Quantum Monte Carlo for the electronic structure of atomic systems

A. Sarsa, E. Buendía, F. J. Gálvez and P. Maldonado

Departamento de Física. Universidad de Córdoba Spain

Departamento de Física At., Mol. y Nucl. Universidad de Granada Spain

QMC for the electronic structure of atoms. OUTLINE

- Introduction
- Correlations with Monte Carlo
- Relativistic Corrections
- Results
- Conclusions and perspectives

QMC for the electronic structure of atoms. OUTLINE

- Introduction
- Correlations with Monte Carlo
- Relativistic Corrections
- Results
- Conclusions and perspectives

QMC for the electronic structure of atoms. OUTLINE

- Introduction
- Correlations with Monte Carlo
- Relativistic Corrections
- Results
- Conclusions and perspectives

QMC for the electronic structure of atoms. OUTLINE

- Introduction
- Correlations with Monte Carlo
- Relativistic Corrections
- Results
- Conclusions and perspectives

QMC for the electronic structure of atoms. OUTLINE

- Introduction
- Correlations with Monte Carlo
- Relativistic Corrections
- Results
- Conclusions and perspectives

INTRODUCTION

- Quantum Monte Carlo methods
- Electronic structure of atoms
- Importance of relativity and correlations

INTRODUCTION

- Quantum Monte Carlo methods
- Electronic structure of atoms
- Importance of relativity and correlations

INTRODUCTION

- Quantum Monte Carlo methods
- Electronic structure of atoms
- Importance of relativity and correlations

Quantum Monte Carlo methods

- Provide the exact ground state energy of many boson

Quantum Monte Carlo methods

- Provide the exact ground state energy of many boson
- Provide a very accurate ground state energy of many fermion

Quantum Monte Carlo methods

- Provide the exact ground state energy of many boson
- Provide a very accurate ground state energy of many fermion
- Based on random walks on the configuration space

Quantum Monte Carlo methods

- Provide the exact ground state energy of many boson
- Provide a very accurate ground state energy of many fermion
- Based on random walks on the configuration space
- Developed about 40 ago for nuclear problems

Quantum Monte Carlo methods

- Provide the exact ground state energy of many boson
- Provide a very accurate ground state energy of many fermion
- Based on random walks on the configuration space
- Developed about 40 ago for nuclear problems
- First seventies applications to liquid helium at zero temperature

Quantum Monte Carlo methods

- Provide the exact ground state energy of many boson
- Provide a very accurate ground state energy of many fermion
- Based on random walks on the configuration space
- Developed about 40 ago for nuclear problems
- First seventies applications to liquid helium at zero temperature
- First eighties applications to electronic structure of atoms

Quantum Monte Carlo methods

- Provide the exact ground state energy of many boson
- Provide a very accurate ground state energy of many fermion
- Based on random walks on the configuration space
- Developed about 40 ago for nuclear problems
- First seventies applications to liquid helium at zero temperature
- First eighties applications to electronic structure of atoms
- A simplification of the method was developed in that period

Quantum Monte Carlo methods

- Provide the exact ground state energy of many boson
- Provide a very accurate ground state energy of many fermion
- Based on random walks on the configuration space
- Developed about 40 ago for nuclear problems
- First seventies applications to liquid helium at zero temperature
- First eighties applications to electronic structure of atoms
- A simplification of the method was developed in that period
- Nowadays used for homogeneous and non homogeneous systems

Electronic structure of atoms

- Experimental ionization potentials, electron affinities and excitation energies are known very accurately

Electronic structure of atoms

- Experimental ionization potentials, electron affinities and excitation energies are known very accurately
- Hartree-Fock is the starting point theoretically. Not very reliable

Electronic structure of atoms

- Experimental ionization potentials, electron affinities and excitation energies are known very accurately
- Hartree-Fock is the starting point theoretically. Not very reliable
- Importance of correlations and relativistic effects

Electronic structure of atoms

- Experimental ionization potentials, electron affinities and excitation energies are known very accurately
- Hartree-Fock is the starting point theoretically. Not very reliable
- Importance of correlations and relativistic effects
- The ions are hard to describe

Electronic structure of atoms

- Experimental ionization potentials, electron affinities and excitation energies are known very accurately
- Hartree-Fock is the starting point theoretically. Not very reliable
- Importance of correlations and relativistic effects
- The ions are hard to describe
- Quantum Chemistry methods (CI and CC) have been applied for some cases

Electronic structure of atoms

- Quantum Monte Carlo have been mostly used for the ground state of light $Z \leq 10$ atoms

Electronic structure of atoms

- Quantum Monte Carlo have been mostly used for the ground state of light $Z \leq 10$ atoms
- Quantum Monte Carlo can be applied to some excited states. Wave functions with the proper values of the angular momentum and parity are needed

Electronic structure of atoms

- Quantum Monte Carlo have been mostly used for the ground state of light $Z \leq 10$ atoms
- Quantum Monte Carlo can be applied to some excited states. Wave functions with the proper values of the angular momentum and parity are needed
- For heavier systems no extra technical difficulties arise.

Electronic structure of atoms

- Quantum Monte Carlo have been mostly used for the ground state of light $Z \leq 10$ atoms
- Quantum Monte Carlo can be applied to some excited states. Wave functions with the proper values of the angular momentum and parity are needed
- For heavier systems no extra technical difficulties arise.
    - The computational time grows

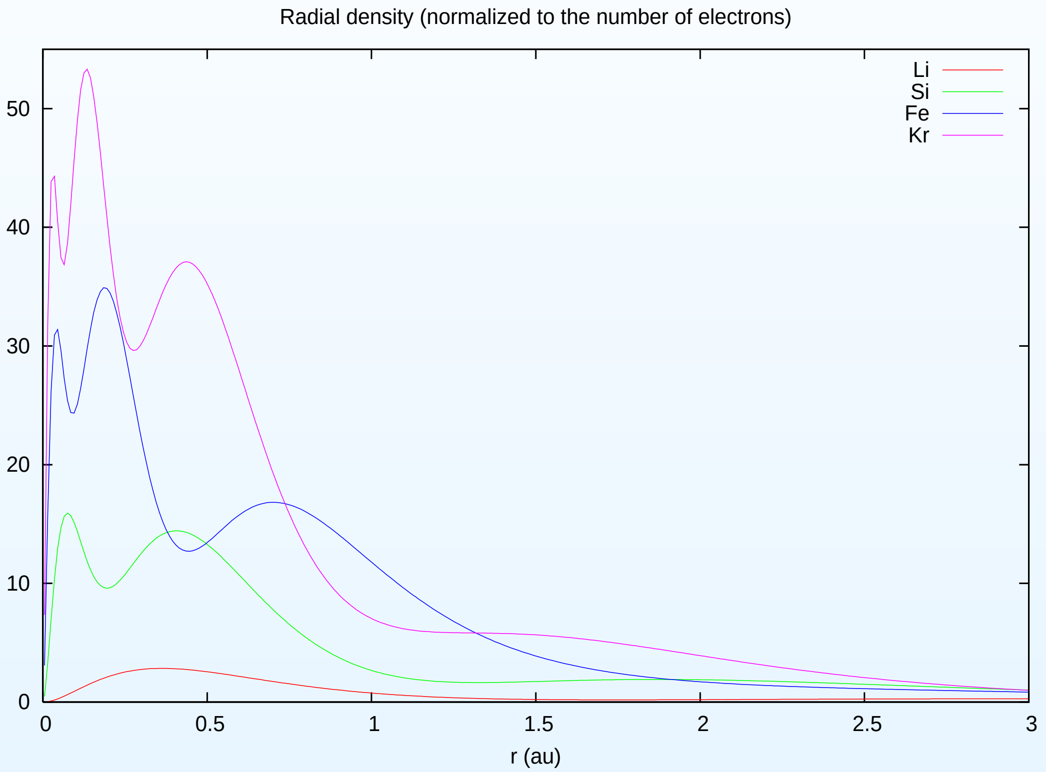
Electronic structure of atoms

- Quantum Monte Carlo have been mostly used for the ground state of light $Z \leq 10$ atoms
- Quantum Monte Carlo can be applied to some excited states. Wave functions with the proper values of the angular momentum and parity are needed
- For heavier systems no extra technical difficulties arise.
  - The computational time grows
  - Electron density becomes more inhomogeneous (shell structure, the size of the atoms hardly grows with N)

Electronic structure of atoms

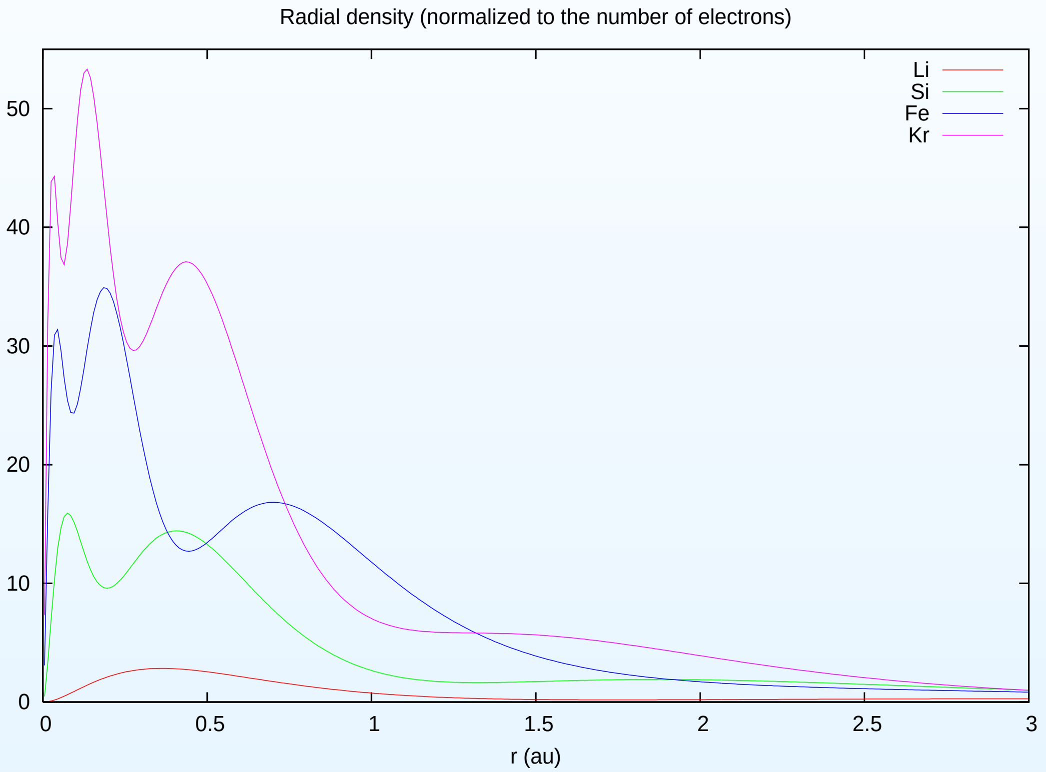
-

Electronic structure of atoms

- 

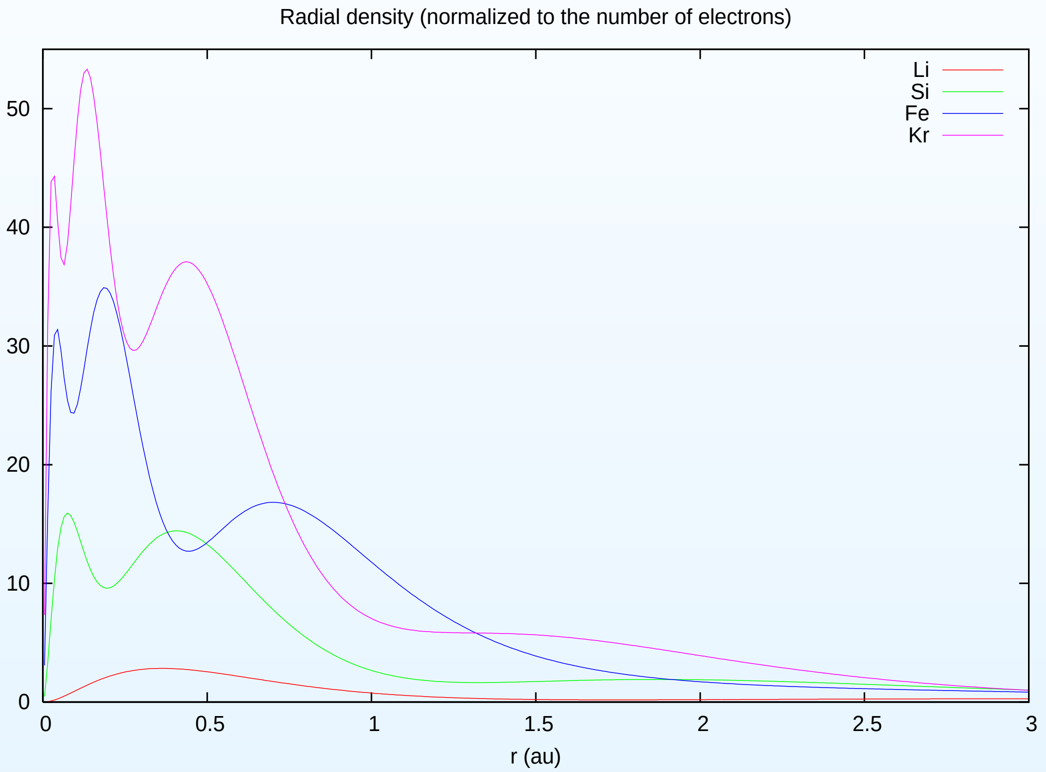
Electronic structure of atoms

-



- The convergence of the Monte Carlo is reduced

Electronic structure of atoms

- 

- The convergence of the Monte Carlo is reduced
- For heavier systems the importance of relativistic effects increases

Importance of relativity and correlations

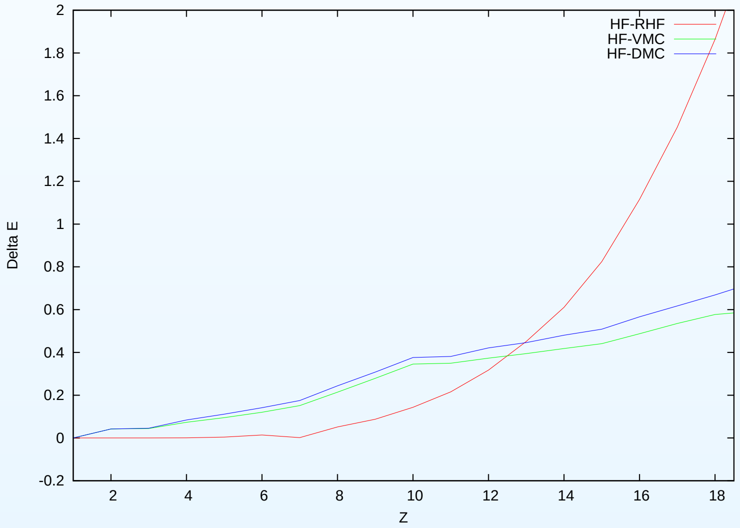
- For the ground state energy relativistic effects are **MORE** important than correlations for $Z \geq 12$.

$E_{\text{Rel}} - E_{\text{HF}}$: Relativistic correction, $E_{\text{DMC}} - E_{\text{HF}}$: Correlation energy, $E_{\text{VMC}} - E_{\text{HF}}$: Correlation Energy

$\Delta E \leq 2$ h Atomic units

Importance of relativity and correlations

- For the ground state energy relativistic effects are **MORE** important than correlations for $Z \geq 12$.



$E_{\mathrm{Rel}} - E_{\mathrm{HF}}$: Relativistic correction, $E_{\mathrm{DMC}} - E_{\mathrm{HF}}$: Correlation energy, $E_{\mathrm{VMC}} - E_{\mathrm{HF}}$: Correlation Energy

$\Delta E \leq 2$ h Atomic units

Importance of relativity and correlations

- For the ground state energy relativistic effects are **MORE** important than correlations for $Z \geq 12$.

Left $19 \leq Z \leq 36$, $0 \leq \Delta E \leq 60$

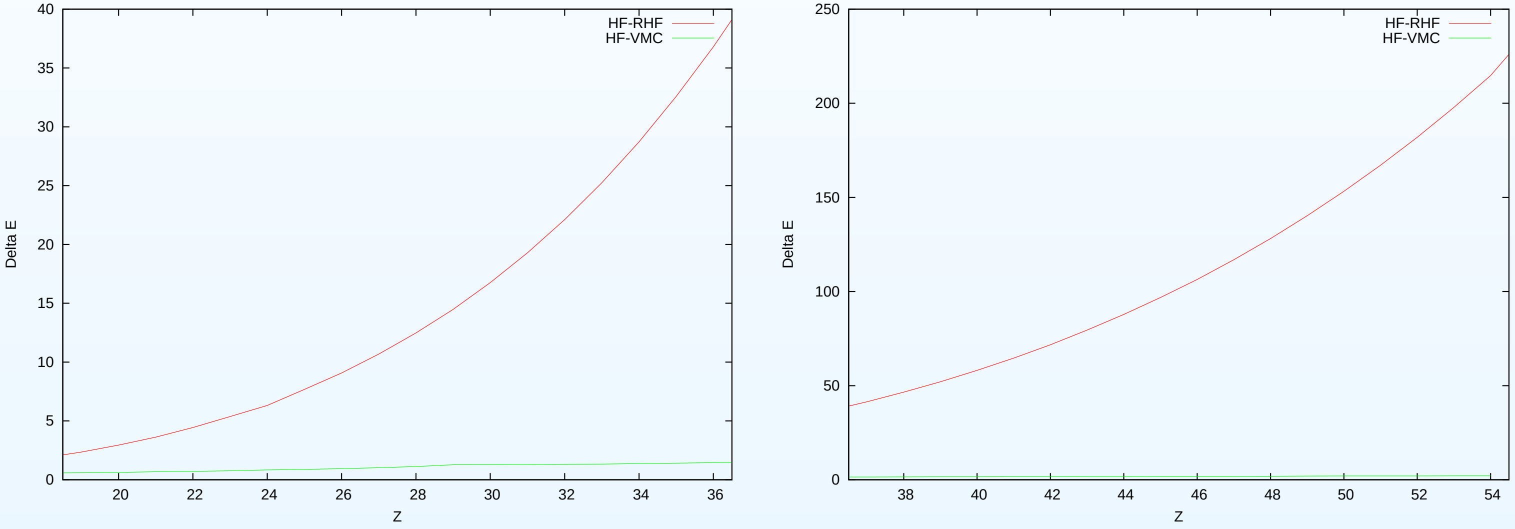
Right $37 \leq Z \leq 54$, $0 \leq \Delta E \leq 250$

Relativistic correction, VMC Correlation energy

Atomic units

Importance of relativity and correlations

- For the ground state energy relativistic effects are **MORE** important than correlations for $Z \geq 12$.



Left $19 \leq Z \leq 36$, $0 \leq \Delta E \leq 60$

Right $37 \leq Z \leq 54$, $0 \leq \Delta E \leq 250$

Relativistic correction, VMC Correlation energy

Atomic units

Importance of relativity and correlations

- Relativistic effects many take place mainly in the inner core

Importance of relativity and correlations

- Relativistic effects many take place mainly in the inner core
- Less importance is expected for differences of energies of configurations differing in the outermost shells.
  Correction to the Ionization potential in atomic units

Left $2 \leq Z \leq 18$, $-0.03 \leq \Delta E \leq 0.07$

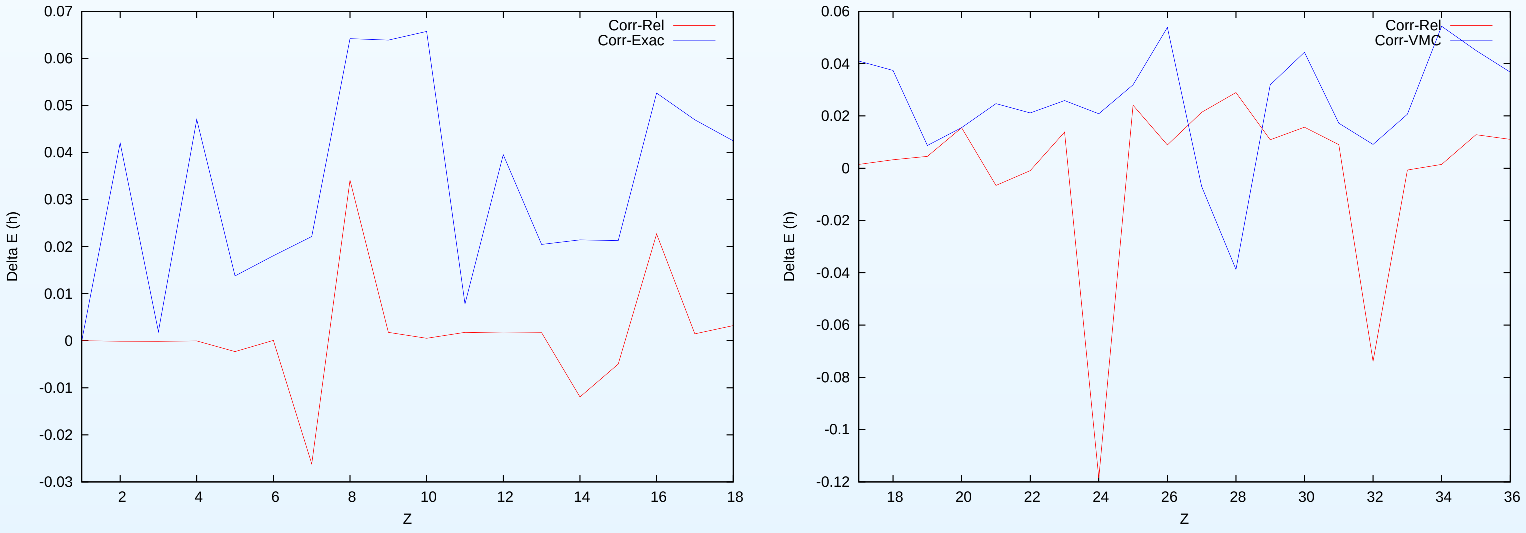
Right $19 \leq Z \leq 36$, $-0.12 \leq \Delta E \leq 0.06$

Relativistic correction, Correlation energy

Importance of relativity and correlations

- Relativistic effects many take place mainly in the inner core
- Less importance is expected for differences of energies of configurations differing in the outermost shells.

Correction to the Ionization potential in atomic units



Left $2 \leq Z \leq 18$, $-0.03 \leq \Delta E \leq 0.07$

Right $19 \leq Z \leq 36$, $-0.12 \leq \Delta E \leq 0.06$

Relativistic correction, Correlation energy

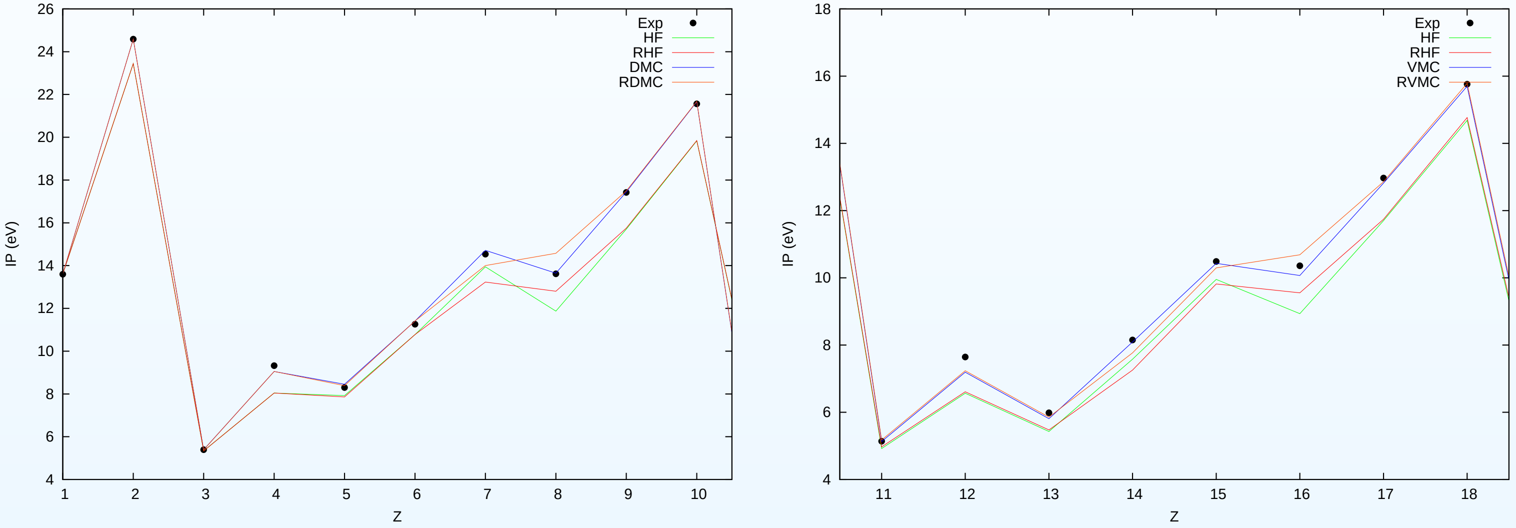
Importance of relativity and correlations

- Ionization Potential

Ionization potential **Left** $2 \leq Z \leq 10$ (Ne) **Right** $11 \leq Z \leq 18$ (Ar)
Points: experimental, HF, Relativity, Correlations,
Relativity+Correlations

Importance of relativity and correlations

- Ionization Potential



Ionization potential **Left** $2 \leq Z \leq 10$ (Ne) **Right** $11 \leq Z \leq 18$ (Ar)

Points: experimental, HF, Relativity, Correlations, Relativity+Correlations

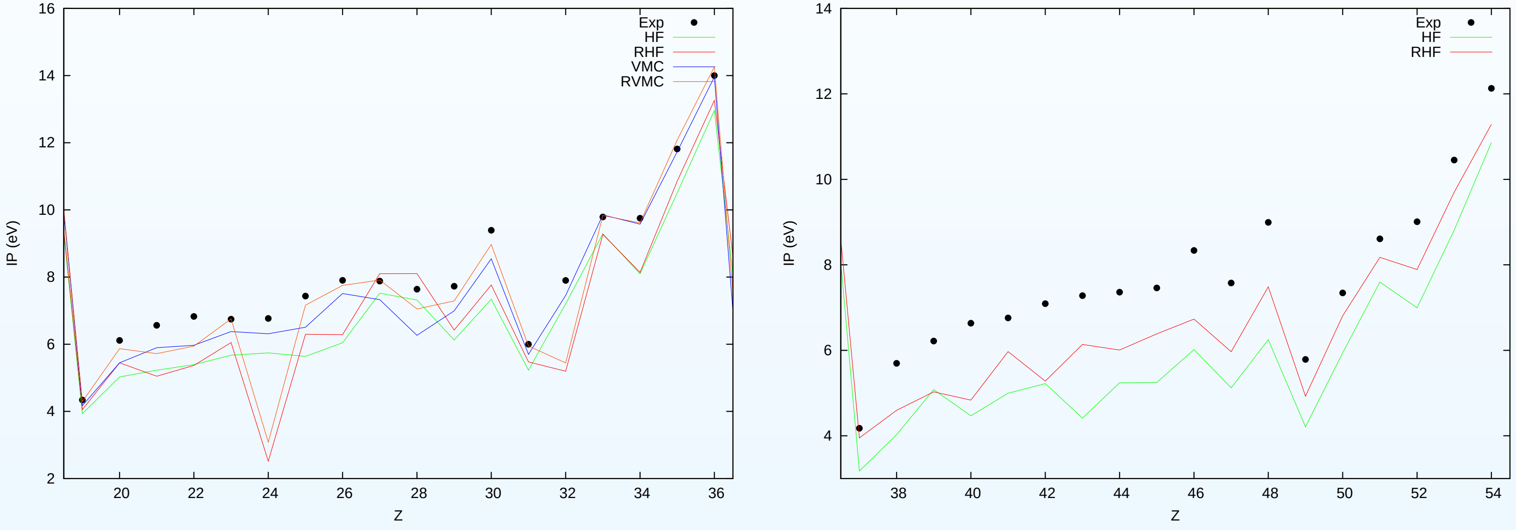
Importance of relativity and correlations

- Ionization Potential

Ionization potential **Left** $19 \leq Z \leq 36$ (Kr) **Right** $36 \leq Z \leq 54$ (Xe)
Points: experimental, HF, Relativity, Correlations,
Relativity+Correlations

Importance of relativity and correlations

- Ionization Potential



Ionization potential **Left** $19 \leq Z \leq 36$ (Kr) **Right** $36 \leq Z \leq 54$ (Xe)

Points: experimental, HF, Relativity, Correlations, Relativity+Correlations

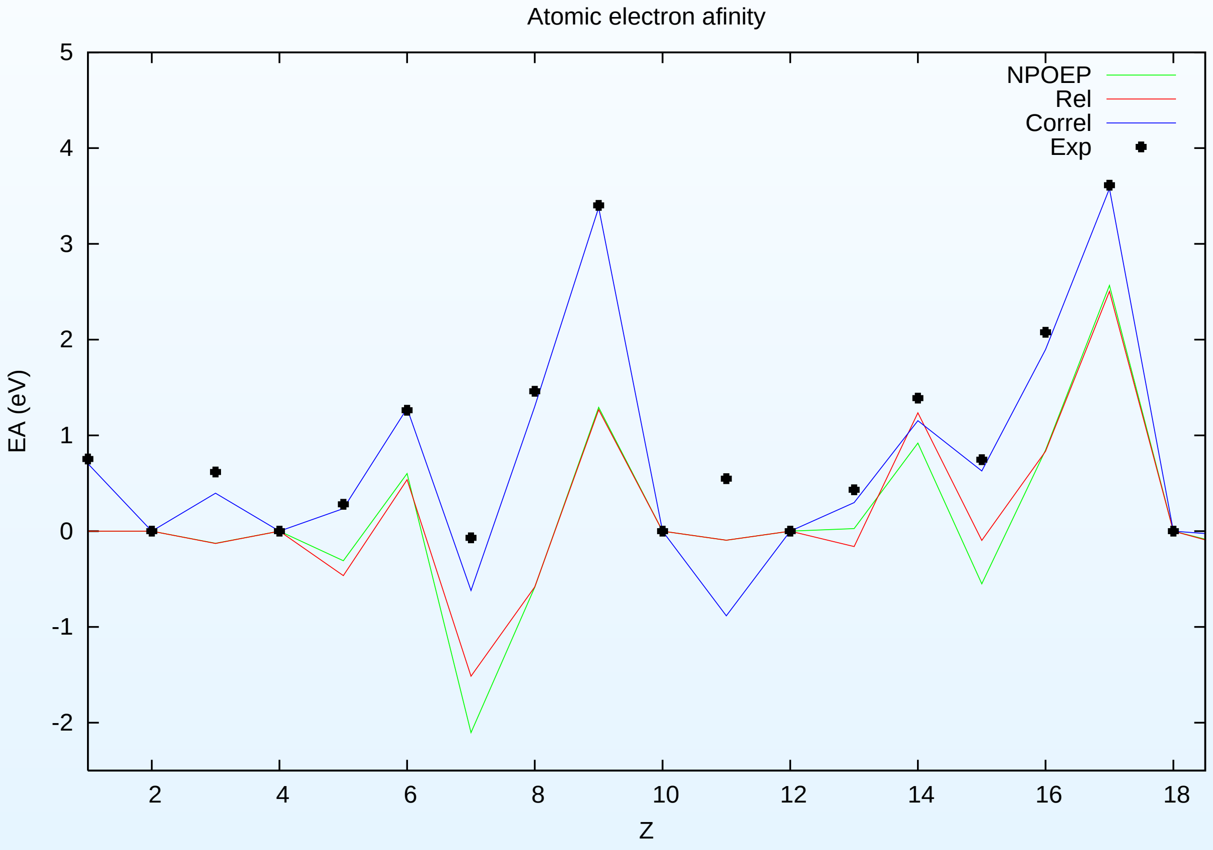
Importance of relativity and correlations

- Electron Affinity

Relativistic correction, Correlation energy, Non relativistic non correlated

Importance of relativity and correlations

- Electron Affinity



Relativistic correction, Correlation energy, Non relativistic non correlated

Importance of relativity and correlations

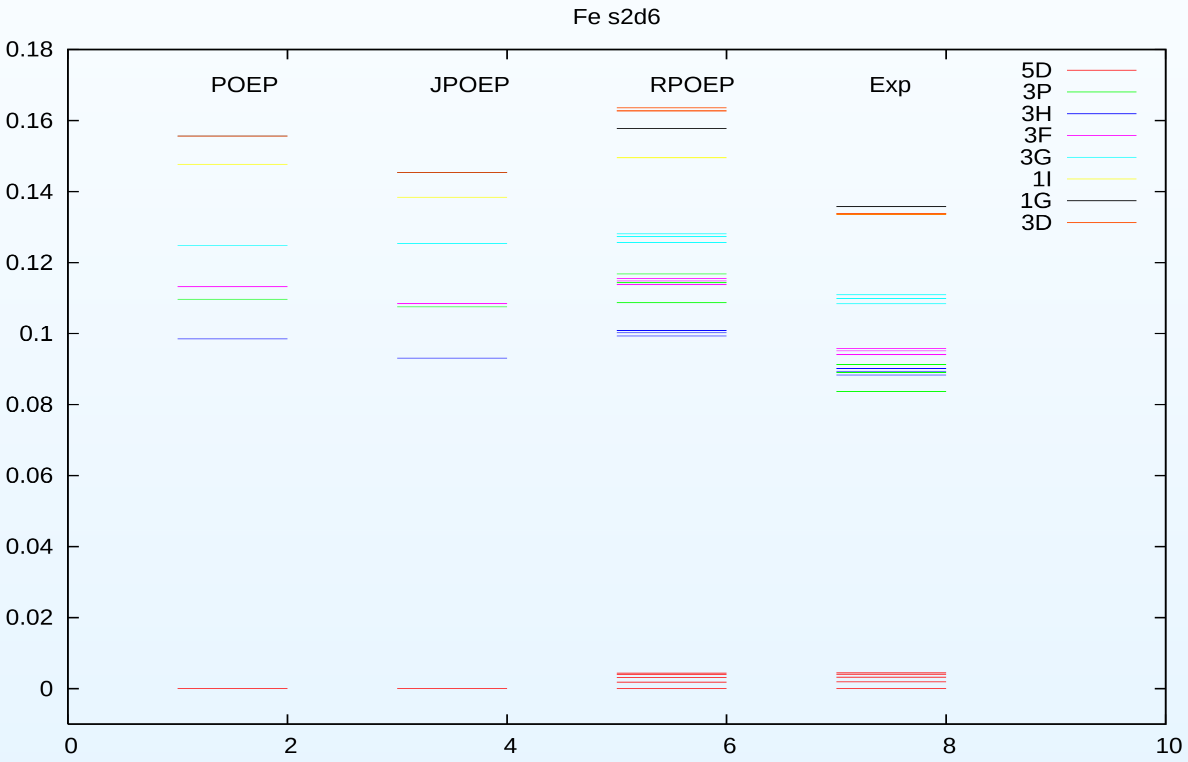
- Low lying spectrum of the Fe atom

POEP no relativity no correlations, JPOEP correlations without relativity, RPOEP relativity without correlations,

←

Importance of relativity and correlations

- Low lying spectrum of the Fe atom



POEP no relativity no correlations, JPOEP correlations without relativity, RPOEP relativity without correlations,

←

CORRELATIONS WITH MONTE CARLO

- Variational Monte Carlo
- Quantum Monte Carlo

CORRELATIONS WITH MONTE CARLO

- Variational Monte Carlo
- Quantum Monte Carlo

Variational Monte Carlo

- In order to get accurate results from Quantum Monte Carlo is convenient to have an accurate wave function for the system

Variational Monte Carlo

- In order to get accurate results from Quantum Monte Carlo is convenient to have an accurate wave function for the system
- Having an approximate wave function containing the most relevant dynamical elements of the system is important by itself

Variational Monte Carlo

- In order to get accurate results from Quantum Monte Carlo is convenient to have an accurate wave function for the system
- Having an approximate wave function containing the most relevant dynamical elements of the system is important by itself
- A functional form is chosen with some free parameters fixed variationally

Variational Monte Carlo

- In order to get accurate results from Quantum Monte Carlo is convenient to have an accurate wave function for the system
- Having an approximate wave function containing the most relevant dynamical elements of the system is important by itself
- A functional form is chosen with some free parameters fixed variationally
- Approximate description of other properties than the energy such as electron densities

Variational Monte Carlo

- Non-relativistic calculation

Variational Monte Carlo

- Non-relativistic calculation
- Monte Carlo quadrature is used for calculating the expectation values of the energy

Variational Monte Carlo

- Non-relativistic calculation
- Monte Carlo quadrature is used for calculating the expectation values of the energy
- This allows for any form of the trial wave function (no analytic integral is needed)

Variational Monte Carlo

- Non-relativistic calculation
- Monte Carlo quadrature is used for calculating the expectation values of the energy
- This allows for any form of the trial wave function (no analytic integral is needed)
- Compact form of the wave functions with a small number of free parameters are used typically

Variational Monte Carlo

- Non-relativistic calculation
- Monte Carlo quadrature is used for calculating the expectation values of the energy
- This allows for any form of the trial wave function (no analytic integral is needed)
- Compact form of the wave functions with a small number of free parameters are used typically
- Energy minimization or variance minimization or a mixture of both is employed to fix the free parameters

Variational Monte Carlo

- In the problem of the electronic structure of atoms the following ansatz is widely used

$$\Psi_t(R) = F(r_i, r_{ij})\Phi \tag{1}$$

Variational Monte Carlo

- In the problem of the electronic structure of atoms the following ansatz is widely used

$$\Psi_t(R) = F(r_i, r_{ij})\Phi \tag{2}$$

  - Φ, the model function, is a Slater determinant of a linear combination of them, usually with the proper L and S values of the state

Variational Monte Carlo

- In the problem of the electronic structure of atoms the following ansatz is widely used

$$\Psi_t(R) = F(r_i, r_{ij})\Phi \tag{3}$$

  - Φ, the model function, is a Slater determinant of a linear combination of them, usually with the proper L and S values of the state
  - F is a generalized Jastrow factor

Variational Monte Carlo

- In the problem of the electronic structure of atoms the following ansatz is widely used

$$\Psi_t(R) = F(r_i, r_{ij})\Phi \tag{4}$$

  - Φ, the model function, is a Slater determinant of a linear combination of them, usually with the proper L and S values of the state
  - F is a generalized Jastrow factor
- In Φ the inter-electronic distance, r_{ij} is not included explicitly

Variational Monte Carlo

- In the problem of the electronic structure of atoms the following ansatz is widely used

$$\Psi_t(R) = F(r_i, r_{ij})\Phi \tag{5}$$

  - ○ Φ, the model function, is a Slater determinant of a linear combination of them, usually with the proper L and S values of the state
  - ○ F is a generalized Jastrow factor
- In Φ the inter-electronic distance, r_{ij} is not included explicitly
- Φ is fixed by using Hartree-Fock, Optimized Effective Potential or Multi-Configuration Hartree-Fock methods.

Variational Monte Carlo

- The linear coefficients of the Multi-Configuration expansion can be optimized along with the Jastrow factor

Variational Monte Carlo

- The linear coefficients of the Multi-Configuration expansion can be optimized along with the Jastrow factor
- This ansatz provides accurate results for atoms and cations up to 36 electrons *Buendía et al.* CPL **436** 352 (2007)

Variational Monte Carlo

- The linear coefficients of the Multi-Configuration expansion can be optimized along with the Jastrow factor
- This ansatz provides accurate results for atoms and cations up to 36 electrons *Buendía et al.* CPL **436** 352 (2007)
- Modifying the orbitals in the Monte Carlo optimization is harder.

Variational Monte Carlo

- The linear coefficients of the Multi-Configuration expansion can be optimized along with the Jastrow factor
- This ansatz provides accurate results for atoms and cations up to 36 electrons *Buendía et al.* CPL **436** 352 (2007)
- Modifying the orbitals in the Monte Carlo optimization is harder.
- Very accurate VMC and DMC have been very recently obtained using back-flow and hundreds of determinants for $3 \leq Z \leq 10$ atoms, *Brown et al.* JCP **126** 224110 (2007)

Variational Monte Carlo

- It is important for F to include dependence on r_i, the distance of the electron i to the nucleus.

Variational Monte Carlo

- It is important for F to include dependence on r_i, the distance of the electron i to the nucleus.

VMC Ground state energy of some atoms in hartree. Second rows percentage of correlation energy. F_{ee} only e-e correlations and $F_{\mathrm{ee-en}}$ e-e and e-n correlations.

Atom	HF	F_{ee}	$F_{\mathrm{ee-en}}$	Exact
Be	-14.57302313	-14.6073(2)	-14.64672(2)	-14.66736
		36	78	
N	-54.40093415	-54.447(1)	-54.5526(2)	-54.5892
		25	80	
Ne	-128.5470980	-128.621(1)	-128.8930(7)	-128.9376
		19	89	

Variational Monte Carlo

- A parameterization of the correlation factor leading to accurate results is

$$F = e^{\sum_{i<j} U_{ij}} \tag{6}$$

and

$$U_{ij} = \sum_{k=1}^{N_c} c_k \left(\bar{r}_i^{m_k} \bar{r}_j^{n_k} + \bar{r}_i^{n_k} \bar{r}_j^{m_k} \right) \bar{r}_{ij}^{o_k} \tag{7}$$

where

$$\bar{r}_i = \frac{b\, r_i}{1 + b\, r_i}, \quad \bar{r}_{ij} = \frac{d\, r_{ij}}{1 + d\, r_{ij}}$$

Variational Monte Carlo

- A parameterization of the correlation factor leading to accurate results is

$$F = e^{\sum_{i<j} U_{ij}} \tag{8}$$

and

$$U_{ij} = \sum_{k=1}^{N_c} c_k (\bar{r}_i^{m_k} \bar{r}_j^{n_k} + \bar{r}_i^{n_k} \bar{r}_j^{m_k}) \bar{r}_{ij}^{o_k} \tag{9}$$

where

$$\bar{r}_i = \frac{b\, r_i}{1 + b\, r_i}, \quad \bar{r}_{ij} = \frac{d\, r_{ij}}{1 + d\, r_{ij}}$$

- m_k, n_k and o_k are given, b and d are usually fixed to one and c_k are the free parameters

Variational Monte Carlo

- The functional form is based on a averaged back-flow type correlation

Variational Monte Carlo

- The functional form is based on a averaged back-flow type correlation
- Presents the correct long and short range behaviors expected for this correlation

Variational Monte Carlo

- The functional form is based on a averaged back-flow type correlation
- Presents the correct long and short range behaviors expected for this correlation
- The total energy, and the variance present a simple dependence on the free parameters.

Variational Monte Carlo

- The functional form is based on a averaged back-flow type correlation
- Presents the correct long and short range behaviors expected for this correlation
- The total energy, and the variance present a simple dependence on the free parameters.
- The electron-electron cusp condition is imposed exactly.

Variational Monte Carlo

- The functional form is based on a averaged back-flow type correlation
- Presents the correct long and short range behaviors expected for this correlation
- The total energy, and the variance present a simple dependence on the free parameters.
- The electron-electron cusp condition is imposed exactly.
- This is an analytic property of the exact wave function that leads to a faster convergence of approximate wave functions and condition and reduces the statistical error of Monte Carlo simulations (removes some divergences of the local energy)

Quantum Monte Carlo

- Calculates numerically the Green’s function of a quantum system

Quantum Monte Carlo

- Calculates numerically the Green's function of a quantum system
- The Green's function is built as a large set of random walks

Quantum Monte Carlo

- Calculates numerically the Green’s function of a quantum system
- The Green’s function is built as a large set of random walks
- The dynamics of the random walks is given by a probability distribution function and a transition probability

Quantum Monte Carlo

- Calculates numerically the Green's function of a quantum system
- The Green's function is built as a large set of random walks
- The dynamics of the random walks is given by a probability distribution function and a transition probability
- The probability distribution must be non-negative. This leads to the sign problem

Quantum Monte Carlo

- Calculates numerically the Green’s function of a quantum system
- The Green’s function is built as a large set of random walks
- The dynamics of the random walks is given by a probability distribution function and a transition probability
- The probability distribution must be non-negative. This leads to the sign problem
- If the nodes are known approximately, an upper bound to the exact energy is obtained

Quantum Monte Carlo

- Several algorithms have been proposed to produce the random walks

Quantum Monte Carlo

- Several algorithms have been proposed to produce the random walks
- Here we shall focus on two of them that provide the same results

Quantum Monte Carlo

- Several algorithms have been proposed to produce the random walks
- Here we shall focus on two of them that provide the same results
  - Diffusion Monte Carlo

Quantum Monte Carlo

- Several algorithms have been proposed to produce the random walks
- Here we shall focus on two of them that provide the same results
    - Diffusion Monte Carlo
    - Green's function Monte Carlo

Quantum Monte Carlo

- Several algorithms have been proposed to produce the random walks
- Here we shall focus on two of them that provide the same results
  - Diffusion Monte Carlo
  - Green’s function Monte Carlo
- In order to apply Quantum Monte Carlo is **very convenient** to have an approximate wave function of the system Nodal surface and Importance Sampling

Quantum Monte Carlo

- Several algorithms have been proposed to produce the random walks
- Here we shall focus on two of them that provide the same results
    - Diffusion Monte Carlo
    - Green’s function Monte Carlo
- In order to apply Quantum Monte Carlo is **very convenient** to have an approximate wave function of the system Nodal surface and Importance Sampling
- If no importance sampling is used, the statistical error would be unacceptable

Quantum Monte Carlo

- The random walks are done by proposing moves in the configuration space

Quantum Monte Carlo

- The random walks are done by proposing moves in the configuration space
- The moves are accepted or refused according to a given transition probability and the probability distribution function

Quantum Monte Carlo

- The random walks are done by proposing moves in the configuration space
- The moves are accepted or refused according to a given transition probability and the probability distribution function
- If too many moves are refused the algorithm is inefficient and the statistical error is big

Quantum Monte Carlo

- The random walks are done by proposing moves in the configuration space
- The moves are accepted or refused according to a given transition probability and the probability distribution function
- If too many moves are refused the algorithm is inefficient and the statistical error is big
- Importance sampling is a technique that favors moves that are likely to be accepted. Efficiency is greatly improved

Quantum Monte Carlo

- The random walks are done by proposing moves in the configuration space
- The moves are accepted or refused according to a given transition probability and the probability distribution function
- If too many moves are refused the algorithm is inefficient and the statistical error is big
- Importance sampling is a technique that favors moves that are likely to be accepted. Efficiency is greatly improved
- Importance sampling needs an approximate wave function. Ideal importance sampling is done with the exact wave function.

Quantum Monte Carlo

- The random walks are done by proposing moves in the configuration space
- The moves are accepted or refused according to a given transition probability and the probability distribution function
- If too many moves are refused the algorithm is inefficient and the statistical error is big
- Importance sampling is a technique that favors moves that are likely to be accepted. Efficiency is greatly improved
- Importance sampling needs an approximate wave function. Ideal importance sampling is done with the exact wave function.
- Wave function and its derivatives must be computed to propose the move

Quantum Monte Carlo: Diffusion Monte Carlo

- In the Diffusion Monte Carlo, an approximate Green’s function is sampled

Quantum Monte Carlo: Diffusion Monte Carlo

- In the Diffusion Monte Carlo, an approximate Green's function is sampled
- A parameter, called time step, controls the approximation. In the limit of zero time step the exact energy is obtained

Quantum Monte Carlo: Diffusion Monte Carlo

- In the Diffusion Monte Carlo, an approximate Green's function is sampled
- A parameter, called time step, controls the approximation. In the limit of zero time step the exact energy is obtained
- Finite time step is needed for carrying out the simulation

Quantum Monte Carlo: Diffusion Monte Carlo

- In the Diffusion Monte Carlo, an approximate Green’s function is sampled
- A parameter, called time step, controls the approximation. In the limit of zero time step the exact energy is obtained
- Finite time step is needed for carrying out the simulation
- Simulations at different time steps. The energy is obtained by extrapolation

Quantum Monte Carlo: Diffusion Monte Carlo

- In the Diffusion Monte Carlo, an approximate Green's function is sampled
- A parameter, called time step, controls the approximation. In the limit of zero time step the exact energy is obtained
- Finite time step is needed for carrying out the simulation
- Simulations at different time steps. The energy is obtained by extrapolation
- For atoms, the larger Z the smaller the time steps

Quantum Monte Carlo: Diffusion Monte Carlo

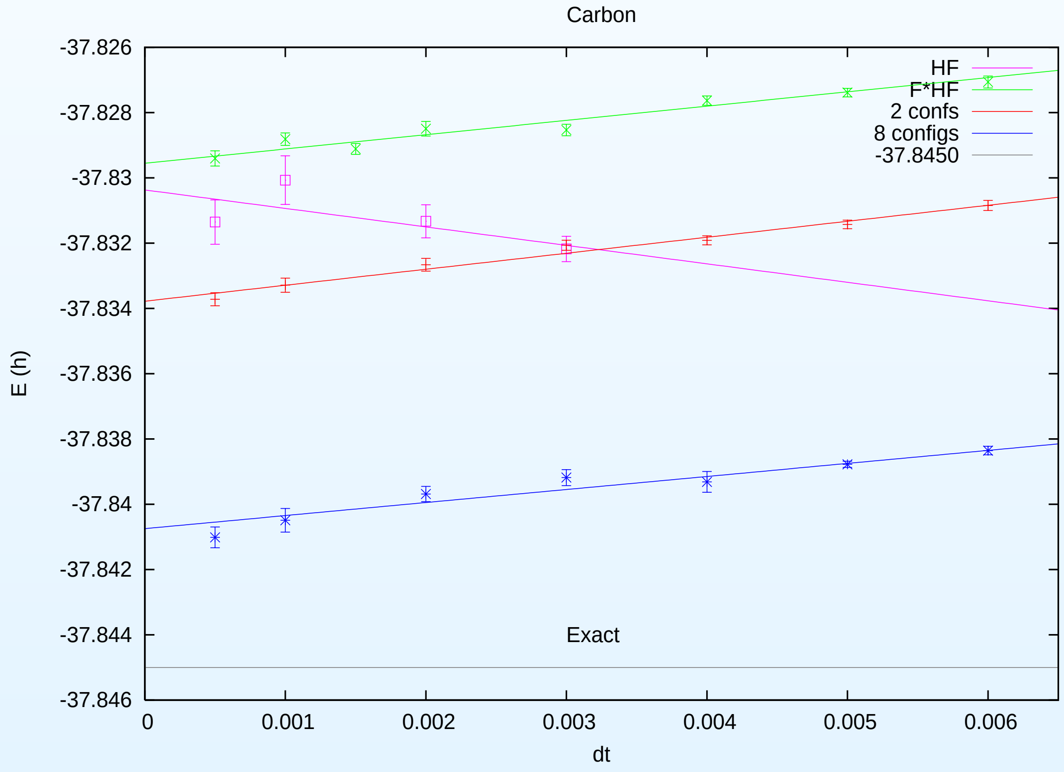
- The value of the extrapolated energy has a systematic error due to the approximate nodal surface

Quantum Monte Carlo: Diffusion Monte Carlo

- The value of the extrapolated energy has a systematic error due to the approximate nodal surface
-

Quantum Monte Carlo: Diffusion Monte Carlo

- The value of the extrapolated energy has a systematic error due to the approximate nodal surface
-



Quantum Monte Carlo: Green’s Function Monte Carlo

- The exact Green’s function (with the nodal error) is sampled

Quantum Monte Carlo: Green’s Function Monte Carlo

- The exact Green’s function (with the nodal error) is sampled
- The Green’s function is expanded in a Born series.

Quantum Monte Carlo: Green’s Function Monte Carlo

- The exact Green’s function (with the nodal error) is sampled
- The Green’s function is expanded in a Born series.
- To build the series an approximate Green’s function is used

Quantum Monte Carlo: Green’s Function Monte Carlo

- The exact Green’s function (with the nodal error) is sampled
- The Green’s function is expanded in a Born series.
- To build the series an approximate Green’s function is used
- The series is summed exactly by using Monte Carlo.

Quantum Monte Carlo: Green’s Function Monte Carlo

- The exact Green’s function (with the nodal error) is sampled
- The Green’s function is expanded in a Born series.
- To build the series an approximate Green’s function is used
- The series is summed exactly by using Monte Carlo.
- The results coincide with the extrapolated Diffusion Monte Carlo

Quantum Monte Carlo: Green’s Function Monte Carlo

- The exact Green’s function (with the nodal error) is sampled
- The Green’s function is expanded in a Born series.
- To build the series an approximate Green’s function is used
- The series is summed exactly by using Monte Carlo.
- The results coincide with the extrapolated Diffusion Monte Carlo

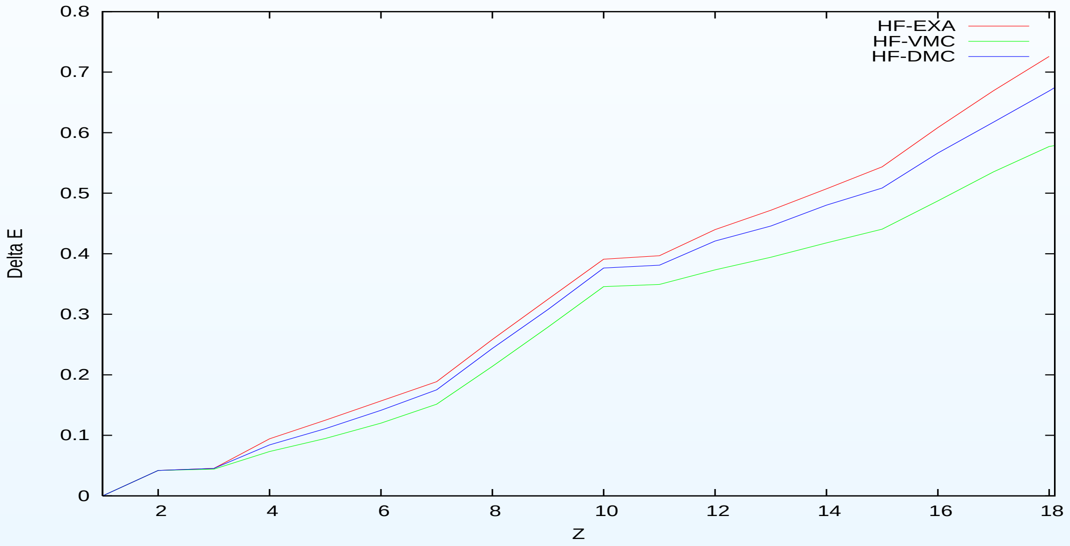
Ground state energy of the Beryllium atom in hartree

Method	Single Configuration	Two Configurations
VMC	-14.64625(4)	-14.66282(3)
DMC	-14.65740(8)	-14.66710(4)
GFMC	-14.65747(8)	-14.66717(5)
HF	-14.57302313	
Exact	-14.66736	

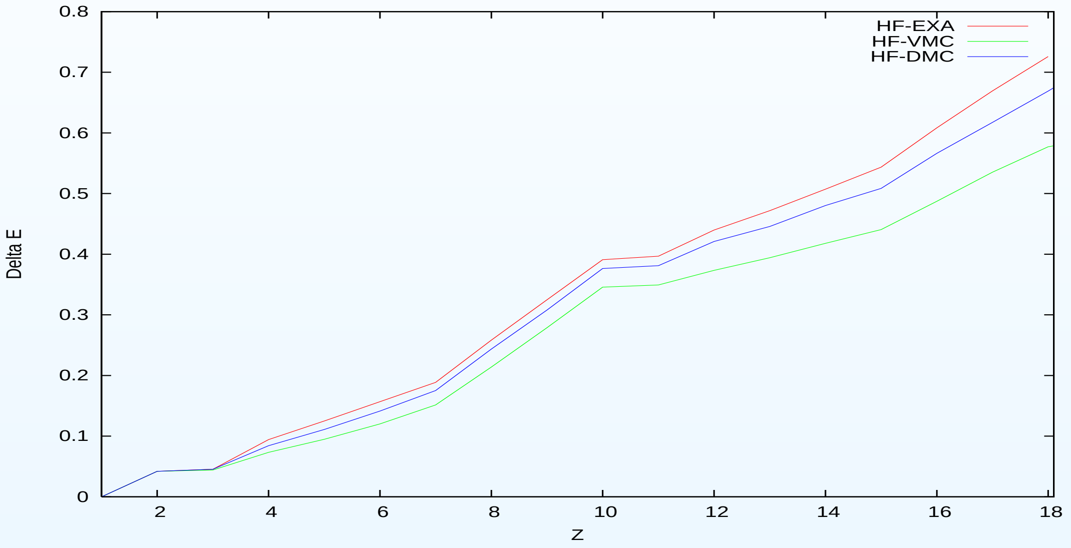
Monte Carlo Methods: Performance

-

Monte Carlo Methods: Performance

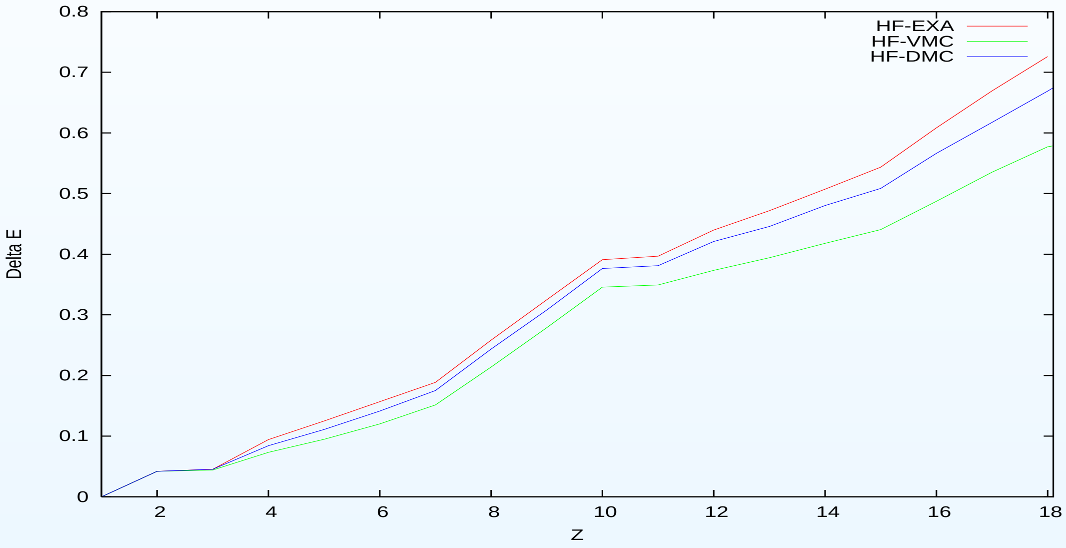
- 

Monte Carlo Methods: Performance

- 

- The correlation energy is the difference between the energy obtained in a given approximation and the Hartree-Fock energy

Monte Carlo Methods: Performance

- 

- The correlation energy is the difference between the energy obtained in a given approximation and the Hartree-Fock energy
- For atoms and cations with less than 18 electrons the non relativistic energy has been estimated. Is taken as exact here.

←

RELATIVISTIC CORRECTIONS

- Optimized Effective Potential Method
- Hamiltonian

RELATIVISTIC CORRECTIONS

- Optimized Effective Potential Method
- Hamiltonian

Optimized Effective Potential Method

- Solution of the N electron problem not including correlations

Optimized Effective Potential Method

- Solution of the N electron problem not including correlations
- Approximation to the Hartree-Fock method (relative differences below 0.01$\%$)

Optimized Effective Potential Method

- Solution of the N electron problem not including correlations
- Approximation to the Hartree-Fock method (relative differences below 0.01$\%$)
- Variational approach based on trial wave functions written as linear combination of Slater determinants

Optimized Effective Potential Method

- Solution of the N electron problem not including correlations
- Approximation to the Hartree-Fock method (relative differences below 0.01$\%$)
- Variational approach based on trial wave functions written as linear combination of Slater determinants
- The trial function is taken to have the angular momentum of the state under study

Optimized Effective Potential Method

- Solution of the N electron problem not including correlations
- Approximation to the Hartree-Fock method (relative differences below 0.01$\%$)
- Variational approach based on trial wave functions written as linear combination of Slater determinants
- The trial function is taken to have the angular momentum of the state under study
- Can be single or multi configuration anstatz

Optimized Effective Potential Method (OEP)

- The occupied orbitals are eigenfunctions of a single particle hamiltonian

Optimized Effective Potential Method (OEP)

- The occupied orbitals are eigenfunctions of a single particle hamiltonian
- The potential in the single particle hamiltonian is taken to be central

Optimized Effective Potential Method (OEP)

- The occupied orbitals are eigenfunctions of a single particle hamiltonian
- The potential in the single particle hamiltonian is taken to be central
- With these orbitals the Slater determinants are build

Optimized Effective Potential Method (OEP)

- The occupied orbitals are eigenfunctions of a single particle hamiltonian
- The potential in the single particle hamiltonian is taken to be central
- With these orbitals the Slater determinants are build
- Then the expectation value of the N-electron hamiltonian is evaluated

Optimized Effective Potential Method (OEP)

- The occupied orbitals are eigenfunctions of a single particle hamiltonian
- The potential in the single particle hamiltonian is taken to be central
- With these orbitals the Slater determinants are build
- Then the expectation value of the N-electron hamiltonian is evaluated
- The total energy is a functional of the effective potential. Optimized potential fixed variationally.

Optimized Effective Potential Method

- The method can be straightforwardly extended to multi-configurations. All of the orbitals are eigenfunctions of the same single particle hamiltonian

Optimized Effective Potential Method

- The method can be straightforwardly extended to multi-configurations. All of the orbitals are eigenfunctions of the same single particle hamiltonian
- The method can be straightforwardly extended to relativistic hamiltonian. No perturbative treatment of relativistic effects (at this non correlated level)

Optimized Effective Potential Method

- The method can be straightforwardly extended to multi-configurations. All of the orbitals are eigenfunctions of the same single particle hamiltonian
- The method can be straightforwardly extended to relativistic hamiltonian. No perturbative treatment of relativistic effects (at this non correlated level)
- The method can be used for excited states. No problems with orthogonality appear.

Optimized Effective Potential Method

- The method can be straightforwardly extended to multi-configurations. All of the orbitals are eigenfunctions of the same single particle hamiltonian
- The method can be straightforwardly extended to relativistic hamiltonian. No perturbative treatment of relativistic effects (at this non correlated level)
- The method can be used for excited states. No problems with orthogonality appear.
- The equations can be solved very accurately.

Optimized Effective Potential Method

- The method can be straightforwardly extended to multi-configurations. All of the orbitals are eigenfunctions of the same single particle hamiltonian
- The method can be straightforwardly extended to relativistic hamiltonian. No perturbative treatment of relativistic effects (at this non correlated level)
- The method can be used for excited states. No problems with orthogonality appear.
- The equations can be solved very accurately.
- Numerical solution of the single-particle Schrödinger or Dirac equation; Parameterization of the effective potential

Optimized Effective Potential Method: Algorithm

- The terms are built in terms of the configuration, either single configuration or multi-configuration. The occupied orbitals are selected and the coupling coefficients are calculated

Optimized Effective Potential Method: Algorithm

- The terms are built in terms of the configuration, either single configuration or multi-configuration. The occupied orbitals are selected and the coupling coefficients are calculated
- Starting values for the parameters of the effective potential are proposed. Potential is taken to be central.

Optimized Effective Potential Method: Algorithm

- The terms are built in terms of the configuration, either single configuration or multi-configuration. The occupied orbitals are selected and the coupling coefficients are calculated
- Starting values for the parameters of the effective potential are proposed. Potential is taken to be central.
- The occupied orbitals are calculated as the single particle eigenfunctions of the Schrödinger or Dirac equation with the potential

Optimized Effective Potential Method: Algorithm

- The terms are built in terms of the configuration, either single configuration or multi-configuration. The occupied orbitals are selected and the coupling coefficients are calculated
- Starting values for the parameters of the effective potential are proposed. Potential is taken to be central.
- The occupied orbitals are calculated as the single particle eigenfunctions of the Schrödinger or Dirac equation with the potential
- The trial wave function is built and the expectation value of the N-electron relativistic hamiltonian is computed

Optimized Effective Potential Method: Algorithm

- The terms are built in terms of the configuration, either single configuration or multi-configuration. The occupied orbitals are selected and the coupling coefficients are calculated
- Starting values for the parameters of the effective potential are proposed. Potential is taken to be central.
- The occupied orbitals are calculated as the single particle eigenfunctions of the Schrödinger or Dirac equation with the potential
- The trial wave function is built and the expectation value of the N-electron relativistic hamiltonian is computed
- The energy is minimized with respect to the parameters of the effective potential

Hamiltonian

- The relativistic hamiltonian used here is

$$H = \sum_{i=1}^{N} h_D(i) + \sum_{i<j} V_{ij} \tag{10}$$

$\longrightarrow$

Hamiltonian

- The relativistic hamiltonian used here is

$$H = \sum_{i=1}^{N} h_D(i) + \sum_{i<j} V_{ij} \tag{11}$$

$\longrightarrow$

- $h_D(i)$ is the Dirac hamiltonian with a central potential $V_n(r)$

$$h_D(i) = c\vec{\alpha}_i \cdot \vec{p}_i + c^2\beta_i + V_n(r)$$

$V_n(r)$ is the electrostatic potential of a sphere with uniform charge distribution

Hamiltonian

- The two body potential V_{ij} in

Hamiltonian

- The two body potential V_{ij} in
    - Coulomb gauge

Hamiltonian

- The two body potential V_{ij} in
  - Coulomb gauge
  - Only two-body interactions

Hamiltonian

- The two body potential V_{ij} in
    - Coulomb gauge
    - Only two-body interactions
    - Only one photon-exchange (lowest order)

Hamiltonian

- The two body potential V_{ij} in
    - Coulomb gauge
    - Only two-body interactions
    - Only one photon-exchange (lowest order)
    - Keeping to order $1/c^2$ inclusive (Breit)

Hamiltonian

- The two body potential V_{ij} in
  - Coulomb gauge
  - Only two-body interactions
  - Only one photon-exchange (lowest order)
  - Keeping to order $1/c^2$ inclusive (Breit)
- $$V_{ij} = \frac{1}{r_{ij}} - B(i,j)$$

$$B(i,j) = \frac{\vec{\alpha}_i \cdot \vec{\alpha}_j}{2r_{ij}} - \frac{(\vec{\alpha}_i \cdot \vec{r}_{ij})(\vec{\alpha}_j \cdot \vec{r}_{ij})}{2r_{ij}^3}$$

Relativistic Optimized Effective Potential solution

- The spinors in the Slater determinant are taken to be the eigen-functions of the following Dirac hamiltonian

$$h_D[V] = c\vec{\alpha}\cdot\vec{p} + c^2\beta + V(r)$$

Relativistic Optimized Effective Potential solution

- The spinors in the Slater determinant are taken to be the eigen-functions of the following Dirac hamiltonian

$$h_D[V] = c\vec{\alpha} \cdot \vec{p} + c^2\beta + V(r)$$

- $V(r)$ is the parameterized effective potential

Relativistic Optimized Effective Potential solution

- The spinors in the Slater determinant are taken to be the eigen-functions of the following Dirac hamiltonian

$$h_D[V] = c\vec{\alpha} \cdot \vec{p} + c^2\beta + V(r)$$

- $V(r)$ is the parameterized effective potential
- All of the occupied orbitals are obtained by solving the equation

$$h_D[V]\phi_{nljm}(q) = \epsilon_{njl}\phi_{nljm}(q)$$

Relativistic Optimized Effective Potential solution

- The spinors in the Slater determinant are taken to be the eigen-functions of the following Dirac hamiltonian

$$h_D[V] = c\vec{\alpha}\cdot\vec{p} + c^2\beta + V(r)$$

- $V(r)$ is the parameterized effective potential
- All of the occupied orbitals are obtained by solving the equation

$$h_D[V]\phi_{nljm}(q) = \epsilon_{njl}\phi_{nljm}(q)$$

- With the spinors the expectation value of the relativistic hamiltonian is evaluated

Relativistic Optimized Effective Potential solution

- The spinors in the Slater determinant are taken to be the eigen-functions of the following Dirac hamiltonian

$$h_D[V] = c\vec{\alpha}\cdot\vec{p} + c^2\beta + V(r)$$

- $V(r)$ is the parameterized effective potential
- All of the occupied orbitals are obtained by solving the equation

$$h_D[V]\phi_{nljm}(q) = \epsilon_{njl}\phi_{nljm}(q)$$

- With the spinors the expectation value of the relativistic hamiltonian is evaluated
- The total energy is minimized with respect to the parameters of the effective potential

$\longleftarrow$

RESULTS:Excited states of C isoelectronic

- We study here the ^{3}P, ^{1}D and ^{1}S, terms of the configuration

$$1s^2 2s^2 2p^2$$

RESULTS:Excited states of C isoelectronic

- We study here the ^{3}P, ^{1}D and ^{1}S, terms of the configuration

$$1s^2 2s^2 2p^2$$

- Effects of electronic correlations with Z

RESULTS:Excited states of C isoelectronic

- We study here the ^{3}P, ^{1}D and ^{1}S, terms of the configuration

$$1s^2 2s^2 2p^2$$

- Effects of electronic correlations with Z
- Order of the states. Interpretation of Hund rules

RESULTS:Excited states of C isoelectronic

- We study here the ^{3}P, ^{1}D and ^{1}S, terms of the configuration

$$1s^2 2s^2 2p^2$$

- Effects of electronic correlations with Z
- Order of the states. Interpretation of Hund rules
- Variational Monte Carlo

RESULTS:Excited states of C isoelectronic

- We study here the ^{3}P, ^{1}D and ^{1}S, terms of the configuration

$$1s^2 2s^2 2p^2$$

- Effects of electronic correlations with Z
- Order of the states. Interpretation of Hund rules
- Variational Monte Carlo
- Multi-Configuration model function

$$\Psi_t = F\Phi, \quad [2s^2 2p^2,\ 2p^4, 2s2p^2 3s, 2s2p^2 3p, 2p2p^2 3d]$$

RESULTS:Excited states of C isoelectronic (au)

Ion	Term	E_{POEP}	E_{MCOEP}	E	E^{1}_{exact}
C	^{3}P	-37.68862	$-37.75273[40.1]$	$-37.8295(1)[90.1]$	-37.8450
	^{1}D	-37.63132	$-37.69311[36.9]$	$-37.7829(1)[90.6]$	-37.7986
	^{1}S	-37.54982	$-37.62339[37.4]$	$-37.7287(1)[91.0]$	-37.7464
N^{+}	^{3}P	-53.88801	$-53.95734[41.6]$	$-54.0398(1)[91.2]$	-54.0545
	^{1}D	-53.80713	$-53.87305[37.1]$	$-53.9697(3)[91.6]$	-53.9847
	^{1}S	-53.68973	$-53.77473[39.4]$	$-53.8882(1)[91.9]$	-53.9056
Ne^{4+}	^{3}P	-120.54357	$-120.62591[43.9]$	$-120.7149(2)[91.4]$	-120.7310
	^{1}D	-120.39679	$-120.47959[42.2]$	$-120.5794(1)[93.1]$	-120.5930
	^{1}S	-120.18032	$-120.30168[46.8]$	$-120.4247(1)[94.2]$	-120.4398

[1] Davidson et al. Phys. Rev. A **44**, 7071 (1991) and http://physics.nist.gov/PhysRefData/ASD/index.html

RESULTS:Excited states of C isoelectronic

- Correlation energy around 40% with $F = 1$ and higher than 90% with the correlation factor

RESULTS:Excited states of C isoelectronic

- Correlation energy around 40% with $F = 1$ and higher than 90% with the correlation factor
- The virial theorem is fulfilled with accuracy higher than 99.9%. The energetic ordering of the states is governed by

RESULTS:Excited states of C isoelectronic

- Correlation energy around 40% with $F = 1$ and higher than 90% with the correlation factor
- The virial theorem is fulfilled with accuracy higher than 99.9%. The energetic ordering of the states is governed by
    - $V_{en} = Z\langle r^{-1}\rangle$ electron-nucleus potential energy

RESULTS:Excited states of C isoelectronic

- Correlation energy around 40% with $F = 1$ and higher than 90% with the correlation factor
- The virial theorem is fulfilled with accuracy higher than 99.9%. The energetic ordering of the states is governed by
  - $V_{en} = Z\langle r^{-1}\rangle$ electron-nucleus potential energy
  - $V_{ee} = \langle r_{12}^{-1}\rangle$ electron-energy potential energy

RESULTS:Excited states of C isoelectronic

- Correlation energy around 40% with $F = 1$ and higher than 90% with the correlation factor
- The virial theorem is fulfilled with accuracy higher than 99.9%. The energetic ordering of the states is governed by
    - $V_{en} = Z\langle r^{-1}\rangle$ electron-nucleus potential energy
    - $V_{ee} = \langle r_{12}^{-1}\rangle$ electron-energy potential energy
- The lower E the higher $|V_{en}|$

RESULTS:Excited states of C isoelectronic

- Correlation energy around 40% with $F = 1$ and higher than 90% with the correlation factor
- The virial theorem is fulfilled with accuracy higher than 99.9%. The energetic ordering of the states is governed by
  - $V_{en} = Z\langle r^{-1}\rangle$ electron-nucleus potential energy
  - $V_{ee} = \langle r_{12}^{-1}\rangle$ electron-energy potential energy
- The lower E the higher $|V_{en}|$
- For C and N^{+} the lower E the greater V_{ee}

RESULTS:Excited states of C isoelectronic

- Correlation energy around 40% with $F = 1$ and higher than 90% with the correlation factor
- The virial theorem is fulfilled with accuracy higher than 99.9%. The energetic ordering of the states is governed by
    - $V_{en} = Z\langle r^{-1}\rangle$ electron-nucleus potential energy
    - $V_{ee} = \langle r_{12}^{-1}\rangle$ electron-energy potential energy
- The lower E the higher $|V_{en}|$
- For C and N$^+$ the lower E the greater V_{ee}
- For the other cations the lower E the greater V_{ee}

RESULTS:Excited states of C isoelectronic

- The lower E the lower the probability of finding two electrons at the same position

RESULTS:Excited states of C isoelectronic

- The lower E the lower the probability of finding two electrons at the same position
- The average size of the atom $\langle r \rangle$ grows with the energy

RESULTS:Excited states of C isoelectronic

- The lower E the lower the probability of finding two electrons at the same position
- The average size of the atom $\langle r \rangle$ grows with the energy
- The ground state presents the less extended $e - e$ distribution and the ^{1}S the most extended one.

RESULTS:Excited states of C isoelectronic

- The lower E the lower the probability of finding two electrons at the same position
- The average size of the atom $\langle r \rangle$ grows with the energy
- The ground state presents the less extended $e - e$ distribution and the ^{1}S the most extended one.
- Angular correlations $\langle \vec{r}_1 \cdot \vec{r}_2 \rangle$. Is negative for all of the systems; depends on the state.

RESULTS:Excited states of C isoelectronic

- Angular correlations in momentum space $\langle \vec{p}_1 \cdot \vec{p}_2 \rangle$ As the kinetic energy

$$\langle T \rangle = \frac{1}{5} \left[\langle P^2 \rangle + \frac{1}{4} \langle p_{12}^2 \rangle \right]$$

RESULTS:Excited states of C isoelectronic

- Angular correlations in momentum space $\langle \vec{p}_1 \cdot \vec{p}_2 \rangle$ As the kinetic energy

$$\langle T \rangle = \frac{1}{5} \left[\langle P^2 \rangle + \frac{1}{4} \langle p_{12}^2 \rangle \right]$$

  - $\langle p_{12}^2 \rangle$ relative moment of a pair of electrons

RESULTS:Excited states of C isoelectronic

- Angular correlations in momentum space $\langle \vec{p}_1 \cdot \vec{p}_2 \rangle$ As the kinetic energy

$$\langle T \rangle = \frac{1}{5} \left[\langle P^2 \rangle + \frac{1}{4} \langle p_{12}^2 \rangle \right]$$

  - $\langle p_{12}^2 \rangle$ relative moment of a pair of electrons
  - $\langle P^2 \rangle$ moment of the center of mass of a pair of electrons

RESULTS:Excited states of C isoelectronic

- Angular correlations in momentum space $\langle \vec{p}_1 \cdot \vec{p}_2 \rangle$ As the kinetic energy

$$\langle T \rangle = \frac{1}{5}\left[\langle P^2 \rangle + \frac{1}{4}\langle p_{12}^2 \rangle\right]$$

  - $\langle p_{12}^2 \rangle$ relative moment of a pair of electrons
  - $\langle P^2 \rangle$ moment of the center of mass of a pair of electrons

- And

$$\langle \vec{p}_1 \cdot \vec{p}_2 \rangle = \langle P^2 \rangle - \frac{1}{4}\langle p_{12}^2 \rangle$$

RESULTS:Excited states of C isoelectronic

- Angular correlations in momentum space $\langle \vec{p}_1 \cdot \vec{p}_2 \rangle$ As the kinetic energy

$$\langle T \rangle = \frac{1}{5}\left[\langle P^2 \rangle + \frac{1}{4}\langle p_{12}^2 \rangle\right]$$

  - ○ $\langle p_{12}^2 \rangle$ relative moment of a pair of electrons
  - ○ $\langle P^2 \rangle$ moment of the center of mass of a pair of electrons

- And

$$\langle \vec{p}_1 \cdot \vec{p}_2 \rangle = \langle P^2 \rangle - \frac{1}{4}\langle p_{12}^2 \rangle$$

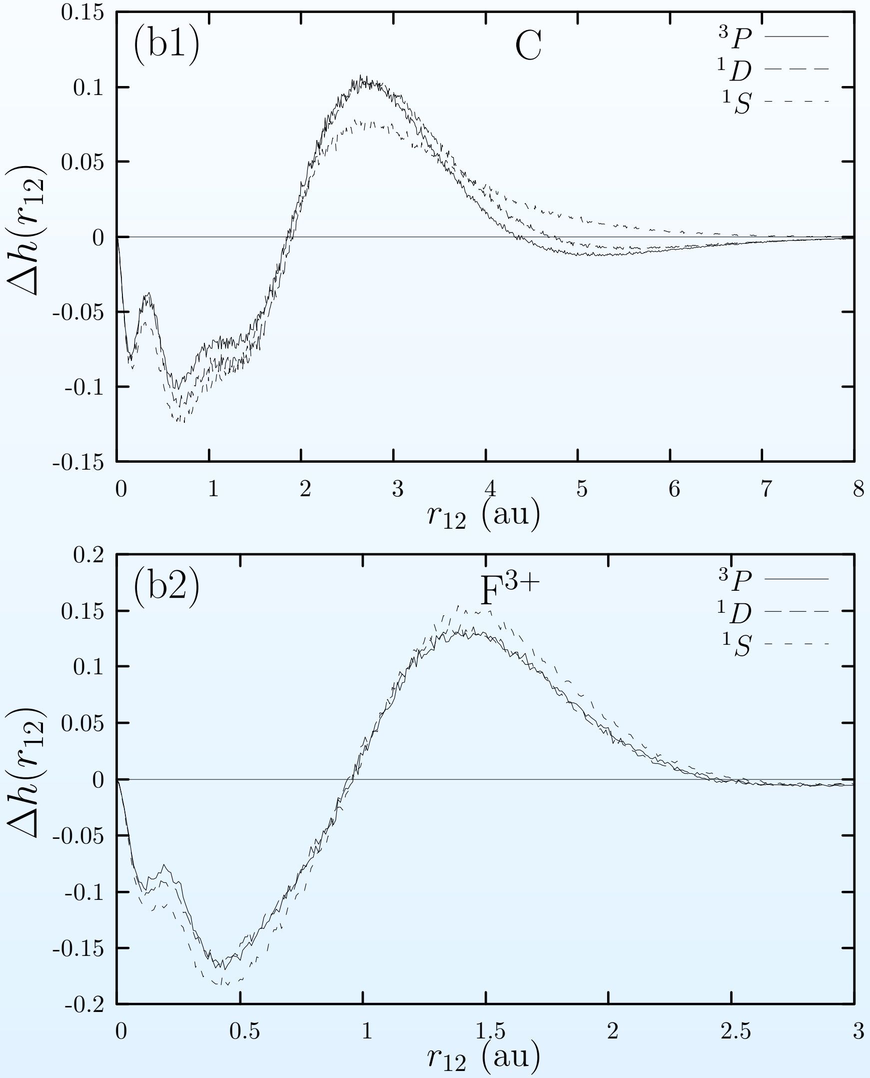
- Negative $\langle \vec{p}_1 \cdot \vec{p}_2 \rangle$ as is the case means that the main contribution to the kinetic energy comes from the interelectronic movement.

RESULTS:Excited states of C isoelectronic

- Coulomb hole

RESULTS:Excited states of C isoelectronic

- Coulomb hole

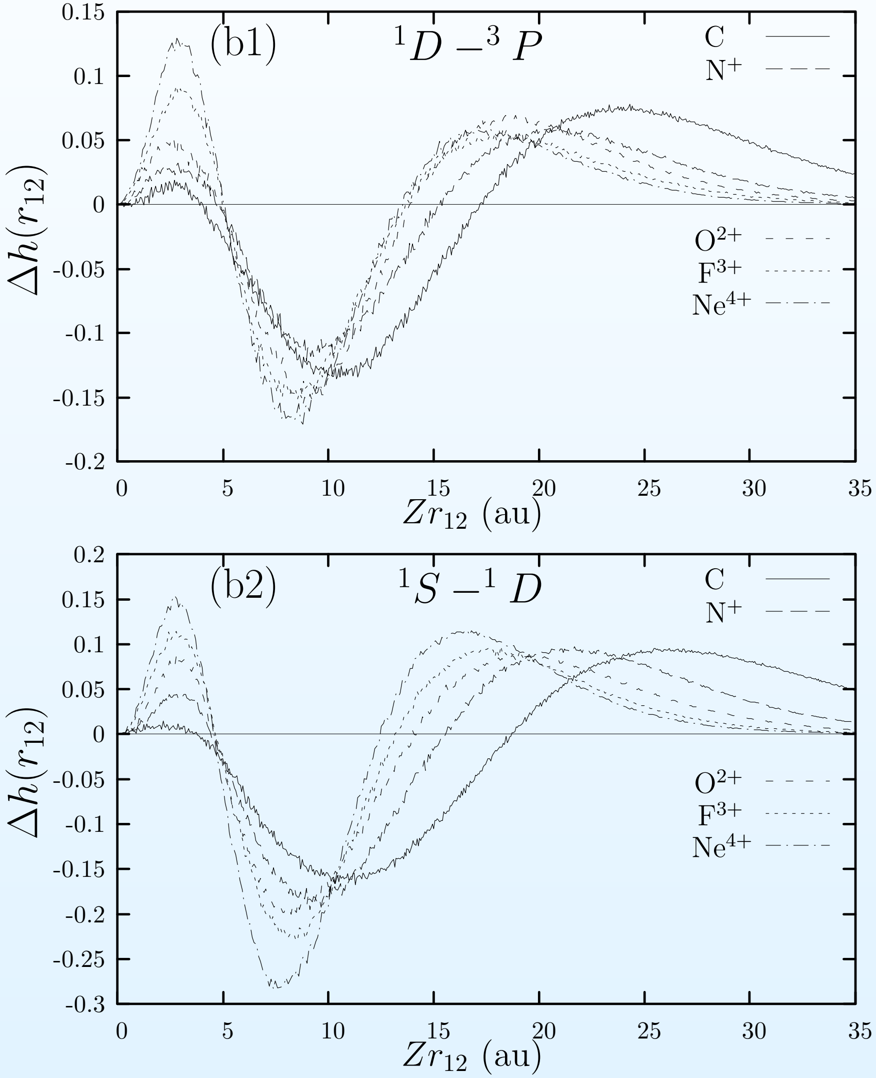


RESULTS:Excited states of C isoelectronic

- Relative interelectronic charge distribution

RESULTS:Excited states of C isoelectronic

- Relative interelectronic charge distribution



RESULTS:Ground state energy of Mg and Al

	HF	VMC-SC	VMC-CI	VMC[1]
Mg	-199.61464	-199.9865(5)[85]	-200.0002(4)[88]	-200.0002(5)[8
	DMC-SC	DMC-CI(2)	DMC[1]	MR-SDCI[2]
	-200.0340(7)[96]	-200.0390(6)[97]	-200.0389(5)[97]	-200.02520[94
	HF	VMC-SC	VMC-CI	VMC[1]
Al	-241.8767	-242.2685(5)[84]	-242.2751(5)[85]	-242.2124(9)[7
	DMC-SC	DMC-CI(2)	DMC[1]	MR-SDCI[2]
	-242.3200(7)[95]	-242.3250(7)[96]	-242.3265(10)[96]	-242.31673[94

[1] Casula et al. JCP **119** 6500 (2003), [2] Meyer et al. CP **191** 213 (1995), [3] Chakravorty et al. PRA **47** 3649 (1993)

RESULTS:Excited states of Fe (au)

	POEP		JPOEP		Exp.	
Term	$3d^6 4s^2$	$3d^7 4s^1$	$3d^6 4s^2$	$3d^7 4s^1$	$3d^6 4s^2$	$3d^7 4s^1$
^5D	0.0		0.0		0.0	
^5F		0.065		-0.001(3)		0.032
^5P		0.137		0.055(4)		0.080
^3H	0.098		0.093(5)		0.089	
^3G	0.125		0.124(4)		0.108	
^1G		0.157		0.078(5)		0.112
^3D		0.175		0.097(4)		0.119
^1I	0.148		0.138(4)		0.134	
^1G	0.156		0.145(4)		0.136	

RESULTS:Ionization potential electron affinity of Fe

	NPOEP	RNPOEP	VMC[1]	VMC
E(au)	-1262.42539	-1271.52694	-1263.20(2)	-1263.376(2)
IP(eV)	6.4372	6.7172		7.51(8)
EA(eV)	-2.4191	-2.5796		-0.11(8)

	GFMC	R-VMC	R-GFMC	Exp
E (au)	-1263.550(4)			
IP(eV)	7.6(2)	7.88(8)	7.9(2)	7.9024
EA(eV)		-0.27(8)		0.151(3)

[1] Foulkes et al. RMP **73** 33 (2001)

Exp from http://physics.nist.gov/PhysRefData/ASD/index.html

RESULTS:Excitation energy (au) of Fe, [Ar]$3d^6 4s^2\ {}^1S$

	E	ΔE
POEP	-1262.254729	0.181594
VMC-JPOEP	-1263.203(4)	0.173(6)
GFMC-JPOEP	-1263.34(4)	0.24(5)
Ion Pot		0.290408

Non correlated (POEP) and VMC gives an state within the discrete spectrum. GFMC gives a correction in the proper (experimental) direction

RESULTS: Ionization potential (eV)

	OEP	VMC(1)	VMC(2)	DMC(1)	DMC(2)	Exp
Li	5.3419138	5.3926(5)		5.3914(4)		5.39
Be	8.0444562	8.807(4)	9.258(8)	9.051(2)	9.3199(4)	9.32
B	7.9317234	8.376(3)	7.933(4)	8.452(3)	8.153(3)	8.30
C	10.786462	11.343(5)	10.950(4)	11.410(7)	11.129(5)	11.26
N	13.957512	14.686(5)	14.351(5)	14.713(5)	14.487(5)	14.53
O	11.885734	13.46(1)		13.62(2)		13.62
F	15.718087	17.41(1)		17.44(1)		17.42
Ne	19.844827	21.630(3)		21.660(4)		21.56

RESULTS: Electron affinity (eV)

	OEP	VMC(1)	VMC(2)	DMC(1)	DMC(2)	Exp
Li	-0.122311	0.365(2)	0.5728(8)	0.559(2)	0.619(1)	0.618049
B	-0.267741	0.238(3)	0.006(4)	0.337(4)	0.177(3)	0.279723
C	0.550339	1.291(5)	1.101(4)	1.336(8)	1.219(5)	1.262118
O	-0.535772	1.31(1)		1.36(2)		1.461112
F	1.363416	3.39(2)		3.44(1)		3.4011887

(1) and (2) stand for one or two configurations in the trial wave function.

CONCLUSIONS AND PERSPECTIVES

- Variational Monte Carlo and Quantum Monte Carlo have been used to study electronic structure of atoms

CONCLUSIONS AND PERSPECTIVES

- Variational Monte Carlo and Quantum Monte Carlo have been used to study electronic structure of atoms
- Relativistic corrections are included perturbativelly

CONCLUSIONS AND PERSPECTIVES

- Variational Monte Carlo and Quantum Monte Carlo have been used to study electronic structure of atoms
- Relativistic corrections are included perturbativelly
- Densities, excitation energies, ionization potential and electron affinities are calculated and compared with the experimental results

CONCLUSIONS AND PERSPECTIVES

- Variational Monte Carlo and Quantum Monte Carlo have been used to study electronic structure of atoms
- Relativistic corrections are included perturbativelly
- Densities, excitation energies, ionization potential and electron affinities are calculated and compared with the experimental results
- Study of correlation and relativistic effects

CONCLUSIONS AND PERSPECTIVES

- Improvement of the trial wave function.

CONCLUSIONS AND PERSPECTIVES

- Improvement of the trial wave function.
- Extend the study to more atoms

CONCLUSIONS AND PERSPECTIVES

- Improvement of the trial wave function.
- Extend the study to more atoms
- Consider relativity and correlations simultaneously, at least in VMC

CONCLUSIONS AND PERSPECTIVES

- Improvement of the trial wave function.
- Extend the study to more atoms
- Consider relativity and correlations simultaneously, at least in VMC
- Study molecular systems

CONCLUSIONS AND PERSPECTIVES

- Improvement of the trial wave function.
- Extend the study to more atoms
- Consider relativity and correlations simultaneously, at least in VMC
- Study molecular systems
- Thank you

←