QMC and the CASINO Program: Exam

Saturday 9th August, 2014

Duration: 73 minutes and 27 seconds.

Instructions: *do as many questions as you wish; feel free to look up the answers in books, manuals, papers, the Internet, etc.; Hartree atomic units are used throughout.*

Scoring: *each of questions 1–5 is worth 10 points, divided as indicated; bonus points are awarded for being funny, inventive or otherwise amusing in the opinion of the examiner; the maximum score is 50 points.*

1. The imaginary-time Schrödinger equation for a many-electron system is

$$\left(\hat{H} - E_T\right) \Phi(\mathbf{R}, t) = -\frac{\partial \Phi\left(\mathbf{R}, t\right)}{\partial t} \ ,$$

where the wave function $\Phi(\mathbf{R}, t)$ is a function of point $\mathbf{R}$ in configuration space and imaginary time t, E_T is the reference energy and

$$\hat{H} = -\frac{1}{2}\nabla^2 + U(\mathbf{R})$$

is the Hamiltonian operator, where U is the potential energy.

(a) By expanding Φ in terms of the eigenfunctions of the Hamiltonian, prove that the excited-state components of Φ die away exponentially relative to the ground state. [3]

(b) Let $f(\mathbf{R}, t) = \Phi(\mathbf{R}, t)\Psi(\mathbf{R})$, where $\Psi(\mathbf{R})$ is an approximation to the ground-state wave function.

(i) Prove that f satisfies the importance-sampled imaginary-time Schrödinger equation

$$-\frac{1}{2}\nabla^2 f(\mathbf{R}, t) + \nabla \cdot [\mathbf{V}(\mathbf{R}) f(\mathbf{R}, t)] + [E_L(\mathbf{R}) - E_T]\, f(\mathbf{R}, t) = -\frac{\partial f\left(\mathbf{R}, t\right)}{\partial t} \ ,$$

where $\mathbf{V}(\mathbf{R}) = \Psi^{-1}(\mathbf{R})\nabla\Psi(\mathbf{R})$ and $E_L(\mathbf{R}) = \Psi^{-1}(\mathbf{R})\hat{H}\Psi(\mathbf{R})$. [4]

(ii) Explain the consequences of the importance-sampling transformation for the diffusion Monte Carlo algorithm. [3]

2. (a) Explain why the nodes of the trial wave function are of particular importance in the diffusion Monte Carlo method. [3]

(b) State at least two possible ways in which one can modify a Slater–Jastrow wave function to improve its nodes. [3]

(c) State which of the following relates to wave-function nodes: *Fermat's Last Theorem*, the *Nodal Theorem*, the *Jigsaw Theorem*, the *Tiling Theorem*, the *Fur Bikini Theorem* or the *Puzzle Theorem*. [2]

(d) The Hartree–Fock wave function for a beryllium atom is the product of up-spin and down-spin determinants:

$$\Psi_{\mathrm{HF}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \begin{vmatrix} \phi_1(r_1) & \phi_2(r_1) \\ \phi_1(r_2) & \phi_2(r_2) \end{vmatrix} \begin{vmatrix} \phi_1(r_3) & \phi_2(r_3) \\ \phi_1(r_4) & \phi_2(r_4) \end{vmatrix} \ ,$$

where r_i is the distance from the ith electron to the nucleus.

(i) Describe the shape of the nodes of Ψ_{HF} as seen by electron 1. [1]

(ii) Explain why a multideterminant expansion can radically change the shape of the nodes, whereas backflow cannot. [1]

3. (a) Explain what is meant by the *Kato cusp conditions*. Explain why it is important to impose the cusp conditions on a QMC trial wave function and describe what happens in QMC calculations if they are not satisfied. [5]

(b) Consider a Slater–Jastrow wave function for an N-electron system ($N_\uparrow$ spin-up electrons and $N_\downarrow$ spin-down electrons),

$$\Psi(\mathbf{R}) = \exp\left[J(\mathbf{R})\right] \begin{vmatrix} \psi_1^\uparrow(\mathbf{r}_1) & \cdots & \psi_{N_\uparrow}^\uparrow(\mathbf{r}_1) \\ \vdots & \ddots & \vdots \\ \psi_1^\uparrow(\mathbf{r}_{N_\uparrow}) & \cdots & \psi_{N_\uparrow}^\uparrow(\mathbf{r}_{N_\uparrow}) \end{vmatrix} \begin{vmatrix} \psi_1^\downarrow(\mathbf{r}_{N_\uparrow+1}) & \cdots & \psi_{N_\downarrow}^\downarrow(\mathbf{r}_{N_\uparrow+1}) \\ \vdots & \ddots & \vdots \\ \psi_1^\downarrow(\mathbf{r}_N) & \cdots & \psi_{N_\downarrow}^\downarrow(\mathbf{r}_N) \end{vmatrix} .$$

(i) Explain why it is not possible to impose the electron–electron cusp conditions on Slater determinants. [3]

(ii) Consider applying a backflow transformation to a Slater–Jastrow wave function. Explain why the backflow displacement $\boldsymbol{\xi}_i(\mathbf{R})$ of the ith particle of a system must be constrained to be zero when $\mathbf{r}_i$ coincides with the position of an all-electron nucleus. [2]

4. (a) Explain why the variance of the local-energy distribution is a valid objective function to minimize in order to optimize a wave function. [4]

(b) Explain why it is relatively difficult to optimize parameters that affect the nodal surface of the trial wave function by unreweighted variance minimization. [2]

(c) List and briefly describe other approaches for optimizing parameters in QMC. [4]

5. (a) (i) State how the variance of the local-energy distribution $\sigma^2_{E_L}$ is related to the standard error in the mean energy $\sigma_{\bar{E}}$. [3]

(ii) Describe how $\sigma^2_{E_L}$ can be reduced for a given system. [2]

(b) Suppose you run a variational Monte Carlo calculation and afterwards you realize that you need to reduce the standard error in the mean energy by a factor of two. How long does the continuation run need to be? [2]

(c) Explain what is meant by *serial correlation*. Describe the reblocking algorithm, and explain why it works. Draw a picture of a typical reblocking plot to aid your answer. [3]

6. Who is the best looking of the TTI Summer School staff? Is it (a) Neil Drummond, (b) Mike Towler or (c) Sam Azadi? FYI, Mike marks the exam.

Comments and suggestions

Do you have any comments or suggestions regarding the summer school?

Do you have any comments or suggestions regarding CASINO? Do you find it user-friendly? What do you think could be improved?