

# Accuracy of the Pseudopotential and Fixed-Node Approximations in Quantum Monte Carlo



Richard G. Hennig and C. J. Umrigar

How to go beyond the fixed-node approximation for C<sub>2</sub> and Si<sub>2</sub> dimer? How accurate are different forms of the pseudopotential for silicon?

#### **Quantum Monte Carlo calculations**

- Reduction of fixed-node error by optimizing multi-determinant wave function
- Energy and bond length of C<sub>2</sub> and Si<sub>2</sub> dimer
  compared to quantum chemistry and experiment
- Comparison of different Si pseudopotentials



Pseudopotentials accurate for Si<sub>2</sub> and defects with HF most accurate. Fixed-node error can differ dramatically for seemingly similar systems.

# Outline

### **1. Accuracy fixed-node approximation for C**<sub>2</sub>

- Multi-determinant trial wave function
- Optimization of determinantal parameters

#### 2. Accuracy for C<sub>2</sub> and Si<sub>2</sub> dimer and defects

• Comparison of binding energy and bond length with quantum chemistry and experiment

### 3. Pseudopotentials for Si<sub>2</sub> and crystalline Si

- Troullier-Martins, Vanderbilt-85 & Dolg form
- HF, LDA and PBE functionals



QMC method and software Defect calculations DFT and pseudopotential code

Advice and discussions

Funding and computer resources

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# **Importance of Defects in Silicon Devices**

### **Motivation**

- Ion implantation-induced interstitials precipitate as extended {311} defects
- Dopant transient enhanced diffusion
- Radiation damage





- Device simulations require accurate defect properties as input
- Sandia QASPR Project (Qualification Alternatives to Sandia Pulsed Reactor)
- Device simulation code CHARON

Provide accurate defect properties with known uncertainty

### **Accuracy of density functionals for defects**

Climbing "Jacob's ladder" of density functionals improves the accuracy for defect formation energies.



Lowest energy barrier from X to H defect is similar in QMC and DFT. The T defect and its barrier are higher in QMC.

# **Benchmark Quantum Monte Carlo Calculations**

### **Stochastic solution of many-body Schrödinger equation:**

- Wave function = Jastrow factor × sum of Slater determinants
- Variational Monte Carlo: Energy optimization [Umrigar & Filippi]
- **Diffusion Monte Carlo:** Ground state projection by imaginary time Schrödinger equation

### **Controlled approximations**

Statistical error (increase sampling size)

Finite-size (larger systems)

Time-step (smaller time step)

Population control (more walkers, projections)

Grid-size (decrease grid spacing)

Fixed node error (for molecules)

## **Uncontrolled approximations**

Fixed node error (for solids) Pseudopotential Pseudopotential locality



**Goal: Reduce error of controllable approximations below 0.1 eV. Estimate error magnitude of uncontrolled approximations.**  **Functional form of trial wave function** 

 $\psi_{t} = \mathcal{J}(r_{i}, r_{j}, r_{ij}) \times \sum d_{n} \mathcal{D}_{n}^{\uparrow} \mathcal{D}_{n}^{\downarrow}$ 

Jastrow factor

*n* Sum of Slater determinant

Determinant

$$\sum d_n {\cal D}_n^{\uparrow} {\cal D}_n^{\downarrow}$$

n

• Up and down spin determinants of single-particle orbitals

**Jastrow** 
$$\mathcal{J}(r_i, r_j, r_{ij}) = \prod_{\alpha i} \exp(A_{\alpha i}) \prod_{ij} \exp(B_{ij}) \prod_{\alpha ij} \exp(C_{\alpha ij})$$
  
electron-ion electron-electron electron-electron-ion correlations  
Jastrow parameters  $\propto N_{\text{atomtype}}$   
Determinantal coefficients  $\propto e^{N_{\text{atom}}}$ 

**Power of QMC:** 

Jastrow parameters do the work of determinantal coefficients.

# **Energy optimization methods**

Minimizing the energy on a finite set of MC points, requires a very large MC sample and is highly inefficient.

The following three methods avoid this by using an expression that for an infinite MC sample minimizes the energy and for a finite set cancels most of the fluctuations.

### **1. Modified Newton method:**

Umrigar, Filippi PRL 94, 150201 (2005); Sorella PRB 71, 241103 (2005)

#### 2. Linear method for non-linear parameters:

Extension by Umrigar, Toulouse & Filippi of linear parameter method by Nightingale, Melik-Alaverdian, PRL 87, 043401 (2001)

#### 3. Perturbative method:

Modification by Toulouse & Umrigar of perturbative EFP method by Scemama-Filippi and EFP method by Fahy-Filippi-Prendergast-Schautz



Fixed-node error of 1 eV reduced by multi-determinant wave function. Optimization of determinant coefficients improves convergence.

## **Energy Extrapolation**



- Large fixed node error of 1 eV for C<sub>2</sub> dimer
- Energy converges rapidly with number of determinants
- Extrapolation required to obtain accurate total energies
- Choice: Linear extrapolation with respect to sum of CSF coefficients
- Cancellation of error desired for calculation of energy differences

### **Cancellation of error for C<sub>2</sub> dimer**



- Smaller error in DMC, still requires error cancellation
- Use equivalent basis sets for atom and dimer calculations
- Include all excitations within small space of orbitals
- CAS-MCSCF wave function provides excellent error cancellation in QMC

**Binding energy of C<sub>2</sub> and Si<sub>2</sub>** 



- No systematic improvement in DFT
- Slow convergence with number of determinants in MCSCF
- $\bullet$  Error cancellation by CAS-MCSCF necessary for  $C_2$  but not  $Si_2$
- Dramatically different fixed node errors for seemingly different systems C<sub>2</sub>: 1 eV and Si<sub>2</sub>: 0.1 eV

# **Bond length of C<sub>2</sub> and Si<sub>2</sub>**



- Bond length less sensitive to Hamiltonian
- Accurate geometries from DFT and quantum chemistry

## **Pseudopotential accuracy for energies**



- LDA pseudopotential overbinds, PBE improves, HF falls in between
- Experimental energy not accurate enough to distinguish

# **Pseudopotential accuracy for geometries**



- Large differences in bond length for different pseudopotentials
- Small dependence on r<sub>c</sub> for all types of potentials
- HF pseudopotential most accurate for geometries



• Shirley HF pseudopotentials twice as efficient as others

## **Pseudopotential efficiency for Si**



#### **More efficient pseudopotentials for:**

- Larger r<sub>c</sub>
- Smaller non-locality in Vanderbilt construction



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#### **Chemical accuracy for binding energies and bond lengths requires**

• Optimized multi-determinant wave function for  $C_2$  and  $Si_2$  dimension

#### **Fixed-node approximation**

- Small error of 0.1 eV for  $Si_2$
- Large error of 1 eV for C<sub>2</sub>

#### **Pseudopotential error**

- Small for Si<sub>2</sub> with PBE and HF pseudopotentials
- Best geometries for HF pseudopotential



Fixed-node error can differ dramatically for seemingly similar systems.

## **From Compact to Extended Defects**

#### **Ion Implantation**



## **Interstitial Defects in Crystalline Silicon**

#### DMC for 16 atom defect cells

#### HF vs. LDA pseudopotentials

LDA vs. GGA orbitals



Pseudopotential error < 0.2 eV

Indication of small fixed-node error

Both pseudopotentials and orbitals result in accurate defect energies. Pseudopotential and fixed-node approximation might be accurate.