Ground State Energy of He atom calculated using Variational Quantum Monte-Carlo Method

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Here, we search for the ground state energy of He atom using the variational monte-carlo (VMC) method. It is found to be approximately -2.896 hartrees.

I. METHODS

According to the quantum statistical mechanics, the average energy of the Helium atom can be computed as

$$\langle E\rangle = \frac{\int d\mathbf{r}_1 d\mathbf{r}_2 \psi^*(\mathbf{r}_1,\mathbf{r}_2) H\psi(\mathbf{r}_1,\mathbf{r}_2)}{\int d\mathbf{r}_1 d\mathbf{r}_2 \psi^*(\mathbf{r}_1,\mathbf{r}_2)} \quad (1)$$

$$= \int d\mathbf{r}_1 d\mathbf{r}_2 \rho(\mathbf{r}_1,\mathbf{r}_2) E_L(\mathbf{r}_1,\mathbf{r}_2), \quad (2)$$

where the Hamiltonian for the system of two electrons interactiong with each other and the heavy nucleus in atomic units ($m = c = \hbar = 1$) is

$$H = -\frac{1}{2}\nabla^2_{\mathbf{r}_1} - \frac{1}{2}\nabla^2_{\mathbf{r}_2} - \frac{2}{|\mathbf{r}_1|} - \frac{2}{|\mathbf{r}_2|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (3)$$

Here, the local energy is given by

$$E_L(\mathbf{r}_1,\mathbf{r}_2) \equiv \frac{1}{\psi(\mathbf{r}_1,\mathbf{r}_2)} H\psi(\mathbf{r}_1,\mathbf{r}_2), \quad (4)$$

and the distribution function is given by

$$\rho(\mathbf{r}_1,\mathbf{r}_2) \equiv \frac{\psi^*(\mathbf{r}_1,\mathbf{r}_2)\psi(\mathbf{r}_1,\mathbf{r}_2)}{\int d\mathbf{r}_1 d\mathbf{r}_2 \psi^*(\mathbf{r}_1,\mathbf{r}_2)\psi(\mathbf{r}_1,\mathbf{r}_2)}. \quad (5)$$

In the expressions above ψ is the two electron wave function, and $\mathbf{r}_1$ and $\mathbf{r}_2$ are their corresponding positions. We compute the multivariable integral using the Monte-Carlo method as follows.

$$\langle E\rangle = \frac{1}{M}\sum_i^M E_L(\mathbf{r}_{1i},\mathbf{r}_{2i}) + \mathcal{O}(\frac{1}{\sqrt{M}}) \quad (6)$$

where $\mathbf{r}_{1i}$ and $\mathbf{r}_{2i}$ are chosen according to the distribution function $\rho(\mathbf{r}_1,\mathbf{r}_2)$. Our choice of the variational wave function is

$$\psi_{ab}(\mathbf{r}_1,\mathbf{r}_2) = e^{-2\frac{\mathbf{r}_1+a\mathbf{r}_1^2}{1+\mathbf{r}_1}} e^{-2\frac{\mathbf{r}_2+a\mathbf{r}_2^2}{1+\mathbf{r}_2}} e^{\frac{1}{2}\frac{\mathbf{r}_{12}}{1+b\mathbf{r}_{r12}}}, \quad (7)$$

where a and b are the variational parameters. By changing a and b we search for the ground state energy of the system.

The short description of the numerical procedure is the following. First we generate 500 walkers (each has six coordinates) with randomly selected inintial positions between -0.5 and 0.5. Then we propose a trial step $\mathbf{R'} = \mathbf{R} + \delta(2.0 * \mathcal{U} - 1.0)$ for each walker. Here, U is a random number drawn from a uniform distribution. If $\psi(\mathbf{R'})/\psi(\mathbf{R}) > \mathcal{U}$ the step is accepted, otherwise, rejected. The the local energy is computed for the given distribution of walkers according to their current positions. In computing the local energy we use a numerical derivative of the wave function. The average energy is then computed by taking the averge over 1000 samples. We perform the procedure by varying the variational parameters between 0.0 and 1.5.

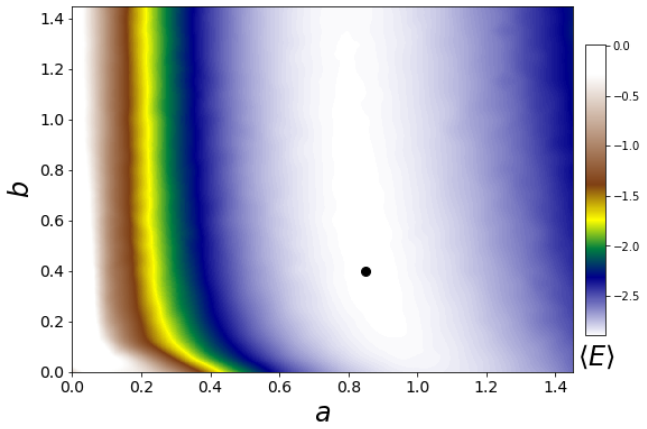

FIG. 1. Ground state energy of He as a function of variational parameters a and b. The mininmum point on the energy surface is shown by the black marker.

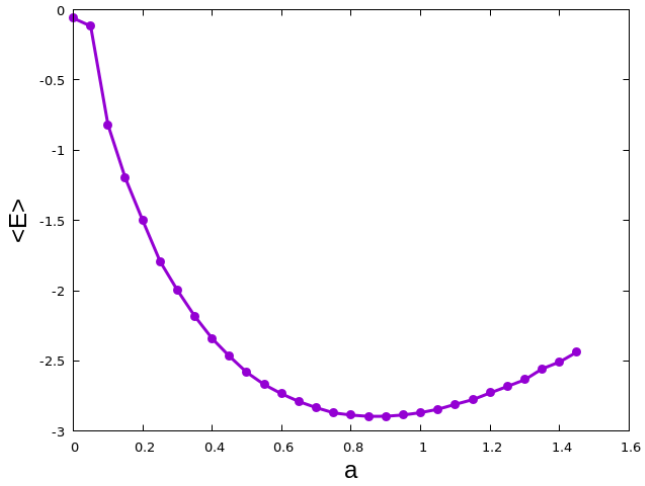

FIG. 2. Ground state energy as a function of a at $b = 0.40$.

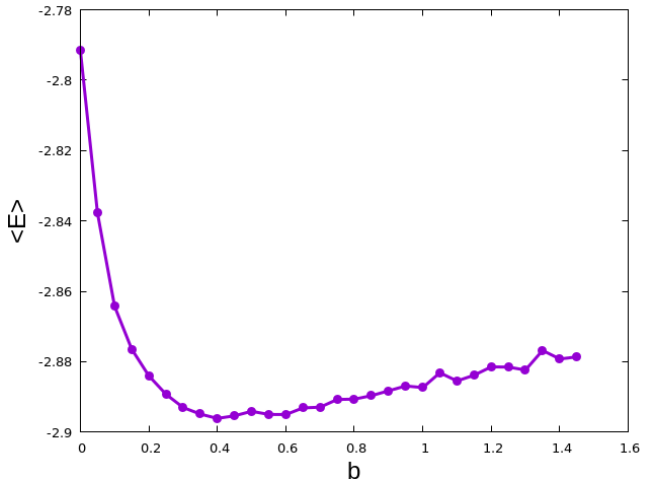

FIG. 3. Ground state energy as a function of b at $a = 0.85$.

II. RESULTS

In Fig. **??**, we present $\langle E \rangle$ as a function of the variational paramemeters a and b in false color plot. Its minimum value is marked by the black circular marker. It is illustrative to see the cut along the constant values of the variational parameters crosssing this point. They are presented in Fig. **??** and in Fig. **??**. The ground state energy or the minimum point on this energy surface is $E_g \approx -2.896$ hartrees, which correspondes to $a = 0.85$ and $b = 0.40$ variational parameters.

III. CONCLUSIONS

We have computed the average energy of the Helium atom as a function of two variational parameters and obtained its ground state. Our result agrees well with the expreminentally measured value.

APPENDIX: CODES

```
#include<iostream>
#include<fstream>
#include<ctime>
#include<cstdlib>
#include<vector>
#include<cmath>
#include<algorithm>
#include<iomanip>

        using namespace std;

const int Nd = 3;
const int Nw = 500;
double a;
double b;
double dx = 0.2;
double energy;
double random_number(){return (double)rand()/(
    RAND_MAX + 1.0);}

double psi(double re1[], double re2[]){

  double r1 = 0, r2 = 0, r12 = 0;
  for (int i = 0; i < Nd; i++){
    r1 +=  re1[i] * re1[i];
    r2 +=  re2[i] * re2[i];
    r12 += (re1[i] - re2[i]) * (re1[i] - re2[i])
    ;
  }
  r1 = sqrt(r1);
  r2 = sqrt(r2);
  r12 = sqrt(r12);
  double pow = -2.0 *(r1 + a * r1 * r1)/(1.0 +
    r1) - 2.0 * (r2 + a * r2 * r2)/(1.0 + r2) +
    0.5 * r12 / (1.0 + b * r12);
  return exp(pow);
}

double lap(double re1[], double re2[]) {

        double rp[Nd], rm[Nd], del2[Nd];
        double lap1 = 0.0, lap2 = 0.0;
        double h = 0.001;
        for (int i = 0; i < Nd; i++){
                for (int j = 0; j < Nd; j++){
                        if(j==i){
      rp[j] = re1[j] + h;
                        rm[j] = re1[j] - h;
      }
      else {
      rp[j] = re1[j];
                        rm[j] = re1[j];
      }
                }
                del2[i] = psi(rp, re2) - 2.0 *
    psi(re1,re2) + psi(rm,re2);
                lap1 += del2[i]/(h*h);
        }

        for (int i = 0; i < Nd; i++){
                for (int j = 0; j < Nd; j++){
                        if(j==i){
      rp[j] = re2[j] + h;
                        rm[j] = re2[j] - h;
      }
      else {
      rp[j] = re2[j];
                        rm[j] = re2[j];

      }
                }
                del2[i] = psi(re1, rp) - 2.0 *
    psi(re1,re2) + psi(re1,rm);
                lap2 += del2[i]/(h*h);
        }

        return (lap1 + lap2)/psi(re1,re2);
}



double eloc(double re1[], double re2[]){

  double r1 = 0, r2 = 0, r12 = 0;
  for (int i = 0; i < Nd; i++){
    r1 +=  re1[i] * re1[i];
    r2 +=  re2[i] * re2[i];
```

```
    r12 += (re1[i] - re2[i]) * (re1[i] - re2[i])
    ;
  }
  r1 = sqrt(r1);
  r2 = sqrt(r2);
  r12 = sqrt(r12);


  double en = -0.5 * lap(re1,re2) - 2.0/r1 -
    2.0/r2 + 1.0/r12;
//  cout << "en:" << en << endl;
  return en;
}

struct Walker
{
  double r1[Nd], r2[Nd];
};

void initialize_walkers(vector<Walker> & walker)
    {
  for (int i = 0; i < Nw; i++){
    for (int j = 0; j < Nd; j++){
      walker[i].r1[j] = random_number() - 0.5;
      walker[i].r2[j] = random_number() - 0.5;
    }
  }
}

void metropolis_step(vector<Walker> & walker,
    int iw){
  double tempr1[Nd], tempr2[Nd];
  for (int j = 0; j < Nd; j++){
    tempr1[j]  = walker[iw].r1[j];
    tempr2[j]  = walker[iw].r2[j];
    tempr1[j] += dx * (2.0 * random_number() -
    1.0);
    tempr2[j] += dx * (2.0 * random_number() -
    1.0);
  }
  double prp = psi(tempr1,tempr2) * psi(tempr1,
    tempr2);
  double pr  = psi(walker[iw].r1, walker[iw].r2)
     * psi(walker[iw].r1, walker[iw].r2);
  if(prp/pr >= random_number()){
    for (int j = 0; j < Nd; j++){
      walker[iw].r1[j] = tempr1[j];
      walker[iw].r2[j] = tempr2[j];
    }
  }
  energy += eloc(walker[iw].r1, walker[iw].r2);
}

main(){
  srand(time(NULL));
  vector<Walker> walker(Nw);
  initialize_walkers(walker);
  double Nther = 2000;
  ofstream outfile("energy.dat");
  a = 0.0;
  while(a<=1.5){
    b = 0.0;
    while(b<=1.5){
      energy = 0.0;
      for (int j = 0; j < Nther; j++){
        for (int i = 0; i < Nw; i++){
    metropolis_step(walker,i);}
      }
      outfile << a << " "  << b << " " << energy
    /Nw/Nther << endl;
      b += 0.05;
  }
    a += 0.05;
  }

}
```

. /home/omo/advanced_comp_physisc/hw3/vmc_helium.cc