

Variational Quantum Monte-carlo

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Overview

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Section 1

Theory

The goal

The goal is to find the energy of the ground state of several atoms and diatomic molecules.

The Time-independent Schrödinger equation

$$E\psi = -\sum_{j=1}^N \frac{\hbar^2}{2m} \nabla_j^2 \psi + \hat{V}(x)\psi \quad (1)$$

The electron potential

The potential is here:

$$\hat{V}(x) = - \sum_{j=1}^N \frac{Ze^2}{(4\pi\epsilon_0)r_j} + \sum_{i=1, i < j}^N \frac{e^2}{(4\pi\epsilon_0)r_{ij}} \quad (2)$$

We here use atomic units so we can set some variables to 1.

$$m = e = \hbar = 4\pi\epsilon_0 = 1 \quad (3)$$

The full equation.

This reduces the problem to:

$$E\psi = \left[-\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \frac{Z}{r_i} + \sum_{i<j}^N \frac{1}{r_{ij}} \right] \psi(x) \quad (4)$$

Conversion table

We have here worked in atomic units, and to convert between SI units we use the table:

Quantity	SI	Atomic Units
Electron mass, m	$9.109 * 10^{-31} \text{ kg}$	1
Charge, w	$1.602 * 10^{-19} \text{ C}$	1
Planck's reduced constant, \hbar	$1.055 * 10^{-34} \text{ Js}$	1
Permittivity, $4 \pi \epsilon_0$	$1.113 * 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$	1
Energy, $\frac{e^2}{4\pi\epsilon_0 a_0}$	27.211 eV	1
Length, $a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$	$0.529 * 10^{-10}$	1

The Monte Carlo method is a stochastic method for integration using random numbers.

In one dimension this gives:

$$\int_a^b f(x) dx = \frac{1}{m} \left(\sum_{i=1}^m f(x_i) + \mathcal{O}\left(\frac{1}{m}\right) \right) \quad (5)$$

Here x_i are random numbers between a and b .

Monte Carlo in N dimensions

We can extend this to N dimensions.

$$\int \int \dots \int f(x_0, x_1 \dots x_N) dx_0 dx_1 \dots dx_N = \frac{1}{m^N} \left(\sum_{i=1}^m \sum_{i=1}^m \dots \sum_{i=1}^m f(x_0, x_1 \dots x_N) + \mathcal{O}\left(\frac{1}{m}\right) \right) \quad (6)$$

Expectational value of the energy.

The expectational value of the energy is given by:

$$\langle E \rangle = \frac{\int dR \psi^*(R) H(R) \psi(R)}{\int dR \psi^*(R) \psi(R)} \quad (7)$$

Splitting the energy

We rewrite this and split the equation into two parts.

$$\langle E \rangle = \frac{\int |\psi(\mathbf{R})|^2 \frac{\hat{H}\psi(\mathbf{R})}{\psi(\mathbf{R})} d\mathbf{R}}{\int |\psi(\mathbf{R})|^2 d\mathbf{R}} = \int \frac{|\psi(\mathbf{R})|^2}{\int |\psi(\mathbf{R})|^2 d\mathbf{R}} \left(\frac{\hat{H}\psi(\mathbf{R})}{\psi(\mathbf{R})} \right) d\mathbf{R}. \quad (8)$$

The probability function

The trial wave function serves as a mean to define the quantal probability function.

$$P(\mathbf{R}) = \frac{|\psi_T(\mathbf{R})|^2}{\int |\psi_T(\mathbf{R})|^2 d\mathbf{R}} \quad (9)$$

The Local energy

We define the local energy operator

$$\mathbf{E}_L(\mathbf{R}) = \frac{1}{\psi_T(\mathbf{R})} \mathbf{H} \psi_T(\mathbf{R}) \quad (10)$$

An approximation

This gives us the expression:

$$\langle E_L \rangle = \int P(R) E_L(R) dR \approx \frac{1}{N} \sum^N E_L(x_i) \quad (11)$$

That an integral is given by its mean value is a fundamental theorem in calculus.

The variational principle

The variational principle states that the expectation value of the Hamiltonian is an upper bound to the true ground state energy E_0

$$E_0 \leq \langle E \rangle \quad (12)$$

The Slater determinant

To find the wavefunction we use a slater determinant. We see that if two rows are equal the determinant becomes zero. This is in accordance with the pauli principle.

Also the slaterdeterminant is antisymmetric under the interchange of any pair of fermions.

$$\psi_D = \frac{1}{\sqrt{N}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \dots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \dots & \chi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(x_N) & \chi_2(x_N) & \dots & \chi_N(x_N) \end{vmatrix} \quad (13)$$

Splitting the Slater determinant

We can here split the Slater determinant into a up spin part and a downspin part.

$$\psi_D = |S \uparrow| |S \downarrow| \quad (14)$$

The Jastrow factor

To include two-body and higher order correlation effects we need a Jastrow factor.

$$J = \prod_{i < j}^N \exp\left(\frac{a_{ij} r_{ij}}{1 + \beta r_{ij}}\right). \quad (15)$$

Here a_{ij} is 0.25 if the spins of i and j are parallel and 0.5 if they are not.

The complete wavefunction

The complete trial wavefunction becomes

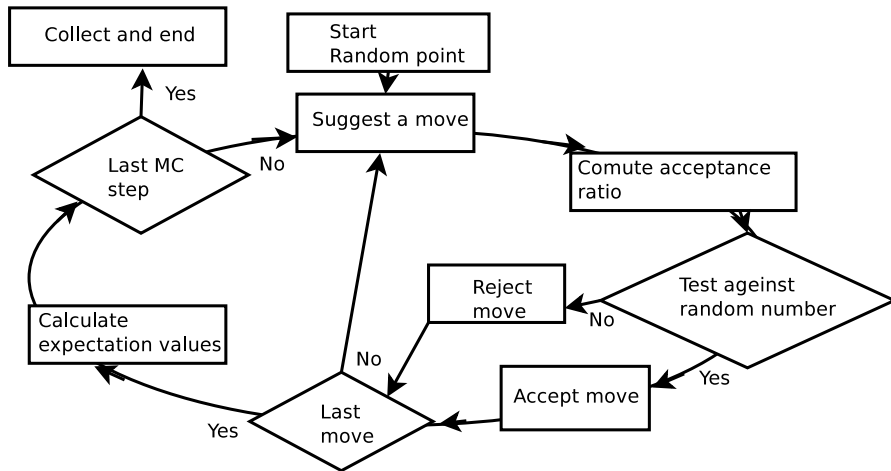
$$\psi \propto |S \uparrow \rangle |S \downarrow \rangle |J \rangle \quad (16)$$

The Hartree-Fock method is used to solve the time-independent Schrödinger equation.

This method uses five major simplifications.

- The Born-Oppenheimer approximation is assumed
- Relativistic effects are neglected
- The solution is a linear combination of basis functions
- The ansatz for the ground state is a Slater determinant
- Electron correlations beyond one-particle-one-hole excitations are neglected

Flowchart of the Metropolis algorithm



$$r_{new} = r_{old} + \chi \quad (17)$$

$$R = \frac{|\psi_{new}|^2}{|\psi_{old}|^2} \quad (18)$$

$$r_{new} = r_{old} + \chi + DF(r_{old})\delta t. \quad (19)$$

$$F(r) = \frac{2}{|\psi(r)|} \nabla |\psi(r)|. \quad (20)$$

$$G(i \rightarrow j) \propto e^{(x_i - x_j - D\delta F(x_i))^2 / 4D\delta\tau}. \quad (21)$$

The Metropolis ratio

$$R = \frac{|S_{\uparrow}^{new}|^2}{|S_{\uparrow}^{old}|^2} \frac{|S_{\downarrow}^{new}|^2}{|S_{\downarrow}^{old}|^2} \frac{J_{new}^2}{J_{old}^2} \frac{G(old, new)}{G(new, old)} \quad (22)$$

The optimized Slater ratio

$$R_S = \frac{|S^{new}|}{|S^{old}|} = \sum_i \chi_i(r_j^{new})(S_{ij}^{old})^{-1}. \quad (23)$$

Finding the Jastrow ratio.

$$\frac{J^{new}}{J^{old}} = \exp\left(\sum_{j=1}^N a_{ij} \left[\frac{r_{ij}^{new}}{1 + \beta r_{ij}^{new}} - \frac{r_{ij}^{old}}{1 + \beta r_{ij}^{old}} \right]\right). \quad (24)$$

The Local energy

$$E_L = \frac{1}{\psi_T} H \psi_T. \quad (25)$$

The complete Local energy

$$E_L = \frac{1}{\psi_T} \left(-\frac{1}{2} \sum_{i=1}^N \nabla_i^2 \right) \psi_T - \sum_{i=1}^N \sum_{n=1}^K \frac{Z_n}{|R_n - r_i|} + \frac{1}{2} \sum_{i \neq j}^n \frac{1}{|r_i - r_j|}. \quad (26)$$

The kinetic energy part

$$\frac{\nabla^2 \psi_T}{\psi_T} = \frac{1}{S_{\uparrow} S_{\downarrow} J} \nabla^2 (S_{\uparrow} S_{\downarrow} J) = \nabla (\nabla S_{\uparrow} S_{\downarrow} J + S_{\uparrow} \nabla S_{\downarrow} J + S_{\uparrow} S_{\downarrow} \nabla J), \quad (27)$$

$$= \frac{1}{S_{\uparrow}} \nabla^2 S_{\uparrow} + \frac{1}{S_{\downarrow}} \nabla^2 S_{\downarrow} + \frac{1}{J} \nabla^2 J + 2 \left(\frac{1}{S_{\uparrow} S_{\downarrow}} \nabla S_{\uparrow} \nabla S_{\downarrow} + \frac{1}{S_{\uparrow} J} \nabla S_{\uparrow} \nabla J + \frac{1}{S_{\downarrow} J} \nabla S_{\downarrow} \nabla J \right). \quad (28)$$

Optimizing the $\nabla_i |S| / |S|$ ratio.

$$\frac{\nabla_i |S|}{|S|} = \sum_k \nabla_i \chi_k(r_i^{new})(S_{ki}^{new})^{-1} \quad (29)$$

Optimizing the $\nabla_i^2 |S|/|S|$ ratio.

$$\frac{\nabla_i^2 |S|}{|S|} = \sum_k \nabla_i^2 \chi_k(r_i^{new})(S_{ki}^{new})^{-1}. \quad (30)$$

Updating the inverse.

$$\tilde{l}_{ij} = \sum_l S_{il}^{new} (S_{lj}^{old})^{-1}. \quad (31)$$

$$(S_{kj}^{new})^{-1} = (S_{kj}^{old})^{-1} - \frac{1}{R_S} (S_{ji}^{old})^{-1} \tilde{l}_{ij} j \neq i. \quad (32)$$

$$(S_{ki}^{new})^{-1} = \frac{1}{R_S} (S_{ki}^{old})^{-1} \text{ else.} \quad (33)$$

Optimizing the $\frac{\nabla_i J}{J}$ Ratio.

$$\frac{\nabla_i J}{J} = \sum_{i < j} \frac{a_{ij}}{r_{ij}} \frac{r_i - r_j}{(1 + \beta r_{ij})^2}. \quad (34)$$

Optimizing the $\frac{\nabla_i^2 J}{J}$ Ratio.

$$\frac{\nabla_i^2 J}{J} = \left| \frac{\nabla_i J}{J} \right|^2 + \sum_{i \neq j} a_{ij} \frac{2}{r_{ij}(1 + \beta r_{ij})^3}. \quad (35)$$

Hydrogenic orbitals

We get the hydrogenic orbitals from the hydrogen equation:

$$E\psi = -\frac{1}{2}\nabla^2\psi + \frac{1}{r}\psi. \quad (36)$$

Quantum numbers

We use here the quantum numbers n, l, m .

- n is the principal quantum number. It can have values $n = 1, 2, 3, \dots$
- l is the orbital momentum. It can have values $l = 0, 1, 2, \dots, n - 1$
- m is the projection of the orbital momentum. It can have values $-l, -l + 1, \dots, 0, 1, 2, \dots, l - 1, l$.

The sperical equation

We split the sperical equation:

$$\psi(r, \theta, \phi) = R(r)P(\theta)F(\phi). \quad (37)$$

The radial part

We find $R(r)$ from `Sympy.physics.hydrogen.R_nl`.

- $R_{nl}(n, l, r, Z=1)$
- n is the main quantum number.
- l is the orbital momentum quantum number.
- r is the radial coordinate.
- Z is the atomic number.

The polar equations

$$P(\theta)F(\phi) = \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_l^m(\cos(\theta)) \exp(im\phi). \quad (38)$$

Legendre polynomial

Here P_l^m is the Legendre polynomial, and is given by the Python function `sympy.assoc_legendre`. It takes as input quantum numbers n and m .

`assoc_legendre(n,m, x)`

- n is the main quantum number.
- m is the projection of the orbital momentum quantum number.
- x is the coordinate used.

The first few Hydrogenic orbitals

$$\exp(-\alpha r), \quad (39)$$

$$(\alpha r - 2)\exp(-\alpha r/2), \quad (40)$$

$$x * \exp(-\alpha r/2), \quad (41)$$

$$y * \exp(-\alpha r/2), \quad (42)$$

$$z * \exp(-\alpha r/2). \quad (43)$$

Gaussian orbitals

An gaussian orbital looks like:

$$\chi_n(x, y, z) = x^i y^j z^k c_n e^{-\alpha_n r^2}. \quad (44)$$

$$i + j + k = n. \quad (45)$$

Where $n = 0, 1, 2, 3, \dots$

Number of orbitals

Letter	n	Orbitals
S	0	1
P	1	3
D	2	6
F	3	10
G	4	15
H	5	21

Table : Number of orbitals per n.

$$(n + 1)(n + 2)/2 \quad (46)$$

All

Basis Set Exchange

3-21++G
 3-21++G*
 3-21G
 3-21G*
 3-21G* Polarization
 3-21GSP
 4-22GSP
 4-22G
 52P
 52P-DKH
 6-31++G
 6-31++G*
 6-31++G**
 6-31+G
 6-311++G(2d,2p)

Search Basis Set Name

Total: 538 published basis sets

W															He														
Li															Be														
Mg															Al														
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr												
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe												
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn												
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr													
																		B	C	N	O	F	Ne						
																		Al	Si	P	S	Cl	Ar						
																		Ge	As	Se	Br	Kr							
																		Sn	Sb	Te	I	Xe							
																		Pb	Bi	Po	At	Rn							
																		U	Np	Pu	Am	Cm	Bk						
																		Cf	Es	Fm	Md	No	Lr						

BASIS SET ECHANGE

v1.2.2

```
# STO-3G EMSL Basis Set Exchange Library 26/01/15 4:47
# Elements References
# -----
# H - Ne: W.J. Hehre, R.F. Stewart and J.A. Pople, J. Chem. Phys. 2657 (1969).
# Na - Ar: W.J. Hehre, R. Ditchfield, R.F. Stewart, J.A. Pople,
# J. Chem. Phys. 2769 (1970).
# K,Ca - : W.J. Pietro, B.A. Levy, W.J. Hehre and R.F. Stewart,
# Ga - Kr: J. Am. Chem. Soc. 19, 2225 (1980).
# Sc - Zn: W.J. Pietro and W.J. Hehre, J. Comp. Chem. 4, 241 (1983) + Gaussian.
# Y - Cd: W.J. Pietro and W.J. Hehre, J. Comp. Chem. 4, 241 (1983). + Gaussian
#
```

\$basis

*

ne STO-3G

*

3 s	
207.0156100	0.15432897
37.7081510	0.53532814
10.2052970	0.44463454
3 s	
8.2463151	-0.09996723
1.9162662	0.39951283
0.6232293	0.70011547
3 p	
8.2463151	0.15591627
1.9162662	0.60768372
0.6232293	0.39195739

*

\$end

Orbitals as a sum of basis functions

The orbital is a sum of basis functions

$$\phi(x, y, z) = \sum_n N_n \chi_n(x, y, z). \quad (47)$$

Normalization equation

We here use the normalization equation:

$$N_n = \left(\frac{2\alpha_n}{\pi} \right)^{3/4} \left[\frac{(8\alpha_n)^{i+j+k} i! j! k!}{(2i)!(2j)!(2k)!} \right]^{1/2}. \quad (48)$$

An example of Gaussian orbitals

As an example we look at a S orbital where we have 3 contracted GTOs.
since $n = 0$ we have $x^0 y^0 z^0 = 1$.

$$\chi_1(x, y, z) = 0.15432897 * \exp(-207.0156100 * r^2), \quad (49)$$

$$\chi_2(x, y, z) = 0.53532814 * \exp(-37.7081510 * r^2), \quad (50)$$

and

$$\chi_3(x, y, z) = 0.44463454 * \exp(-10.2052970 * r^2). \quad (51)$$

Plot of basis functions

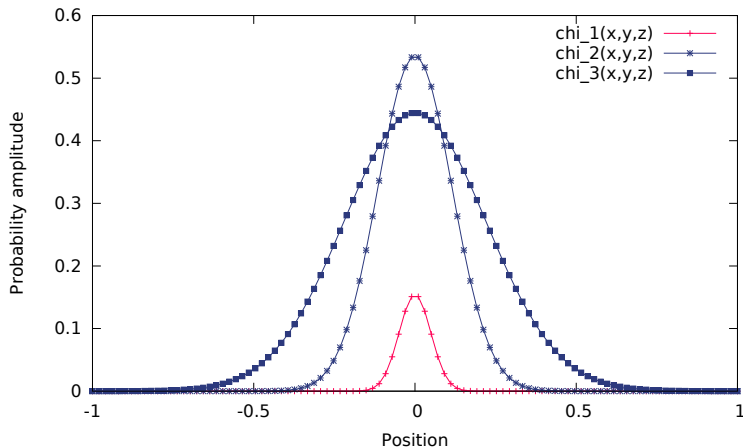


Figure : Here is a plot of χ_1, χ_2 and χ_3

Gradient and Laplacian

We use Sympy to find the gradient and Laplacian of the wavefunctions.

Figure of diatomic molecule

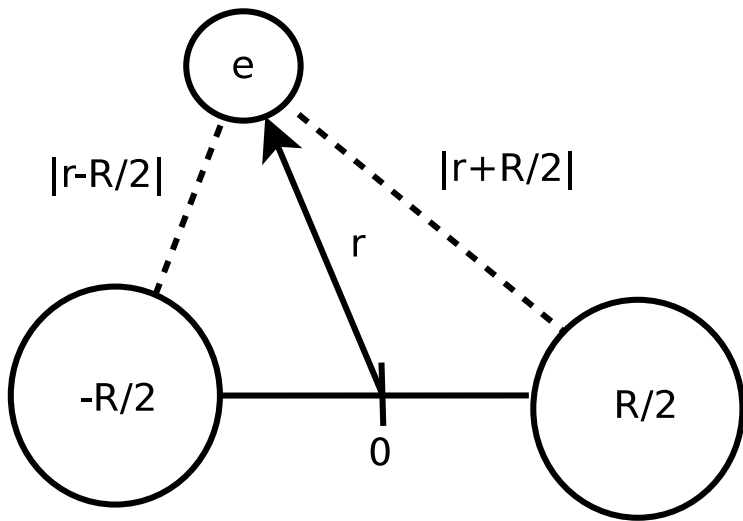


Figure : A diatomic molecule with one of the electrons. Here R and r are vectors.

Hamiltonian of diatomic molecule

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N \left(\frac{Z}{|R/2 + r_i|} + \frac{Z}{|R/2 - r_i|} \right) + \frac{Z^2}{R} + \frac{1}{2} \sum_{i \neq j}^n \frac{1}{|r_i - r_j|}. \quad (52)$$

Wavefunction of diatomic molecule

We use these superpositions every other orbital.

$$\psi^+(r_i, R) = \psi(r + R/2) + \psi(r_i - R/2), \quad (53)$$

$$\psi^-(r_i, R) = \psi(r + R/2) - \psi(r_i - R/2). \quad (54)$$

$$\nabla\psi^+(r_i, R) = \nabla\psi(r + R/2) + \nabla\psi(r_i - R/2), \quad (55)$$

$$\nabla\psi^-(r_i, R) = \nabla\psi(r + R/2) - \nabla\psi(r_i - R/2). \quad (56)$$

Laplacian of diatomic molecule

$$\nabla^2\psi^+(r_i, R) = \nabla^2\psi(r + R/2) + \nabla^2\psi(r_i - R/2), \quad (57)$$

$$\nabla^2\psi^-(r_i, R) = \nabla^2\psi(r + R/2) - \nabla^2\psi(r_i - R/2). \quad (58)$$

A variant of Newtons method

$$x_{i+1} = x_i - \nabla f(x_i) / \nabla^2 f(x_i). \quad (59)$$

The derivatives

$$\nabla f(x_m) = ((f(x_{m+h}) - f(x_{m-h}))/ (2h)). \quad (60)$$

$$\nabla^2 f(x_m) = ((f(x_{m+h}) - 2f(x_m) + f(x_{m-h}))/ (h^2)). \quad (61)$$

The VMC algorithm is very easy to paralellize. Just run several runs with different seed and take the average.

$$N_i = (aN_{i-1} + c)MOD(M) \quad (62)$$

Here a , c and M are constants. The variable M should be as large as possible. This gives a random number between 0 and 1 with the equation

$$x_i = N_i/M \quad (63)$$

Section 2

Results

Hydrogenic orbitals with Jastrow.

Type	α	β	VMC	real	rel	σ
He	1.811	0.50	-2.890	-2.9037	0.47%	1.409e-3
Be	3.97	0.10	-14.50	-14.6674	1.14%	4.282e-3
Ne	10.28	0.083	-127.86	-128.9383	0.84%	1.143e-2
Ar	18.55	0.168	-524.2	-527.544	0.63%	5.828e-2
Kr	35.3	0.40	-2745	-2753.055	0.26%	7.358e-1

α is always less than charge. β decreases then increases. Average is 0.668%.

Hydrogenic orbitals without Jastrow

Type	α	VMC	real	rel	σ
He	1.687	-2.848	-2.9037	1.92%	3.301e-3
Be	3.378	-14.22	-14.667	3.05%	8.535e-3
Ne	7.850	-122.0	-128.938	5.38%	3.426e-2
Ar	14.56	-502.9	-527.544	4.67%	2.291e-1
Kr	28.47	-2674	-2753.055	2.84%	3.081

α is less than charge. Average is 3.572%.

Gaussian orbitals with Jastrow

Type	β	VMC	real	rel	σ
He	0.65	-2.84	-2.9037	2.19%	2.569e-3
Be	0.80	-14.44	-14.667	1.55%	7.897e-3
Ne	2.20	-126.5	-128.938	1.89%	5.696e-2
Ar	2.70	-520.8	-527.544	1.28%	4.164e-1
Kr	2.90	-2718.2	-2753.055	1.23%	30.50

β increases. Average is 1.628%

Gaussian orbitals without Jastrow

Type	VMC	real	rel	σ
He	-2.81	-2.9037	3.23%	3.546e-3
Be	-14.35	-14.667	2.16%	1.048e-2
Ne	-126.64	-128.938	1.78%	2.282e-1
Ar	-522.7	-527.544	0.92%	7.816e-1
Kr	-2715.1	-2753.055	1.34%	42.97

No α or β . Average is 1.887%

Averages atoms

Hydro /w jast	Hydro /wo jast	Gauss /w jast	Gauss /wo jast
0.668%	3.571%	1.629%	1.887%

Molecule. Hydrogenic orbitals with Jastrow

Type	R	VMC	α	β	real	rel	σ
H_2	1.4	-1.158	1.296	14.5	-1.1746	1.413%	1.78e-3
Li_2	5.051	-14.745	2.782	0.41	-14.995	1.670%	4.492e-3
Be_2	4.63	-28.820	3.801	0.32	-29.339	1.767%	5.552e-3
B_2	3.005	-48.233	4.805	0.264	-49.418	2.399%	8.595e-3
C_2	2.3481	-73.164	5.662	0.4741	-75.923	3.6339%	1.394e-2
N_2	2.068	-105.63	6.578	0.5044	-109.54	3.571%	2.141e-2
O_2	2.282	-145.3	7.526	0.519	-150.33	3.343%	3.641e-2

α begins over the charge and ends under the charge. β decreases then increases. The average is 2.543%.

Molecule. Hydrogenic orbitals without Jastrow

Type	R	VMC	α	real	rel	σ
H_2	1.4	-1.128	1.190	1.1746	3.967%	2.456e-2
Li_2	5.051	-14.587	2.547	-14.995	2.724%	6.268e-3
Be_2	4.63	-28.423	3.381	-29.339	3.121%	1.380e-2
B_2	3.005	-47.225	4.146	-49.4184	4.438%	2.704e-2
C_2	2.3481	-71.820	4.936	-75.923	5.404%	3.948e-2
N_2	2.068	-103.37	5.671	-109.54	5.635%	4.923e-2
O_2	2.282	-142.07	6.416	-150.321	5.493%	5.939e-2

α begins above charge and end below. The average is 4.397%.

Molecule, Gaussian orbitals with Jastrow

Type	R	VMC	β	real	rel	σ
H_2	1.4	-1.148	0.457	-1.1746	2.264%	1.572e-3
Li_2	5.051	-14.724	1.012	-14.995	1.810%	5.462e-3
Be_2	4.63	-28.686	38.25	-29.339	2.224%	1.258e-2
B_2	3.005	-48.230	1.041	-49.4184	2.405%	2.119e-2
C_2	2.3481	-72.515	6.409	-75.923	4.489%	3.330e-2
N_2	2.068	-105.9	1.627	-109.54	3.325%	4.797e-2
O_2	2.282	-146.4	6.641	-150.321	2.612%	7.520e-2

β does not seem to follow any pattern. The average is 2.733%.

Molecule. Gaussian orbitals without Jastrow

Type	R	VMC	real	rel	σ
H_2	1.4	-1.117	-1.1746	4.904%	2.399e-3
Li_2	5.051	-14.626	-14.995	2.464%	6.016e-3
Be_2	4.63	-28.686	-29.339	2.224%	1.241e-2
B_2	3.005	-46.912	-49.4184	5.0718%	2.749e-2
C_2	2.3481	-72.432	-75.923	4.5980%	3.186e-2
N_2	2.068	-105.86	-109.54	3.3615%	4.522e-2
O_2	2.282	-146.2	-150.321	2.7452%	8.565e-2

The average is 3.624%

Averages molecules.

Hydro /w jast	Hydro /wo jast	Gauss /w jast	Gauss /wo jast
2.543%	4.397%	2.733%	3.624%

Timegraphs atoms.

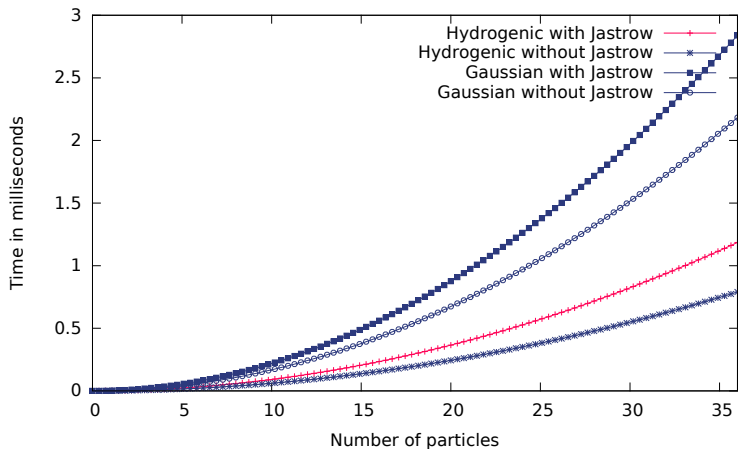


Figure : In this plot we see time (in milliseconds) per cycle per number of particles for Atoms.

Timegraphs molecules

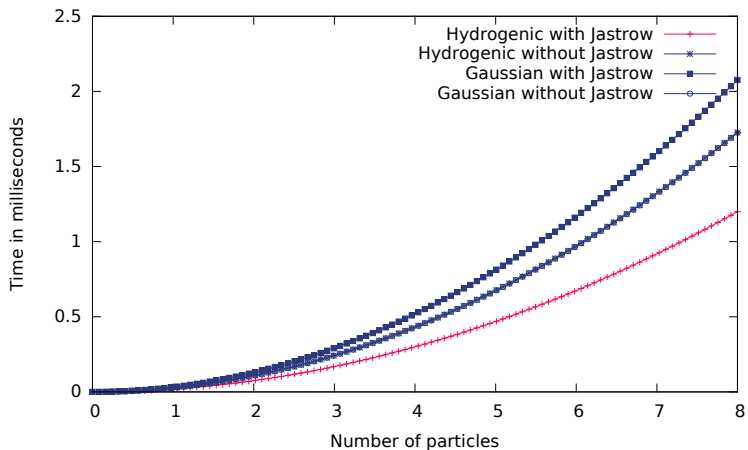


Figure : In this plot we see time (in milliseconds) per cycle per number of particles for Molecules.

Conclusions

We conclude that the VMC algorithm works.
Hydrogenic and Gaussain orbitals both works fine.

Further work

Heavier and more complex molecules.