Cornell Basic Training Lab for QMC Module: Variational and Diffusion Monte Carlo for ground and 1^{st} excited state of 2-electron atom/ion

Tyler Anderson and Cyrus Umrigar

I. INTRODUCTION

We will implement toy VMC and DMC programs in Python to calculate the ${}^1S$ ground states of He and H^-, and the ${}^3S$ first excited state of Helium. Of course the same program could be used for the ${}^1S$ and ${}^3S$ states of any 2-electron ion. VMC will give a variational upper bound for all the three states, whereas DMC will give the exact energies (aside from statistical error and Trotter error, both of which can be systematically reduced with a relatively modest increase in computer time). The program is a "toy" in that a) it will work only for 2-electron atoms/ions, b) we will use much simpler trial wavefunctions than we would in a research code for these systems, and c) that we will not be concerned very much about fast execution. Nevertheless, this program will illustrate some of the important concepts in VMC and DMC.

Most of the code is already written, but some lines are missing (look for "XXX" in the code) and you have to provide them. We will build up the code in steps, testing each step as we go. The parts of this writeup where you have to provide answers are in blue. As you perform the various programming tasks, fill out the corresponding portions of this writeup. When you are all done, you will submit the completed writeup.

For a 2-electron atom, the general Hamiltonian for a molecule

$$H = -\frac{1}{2}\sum_{i}^{N_{\rm elec}} \nabla_i^2 + \sum_{\alpha}^{N_{nuc}}\sum_{\beta}^{\alpha-1} \frac{Z_\alpha Z_\beta}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} - \sum_{\alpha}^{N_{nuc}}\sum_{i}^{N_{\rm elec}} \frac{Z_\alpha}{|\mathbf{r}_\alpha - \mathbf{r}_i|} + \sum_{i}^{N_{\rm elec}}\sum_{j}^{i-1} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{1}$$

reduces to

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}},$$

where the nucleus is at the origin, $r_i = |\mathbf{r}_i|$ and $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$.

II. SIMPLE GROUND STATE TRIAL WAVEFUNCTION

A frequently used ansatz for molecular wavefunctions is the multi-Slater-Jastrow form:

$$\Psi_T(\mathbf{r}_1 \cdots \mathbf{r}_n) \;=\; D \times J = \left(\sum_{i}^{N_{det}} d_i \mathrm{D}_i^{\uparrow}\,\mathrm{D}_i^{\downarrow}\right) \times \prod_{i<j,\alpha} J(r_{ij}, r_{i\alpha}, r_{j\alpha}) \tag{2}$$

$\mathrm{D}^{\uparrow}$ and $\mathrm{D}^{\downarrow}$ are determinants of single-particle orbitals ϕ for up (↑) and down (↓) spin electrons respectively. Here we use a much simplified form of the above:

$$\psi\left(\mathbf{r}_1, \mathbf{r}_2\right) \;=\; D \times J = \phi(r_1)\phi(r_2)J(r_{12}). \tag{3}$$

The simplifications we have made are that instead of using multiple determinants, we use just a single up-spin and down-spin determinant (which reduce here to just 1-body orbitals), and that the 3-body (e-e-n) Jastrow has been replaced by just a 2-body (e-e) Jastrow,

$$J\left(r_{12}\right) = \exp\left\{\frac{b_1 r_{12}}{1+b_2 r_{12}}\right\}. \tag{4}$$

Further, we choose the orbitals to be just a single exponential (as is the case for the ground state of a hydrogenic atom), i.e.,

$$\phi\left(r_i\right) = e^{-\zeta r_i}. \tag{5}$$

Note that we do not bother with normalization factors, since they drop out when one does QMC.

$$D(\mathbf{r}_1,\mathbf{r}_2) = e^{-\zeta(r_1+r_2)} \tag{6}$$

$$\frac{\nabla D(\mathbf{r}_1,\mathbf{r}_2)}{D(\mathbf{r}_1,\mathbf{r}_2)} = \frac{\nabla_1 D(\mathbf{r}_1,\mathbf{r}_2)+\nabla_2 D(\mathbf{r}_1,\mathbf{r}_2)}{D(\mathbf{r}_1,\mathbf{r}_2)} = -\zeta(\hat{r}_1+\hat{r}_2) \tag{7}$$

$$\frac{\nabla^2 D(\mathbf{r}_1,\mathbf{r}_2)}{D(\mathbf{r}_1,\mathbf{r}_2)} = \frac{\nabla_1^2 D(\mathbf{r}_1,\mathbf{r}_2)+\nabla_2^2 D(\mathbf{r}_1,\mathbf{r}_2)}{D(\mathbf{r}_1,\mathbf{r}_2)} = 2\zeta\left(\zeta-\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\right) \tag{8}$$

$$J(r_{12}) = e^{\frac{b_1 r_{12}}{(1+b_2 r_{12})}} \tag{9}$$

$$\frac{\nabla J(r_{12})}{J(r_{12})} = \frac{\nabla_1 J(\mathbf{r}_1,\mathbf{r}_2)+\nabla_2 J(\mathbf{r}_1,\mathbf{r}_2)}{J(r_{12})} = \frac{b_1}{(1+b_2 r_{12})^2}\hat{r}_{12} \tag{10}$$

$$\frac{\nabla^2 J(\mathbf{r}_1,\mathbf{r}_2)}{J(r_{12})} = \frac{\nabla_1^2 J(\mathbf{r}_1,\mathbf{r}_2)+\nabla_2^2 J(\mathbf{r}_1,\mathbf{r}_2)}{J(r_{12})} = \frac{2b_1}{(1+b_2 r_{12})^2}\left(\frac{2}{r_{12}}+\frac{b_1}{(1+b_2 r_{12})^2}-\frac{2b_2}{(1+b_2 r_{12})}\right) \tag{11}$$

$$\mathbf{V} \equiv \frac{\nabla(DJ)}{DJ} = \frac{\nabla D}{D}+\frac{\nabla J}{J} \tag{12}$$

$$\frac{\nabla^2(DJ)}{DJ} = \frac{\nabla^2 D}{D}+\frac{\nabla^2 J}{J}+2\frac{\nabla D\cdot\nabla J}{DJ} \tag{13}$$

We will refer to the $3N_{\text{elec}} = 6$ dimensional vector, $\mathbf{V}$ as the drift velocity.

Plugging in this wavefunction and Hamiltonian, one can show that the local energy is given by

$$\begin{aligned} E_L = \frac{1}{\psi}H\psi = -\zeta^2+(\zeta-Z)\left(\frac{1}{r_1}+\frac{1}{r_2}\right)+\frac{1}{r_{12}}\left(1-\frac{2b_1}{\left(1+b_2 r_{12}\right)^2}\right) \\ +\frac{2b_1 b_2}{\left(1+b_2 r_{12}\right)^3}-\frac{b_1^2}{\left(1+b_2 r_{12}\right)^4}+\frac{\zeta b_1}{\left(1+b_2 r_{12}\right)^2}\hat{r}_{12}\cdot\left(\hat{r}_1-\hat{r}_2\right). \end{aligned} \tag{14}$$

Q1. Implement these two components of the wavefunction and their gradients and Laplacians in wavefunction.py:
Within wavefunction.py there are functions that test your implementation by calculating the gradients and Laplacians numerically, and print out the difference between the numerical evaluation and the analytic one. The numerical

evaluation is done for different discretization steps, Δ. It does this test for the determinantal and the Jastrow parts separately before doing the product wavefunction to help you debug each part separately. Once you think it is working, fill out the table below to show what you get for the Slater-Jastrow wavefunction.

TABLE I. Check that gradient and Laplacian are consistent with the wavefunction for the Slater-Jastrow wavefunction. (Should do this check for each form of the wavefunction before going further.)

Δ	gradient error	Laplacian error
1×10^{-3}	3.34×10^{-7}	1.16×10^{-6}
1×10^{-4}	3.35×10^{-9}	2.67×10^{-8}
1×10^{-5}	3.65×10^{-11}	5.81×10^{-6}
1×10^{-6}	1.59×10^{-10}	1.31×10^{-3}
1×10^{-7}	1.08×10^{-9}	1.42×10^{-1}
1×10^{-8}	1.37×10^{-8}	8.17

Why is there an optimal value of Δ for both the gradient and the Laplacian? Why is the optimal Δ larger for the Laplacian than for the gradient?
Because there is a tradeoff between truncation error and round off error. The roundoff error is more severe for the Laplacian because it is a higher derivative, so one cannot go to as small a Δ.

The form of the wavefunction above has 3 variational parameters, ζ, b_1, b_2. However, instead of choosing all of them to minimize the energy, we will choose two of them to avoid having any divergences in the local energy, i.e., we will impose *cusp conditions*. What values must two of these parameters take to do this?
$\zeta = 2,\ b_1 = 1/2$

After having imposed the cusp conditions, there are no divergences in E_L. Is E_L continuous now?
Hint: Look at the last term of E_L in Eq. 14.
Consider both electrons infinitesmally close to the nucleus. The dot product changes discontinuously when say electron 1 moves from being on the same side of the nucleus as electron 2, to being on the opposite side. So, imposing the cusp-condition got rid of the divergence in E_L but there is still a discontinuity. This discontinuity is not terribly important because it is fairly rare for both electrons to be very close to the nucleus.

III. METROPOLIS-HASTINGS METHOD AND VARIATIONAL MONTE CARLO

We discussed during the lectures that one can greatly improve the sampling efficiency (reduce T_corr) by making a good choice for the Metropolis-Hastings proposal probability. Here, we will not go for the optimal choice, which is a bit complicated to implement, but instead we will make a choice which is reasonably good and has the virtue that we can reuse it when we implement diffusion Monte Carlo, namely:

$$T(\mathbf{R}_\mathrm{f}|\mathbf{R}_\mathrm{i}) = \frac{1}{(2\pi\tau)^{3/2}} \exp\left[\frac{-(\mathbf{R}_\mathrm{f} - \mathbf{R}_\mathrm{i} - \mathbf{V}(\mathbf{R}_\mathrm{i})\tau)^2}{2\tau}\right], \quad \mathbf{V}(\mathbf{R}_\mathrm{i}) = \frac{\nabla\Psi(\mathbf{R}_\mathrm{i})}{\Psi(\mathbf{R}_\mathrm{i})} \tag{15}$$

$$A(\mathbf{R}_\mathrm{f}|\mathbf{R}_\mathrm{i}) = \min\left\{1, \frac{T(\mathbf{R}_\mathrm{i}|\mathbf{R}_\mathrm{f})\ |\Psi|^2(\mathbf{R}_\mathrm{f})}{T(\mathbf{R}_\mathrm{f}|\mathbf{R}_\mathrm{i})\ |\Psi|^2(\mathbf{R}_\mathrm{i})}\right\}. \tag{16}$$

Given the initial position $\mathbf{R}_\mathrm{i}$, the proposed coordinate $\mathbf{R}_\mathrm{f}$ is chosen as:

$$\mathbf{R}_{\rm f} = \mathbf{R}_{\rm i} + \mathbf{V}(\mathbf{R}_{\rm i})\tau + \sqrt{\tau}N \tag{17}$$

where N is a normally distributed random variable. The second and third terms are called the drift and diffusion terms, respectively.

We can check whether we have implemented this correctly by running Metropolis-Hastings on a wavefunction where we know the kinetic energy and potential energy analytically, e.g., the Slater part of our Slater-Jastrow wavefunction. This is something that many of us did in our elementary quantum mechanics classes. We have

$$\begin{aligned} E_{\rm kin} &= \frac{\langle -\frac{1}{2}(\nabla_1^2 + \nabla_2^2)D\rangle}{\langle D\rangle} = \zeta^2 && (18)\\ E_{en} &= \frac{\langle -Z(\frac{1}{r_1} + \frac{1}{r_1})D\rangle}{\langle D\rangle} = -2Z\zeta && (19)\\ E_{ee} &= \frac{\langle (\frac{1}{r_{12}})D\rangle}{\langle D\rangle} = \frac{5}{8}\zeta && (20) \end{aligned}$$

So, we have

$$E(\zeta) = \zeta^2 - 2Z\zeta + \frac{5}{8}\zeta \tag{21}$$

which has a minimum of

$$E_{\rm min} = -\left(Z - \frac{5}{16}\right)^2, \quad \text{for} \quad \zeta = Z - \frac{5}{16}. \tag{22}$$

However, to test the program, you can do whatever value of ζ you like and compare to Eqs. 18, 19+20, 21.

Q2. Implement Metropolis-Hastings, try wavefunction for He and H$^-$:
Edit qmc.py to implement Eqs. 15, 16, and 17. Now you should have a functional VMC program. To test for correctness, set wavefunction_type in the input to “Slater" (or you can keep it as “Slater-Jastrow" and just set $b_1 = 0$) and run the program for some value of ζ and check that you get the expected value.

Why is the statistical error of the energy much smaller than that of its components?
Because the energy has zero-variance when $\Psi_{\rm T} = \Psi_0$, whereas its components have finite variance.

Once you have Metropolis-Hastings working for “Slater" it will also work for “Slater-Jastrow". So, now you can run it for various values of our one variational parameter, b_2 and fill out the blank spots in the table below. You can go to the runs:

```
cd runs/He_1S
../run vmc_He*inp &
```

So, you are doing a 1-parameter optimization by hand. In a research-level QMC program it is a simple matter to optimize a wavefunction with a few dozen parameters to get an accuracy of better than a microHartree for such simple systems, as shown at the bottom of Table II.

TABLE II. Variational energy, statistical error, σ, and $T_{\rm corr}$ for various simple He atom wavefunctions in Hartree units. The statistical error in the last digit of $E_{\rm VMC}$ is shown in parentheses.

wavefunction	ζ	b_1	b_2	$E_{\rm vmc}$ (stat error)	σ	$T_{\rm corr}$
$e^{-\zeta(r_1+r_2)}$	2	–	–	−2.75	–	–
$e^{-\zeta(r_1+r_2)}$	1.6875	–	–	−2.84765	–	–
$\Psi_{\rm HF} = \psi(r_1)\psi(r_2)$	–	–	–	−2.86168	–	–
$e^{-\zeta(r_1+r_2)+\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	2.	0.5	0	−2.85623(76)	0.490	3.9
$e^{-\zeta(r_1+r_2)+\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	2.	0.5	0.1	−2.87630(58)	0.370	4.0
$e^{-\zeta(r_1+r_2)+\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	2.	0.5	0.15	−2.87721(58)	0.335	4.8
$e^{-\zeta(r_1+r_2)+\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	2.	0.5	0.2	−2.87592(59)	0.312	5.7
$e^{-\zeta(r_1+r_2)+\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	2.	0.5	0.3	−2.86999(64)	0.292	7.7
$e^{-\zeta(r_1+r_2)+\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	2.	0.5	0.4	−2.86237(70)	0.296	9.0
$e^{-\zeta(r_1+r_2)+\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	2.	0.5	0.5	−2.85529(77)	0.312	9.7
57-parameter wavefn	2.	0.5	–	−2.903724(0)	0.003	1.1

What is the value of b_2 (to 2 digit precision) that minimized the energy?
Is the statistical error minimum (for a given # of MC steps) also minimized for about the same value?
What about σ and $T_{\rm corr}$?

Once you have a near optimal value of b_2, find a near-optimal value of the time-step τ, by filling out the following table. Use the same values of N_s and N_b for all the τ, but make sure that N_s is large enough that you are not significantly underestimating $T_{\rm corr}$ and that N_b is large enough that you have enough statistics.

TABLE III. Test for near-optimal τ.

τ	$E_{\rm vmc}$ (stat error)	σ	$T_{\rm corr}$
0.05	−2.87801(73)	0.335	7.5
0.1	−2.87721(58)	0.335	4.8
0.2	−2.87710(56)	0.334	4.4
0.3	−2.87848(60)	0.334	5.2
0.4	−2.87785(74)	0.335	7.9

A. Similar wavefunction for H$^-$

The above wavefunction (with ζ changed appropriately of course) gives reasonable energies for 2-electron positive ions, Li$^+$, Be^{2+}, $\cdots$. The negative ion, H$^-$ ion is stable, i.e., it has a lower energy than H, but it is a bit more challenging than the positive ions.

Q3. Does the above wavefunction predict a stable H$^-$ ion?
Fill out the top 4 lines of Table IV.

B. Better wavefunction for H$^-$

The H$^-$ ion is much more extended than a H or a He atom, and it has a lot of in-out correlation, i.e., much of the time one electron is close to the nucleus and the other electron is far away. So, we can improve upon our wavefunction by having one orbital that is compact and another that is more extended, We replace Eqs. 3 and 5 by

$$\psi\left(\mathbf{r}_1, \mathbf{r}_2\right) \;=\; D \times J = \big(\phi(r_1)\phi_2(r_2) + \phi_2(r_1)\phi(r_2)\big) J\left(r_{12}\right). \tag{23}$$

where ϕ is the same as before and ϕ_2 is

$$\phi_2\left(r\right) = e^{-\zeta_1 r} + (\zeta_1 - Z) r e^{-\zeta_2 r}. \tag{24}$$

Note that we have chosen a form for $\phi_2(r)$ that satisfies the cusp condition, as does $\phi(r)$ in Eq. 5 with $\zeta = Z$.

Q4. Try the better wavefunction for H$^-$:
Use the wavefunction in Eqs. 23, 4, 24 with $\zeta = 1, \zeta_1 = 1.18, \zeta_2 = 0.55, b_2 = 0.27$ to see whether it predicts a stable H$^-$ ion.

TABLE IV. Variational energy, statistical error, σ, and $T_{\rm corr}$ for various simple H$^-$ ion wavefunctions in Hartree units. The statistical error in the last digit of $E_{\rm VMC}$ is shown in parentheses.

wavefunction	ζ	ζ_2	ζ_3	b_1	b_2	$E_{\rm vmc}$ (stat error)	σ	$T_{\rm corr}$
$\phi(r_1)\phi(r_2)e^{\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	1.	–	–	0.5	0.0	$-0.46724(44)$	0.211	4.3
$\phi(r_1)\phi(r_2)e^{\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	1.	–	–	0.5	0.1	$-0.49515(32)$	0.142	4.0
$\phi(r_1)\phi(r_2)e^{\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	1.	–	–	0.5	0.2	$-0.48188(38)$	0.135	8.0
$\phi(r_1)\phi(r_2)e^{\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	1.	–	–	0.5	0.3	$-0.46817(44)$	0.153	8.4
$\big(\phi(r_1)\phi_2(r_2) + \phi_2(r_1)\phi(r_2)\big)e^{\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	1.	1.18	0.55	0.5	0.20	$-0.52516(12)$	0.055	4.6
$\big(\phi(r_1)\phi_2(r_2) + \phi_2(r_1)\phi(r_2)\big)e^{\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	1.	1.18	0.55	0.5	0.25	$-0.526566(89))$	0.046	3.8
$\big(\phi(r_1)\phi_2(r_2) + \phi_2(r_1)\phi(r_2)\big)e^{\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	1.	1.18	0.55	0.5	0.30	$-0.526545(88)$	0.045	3.8
$\big(\phi(r_1)\phi_2(r_2) + \phi_2(r_1)\phi(r_2)\big)e^{\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	1.	1.18	0.55	0.5	0.35	$-0.52587(10)$	0.051	4.2
57-parameter wavefn	1.	–	–	0.5	–	$-0.527751(0)$	–	–

C. 1st excited state of He

The first excited state of He has ^{3}S symmetry. So, now both electrons are spin up, and instead of just taking a product of the orbitals we must form a determinant from the orbitals. Other than that we can use the same form of the orbitals we had above, except for one other small detail. For parallel-spin electrons in 3D, the cusp in the wavefunction is 1/4 rather than 1/2, so use $b_1 = 0.25$. However, since parallel-spin electrons never get very close it does not really matter very much if you forget to do this. So, the wavefunction is

$$\psi\left(\mathbf{r}_1, \mathbf{r}_2\right) = \begin{vmatrix} \phi\left(r_1\right) & \phi\left(r_2\right) \\ \phi_2\left(r_1\right) & \phi_2\left(r_2\right) \end{vmatrix} \exp\left\{\frac{b_1 r_{12}}{1 + b_2 r_{12}}\right\}. \tag{25}$$

There is one other thing we need to take care of for any system where the wavefunction has nodes. The drift velocity, $\mathbf{V}$, in Eq. 12 diverges at nodes. So, on the rare occasions when a walker lands very close to a node, the drift shoots it out a very long distance, and since the probability of the reverse Metropolis-Hastings move is small, the forward move has a low probability of being accepted. This is a problem even in VMC, but becomes a more serious problem in DMC because the local energy diverges to $+\infty$ on one side of the node and to $-\infty$ on the other side. On the $-\infty$ side one can get a multiplicity of walkers that stay stuck there. This problem is easily taken care of by thinking in terms of doing a crude average of the velocity over the time-step τ. Near a node, make a linear approximation for Ψ, in which case $V = 1/r$ where $r = \Psi/|\nabla\Psi|$ is the estimated distance to the node. In that case

$$\begin{aligned}
\frac{\mathrm{d}r}{\mathrm{d}t} &= \frac{1}{r} \\
\frac{r^2(\tau) - r^2(0)}{2} &= \tau \\
r &= \sqrt{(r^2(0) + 2\tau)} \\
\bar{V}\tau &= \frac{r(\tau) - r(0)}{\tau} = \frac{\sqrt{(r^2(0) + 2\tau)} - r(0)}{\tau} \\
\bar{V} &= \frac{-1 + \sqrt{1 + 2V^2\tau}}{V\tau} \\
\bar{\mathbf{V}} &= \frac{-1 + \sqrt{1 + 2V^2\tau}}{V^2\tau}\mathbf{V}
\end{aligned} \tag{26}$$

In the limit of small τ we recover $\bar{\mathbf{V}} = \mathbf{V}$.

Q5. Try this wavefunction for ^{3}S state of He:
Use the wavefunction in Eq. 25, with $\zeta = 2, \zeta_1 = 1.48, \zeta_2 = 0.62$, and various b_2 to compute the energy of the ^{3}S state of He.

TABLE V. Variational energy, statistical error, σ, and $T_{\rm corr}$ for the ^{3}S first excited state of He atom using the wavefunction in Eq. 25 in Hartree units. The statistical error in the last digit of $E_{\rm VMC}$ is shown in parentheses.

wavefunction	ζ	ζ_2	ζ_3	b_1	b_2	$E_{\rm vmc}$ (stat error)	σ	$T_{\rm corr}$
$(\phi(r_1)\phi_2(r_2) - \phi_2(r_1)\phi(r_2))e^{\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	2.	1.48	0.62	0.25	0.30	$-2.17441(10)$	0.041	6.2
$(\phi(r_1)\phi_2(r_2) - \phi_2(r_1)\phi(r_2))e^{\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	2.	1.48	0.62	0.25	0.40	$-2.175043(69)$	0.027	6.3
$(\phi(r_1)\phi_2(r_2) - \phi_2(r_1)\phi(r_2))e^{\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	2.	1.48	0.62	0.25	0.50	$-2.175067(51)$	0.022	5.0
$(\phi(r_1)\phi_2(r_2) - \phi_2(r_1)\phi(r_2))e^{\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	2.	1.48	0.62	0.25	0.60	$-2.175108(46)$	0.024	3.8
$(\phi(r_1)\phi_2(r_2) - \phi_2(r_1)\phi(r_2))e^{\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	2.	1.48	0.62	0.25	0.80	$-2.174948(56)$	0.030	3.4
$(\phi(r_1)\phi_2(r_2) - \phi_2(r_1)\phi(r_2))e^{\frac{b_1 r_{12}}{1+b_2 r_{12}}}$	2.	1.48	0.62	0.25	1.00	$-2.174790(70)$	0.037	3.6
24-parameter wavefn	2.	–	–	0.25	–	$-2.175229(1)$	–	–

IV. DIFFUSION MONTE CARLO

So far we have used VMC to calculate variational upper bounds for the ground states of He and H$^-$, and for the first excited state of He. The energies were accurate to 2, 3, and 4 digits for these 3 systems, respectively.

We will now use DMC to calculate the “exact" energies of these states. By “exact" we mean exact aside for statistical error and time-step (Trotterization) error, since both of these errors can be made systematically smaller by using more computer time. The statistical error goes down as the inverse square root of the computer time and the Trotterization error goes down at least as the inverse of the computer time (by using smaller τ).

Q6. Explain why all the 3 states we calculate have no fixed-node error:

We chose the Metropolis-Hastings proposal probability to be the norm-conserving part of the DMC propagator so that it could do double duty in VMC and DMC. So, now what remains to be done is to edit the `reweight` function in `qmc.py` to multiply the weights of the walkers at each step by

$$w = e^{\tau\left(E_{\mathrm{T}} - 0.5(E_{\mathrm{L}}(\mathbf{R}_{\mathrm{old}}) + E_{\mathrm{L}}(\mathbf{R}_{\mathrm{new}}))\right)} \tag{27}$$

where E_{T} is an estimate of the energy, discussed in ingredient 3 below.

In VMC, the Markov proposal probability is normalized, whereas in PMC methods, such as DMC, the projector is not. This necessitates the following 4 small additional ingredients in PMC methods:

1. **Weights:** The walkers carry weights which change from generation to generation.

2. **Walker population and branching (birth/death):** If we have just a single walker its weight would do a random walk and the contributions of a small fraction of the generations of the walk would dominate, even though the computer time spent on each generation is the same. So, we get around this by having a population of walkers, and employ a *branching* algorithm to keep the weights of the walkers either exactly or approximately the same. There are three branching algorithms that are commonly used – *integerize, split-join* and *stochastic reconfiguration.* The latter two are preferred a bit because they avoid unnecessary fluctuations, but the difference in their performance is not big.

3. **Population control:** By having a walker population and a branching algorithm, we make the weights of the walkers of a given generation approximately the same. However, the total weights of a generation may vary greatly between generations. Hence we need to exercise *population control.* One way to do this is to define

$$E_{\mathrm{T}} = E_{\mathrm{est}} + \frac{\log(W_{\mathrm{target}}/W_{\mathrm{gen}})}{N_{\mathrm{gen}}} \tag{28}$$

   where E_{est} is the best current estimator for the energy, W_{target} is the target weight of a generation, W_{gen} is the weight of the current generation, and N_{gen} controls the strength of the population control. Roughly, N_{gen} is the average number of generations after which the population tends to return to its target value. Larger values of N_{gen} results in a smaller population control bias coming from smaller fluctuations in E_{T} but only modestly larger fluctuations in W_{gen}. Reasonable choices for N_{gen} are say 10 or 100 or $1/\tau$ – it does not matter very much.

4. **Correct for population control error:** Having a fluctuating, rather than a constant E_{T} results in a small positive population control bias, because fluctuations in W_{gen} are correlated with fluctuations in the average energy of the generation and therefore with E_{T}. It is straightforward to correct for this bias (see the pedagogic article) and there is no reason not to do that. However, most practitioners, simply rely on using a large enough population to make the error negligible since it scales as $1/W_{\mathrm{target}}$. For the accuracy we care about in this lab, we will not bother with implementing the correction for the population control bias.

Q7. DMC energies for ^{1}S states of He and H$^-$ and ^{3}S states of He:

Implement Eqs. 27 and 28 in qmc.py. Then calculate the DMC energies for ^{1}S states of He and H$^-$ and ^{3}S states of He to fill out the tables below. We do each of these for a few values of τ to make sure that the time-step error is negligible compared to the desired accuracy and to extrapolate to $\tau = 0$ if necessary. Make sure that N_s is large enough that you are not significantly underestimating T_{corr} and that N_b is large enough that you have enough statistics.

TABLE VI. DMC energy, statistical error, σ, and T_{corr} for various simple He atom wavefunction in Hartree units for various τ. The statistical error in the last digit of E_{VMC} is shown in parentheses.

τ	E_{dmc} (stat error)	σ	T_{corr}
0.005	-2.9010(21)	0.338	75.4
0.01	-2.9025(17)	0.337	51.3
0.02	-2.9019(13)	0.337	29.4
0.05	-2.90127(74)	0.337	9.5
0.1	-2.90215(70)	0.338	8.6
0.15	-2.90238(58)	0.338	5.9
0.2	-2.90203(45)	0.338	3.6
0.25	-2.90367(48)	0.338	4.0
0.30	-2.90569(50)	0.339	4.3
0.40	-2.90958(54)	0.339	5.0

TABLE VII. Same as Table VI but for the H^- ion using the wavefunction in Eq. 23

τ	E_{dmc} (stat error)	σ	T_{corr}
0.02	-0.52827(26)	0.046	65.9
0.05	-0.52761(17)	0.046	29.0
0.1	-0.52775(12)	0.046	12.8
0.2	-0.527682(99)	0.046	9.2
0.4	-0.527863(73)	0.046	5.0
0.5	-0.527873(73)	0.046	5.0
0.6	-0.528024(65)	0.046	4.0
1.0	-0.528162(82)	0.047	6.2

TABLE VIII. Same as Table VI but for the ^{3}S state of He using the wavefunction in Eq. 25

τ	E_{dmc} (stat error)	σ	T_{corr}
0.01	-2.17516(13)	0.024	57.5
0.02	-2.175071(98)	0.024	34.6
0.05	-2.175205(61)	0.024	13.1
0.1	-2.175168(46)	0.024	7.7
0.15	-2.175255(40)	0.024	5.6
0.2	-2.175237(43)	0.023	6.8
0.3	-2.175209(36)	0.024	4.7
0.4	-2.175272(34)	0.023	4.2
0.5	-2.175211(46)	0.023	8.0
0.6	-2.175338(48)	0.023	8.2

How close do you get to the highly accurate values given in the VMC tables?