential from which they were generated $\Rightarrow \mathcal{O}(N)$ variable parameters. Is this sufficient?

Perhaps include unoccupied orbitals $\bar{\phi}_\beta$ within an energy window ΔE

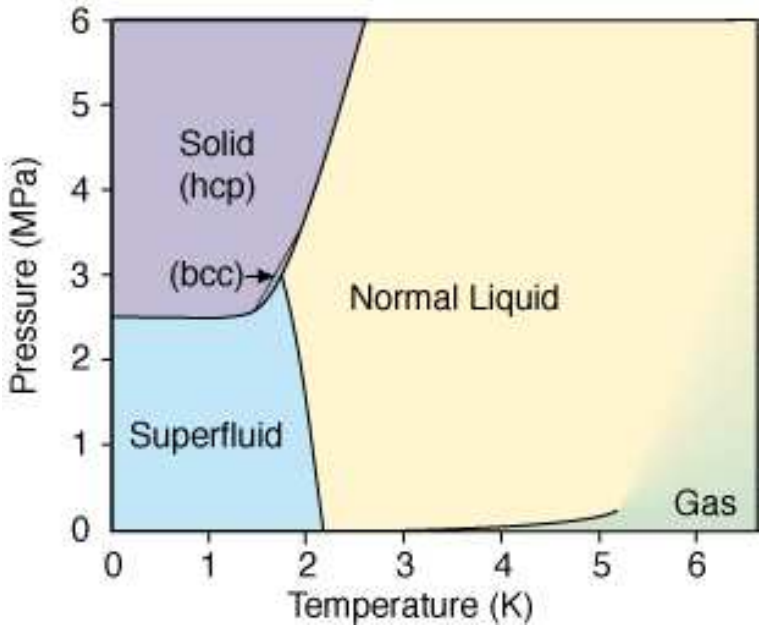
$$\phi'_\alpha = \phi_\alpha + c_{\alpha\beta}\bar{\phi}_\beta$$

Number of unoccupied orbitals in window $\propto N \Rightarrow \mathcal{O}(N^2)$ parameters $c_{\alpha\beta}$

Perhaps vary linear coefficients in basis, $\phi_\alpha(\mathbf{r}) = \sum_i c_i^\alpha \, b_i(\mathbf{r})$?

We need to think more deeply about how to parameterise orbitals

Helium 4 (^{4}He)



Phase diagram of ^{4}He

Ground state of ^{4}He: Bosons $\Rightarrow$ Ψ_0 is nodeless

$$\Psi_0 = \prod_{i<j} e^{-u(|\mathbf{r}_i - \mathbf{r}_j|)} \qquad \text{Pair product form}$$

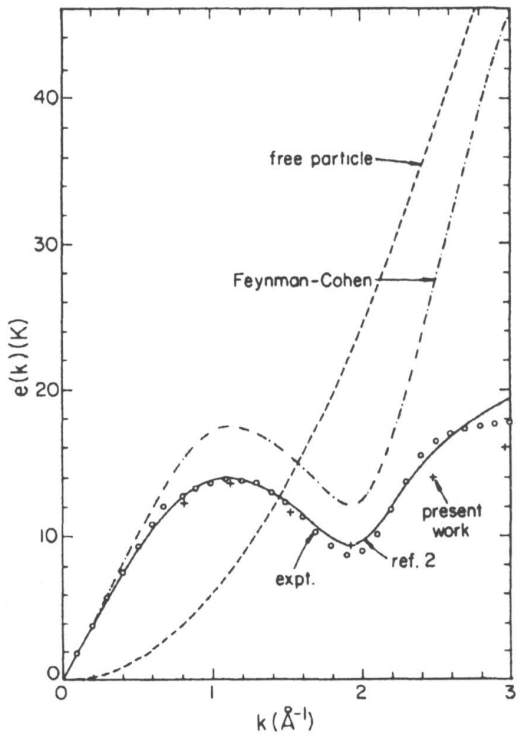
First VMC calculations - McMillan (1965). Describes solid *and* fluid
Backflow important

Feynman's excited state wave functions:

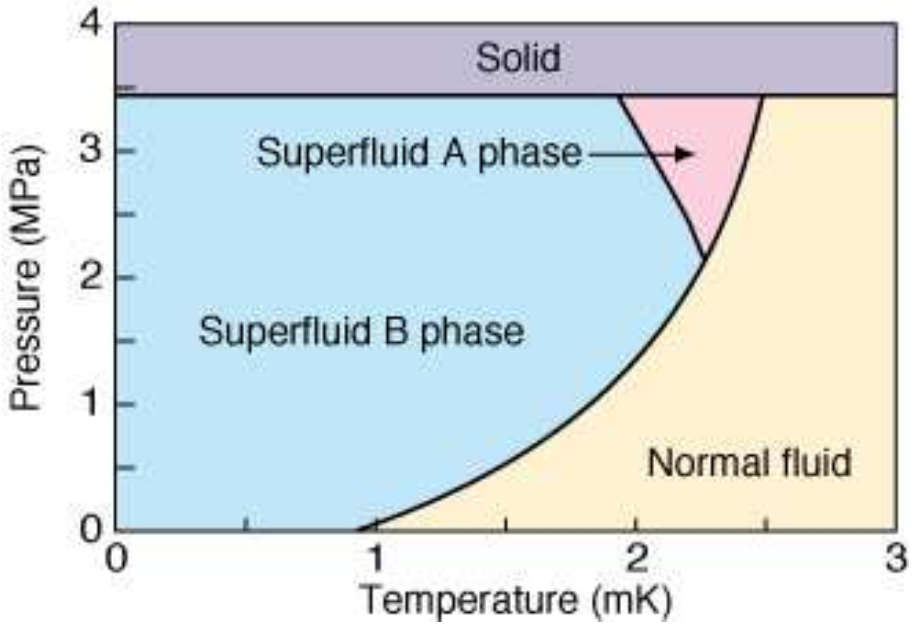
$$\sum_{i=1}^{N} e^{-i\mathbf{k}.\mathbf{r}_i}\,\Psi_0$$

$$\sum_{i=1}^{N} e^{-i\mathbf{k}.\mathbf{r}_i}\left[1+\alpha\sum_{j=1}^{N}\frac{(\mathbf{r}_i-\mathbf{r}_j).\mathbf{k}}{|\mathbf{r}_i-\mathbf{r}_j|^2}\right]\Psi_0$$

With backflow



Helium 3 (^{3}He)



Phase diagram of ^{3}He

Ground state of ^{3}He: Fermions $\Rightarrow$ use Slater-Jastrow with plane waves:

$$e^J \begin{vmatrix} \exp(i\mathbf{k}_1 \cdot \mathbf{r}_1) & \dots & \exp(i\mathbf{k}_1 \cdot \mathbf{r}_N) \\ \exp(i\mathbf{k}_2 \cdot \mathbf{r}_1) & \dots & \exp(i\mathbf{k}_2 \cdot \mathbf{r}_N) \\ \vdots & \vdots & \vdots \\ \exp(i\mathbf{k}_N \cdot \mathbf{r}_1) & \dots & \exp(i\mathbf{k}_N \cdot \mathbf{r}_N) \end{vmatrix}$$

Three-body Jastrow and backflow are important

Helium 3 (^{3}He)

QMC results for ^{3}He are not completely satisfactory

(1) $E_{\rm exp} \simeq -2.5$ K, error in optimised backflow nodes estimated to be ~ 0.25 K (Ceperley *et al.*)
(2) spin susceptibility factor of 2 too small because the wave function for the polarised system is "simpler"

Experimentally - below ~ 1 mK get transition to superfluid of atoms with p-wave pairing - theory similar to BCS

Bouchaud and Lhuillier obtained good energies in QMC with p-wave pairing and no backflow! But these calculations are wrong!!
Energy of pairing of order transition temperature?
Maybe try backflow-pairing, but should not be too optimistic

Two-component plasma/Excitonic insulator/Wigner crystal

Antisymmetrised Geminal Power (AGP) "parent" wave function

$$g(\mathbf{r}_e, \mathbf{r}_h) = \sum_n a_n u_n^*(\mathbf{r}_e)\, v_n(\mathbf{r}_h)$$

Two-component plasma

$$u_n = v_n = e^{i\mathbf{k}_n \mathbf{r}} \quad a_n \neq 0 \quad \text{for } N \text{ plane waves}$$

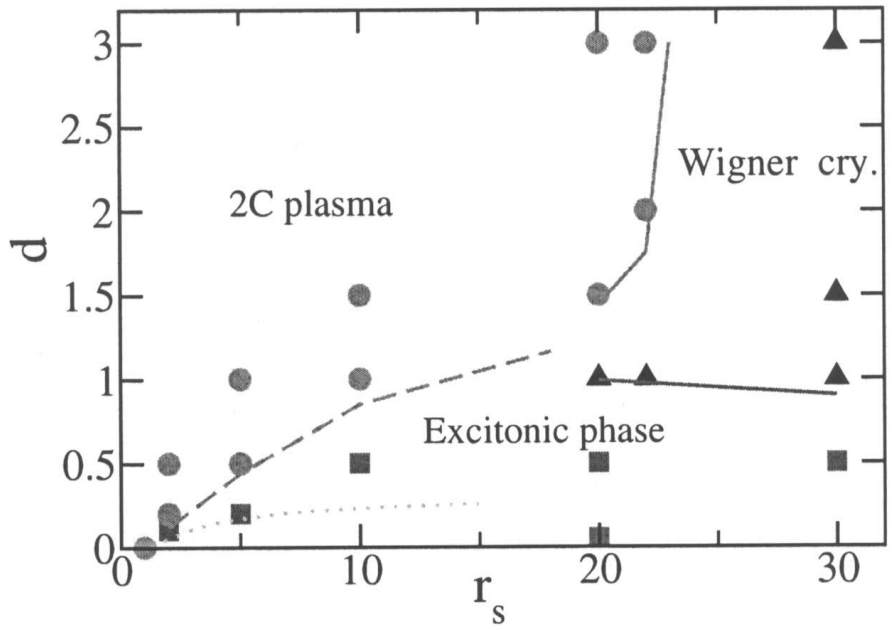
Excitonic insulator

$$u_n = v_n = e^{i\mathbf{k}_n \mathbf{r}} \quad a_n \neq 0 \quad \text{for } > N \text{ plane waves}$$

Wigner crystal

$$\begin{aligned} u_n &= f_e(\mathbf{r}_e - \mathbf{R}_n) \\ v_n &= f_h(\mathbf{r}_h - \mathbf{R}_n) \end{aligned}$$

Electron-hole systems



Phase diagram of electron-hole bilayer from de Palo *et al.* 2002

Try the following pairing function?

$$g(\mathbf{r}_e, \mathbf{r}_h) = \sum_n a_n e^{i\mathbf{G}_n \cdot (\mathbf{r}_e - \mathbf{r}_h)} + \phi(\mathbf{r}_e - \mathbf{r}_h) + \sum_i f_e(\mathbf{r}_e - \mathbf{R}_i) f_h(\mathbf{r}_h - \mathbf{R}_i)$$

Better than adding separate determinants?

A positron in an electron gas

Positron is antiparticle of electron
Can annihilate with electron to give two γ rays
Strong electron-positron pairing attraction

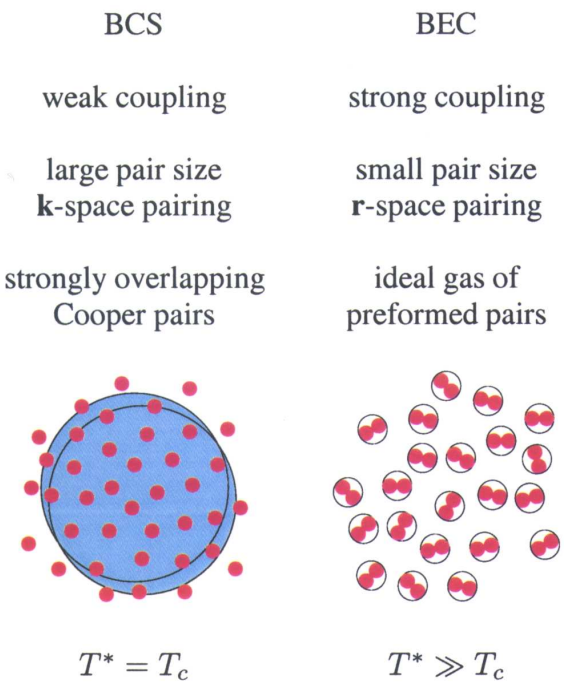
Use different pairing functions for each electronic state:

$$\begin{vmatrix} \psi_1(\mathbf{r}_1 - \mathbf{r}_p) & \dots & \psi_1(\mathbf{r}_N - \mathbf{r}_p) \\ \psi_2(\mathbf{r}_1 - \mathbf{r}_p) & \dots & \psi_2(\mathbf{r}_N - \mathbf{r}_p) \\ \vdots & \vdots & \vdots \\ \psi_N(\mathbf{r}_1 - \mathbf{r}_p) & \dots & \psi_N(\mathbf{r}_N - \mathbf{r}_p) \end{vmatrix}$$

Pickard, Drummond, and Needs

BCS-BEC crossover in ultracold Fermi gases

Bardeen-Cooper-Schrieffer superfluid $\leftrightarrow$ molecular Bose-Einstein Condensate



At the crossover get "universal behaviour" independent of details of interaction ($unitary\ limit$) - Very fashionable!
Many things to vary - can tune interactions by varying applied B field, etc.

Plenty of work for QMC!

Conclusions

- Current understanding of many-body wave functions revolves around four basic ideas (determinants/permanents, Jastrow factors, pairing, backflow)

- Use the four ideas in a physically motivated combination

- We need to think more deeply about how to parameterise orbitals

- Recently we have been concentrating on improving CASINO and making better wave functions - now we have to prove it is useful!