

Ab-initio Approaches to Quantum-mechanical Many-electron Problem

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SCIENTIFIC INNOVATION THROUGH INTEGRATION

Introduction



ab-initio -- from the beginning

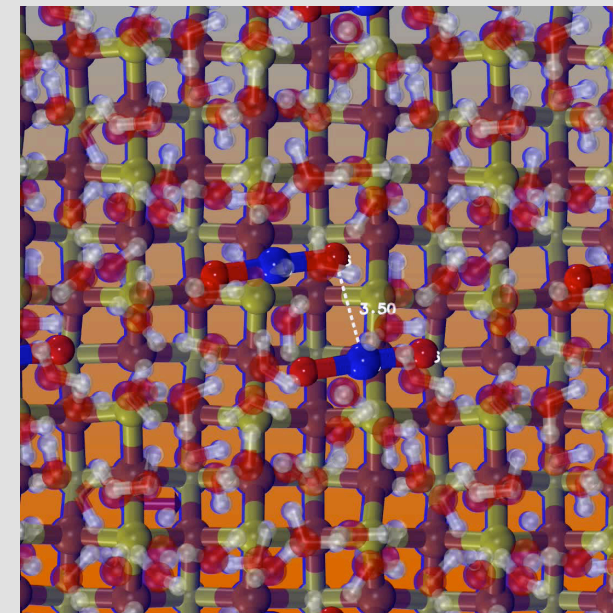
The Concise Oxford Dictionary. Oxford University Press, 2001

ab-initio calculation -- A method of calculating atomic and molecular structure directly from the first principles of quantum mechanics, without using quantities derived from experiment (such as ionization energies found by spectroscopy) as parameters.

A Dictionary of Chemistry. Oxford University Press, 2000.

Classical vs Ab-Initio Methods

CLASSICAL METHODS	AB-INITIO METHODS
Phenomenological potential energy surface (<i>typically two body contributions</i>)	Potential energy surface calculated directly from the Schrodinger equation (<i>many-body terms included automatically</i>)
Difficult to describe bond breaking/making	Describes bond breaking/making
Electronic properties are <u>not</u> available	Electronic spectra included in calculation
Can do millions of particles	Limited to 1500 atoms with significant dynamics



AIMD simulation of U(VI)-U(VI) dimerization on solvated Mackinawite surface(300°K)

greater range of task counts, we reduced the number of MPI tasks per node below 16. This necessitates restricting the number of threads to one thread/MPI task to ensure that each MPI task could use more than one but not more than one core for its computation. The resulting strong scaling curve is plotted in Fig. 1. The reduced efficiency at high number of MPI tasks is due to the fact that building the linear system with a large principal submatrix becomes more expensive (more communication) and is used less efficiently. For example, there is an average of 8, 4, 2, 1 and 0.5 columns of data for, respectively, for the number of tasks utilized

Many-Electron Problem



- Many-electron Hamiltonian

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_{r_i}^2 + \sum_i v_{ion}(r_i) + \sum_{i>j} \frac{1}{|r_i - r_j|}$$

- Schrödinger equation

$$\hat{H}\Psi = E\Psi$$

Many-electron wavefunction



- Antisymmetrical (Pauli exclusion principle)

$$\Psi(r_1, r_2) = -\Psi(r_2, r_1)$$

- Slater determinants expansion

$$\Psi(r_1, r_2, \dots, r_N) = \sum_{i_1 < i_2 < \dots < i_N} \alpha_{i_1 i_2 \dots i_N} A[\psi_{i_1}(r_1) \psi_{i_2}(r_2) \dots \psi_{i_N}(r_N)]$$

- Example: two particle system

$$\Psi(r_1, r_2) = \sum_{i < j} \alpha_{ij} (\psi_i(r_1) \psi_j(r_2) - \psi_i(r_2) \psi_j(r_1))$$

Variational Principle



- Formally equivalent to Schrödinger equation

$$E = \min_{\Psi} \left[\frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \right]$$



$$\hat{H}\Psi = E\Psi$$

- In practice minimization is always performed over some restricted space
- Example Methods – HF, CI, MCSCF, CCSD,...

Hartree-Fock (HF) Method



- Wavefunction as a single Slater determinant

$$\Psi^{HF}(r_1, r_2, \dots, r_N) = A[\psi_1(r_1)\psi_2(r_2)\dots\psi_N(r_N)]$$

- Variational Principle

$$\frac{\delta}{\delta\psi_i} \langle \Psi^{HF} | H | \Psi^{HF} \rangle = 0, \quad \langle \psi_i | \psi_j \rangle = \delta_{ij}$$

- Hartree-Fock Equations

$$\left[-\frac{1}{2} \nabla^2 + v_{ion}(r) + \sum_j \int \frac{|\psi_j(r')|^2}{|r-r'|} dr' \right] \psi_i(r) - \sum_j \psi_j(r) \int \frac{\psi_j(r')\psi_i(r')}{|r-r'|} dr' = \epsilon_i \psi_i(r)$$

Perturbation Approach



- Identify solvable reference part and the perturbation

$$\hat{H} = \hat{H}_{ref} + \lambda \hat{H}_{pert}$$

- Expand in powers of λ

$$E = E_{ref} + \lambda E_1 + \lambda^2 E_2 + \dots$$

- *All corrections are expressed in terms of H_{ref}
Moller-Plesset perturbation theory (MP2, ...)*

Density-Functional Theory (DFT)



- 1) Hohenberg-Kohn theorem(s) : $n(r) \rightarrow \Psi(r_1, r_2, r_3, \dots)$
 - Kohn-Sham DFT starts assumes $n(r)$ expanded in terms of non-interacting orbitals
 - $n(r) \equiv \sum_{i=1}^N |\psi_i|^2$

2) DFT as a self-consistent perturbation theory

$$\hat{H} = \underbrace{-\frac{1}{2} \sum [\nabla_i^2 + v_{ion}(r_i) + v_{eff}(r_i)]}_{\text{Reference Hamiltonian}} + \underbrace{\left[\sum_{i>j} \frac{1}{|r_i - r_j|} - \sum v_{eff}(r_i) \right]}_{\text{perturbation}}$$

The effective potential is adjusted to bring the reference system closer to the real system and thus minimize the expansions errors

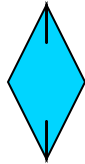
Optimal Effective Potential



$$E = E_{ref} + \lambda E_1 + \lambda^2 E_2 + \dots + \Delta E$$

$$\frac{\delta \Delta E}{\delta v_{eff}(r)} = 0$$

Optimal
Effective
Potential



Density of the reference
system coincides with true
density

Exchange-correlation potential



$$v_{eff}(r) = \int \frac{n(r')}{|r - r'|} dr' + v_{xc}(r)$$

How to determine $v_{xc}(r)$

- perturbation expansion (OEP, etc)
- slow varying density approximation (LDA)
- semi ad hoc guesses fitted to an experimental data (GGA, B3LYP,...)

Kohn-Sham Equations



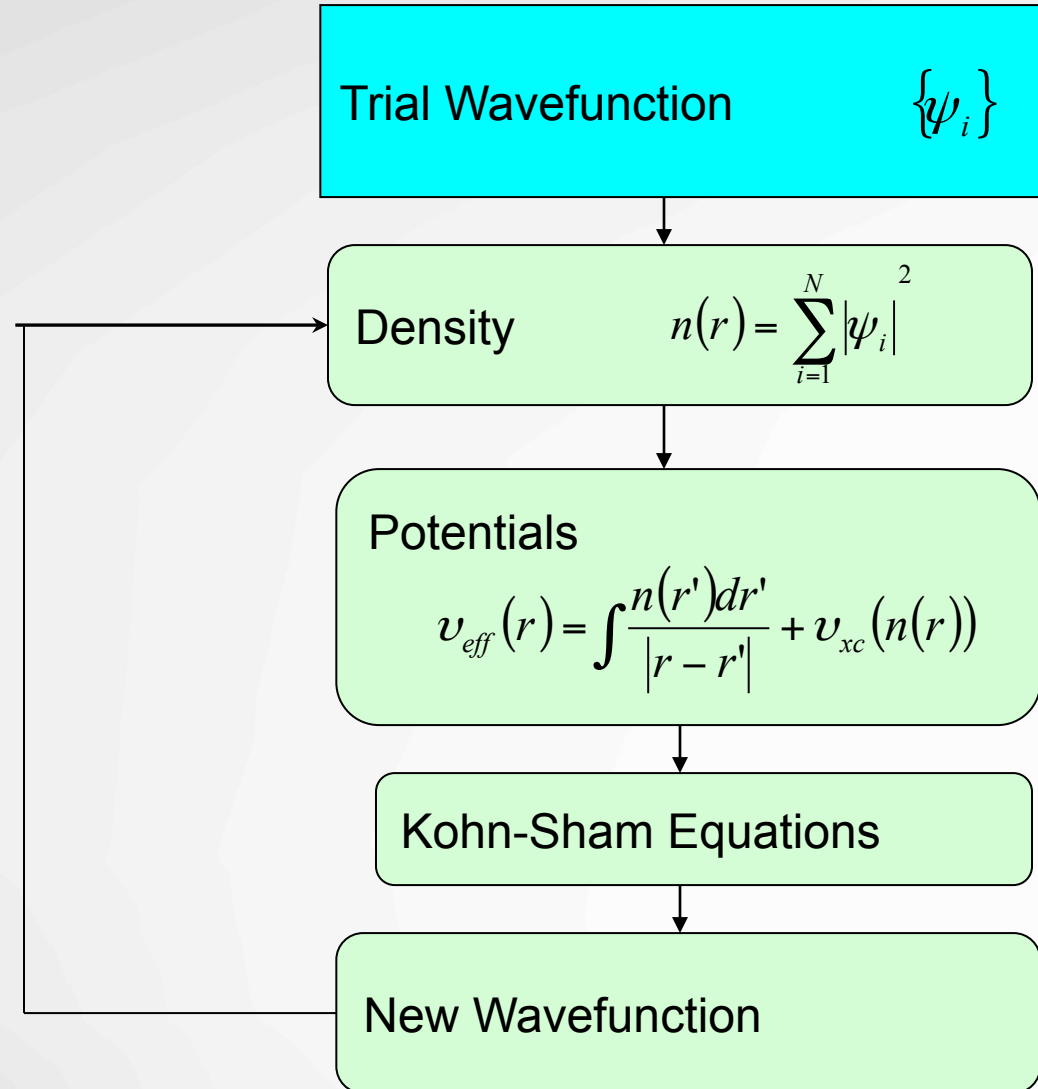
- Nonlinear eigenvalue problem

$$\left(-\frac{1}{2} \nabla^2 + v_{ion} + v_H[n] + v_{xc}[n] \right) \psi_i = e_i \psi_i$$

$$n(r) = \sum_{i=1}^N |\psi_i|^2$$

- Require self-consistent solution

Self-Consistent Loop



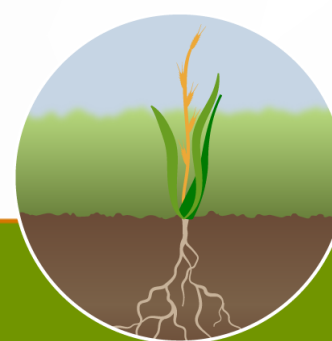
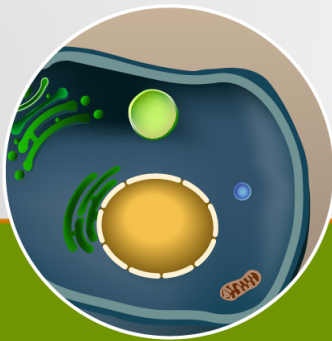
Conclusion



- Ab-initio methods can solve problems which are outside the scope of classical simulations.
- Ab-initio methods are demanding in terms of computing resources
- Density-functional methods provide a good mix of accuracy and efficiency
- Parallel computers and software (e.g. NWChem) are a must for practical applications of ab-initio methods.

Introduction to Plane-Wave Basis Sets and Pseudopotential Theory

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SCIENTIFIC INNOVATION THROUGH INTEGRATION

Kohn-Sham Equations



- ▶ Nonlinear eigenvalue equations

$$\left(-\frac{1}{2} \nabla^2 + v_{ion} + v_H[n] + v_{xc}[n] \right) \psi_i = e_i \psi_i$$

$$n(r) = \sum_{i=1}^N |\psi_i|^2$$

- ▶ Require self-consistent solution
- ▶ In order to solve these equations we need to expand the wavefunctions Ψ in a basis set

$$\psi_i = \sum_{\alpha} c_{\alpha} \varphi_{\alpha}$$

Gaussian DFT Versus Plane-Wave DFT



Gaussian Basis Set

Parallel Efficient

All-Electron

- Core regions included in calculation
- First row transition metals can readily be calculated

Ab Initio MD expensive

- Pulay forces

Different basis sets for molecules and solids

High-Level Methods worked out

PlaneWave Basis Set

Parallel Efficient

Requires pseudopotentials to be efficient

- Not all-electron
- Core region not included
- First row transition metals are difficult
 - Norm-conserving pseudopotentials of the nodeless 3d states require large plane-wave basis sets
 - Significant overlap between the valence 3d states and core densities

Efficient Ab Initio MD

- Car-Parrinello

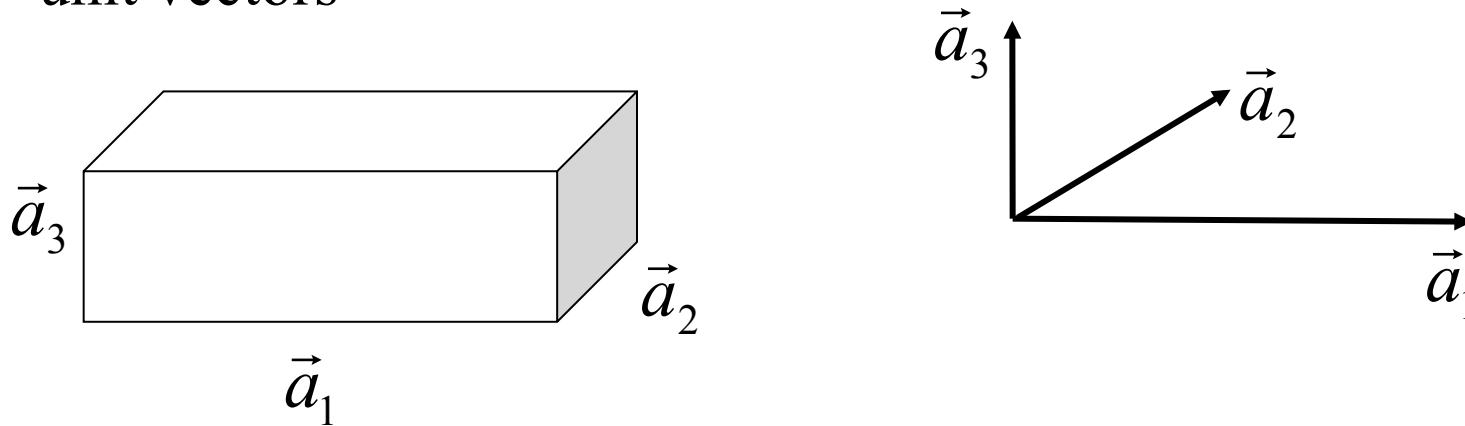
Same basis set for molecules and solids

Still work to be done to make High-level methods work well

Plane-Wave Basis Sets



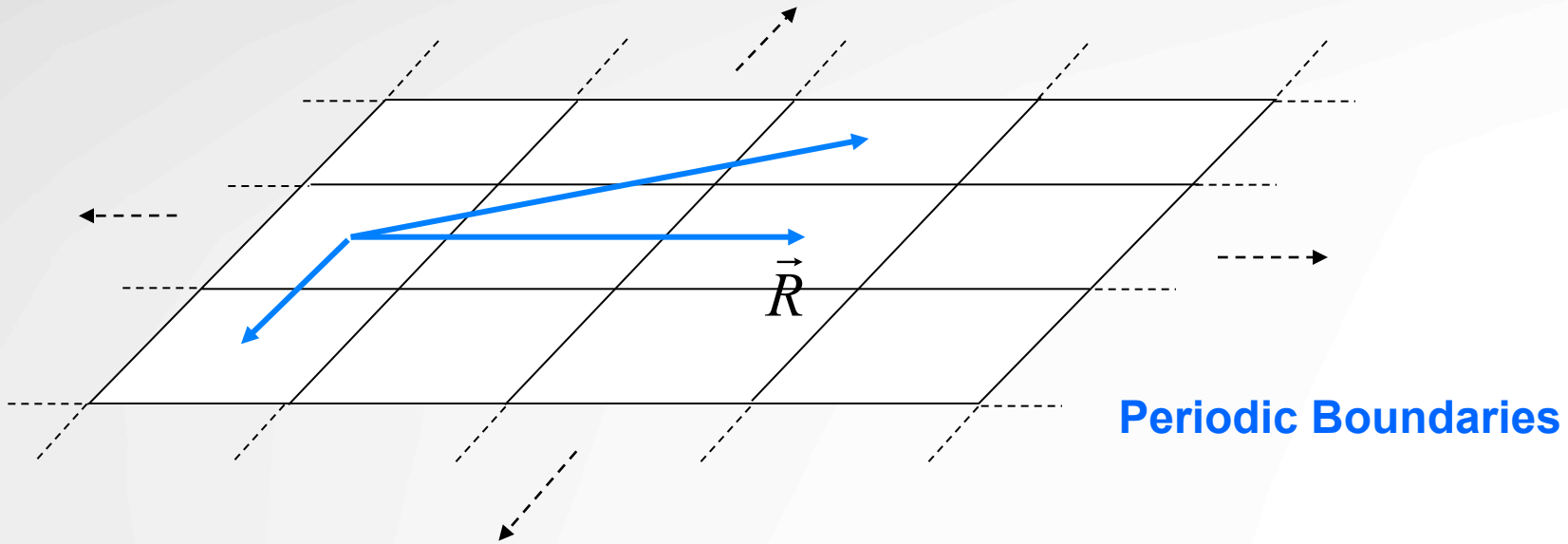
System is assumed to be placed inside a unit cell defined by the unit vectors



The volume of the unit cell is

$$\Omega = [\vec{a}_1, \vec{a}_2, \vec{a}_3] = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$$

Plane-Wave Basis Sets



$$\vec{r} \rightarrow \vec{r} + \vec{R}$$

where

$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3, \quad n_1, n_2, n_3 = \text{integers}$$



Plane-Wave Basis Sets

$$u_n(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \tilde{\psi}_n(\vec{G}) e^{i\vec{G}\cdot\vec{r}} \quad \text{Plane-wave Expansion}$$

Since our system is periodic our plane-wave expansion must consist of only the plane-waves $e^{i\vec{G}\cdot\vec{r}}$ that have the periodicity of the lattice,

We can determine these plane-waves from the following constraint

$$e^{i\vec{G}\cdot(\vec{r} + \vec{R})} = e^{i\vec{G}\cdot\vec{r}}$$



Plane-Wave Basis Sets

It is easy to show from the periodicity constraint that the wave-vectors can be defined in terms of the following reciprocal lattice vectors

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\Omega}$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\Omega}$$

Reciprocal lattice vectors

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\Omega}$$

Wave-vectors that satisfy the periodicity of the lattice

$$\vec{G}_{i_1 i_2 i_3} = \left(i_1 - \frac{N_1}{2} \right) \vec{b}_1 + \left(i_2 - \frac{N_2}{2} \right) \vec{b}_2 + \left(i_3 - \frac{N_3}{2} \right) \vec{b}_3$$

Plane-Wave Basis Sets



The exact form of the plane-wave expansion used in plane-wave code is

$$u_n(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{i_1=1}^{N_1} \sum_{i_2=1}^{N_2} \sum_{i_3=1}^{N_3} \tilde{u}_n(\vec{G}_{i_1 i_2 i_3}) e^{i\vec{G}_{i_1 i_2 i_3} \cdot \vec{r}}$$

The upper-limits of the summation (N_1, N_2, N_3) control the spacing of the real-space grid

$$\vec{r}_{i_1 i_2 i_3} = \left(\frac{i_1}{N_1} - \frac{1}{2} \right) \vec{a}_1 + \left(\frac{i_2}{N_2} - \frac{1}{2} \right) \vec{a}_2 + \left(\frac{i_3}{N_3} - \frac{1}{2} \right) \vec{a}_3$$



Plane-Wave Basis Sets

There is a further truncation of plane wave expansion in plane-wave calculations. Namely, only the reciprocal lattice vectors whose kinetic energy lower than a predefined maximum cutoff energy,

$$\frac{1}{2} |\vec{G}|^2 < E_{cut} \quad \text{Wavefunction Cutoff Energy}$$

are kept in the expansion, while the rest of the coefficients are set to zero. Besides reducing the computational load, this truncation strategy limits the effects of unit cell orientation on the outcome of the calculation.

DFT calculations rarely use a completely converged plane-wave basis, but that convergence is usually unnecessary. However, incomplete basis set calculations using different cell sizes require that each calculation use the same E_{cut}

Plane-Wave Basis Sets



Since the density is the square of the wavefunctions, it can vary twice as rapidly. Hence for translational symmetry to be formally maintained the density, which is also expanded using plane-waves

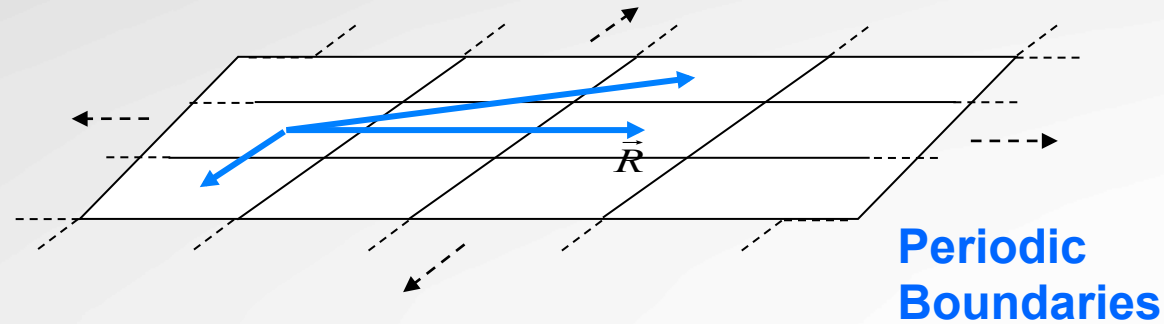
$$\rho(\vec{r}) = \sum_n u_n^*(\vec{r}) u_n(\vec{r}) = \sum_{\vec{G}} \tilde{\rho}(\vec{G}) e^{i\vec{G}\cdot\vec{r}}$$

Should contain 8 times more plane-waves than the corresponding wavefunction expansion

$$\frac{1}{2} |\vec{G}|^2 < 4E_{cut} \quad \text{Density} \quad \text{Cutoff Energy}$$

Often the Density cutoff energy is chosen to be the same as the wavefunction cutoff energy – This approximation is known as dualling

Plane-Wave Basis Sets



In solid-state systems, the plane-wave expansion given by

$$u_n(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \tilde{u}_n(\vec{G}) e^{i\vec{G}\cdot\vec{r}} \quad \text{G-point Plane-wave Expansion}$$

is not complete. Based on the fact that the translation operators $T(\mathbf{R})$ are compatible with the Hamiltonian of the system, $[T(\mathbf{R}), H]=0$, and that not all eigenkets of $T(\mathbf{R})$ can be expanded strictly in terms of the set of eigenkets $|u_n\rangle$. The wavefunction expansion can be generalized

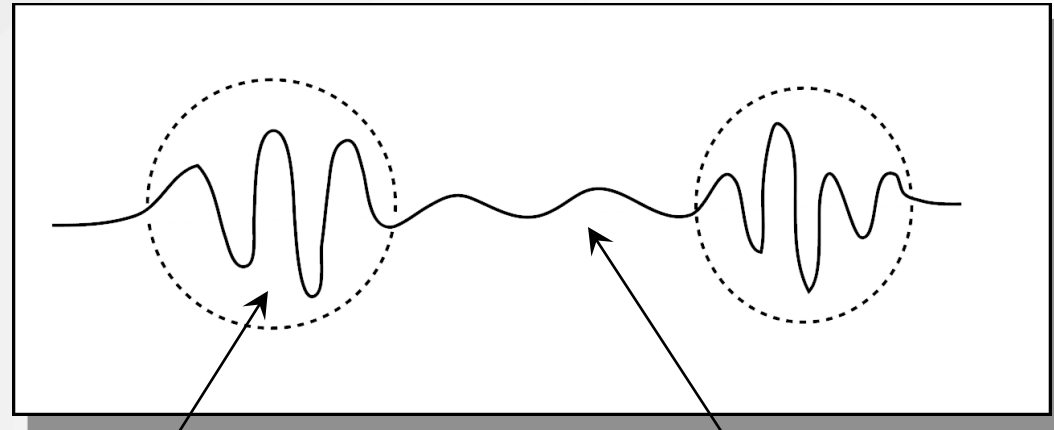
$$|\vec{k}, n\rangle = |\vec{k}\rangle |u_n\rangle \quad \text{or} \quad \psi_{\vec{k}, n}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_n(\vec{r}) \quad \text{Bloch's Theorem}$$

Where \mathbf{k} are all the allowed wave-vectors in the primitive cell of the reciprocal lattice.

Motivations for Pseudopotential Method



Valence wavefunction behavior in a typical molecular system



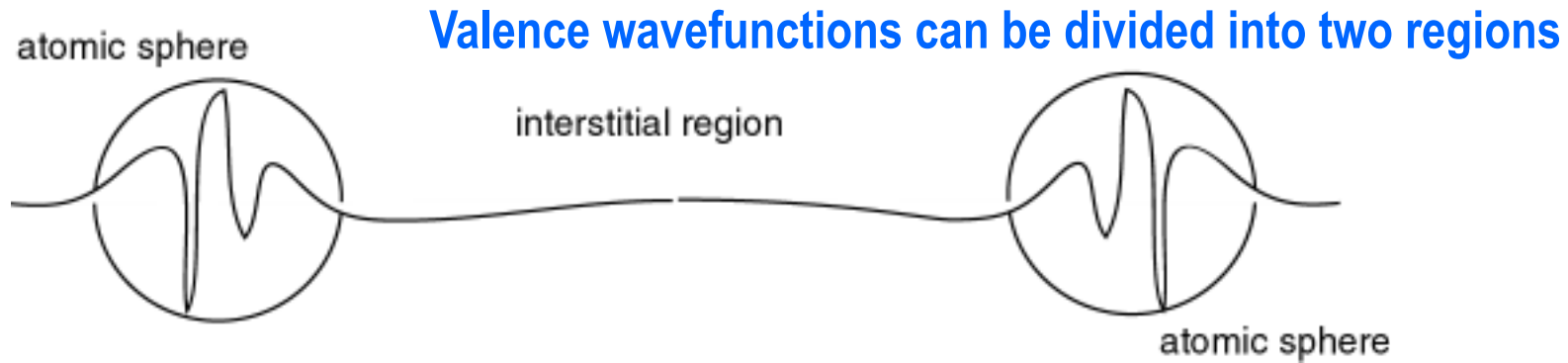
Atomic sphere region:

$$\sum_{\alpha} c_{\alpha} \varphi_{\alpha}(\mathbf{r})$$

Interstitial region:

$$\sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

Pseudopotential Method



OPW

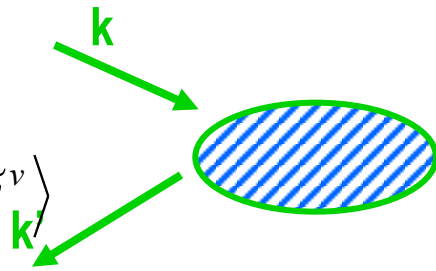
$$|\psi^v\rangle = |\tilde{\psi}^v\rangle - \sum_c |c\rangle\langle c|\tilde{\psi}^v\rangle$$

$$H|\psi^v\rangle = E_v|\psi^v\rangle$$

Pseudopotentials

$$(H + V^R)|\tilde{\psi}^v\rangle = E_v|\tilde{\psi}^v\rangle$$

$$V^R|\tilde{\psi}^v\rangle = \sum_c (E_v - E_c)|c\rangle\langle c|\tilde{\psi}^v\rangle$$

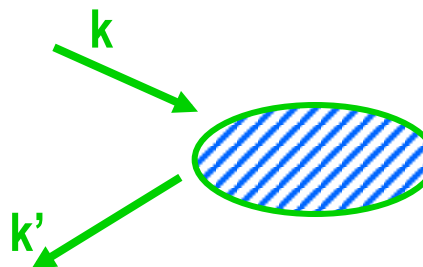


- Core electrons removed
- Strong ionic potential is replaced by a weak pseudopotential
- Valence electrons are described via a smooth pseudowavefunctions
- Loss of wavefunction in core region
- 3d valence states are not well screened

Pseudopotential Method



The pseudopotential method is based on two observations. **First**, in almost any system one could identify a set of the so-called core orbitals which change little from their atomic counterparts. **Second**, the remainder, the so-called valence orbitals, acquire their oscillating behavior mainly due to Pauli exclusion principle or, in plain words, orthogonality constraints to the core orbitals. In pseudopotential approximation the original atoms that constitute a given chemical system are modified by removing core energy levels and enforcing the Pauli exclusion principle via repulsive pseudopotential. This removes the wiggles from the atomic valence orbitals and allows efficient application of plane wave basis set expansion. The resulting pseudoatoms will in general acquire a nonlocal potential term.

$$V(\vec{k}, \vec{k}') |\vec{k}\rangle = |\vec{k}'\rangle$$


Pseudopotential Method



- There are many other ways to define V^R such that $H+V^R$ has the same valence eigenvalues as the actual Hamiltonian.
- Hamann et al. proposed a simple procedure to extract pseudopotentials from atomic calculations, these potentials are designed to have the following properties:
 - ▶ Real and pseudo valence eigenvalues agree for a chosen “prototype” atomic configuration
 - ▶ Real and pseudo atomic valence wavefunctions agree beyond a chosen “core radius” r_c
 - ▶ Real and pseudo valence charge densities agree for $r>r_c$
 - ▶ Logarithmic derivatives and the first energy derivatives agree for $r>r_c$
- This class of pseudopotentials are called norm-conserving pseudopotentials

Constructing a Pseudopotential



Step 1: Solve all-electron eigenvalues and wavefunctions for a reference atom

Step 2: Construct pseudo wavefunction from the all-electron wavefunctions, such that:

- Real and pseudo eigenvalues agree
- Real and pseudo atomic valence wavefunctions agree beyond a chosen “core radius” r_c
- Real and pseudo valence charge densities agree for $r > r_c$
- Logarithmic derivatives and the first energy derivatives agree for $r > r_c$

Step 3: Invert the atomic Schrodinger Equation to obtain a screened pseudopotential

Step 4: Generate an ionic pseudopotential from the screened pseudopotentials

Step 5: Transform the semi-local potential to a non-local form (Kleinman-Bylander)



PAW method

Free-space Boundary Conditions

$$E_{e-e} = \frac{1}{2} \iint_{\Omega} \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'$$

- Technique to implement free-space boundary conditions into plane-wave methods
 - E.J. Bylaska et al, J.Phys.Chem, 100, 6966 (1996).
 - E.J. Bylaska et al, Comp. Phys. Comm.
- Allows us to calculate charged systems
- Implementing Free-Space boundary condition does not significantly degrade performance of plane-wave codes.
- Technique implemented into PAW code.

Figure: accuracy of free-space methods

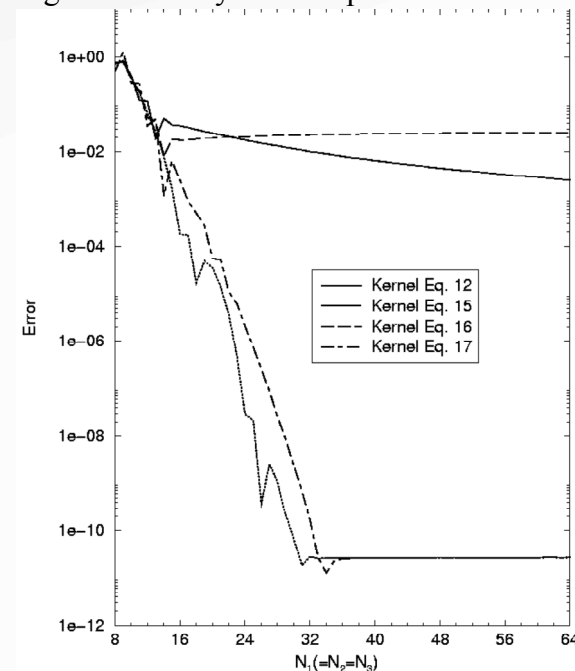


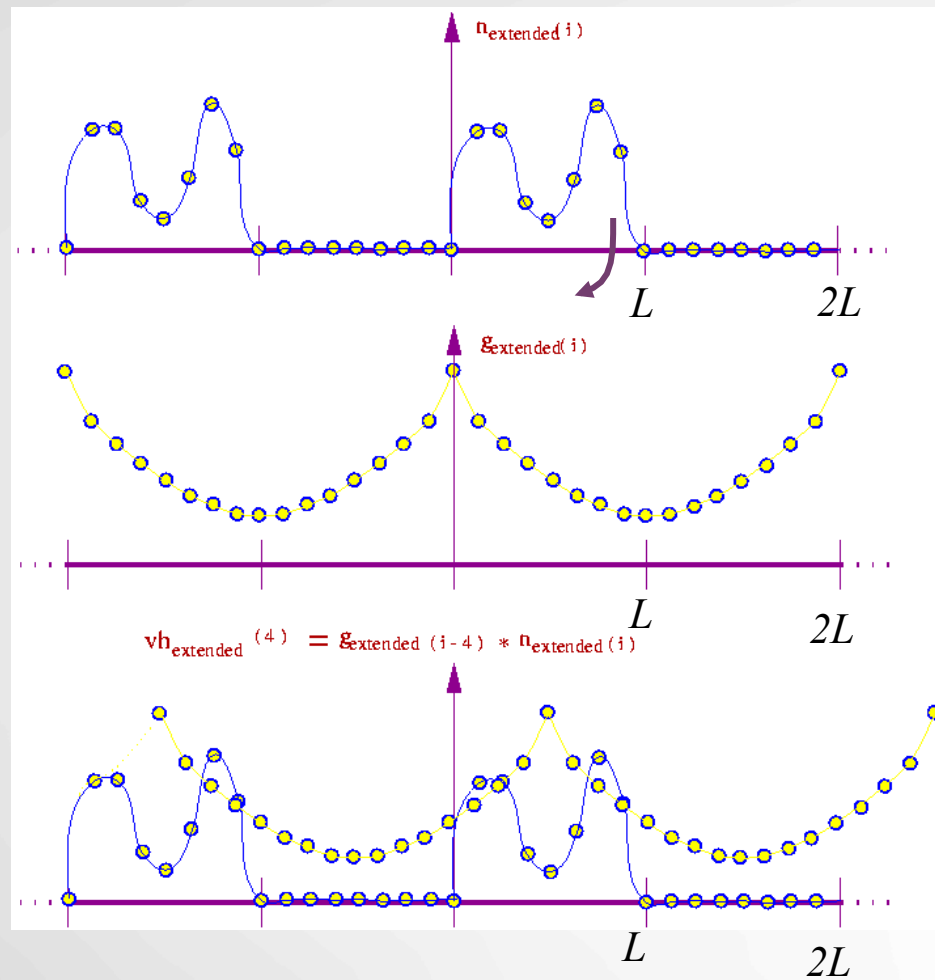
Table 3: Fe³⁺ multiplet structure

	PAW/101Ry	NWChem/VTZ	PSPW/131Ry	CAS(5e,5d)/ecdp	Exp.
⁴ X- ⁶ X	3.3 eV	3.0 eV	6.2 eV**	4.6eV	4.1eV
² X- ⁶ X	4.8 eV	4.6 eV	9.1 eV**	6.6eV	

** semi-core corrections not included.



Aperiodic Convolution: Working in the $[-L,L)^3$ domain



Lack of accuracy comes from cusp in cutoff
Coulomb kernel

Cutoff Coulomb Kernel

$$g(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} g_a(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} & \text{for } |\mathbf{r}| \leq R_{\text{max}} - \delta \\ \frac{1}{|\mathbf{r}|} & \text{otherwise} \end{cases}$$

$$g_a(\mathbf{G}) = \begin{cases} \frac{2\pi(R_{\text{max}})^2}{h^3} & \text{for } |\mathbf{G}| = 0 \\ \frac{4\pi}{h^3|\mathbf{G}|^2} \left(1 - \cos(|\mathbf{G}| R_{\text{max}})\right) & \text{otherwise} \end{cases}$$

$$R_{\text{max}} = \begin{cases} L & \text{(simple cubic)} \\ \frac{\sqrt{2}}{2} L & \text{(face-centered cubic)} \\ \frac{\sqrt{3}}{2} L & \text{(body-centered cubic)} \end{cases}$$

$\delta = \text{small constant}$

Car-Parrinello Molecular Dynamics

Moral: "A man dreams of a miracle and wakes up with loaves of bread"

Erich Maria Remarque



Molecular Dynamics Loop



(1) Compute Forces on atoms, $F_i(t)$ for current atomic configuration, $R_i(t)$

$F_i(t) \leftarrow$

- calculate using classical potentials
(can do large systems and long simulation times)
- calculate directly from first principles by solving many-electron Schrödinger equations
(can treat very complex chemistry, but simulation times are very long)



(2) Update atom positions using Newton's laws

$$\bullet R_i(t+\Delta t) \leftarrow 2 \cdot R_i(t) - R_i(t-\Delta t) + \Delta t^2 / (M_i) \cdot F_i(t)$$



Basic Features of Ab Initio Molecular Dynamics



DFT Equations

$$H\psi_i = \varepsilon_i\psi_i$$

$$H\psi_i(\mathbf{r}) = \left(\begin{array}{l} -\frac{1}{2}\nabla^2 + V_l(\mathbf{r}) + \hat{V}_{NL} + V_H[\rho](\mathbf{r}) \\ +(1-\alpha)V_x[\rho](\mathbf{r}) + V_c[\rho](\mathbf{r}) \end{array} \right) \psi_i(\mathbf{r}) - \alpha \sum_j K_{ij}(\mathbf{r})\psi_j(\mathbf{r})$$

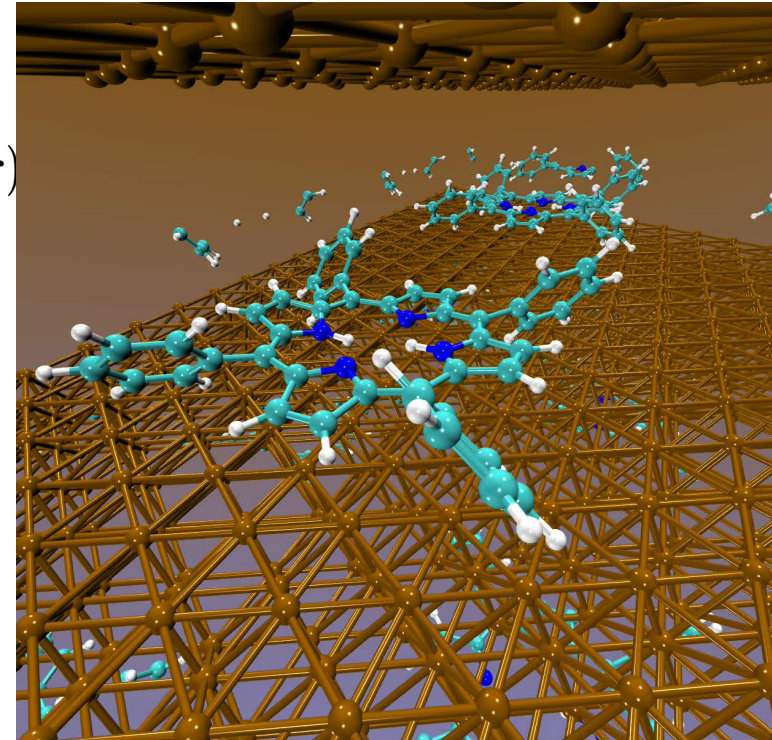


CP dynamics: Ion and wavefunction motion coupled. Ground state energy

$$\mu\ddot{\psi}_i = H\psi_i - \sum_{i=1}^{N_e} \lambda_{ij}\psi_j \quad \mu=0$$

$$M_I\ddot{\mathbf{R}}_I = \mathbf{F}_I \quad \mathbf{F}_I = \sum_{i=1}^{N_e} \langle \psi_i | \frac{\partial H}{\partial \mathbf{R}_I} | \psi_i \rangle$$

Want to do this in **~1second** per step



Plane-wave basis sets, pseudopotentials are used to solve PDE

Pitfalls of Ab Initio Molecular Dynamics



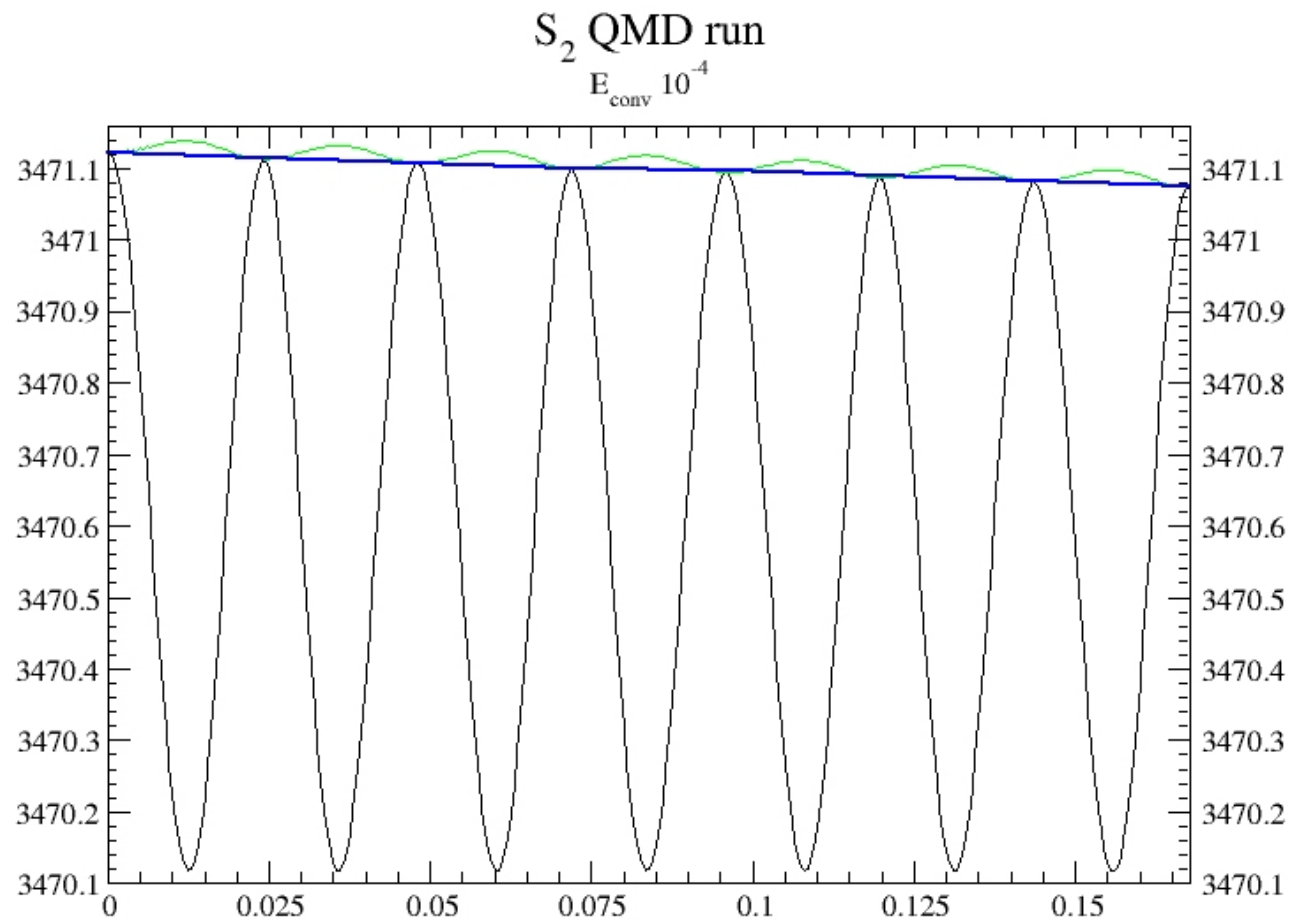
- Expensive?
- *Energy Conservation – Born-Oppenheimer Error*

$$dE/dR = (\delta E/\delta c)(dc/dR) + \delta E/\delta R$$

“Attempts to implement such a dynamical scheme in a straightforward fashion prove to be unstable. Specifically, the atomic dynamics do not conserve energy unless a very high degree of convergence in the electronic structure calculation is demanded. If this is not done the electronic system behaves like a heat sink or source.....”

-- Remler and Madden

${}^3\Sigma_g^-$ - S_2 Energy Surface from QMD Simulation



Car-Parrinello Dynamics



Car and Parrinello suggested that ionic dynamics could be run in parallel with a fictitious electronic dynamics via the following Lagrangean

$$L = \sum_i \frac{1}{2} \mu \langle \dot{\psi}_i | \dot{\psi}_i \rangle + \sum_I \frac{1}{2} M_I \dot{R}_I^2 + E[\{\psi_i\}, \{R_I\}, \text{constraints}]$$

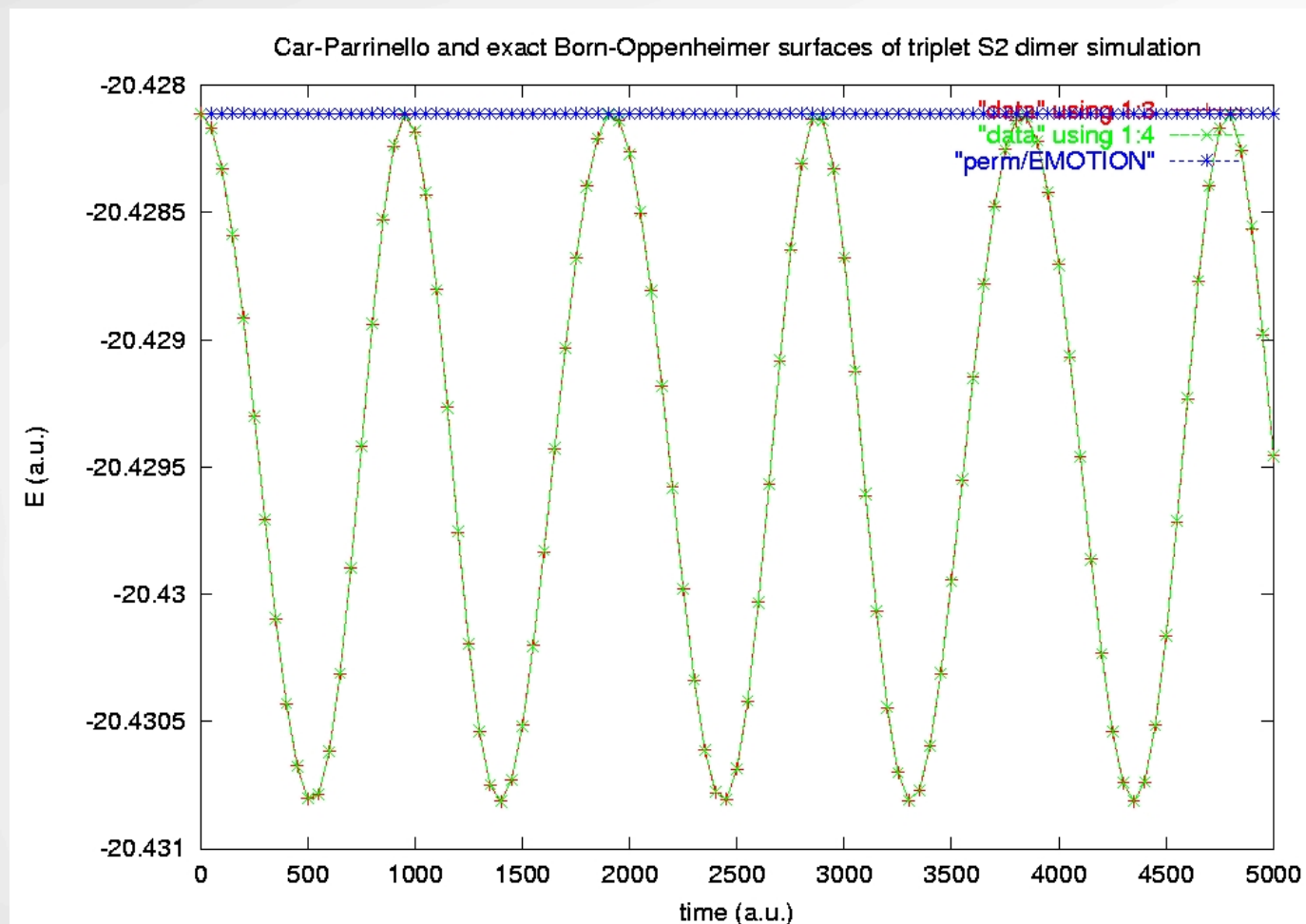
- ▶ Amazingly these equations of motion result in a conservative ionic dynamics that is extremely close to the Born-Oppenheimer surface.
- ▶ The electronic system behaves quasi-adiabatically. That is the electronic system follows the ionic system and there is very little additional motion wandering away from the Born-Oppenheimer surface.

Example 1b: S₂ molecule LDA Car-Parrinello Simulation.



```
title "S2 MD LDA/25Ry"
start s2.md
geometry
S 0.0 0.0 0.0
S 0.0 0.0 1.95
end
pspw
  car-parrinello
    time_step 5.0      #Typically between 1 and 20
    fake_mass 600.0   #Typically between 300 and and 1500
    loop 10 100
  end
  mult 3
end
set nwpw:minimizer 2
task pspw energy
task pspw car-parrinello
```

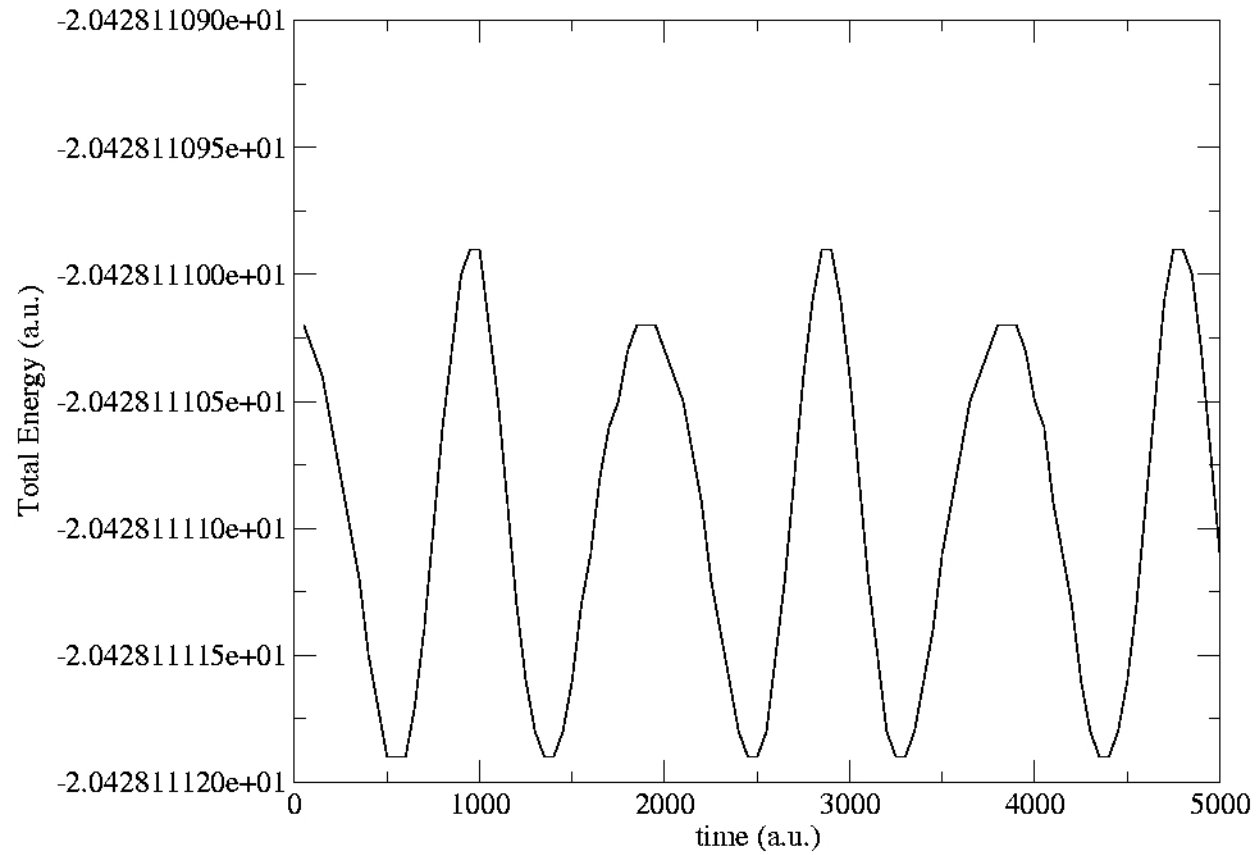
$^3\Sigma_g^-$ S₂ Energy Surface from Car-Parrinello Simulation



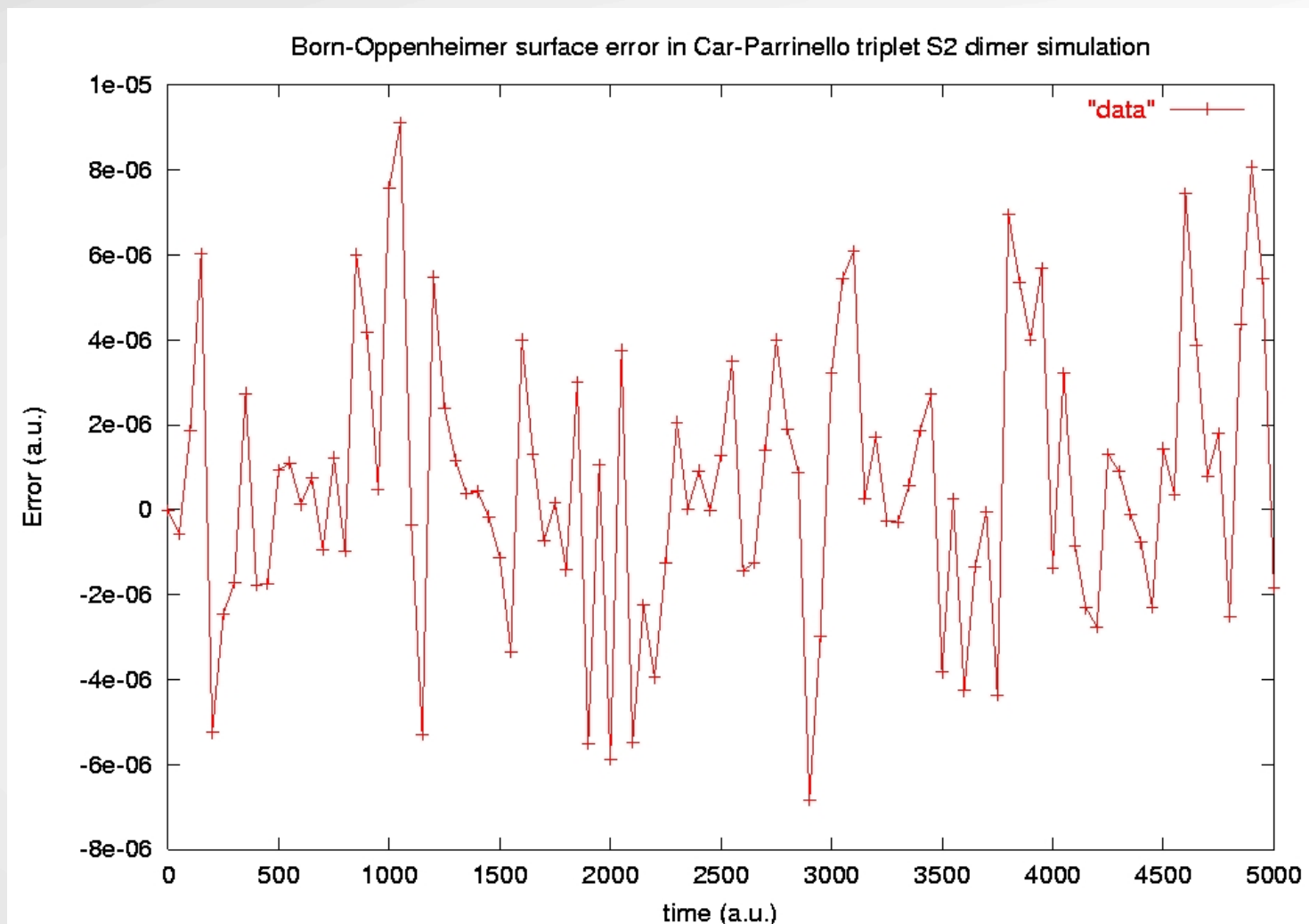
Energy Conservation



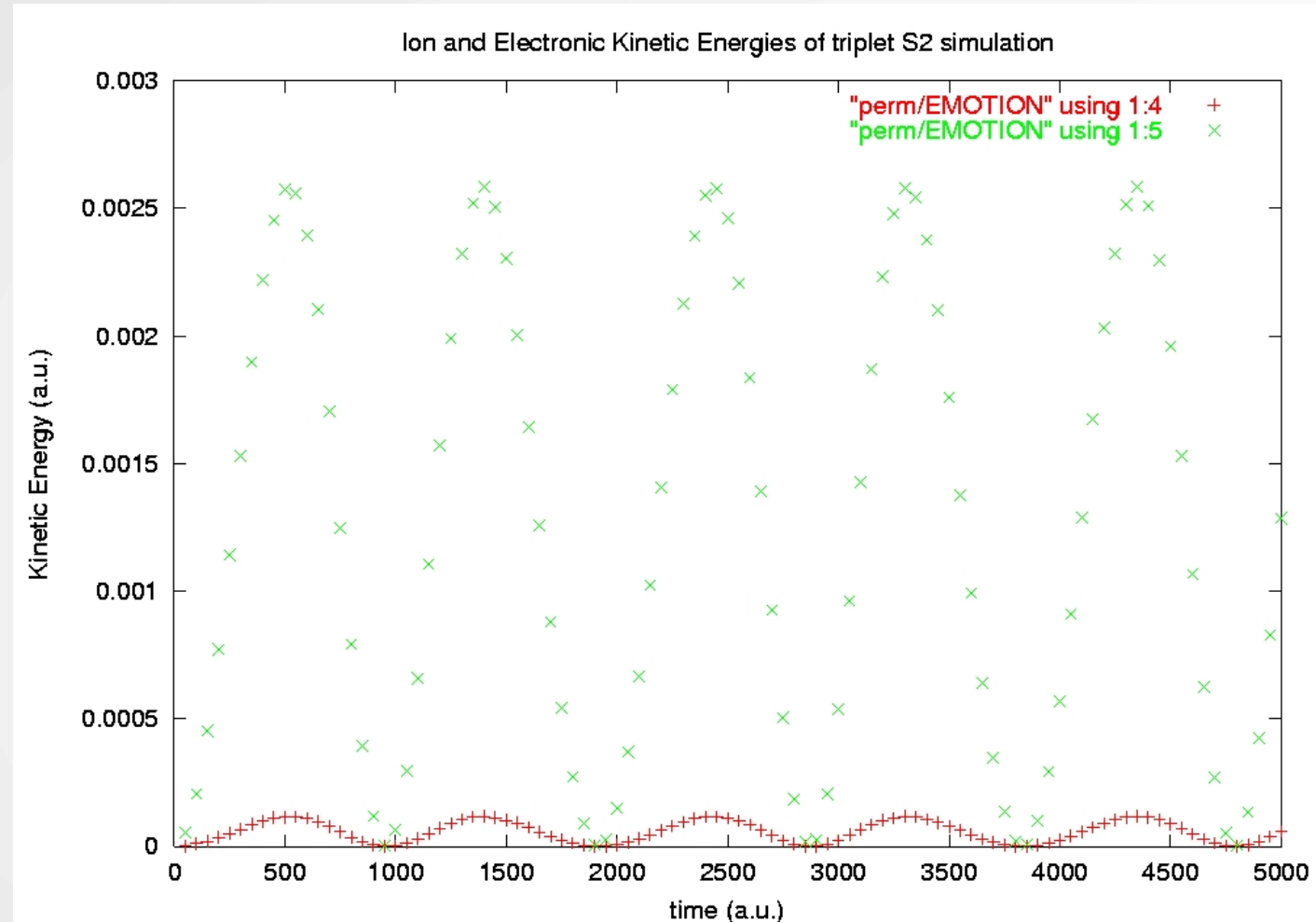
Total Energy Conservation of triplet S2 simulation



Born-Oppenheimer Error



Ionic and Fictitious Electronic Kinetic Energies



A Closer look at Born-Oppenheimer and Car-Parrinello



- Adiabaticity is not built into the Car-Parrinello equations of motion. As pointed out by Remler and Madden
“equipartition principle tells us that the average kinetic energies of all degrees of freedom in the classical system will be equal at equilibrium. The adiabatic state, in which the fictitious system is at a very low temperature and the ionic system is hot is therefore metastable.”
- The metastable motion is the result of a good start-up procedure and the overlap of the fictitious electronic motion with the ionic motion must be small (i.e. Start simulation on BO surface! Also, standard CP works best for large band gap systems)
- Total ionic momentum is NOT rigorously conserved

Ab Initio Molecular Dynamics References



- R. Car and M. Parrinello (1985), “Unified Approach for Molecular Dynamics and Density Functional Theory”, *Phys. Rev. Lett.*, **55**(22), pages 2471-2474.
- R. Car and M. Parrinello (1989), “The Unified Approach for Molecular Dynamics and Density Functional Theory”, in *Simple Molecular Systems at Very High Density*, vol. 186 of NATO ASI Series, series B, Physics, P.P. Loubeyre and N. Boccara (Eds.) (Plenum Press, NY) pages 455-476.
- D.K. Remler, and P.A. Madden (1990), “Molecular dynamics without effective potentials via the Car-Parrinello approach”, *Mol. Phys.*, **70**(6), page 921-966.
- T. Morishita, S. Nose (1999), “Momentum conservation law in the Car-Parrinello method,” *Phys Rev. B.*, **59** (23) pages 15126-15132
- D. Marx and J. Hutter (2000), “Ab Initio Molecular Dynamics: Theory and Implementation”, *Modern Methods and Algorithms for Quantum Chemistry, Proceedings, Second Edition*, J. Grotendorst(Ed.), John von Neumann Institute for Computing, Julich, NIC Series, Vol. 3. (<http://www.fz-juelich.de/nic-series/Volume3/marx.pdf>)
- M. Valiev, E.J. Bylaska, A. Gramada, and J.H. Weare (2002), *First Principle Molecular Dynamics Simulations using Density-Functional Theory*, chapter 56, in Reviews In Modern Quantum Chemistry: A Celebration Of The Contributions Of R. G. Parr, Ed. K.D. Sen (World Scientific, Singapore).