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CONTINUUM QUANTUM MONTE CARLO METHODS

12 - 23 January 2004

RESPONSE FUNCTIONS, EXCITED STATES, MAXIMUM ENTROPY METHOD:

QUANTUM DYNAMICS

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These are preliminary lecture notes, intended only for distribution to participants.

Quantum Dynamics

- What can we do about "real-time" quantum dynamics?

$$f(t) = e^{-it(H-E_T)} f(0)$$

$$f(t) = e^{-t(H-E_T)} f(0)$$

- Clearly very important!! This is what experiments usually probe.
- Feynman argued that full many-body quantum dynamics is exponentially difficult on a classical computer. Amount of memory needed to store and time needed to update, the wavefunction--which can be completely arbitrary-- grows very fast.
- Judge by the progress on quantum scattering calculations:
  - 1950-1970 2 particle problems
  - 1970-1990 3 particle problems
  - 1990-2010 4 particle problems
  - ....

1

QMC-Equilibrium responses

- Feynman's argument does not apply to the sort of things measurable in experiment:
  - Linear response functions
  - Specific cross sections
  - Low temperature dynamics
  - Specific excited states

Where is the limit of what is possible on a classical computer?

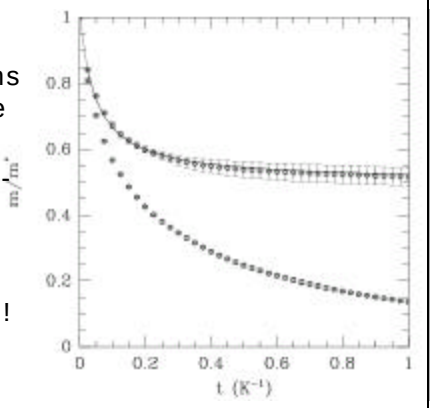
- We will focus on:
  1. Construction of real time response from imaginary time correlations
  2. T=0 excited states
  3. scattering calculations.

2

Effective mass

- Effective mass is gotten from the diffusion constant at low temperature
- At short time KE dominates and $m = m^*$
- At large times, neighboring atoms block the diffusion increasing the mass by a factor of 2.
- Lower curve is for Boltzmannons- they have to return to start position so they move less.
- Diffusion in imaginary time has something to do with excitations!

$$\frac{m}{m^*} = \frac{\left\langle [r(t) - r(0)]^2 \right\rangle}{6lt}$$



3

Imaginary time correlations

- With PIMC (and DMC) we can calculate imaginary time dynamics: $F_O(t) = Z^{-1}\left\langle Oe^{-t\hat{H}}Oe^{-(b-t)\hat{H}}\right\rangle = \left\langle\left\langle O(t)O(t+t)\right\rangle\right\rangle$
  (DMC corresponds to $\beta\to\infty$)
- If we could determine this analytically we could just substitute imaginary values of τ for real values.
- Dynamic structure function is the response to a density perturbation is (e.g. density-density response)

$$S_k(w) = \frac{1}{2p}\int_{-\infty}^{\infty} dt e^{iwt} F_k(t) \quad \text{where } O = \frac{1}{\sqrt{N}}\sum_{i=1}^{N} e^{i\vec{k}\cdot\vec{r}_i}$$

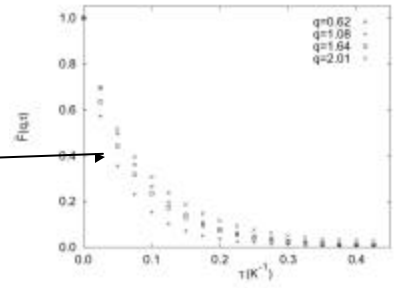
$$F_k(t) = \int_{-\infty}^{\infty} dw e^{-tw} S_k(w)$$

- $S_k(\omega)$ is measured by neutron scattering. We need to invert the "Laplace transform" to get $S_k(\omega)$.

4

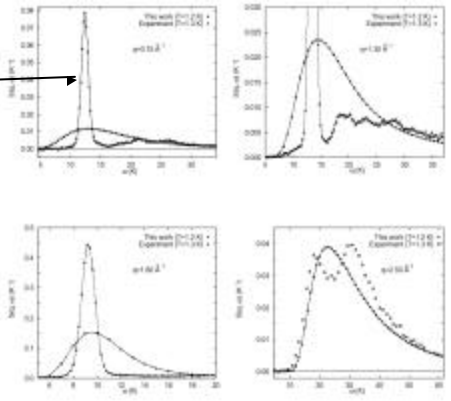
$$F_O(t) = Z^{-1}\left\langle Oe^{-t\hat{H}}Oe^{-(b-t)\hat{H}}\right\rangle$$

Little structure or information in F(q,t)



shown are different q values.

but much in S(q,w). Sharp peaks at the excitations (essentially infinitely narrow lines in the superfluid)



Bayes' theorem

- What is the most probable value of $S_k(\omega)$ given both:
  - the PIMC data, $F_k(t)$ and
  - prior knowledge of $S_k(\omega)$: e.g. $S_k(\omega) \geq 0$
- Bayes' theorem (also used by Laplace)

$$\Pr\left(S(w)\middle|F(t)\right) \propto P_L\left(F(t)\middle|S(w)\right)P_P(S(w))$$

- Likelihood function follows from central limit theorem:

$$P_L\left(F(t)\middle|S(w)\right) \propto \exp\left[-\frac{1}{2}\sum_{t,t'} dF(t)\,s(t,t')^{-1}\,dF(t')\right]$$

$$dF(t) = F(t) - \left\langle F(t)\right\rangle \text{ and } s(t,t') = \left\langle dF(t)\,dF(t')\right\rangle$$

- But what to choose for the prior $P_p(S)$? Typical choice is the "entropy."

$$P_P(S(w)) \propto \exp\left[a\sum_w S(w)\ln\left(S(w)/m(w)\right)\right]$$

6

Now two routes to making the inversion:

1. Sample $S_k(\omega)$. AvEnt Using MCMC, make moves in $S_k(\omega)$ space. Take averages and also get idea of the allowed fluctuations. Model can be defined self consistently
2. Find most probable $S_k(\omega)$. MaxEnt Maximize function. Ok if the p.d.f. is highly peaked. Estimate errors by the curvature at the maximum. Fast to do numerically but makes more assumptions. (coself code)

How do we choose α? Choose it from its own prior function so the strength of the likelihood function and the prior function are balanced. Its prior function is: $P(\alpha)=1/\alpha$.

Determine MC errors by blocking and rotate to direction of independent data.

7

Example: Liquid ^{4}He

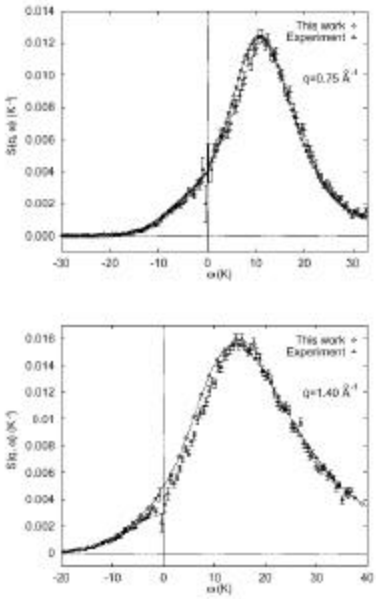
Boninsegni and DMC JLTP ***104****, 339 (1996).*

- Calculate $F_k(\tau)$ using PIMC (UPI code).
- AvEnt works beautifully in normal phase.
- Gives peaks too broad in the superfluid phase. Failure of the entropic prior.
- It makes the assumption that energy modes are uncoupled. This is false! Energy levels repel each other so that if there is energy at one level, energy levels are pushed away from nearby values.
- Would require incredible precision to get sharp features.
- But good method for determining the excitation energy.

8

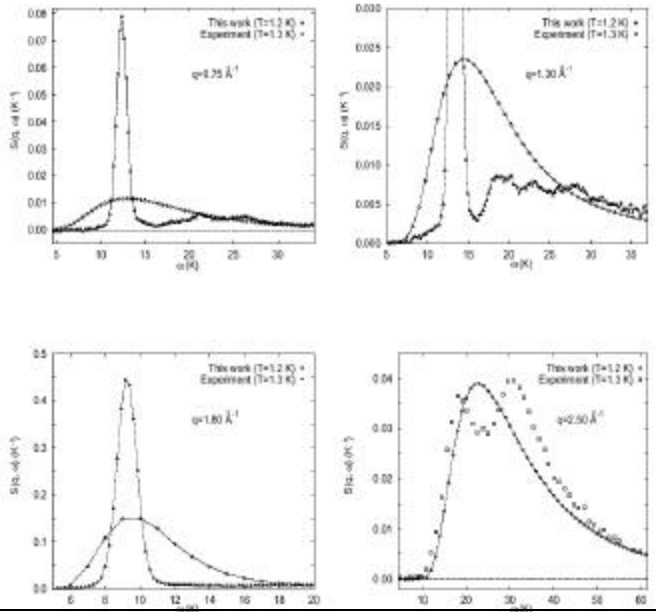
Comparison in normal liquid He phase

- MaxEnt works well in normal phase (T=4K)
- Modes are quantum but independent of each other so that max-ent prior is reasonable.



9

Comparison in Superfluid



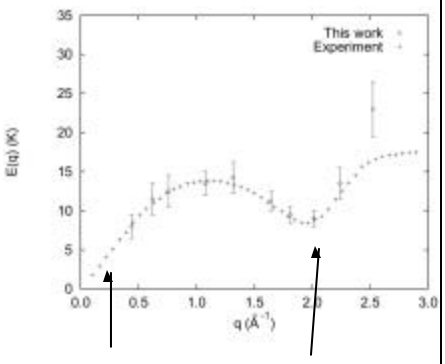
10

Excitation energies

Improvements?

- Better PIMC data, more time values, smaller errors.
- Work in effective hamiltonian space, not energy space.
- Get more information, for example,
  - multiphonon correlation functions
  - Incorporate exchange values
  - Analytic information about response properties

Reasonable excitation energies from MAXENT



Phonons rotons

11

How about T=0K?

- Do reptation so we don't have mixed estimator problem
- Consider Feynman-Cohen trial function for liquid helium excitations. $\Psi_k(R) = \Psi_k(R) r_k$ where $r_k = \sum_i e^{i\mathbf{k}\mathbf{r}_i}$
- Reduces to ground state at k=0. In an atom or solid, simply make an excited state trial function.
- Has momentum k, so orthogonal to other excitations.

$$\Psi(b) = e^{-\frac{b}{2}H}\Psi$$

$$Z(b) = \langle \Psi(b)\Psi(b) \rangle = \langle \Psi e^{-bH}\Psi \rangle = \int dR_0 ... dR_p \Psi(R_0) \langle R_0 e^{-tH} R_1 \rangle .... \langle R_{p-1} e^{-tH} R_p \rangle \Psi(R_p)$$

$$Z(b) = \sum_a |\langle f_a | \Psi \rangle|^2 e^{-bE_a}$$

$$E(b) = \frac{\langle \Psi(b) H \Psi(b) \rangle}{\langle \Psi(b)\Psi(b) \rangle}_b = \frac{\langle E_{L0}(R_0) r_{-k}(0) r_k(b) \rangle_b}{F_k(b)} + l\,k^2$$

$$Z(b) = \langle \Psi_0 r_{-k} e^{-bH} r_k \Psi_0 \rangle = F_k(b)$$

12

Fixed-node method

- Initial distribution is a pdf.
  It comes from a VMC simulation. $f(R,0) = |y_T(R)|^2$
- Drift term pushes walks away from the nodes.
- Impose the condition: $f(R) = 0$ when $y_T(R) = 0.$
- This is the fixed-node BC
- Will give an upper bound to the exact energy, the best upper bound consistent with the FNBC as long as we are looking for the ground state of a given symmetry (and symmetry has a 1D representation).

$$E_{FN} \geq E_0$$

$$E_{FN} = E_0 \text{ if } f_0(R)y(R) \geq 0 \text{ all } R$$

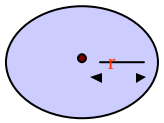
- f(R,t) has a discontinuous gradient at the nodal location.
- Accurate method because Bose correlations are done exactly.
- One needs trial functions with accurate nodes for excited state.

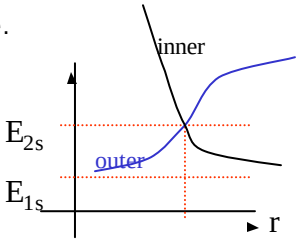
14

Fixed-node approach to excited states

For ground state of a given symmetry, tiling theorem applies to all the pockets of a trial function.

- all pockets are related by symmetry => all energies the same
- What can go wrong if it is not orthogonal? Pockets will be different.
- Consider a H atom in a 2s state.





- You get 2 different energies and they are only identical for the correct node position.
- Problem: no orthogonality to ground state is imposed.

15

Fixed-node calculation of excited states

- Fixed-node hamiltonian messes up matrix elements.

$$Z(b) = \left\langle \Psi e^{-bH} \Psi \right\rangle = \int dR_0 ... dR_p \Psi(R_0) \left\langle R_0 e^{-tH} R_1 \right\rangle .... \left\langle R_{p-1} e^{-tH} R_p \right\rangle \Psi(R_p)$$

$$Z(b) = \sum_a \left| \left\langle f_a \middle| \Psi \right\rangle \right|^2 e^{-bE_a}$$

Use fixed-node Hamiltonian defined for the ground state.

Problem $Z_{FN}(b) = \sum_a \left| \left\langle f_{FNa} \middle| \Psi \right\rangle \right|^2 e^{-bE_{FNa}} \neq Z(b)$

since only $f_{FN0} = f_0$ and $E_{FN0} = E_0$

- Unless you know excited state nodes are correct, you must use bosonic trial function and transient estimate method => Sign problem for all excited states.

16

Linear Basis approach

Assume trial function is a linear combination of known functions: a basis $f_n(R)$.

$$y(R;\mathbf{a}) = \sum_{n=1}^{m} a_n f_n(R)$$

$$E_V(\mathbf{a}) = \frac{\sum_{n,m} a_n^* a_m H_{nm}}{\sum_{n,m} a_n^* a_m N_{nm}}$$

$N_{nm} = \left\langle f_n f_m \right\rangle =$ overlap matrix

$H_{nm} = \left\langle f_n H f_m \right\rangle =$ Hamiltonian matrix H

$N_{nm} = d_{nm}$ in an orthonormal basis N

$$\frac{dE}{d\mathbf{a}} = 2\left[H\mathbf{a} - E_v N\mathbf{a} \right] = 0 \Rightarrow$$

$H\mathbf{a}_l = E_l N\mathbf{a}_l$ generalized eigenvalue problem

17

Properties of solution to GEP

- For a basis of size m, there exist "m" eigenvalues and orthonormal eigenfunctions:

$$y_n(R) = \sum_{k=1}^{m} a_{k,n} f_k(R)$$

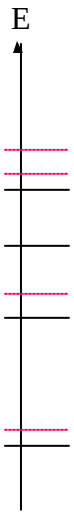
$$\langle y_n y_m \rangle = a_n^* S_{nm} a_m = d_{nm}$$

- McDonald's theorem: the nth eigenvalue in a basis is an upper bound to the nth "exact eigenvalue.

$$E_0 \le E_1 \le E_2 \le \ldots \le E_m$$

$$E_n^{ex} \le E_n$$

- We can always lower all the energies by augmenting the basis
- When basis is complete, we get exact answers!
- Orthogonality taken into account in the solution.



VMC Calculation of excited-state energies

Correlation Function MC: J. Chem. Phys. **89**, 6316 (1988).

- Construct a basis of trial functions spanning excited states in question. $\{f_i(R)\}$ $1 \le i \le M$
- Using VMC calculate all the matrix elements as a function of imaginary time. Must use a bosonic sampling function.

$$P(R) = \sum_n |f_n|^2$$

- Find lowest energy in this basis
- Solve the generalized eigenvalue problem:

$$H_{ij} C_i^l = E^l N_{ij} C_i^l$$

$$N_{ij} \equiv \langle f_i \mid f_j \rangle = \left\langle \frac{f_i^*(R) f_j(R)}{P(R)} \right\rangle$$

$$H_{ij} \equiv \langle f_i | H | f_j \rangle = \left\langle \frac{f_i^*(R) f_j(R) E_{Lj}(R)}{P(R)} \right\rangle$$

- Then E_k is the best upper bound spanned by the basis functions.
- Zero variance applies also to excited states.

Fermi Liquid parameters

- Do by correlated sampling: Do one long MC random walk with a guiding function (something overlapping with all states in question).
- Generate energies of each individual excited state by using a weight function

$$w_a(R) = \frac{f_a(R)}{y_G(R)}$$

$$y_G^2 = \sum_a |f_a(R)|^2$$

- "Optimal Guiding function" is
- Determine particle hole excitation energies by replacing columns:fewer finite size effects this way. Replace columns in slater matrix
- Case where states are orthogonal by symmetry is easier, but non-orthogonal case can also be treated.
- Back flow needed for some excited state since Slater Jastrow has no coupling between unlike spins.

20

Diffusion Monte Carlo method

- The time-evolved basis approaches the exact eigenfunctions:

$$f_i(R;t) = e^{-tH/2} f_i(R)$$

- Using bosonic DMC (no nodes) calculate the N and H as a function of imaginary time. Note, H=dN/dt.

$$N_{ij}(t) \equiv \left\langle f_i \left| e^{-t\hat{H}} \right| f_j \right\rangle = \left\langle f_i^* \left(R(t+t_0)\right) f_j\left(R(t_0)\right) \right\rangle$$

- Use same guiding function for importance sampling.
- Solve the generalized eigenvalue problem:

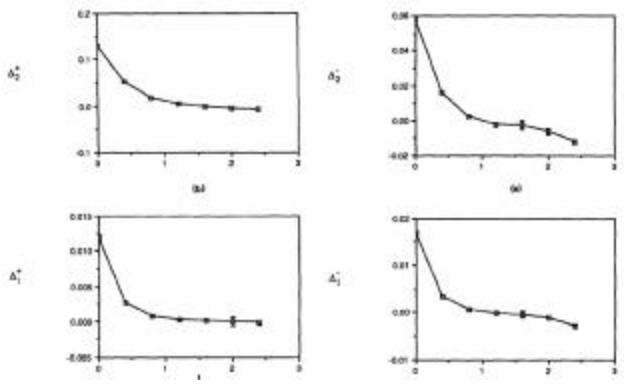
$$H_{ij}(t) a_i^l = E(t)^l N_{ij}(t) a_i^l$$

- Then $E^l(t)$ approaches the exact λ^{th} energy exponentially fast and from above.

21

Typical results

- Look for plateau in energy.
- Error bars grows exponentially in time (sign problem).
- Best results are for lower energy states
- Can use symmetry to reduce matrix size.



22

Remarks on CFMC

- Zero variance principle applies.
- Can treat a large basis and hence get a whole spectrum at once.
- Sign problem is still there. In practice “t” cannot be too large.
- If nodes in the DMC are present, excited state energies will be wrong.
- Maybe MaxEnt methods can do better. But problems working in energy space. Much better in effective Hamiltonian space.
- Used for
  - Vibration excitations
  - Molecular excitations
  - Lattice models.
  - Positronium-positonium scattering (Shumway-DMC)

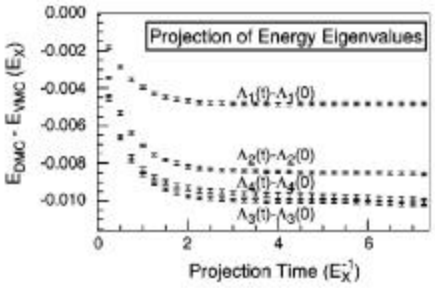
23

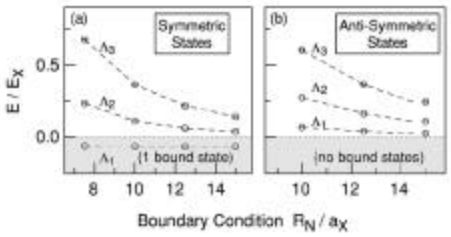
Exciton-Exciton scattering

Shumway and DC, *Phys. Rev. B 63, 165209-165215 (2001).*

- 4-quantum particles
- Boundary conditions and energy determine phase shifts
- Use excited state method to get exact energies inside boundaries.

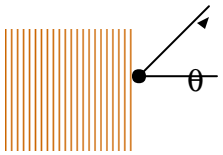
$$r_c \Rightarrow E_0, E_1, E_2, \ldots \Rightarrow k_0, k_1, k_2, \ldots.$$
$$(r_c, k_n) \Rightarrow d(k_n) \Rightarrow s(k)$$





24

Basic 2-body scattering equations



$$y(r) \sim e^{ikr} + f(q)\frac{e^{ikr}}{r} = \sum_{l=0}^{\infty} P_l(\cos q)\left[(2l+1)i^l\, j(kr) + f_l\frac{e^{ikr}}{r}\right]$$

$$\frac{ds}{d\Omega} = \left|f(q)\right|^2 = \sum_{l=0}^{\infty}\left|P_l(\cos q)\, f_l\right|^2$$

$$y(r) \to \sum_{l=0}^{\infty} A_l P_l(\cos q)\frac{\sin(kr - lp/2 - d_l)}{kr} \qquad \text{r: } v(r) = 0$$

$$f_l = \frac{2l+1}{k} e^{id_l}\sin(d_l)$$

$$s_{tot} = \frac{4p}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2 d_l$$

See text books for details

$$\left\{\frac{\hbar^2}{2m}\frac{d^2}{dr^2} - v(r) - \frac{\hbar l(l+1)}{2mr^2}\right\}u_l(r) = Eu_l(r) \qquad E = \frac{\hbar^2 k^2}{2m}$$

$$u_l(r) \to kr\left[\cos(d_l)\, j_l(r) - \sin(d_l)\, n_l(r)\right] \qquad \text{r: } v(r) = 0$$

25