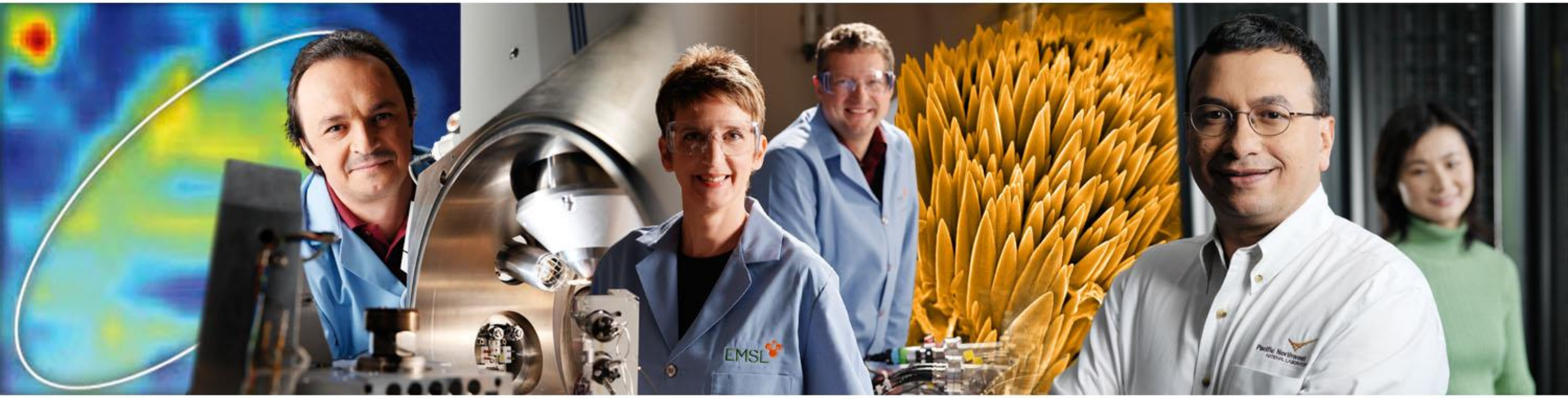
NWChem: Planewave Density Functional Theory



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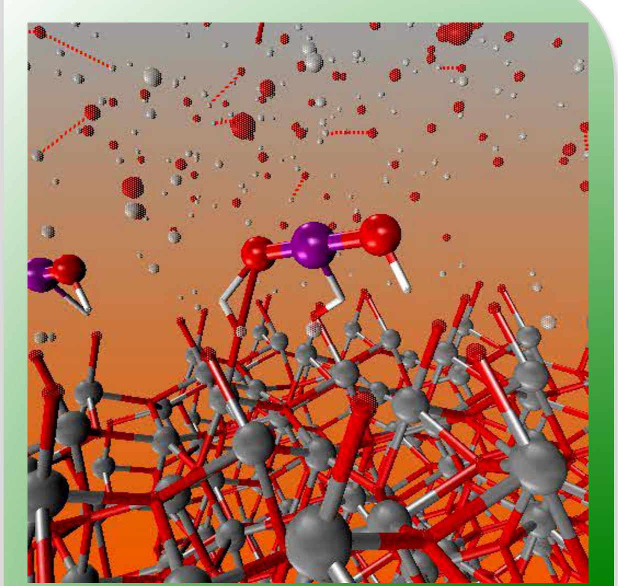
Outline

- Overview of Plane-Wave Density Functional Module in NWChem
  - NWPW capabilities
  - Plane-Wave Basis

- Basic examples:
  - Geometry optimization for S_2 molecule
  - Calculations for diamond
    - Optimizing the unit cell and geometry for an 8 atom supercell of diamond with PSPW
    - Optimizing the unit cell for an 8 atom supercell of diamond with BAND

- AIMD Simulations
  - Car-Parrinello Simulation of S_2 molecule

Plane-Wave Density Functional Theory (NWPW module) in NWChem



AIMD simulation of solvated UO_2^{2+} + 112-Al_2O_3 surface(300°K)

- Highly scalable
- CG, limited memory BFGS, and RMM-DIIS minimization
- Gamma and Band structure capabilities
- Car-Parrinello and Born-Oppenheimer(extended Lagrangian dynamics)
- Constant energy and constant temperature Car-Parrinello
- Fixed atoms in cartesian, SHAKE constraints, translation contraints, and rotation constraints, Metadynamics, PMF
- Hamann, Troullier-Martins, and HGH norm-conserving pseudopotentials with optional semicore corrections
  - Interface for CPI and TETER formats
- PAW
- LDA and PBE96 exchange-correlation potentials (spin-restricted and unrestricted) SIC, pert-OEP, Hartree-Fock and Hybrid Functionals (restricted and unrestricted)
- Fractional occupation,
- Geometry/unitcell optimization, frequency, transition-state searches
- AIMD/MM
- Wannier analysis
- Wavefunction, density, electrostatic, Wannier, ELF plotting
- …..

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Gaussian DFT Versus Plane-Wave DFT

Gaussian Basis Set

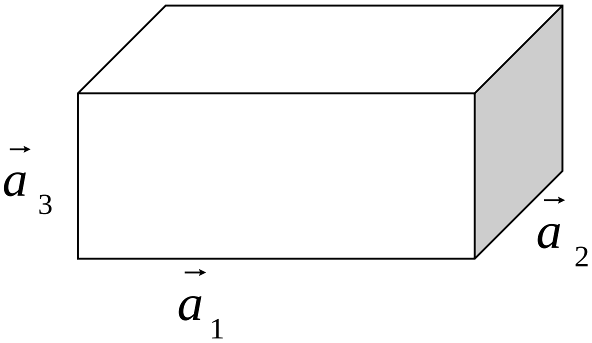
- Parallel Efficient
- All-Electron
  - Core regions included in calculation
  - First row transition metals can readily be calculated
- Ab Initio MD expensive
  - Pulay forces
- Different basis sets for molecules and solids

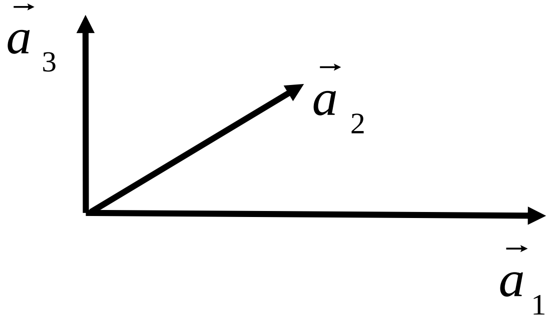
PlaneWave Basis Set

- 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 3s and 3p states
- Efficient Ab Initio MD
  - Car-Parrinello
- Same basis set for molecules and solids

Plane-Wave Basis Sets

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

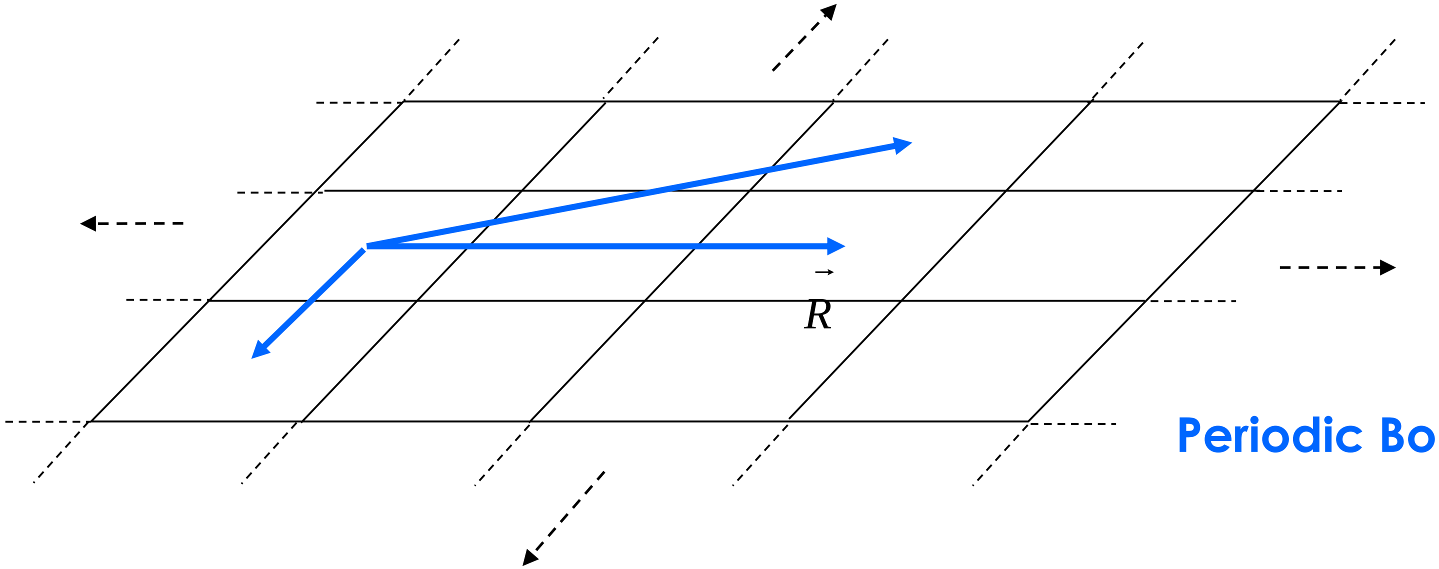




The volume of the unit cell is

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

Plane-Wave Basis Sets



Periodic Boundaries

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

where

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

Plane-Wave Basis Sets

$$u_n(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \tilde{\psi}_n(\vec{G}) e^{i\vec{G}\cdot\vec{r}}$$

Plane-wave Expansion

Since are 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

EMSL

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

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

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

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

Reciprocal lattice vectors

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

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

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,

$$\frac{1}{2}\left|\vec{G}\right|^2 < E_{cut}$$

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

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

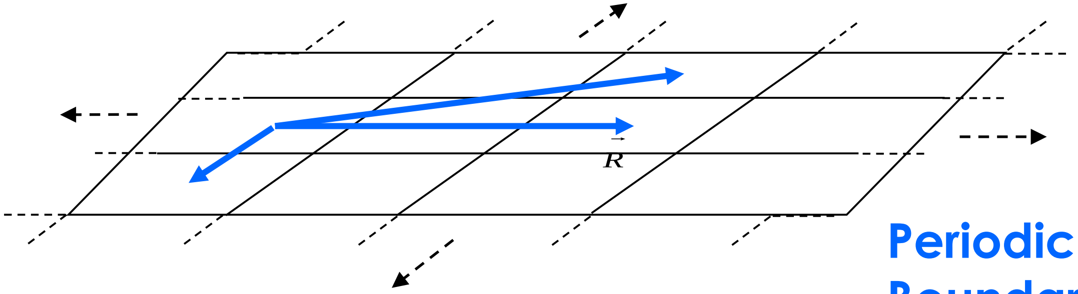
Should contain 8 times more plane-waves than the corresponding wavefunction expansion

$$\frac{1}{2}\left|\vec{G}\right|^2 < 4E_{cut}$$

Density 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



Periodic Boundaries

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

$$u_n(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \tilde{u}_n(\vec{G}) e^{i\vec{G}\cdot\vec{r}}$$

☝–point Plane-wave Expansion

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

$$\left|\vec{k}, n\right\rangle = \left|\vec{k}\right\rangle \left|u_n\right\rangle \quad \text{or} \quad \psi_{\vec{k},n}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_n(\vec{r})$$

Bloch's Theorem

Where *k* are all the allowed wave-vectors in the primitive cell of the reciprocal lattice.

Minimal Input Example

- Minimal input (all defaults)

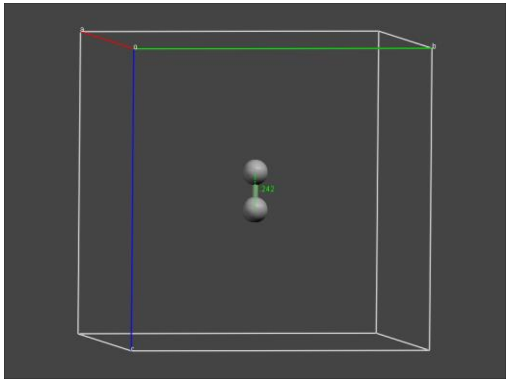
```
geometry
Be 0 0 0
end
task pspw
```

- Performs a closed-shell N^3 DFT calculation using the local density approximation on the beryllium atom.

- Important Keywords: `simulation_cell`, `vectors`, `XC`, `tolerances`

Example Input: S2 molecule LDA geometry opt.

```
echo
title "total energy of s2-dimer LDA/30Ry with PSPW method"
scratch_dir ./scratch
permanent_dir ./perm s
start s2-pspw-energy
geometry
S 0.0 0.0 0.0
S 0.0 0.0 1.88
end
nwpw
   simulation_cell
      SC 20.0
   end
   cutoff 15.0
   mult 3
   xc lda
   lmbfgs
end
task pspw energy
task pspw optimize #optimize geometry
```



The energies from the simulation

```
... == Summary Of Results ==

   number of electrons: spin up= 7.00000 down= 5.00000 (real space)

   total energy              : -0.2041363137E+02 ( -0.10207E+02/ion)
   total orbital energy   : -0.4944372503E+01 ( -0.41203E+00/electron)
   hartree energy          : 0.1680529987E+02 ( 0.14004E+01/electron)
   exc-corr energy         : -0.4320620600E+01 ( -0.36005E+00/electron)
   ion-ion energy           : 0.8455644190E-02 ( 0.42278E-02/ion)

   kinetic (planewave)  : 0.7529965882E+01 ( 0.62750E+00/electron)
   V_local (planewave) : -0.4506036741E+02 ( -0.37550E+01/electron)
   V_nl (planewave)       : 0.4623635248E+01 ( 0.38530E+00/electron)
   V_Coul (planewave) : 0.3361059973E+02 ( 0.28009E+01/electron)
   V_xc. (planewave)     : -0.5648205953E+01 ( -0.47068E+00/electron)
   Virial Coefficient        : -0.1656626150E+01

   orbital energies:
      -0.2001309E+00 ( -5.446eV)
      -0.2001309E+00 ( -5.446eV)
      -0.3294434E+00 ( -8.965eV)      -0.2991148E+00 ( -8.139eV)
      -0.3294435E+00 ( -8.965eV)      -0.2991151E+00 ( -8.139eV)
      -0.3582269E+00 ( -9.748eV)      -0.3352434E+00 ( -9.123eV)
      -0.5632339E+00 ( -15.326eV)    -0.5246249E+00 ( -14.276eV)
      -0.7642738E+00 ( -20.797eV)    -0.7413909E+00 ( -20.174eV)

   Total PSPW energy  : -0.2041363137E+0
```

Optimizing the unit cell and geometry for an 8 atom supercell of diamond with PSPW

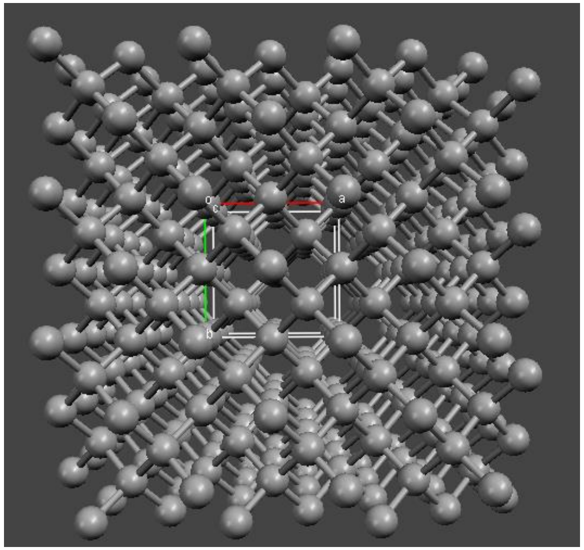
```
title "Diamond 8 atom cubic cell - geometry and unit cell optimization"
echo

permanent_dir ./perm
scratch_dir   ./scratch

start diamond

memory 950 mb

#**** Enter the geometry using fractional coordinates ****
geometry center noautosym noautoz print
  system crystal
    lat_a 3.56d0
    lat_b 3.56d0
    lat_c 3.56d0
    alpha 90.0d0
    beta  90.0d0
    gamma 90.0d0
  end
  C -0.50000d0 -0.50000d0 -0.50000d0
  C  0.00000d0  0.00000d0 -0.50000d0
  C  0.00000d0 -0.50000d0  0.00000d0
  C -0.50000d0  0.00000d0  0.00000d0
  C -0.25000d0 -0.25000d0 -0.25000d0
  C  0.25000d0  0.25000d0 -0.25000d0
  C  0.25000d0 -0.25000d0  0.25000d0
  C -0.25000d0  0.25000d0  0.25000d0
end
 …
```



Optimizing the unit cell and geometry for an 8 atom supercell of diamond with PSPW

```
…

nwpw
  ewald_rcut 3.0
  ewald_ncut 8  #The default value of 1 needs to be increased for small cells
  lmbfgs
  xc pbe96
end

driver
  clear
  maxiter 40
end

set nwpw:cif_filename diamond.opt  # create a CIF file containing optimization history
set includestress .true.          # this option tells driver to optimize the unit cell
task pspw optimize ignore
```

Optimizing the unit cell and geometry for an 8 atom supercell of diamond with PSPW

```
...
     ----------------------
     Optimization converged
     ----------------------

  Step       Energy      Delta E   Gmax     Grms     Xrms     Xmax   Walltime
  ---- ---------------- -------- -------- -------- -------- -------- --------
@    6     -45.07688304 -1.1D-07  0.00037  0.00021  0.00002  0.00003    174.5
                                     ok       ok       ok       ok



                         Geometry "geometry" -> "geometry"
                         ---------------------------------

 Output coordinates in angstroms (scale by  1.889725989 to convert to a.u.)

  No.       Tag          Charge          X              Y              Z
 ---- ---------------- ---------- -------------- -------------- --------------
    1 C                    6.0000     1.82723789     1.82729813     1.82705440
    2 C                    6.0000     0.00000857    -0.00006053     1.82730027
    3 C                    6.0000    -0.00000584     1.82706061     0.00002852
    4 C                    6.0000     1.82712018     0.00006354    -0.00002544
    5 C                    6.0000     2.74074195     2.74072805     2.74088522
    6 C                    6.0000     0.91366407     0.91370055     2.74064976
    7 C                    6.0000     0.91351181     2.74080771     0.91352917
    8 C                    6.0000     2.74078843     0.91348115     0.91365446
```

Optimizing the unit cell and geometry for an 8 atom supercell of diamond with PSPW

```
Lattice Parameters
------------------

lattice vectors in angstroms (scale by  1.889725989 to convert to a.u.)

a1=<   3.654   0.000   0.000 >
a2=<   0.000   3.654   0.000 >
a3=<   0.000   0.000   3.654 >
a=       3.654 b=      3.654 c=       3.654
alpha=  90.000 beta=  90.000 gamma=  90.000
omega=     48.8

reciprocal lattice vectors in a.u.

b1=<   0.910   0.000   0.000 >
b2=<   0.000   0.910   0.000 >
b3=<   0.000   0.000   0.910 >
```

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Optimizing the unit cell and geometry for an 8 atom supercell of diamond with PSPW

```
==============================================================================
                 internuclear distances
------------------------------------------------------------------------------
    center one      |      center two      | atomic units |  angstroms
------------------------------------------------------------------------------
  5 C               |  1 C                 |    2.99027   |    1.58238
  6 C               |  1 C                 |    2.99027   |    1.58238
  6 C               |  2 C                 |    2.99027   |    1.58238
  7 C               |  1 C                 |    2.99026   |    1.58238
  7 C               |  3 C                 |    2.99027   |    1.58238
  8 C               |  1 C                 |    2.99027   |    1.58238
  8 C               |  4 C                 |    2.99027   |    1.58238
------------------------------------------------------------------------------
             number of included internuclear distances:          7
==============================================================================

==============================================================================
                 internuclear angles
------------------------------------------------------------------------------
     center 1       |       center 2       |       center 3       |  degrees
------------------------------------------------------------------------------
  5 C               |  1 C                 |  6 C                 |   109.46
  5 C               |  1 C                 |  7 C                 |   109.48
  5 C               |  1 C                 |  8 C                 |   109.48
  6 C               |  1 C                 |  7 C                 |   109.47
  6 C               |  1 C                 |  8 C                 |   109.46
  7 C               |  1 C                 |  8 C                 |   109.48
  1 C               |  6 C                 |  2 C                 |   109.48
  1 C               |  7 C                 |  3 C                 |   109.47
  1 C               |  8 C                 |  4 C                 |   109.47
------------------------------------------------------------------------------
             number of included internuclear angles:          9
==============================================================================  ...
```

Optimizing the unit cell and geometry for an 8 atom supercell of diamond with PSPW

The C-C bond distance after the geometry optimization is 1.58 Angs. and agrees very well with the experimental value of 1.54 Angs.. Another quantity that can be calculated from this simulation is the cohesive energy.The cohesive energy of a crystal is the energy needed to separate the atoms of the solid into isolated atoms, i.e.

$$E_{coh} = -\left(E_{solid} - \sum_{a} E^{a}_{atom} \right)$$

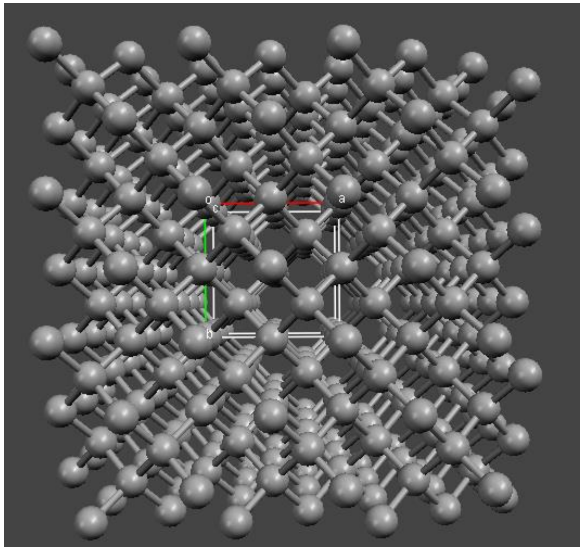
where E_{solid} is the energy of the solid and are the energies of the isolated atoms. In order to calculate the cohesive energy the energy of an isolated carbon atom at the same level of theory and cutoff energy will need to be calculated.

Using this energy and energy of diamond the cohesive energy per atom is calculated to be

$$E_{coh} = -(-45.07688304au/8 - (-5.421213534au)) = 0.2133968au = 5.8eV$$

This value is substantially lower than the experimental value of 7.37*eV*! It turns out this error is a result of the unit cell being too small for the diamond calculation (or too small of a Brillioun zone sampling). In the next section, we show how increasing the Brillouin zone sampling reduces the error in the calculated cohesive energy.

Optimizing the unit cell for an 8 atom supercell of diamond with BAND



```
title "Diamond 8 atom cubic cell - geometry and unit cell optimization"
Echo
permanent_dir ./perm
scratch_dir   ./scratch

start diamond-band
memory 1950 mb

#**** Enter the geometry using fractional coordinates ****
geometry center noautosym noautoz print
  system crystal
    lat_a 3.58d0
    lat_b 3.58d0
    lat_c 3.58d0
    alpha 90.0d0
    beta  90.0d0
    gamma 90.0d0
  end
  C -0.50000d0 -0.50000d0 -0.50000d0
  C  0.00000d0  0.00000d0 -0.50000d0
  C  0.00000d0 -0.50000d0  0.00000d0
  C -0.50000d0  0.00000d0  0.00000d0
  C -0.25000d0 -0.25000d0 -0.25000d0
  C  0.25000d0  0.25000d0 -0.25000d0
  C  0.25000d0 -0.25000d0  0.25000d0
  C -0.25000d0  0.25000d0  0.25000d0
end
set includestress    .true.   # option tells driver to optimize the unit cell
set nwpw:zero_forces .true.   # option zeros the forces on the atoms--> only lattice parameters optimized
```

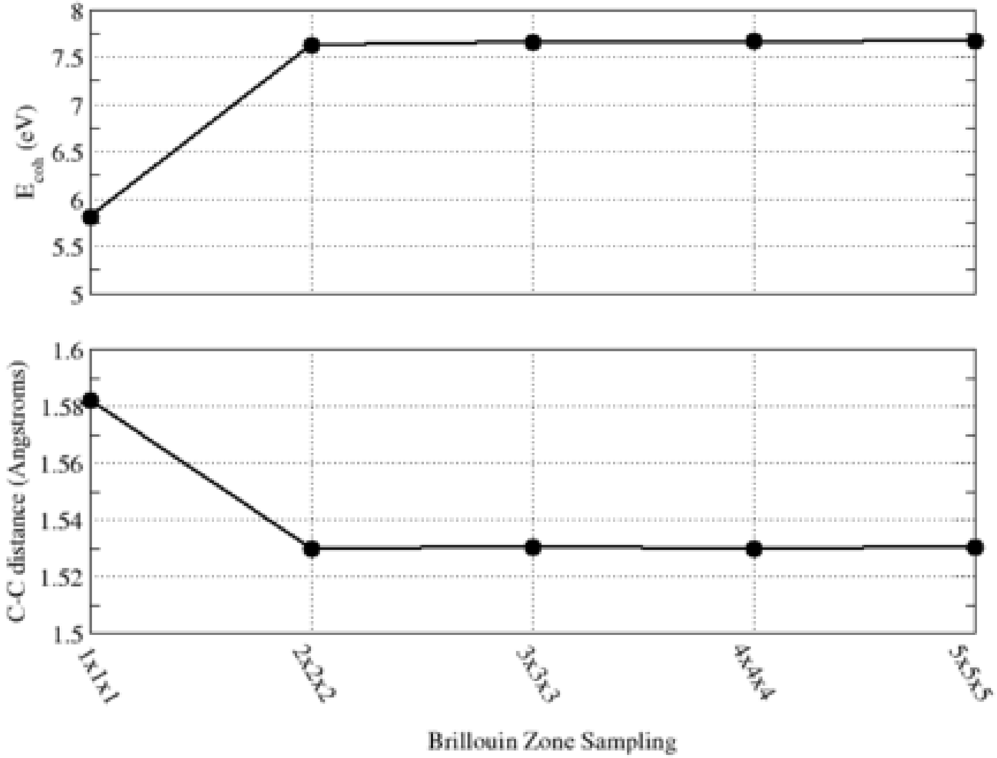
Optimizing the unit cell for an 8 atom supercell of diamond with BAND

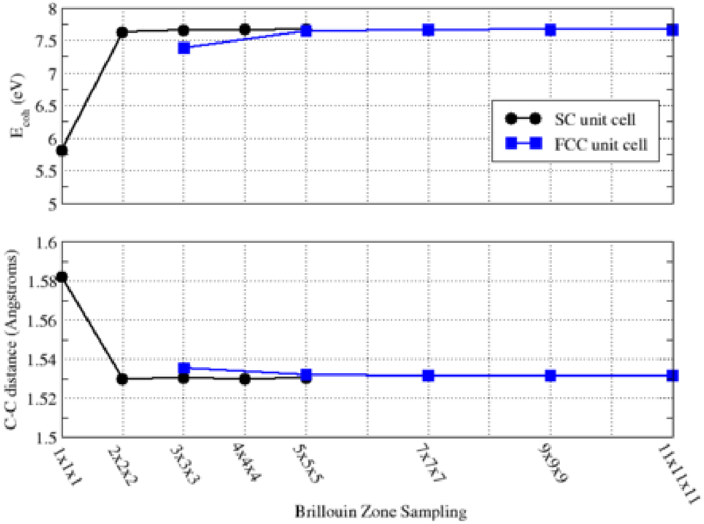
```
nwpw
  ewald_rcut 3.0
  ewald_ncut 8    #The default value of 1 needs to be increased
  lmbfgs
  xc pbe96
end

#1x1x1 k-point mesh
nwpw
  monkhorst-pack 1 1 1
end
set nwpw:cif_filename diamond111.opt
driver; clear; maxiter 40; end; task band optimize ignore

 #2x2x2 k-point mesh
 nwpw
   monkhorst-pack 2 2 2
 end
 set nwpw:cif_filename diamond222.opt
 driver; clear; maxiter 40; end; task band optimize ignore

 #3x3x3 k-point mesh
 nwpw
   monkhorst-pack 3 3 3
 end
 set nwpw:cif_filename diamond333.opt
 driver; clear; maxiter 40; end; task band optimize ignore
```

Optimizing the unit cell for an 8 atom supercell of diamond with BAND

```
#4x4x4 k-point mesh
nwpw
  monkhorst-pack 4 4 4
end
set nwpw:cif_filename diamond444.opt
driver; clear; maxiter 40; end; task band optimize ignore

#5x5x5 k-point mesh
nwpw
  monkhorst-pack 5 5 5
end
set nwpw:cif_filename diamond555.opt
driver; clear; maxiter 40; end; task band optimize ignore
```

Optimizing the unit cell for an 8 atom supercell of diamond with BAND





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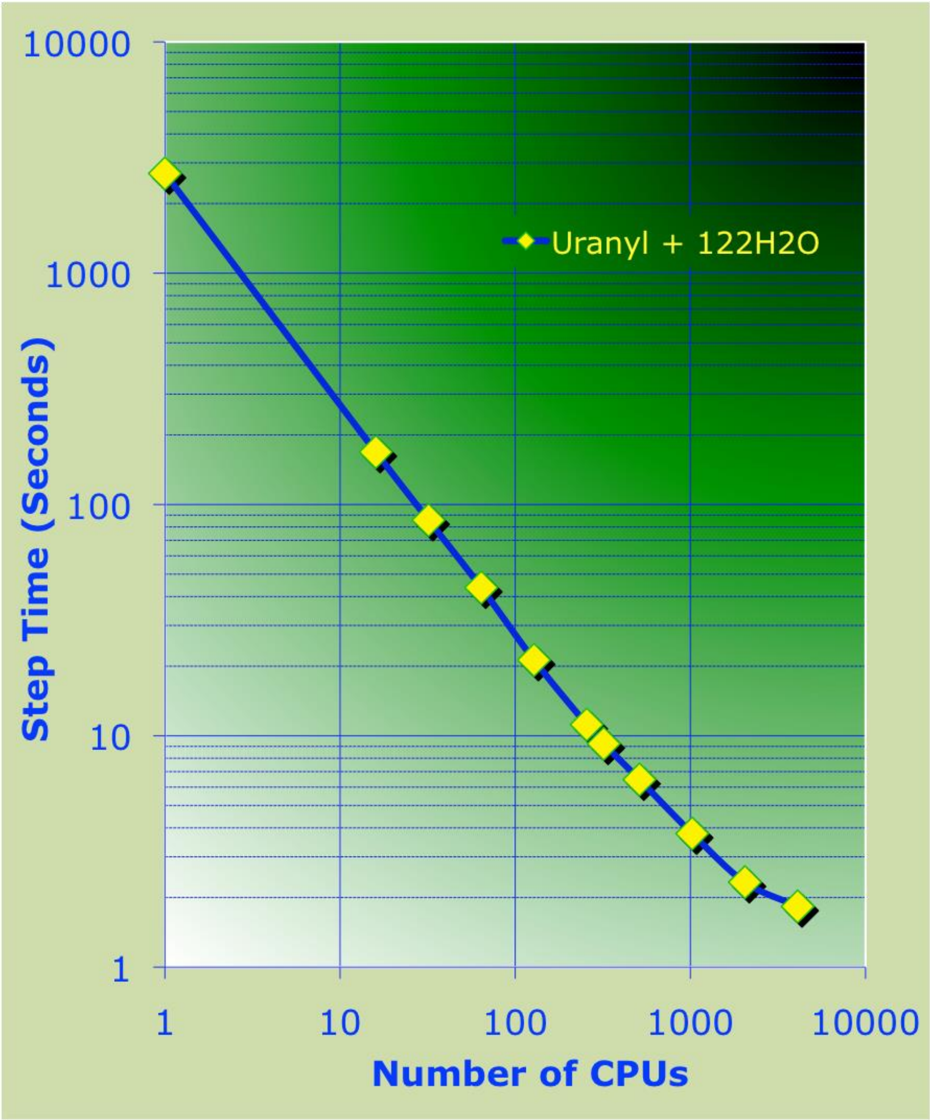
Parallel timings for AIMD simulation of $UO_2^{2+}+122H_2O$



- Development of algorithms for AIMD has progressed in recent years
  - 0.1-10 seconds per step can be obtained on many of today's supercomputers for most AIMD simulations.
  - However, large numbers of cpus are often required
  - 5000 cpus * 10 days → 1.2 million cpu hours
  - Very easy to use up 1-2 million CPUs hours in a single simulation

Conventional MD versus AIMD versus AIMD/MM (QM/MM)

Conventional molecular dynamics	Ab-initio molecular dynamics	Combined ab-initio molecular dynamics/molecular dynamics
Empirical, usually two-body potentials, Difficult to treat reactions	Potential obtained from Schrodinger equation, includes all-body and electronic behavior	Potential in "selected region" obtained from Schrodinger equation, includes all-body and electronic behavior
Empirical potentials parameterized for a small range of PT	Equally applicable under all conditions	Empirical potentials parameterized for a small range of PT
10^5 particles no problem	600 particles with significant dynamics	1000's of particles with significant dynamics
10^3 ps no problem	10's of ps difficult	10's of ps easy
Can be performed on workstations…supercomputers	Still needs supercomputers	Can be performed on workstations…supercomputers

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 simulations times are very long)

(2) Update atom positions using Newtons laws

- $R_I(t+\Delta t) \leftarrow 2*R_I(t) - R_I(t-\Delta t) + \Delta t^2/(M_I)*F_I(t)$

Pitfalls of Ab Initio Molecular Dynamics

- Expensive?

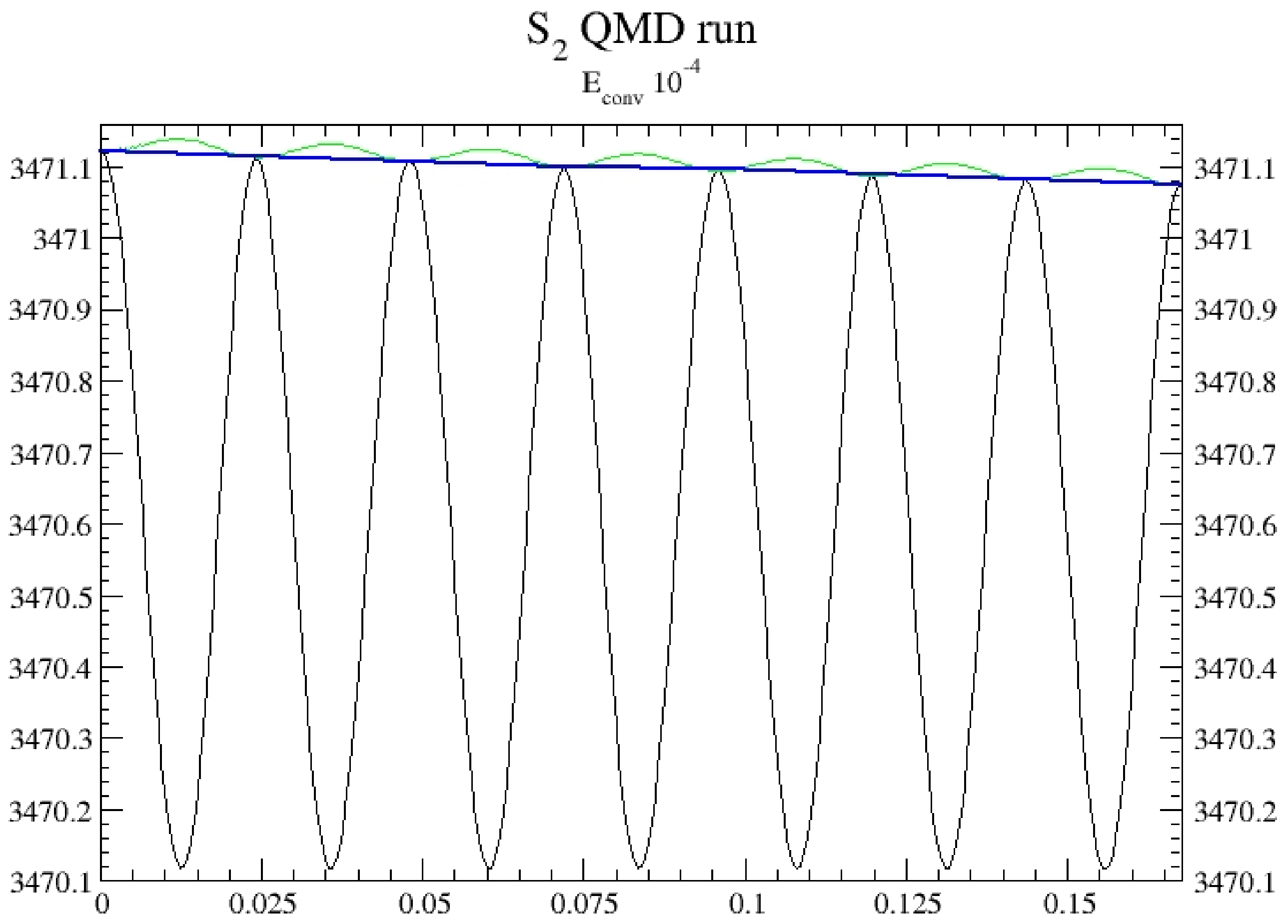
- *Energy Conservation – Born-Oppenheimer Error*

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

"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 ficticious electronic dynamics via the following Lagrangean

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

► 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 electonic system follows the ionic system and there is very little additional motion wandering away from the Born-Oppenheimer surface.

Basic features of ab-initio molecular dynamics

DFT Equations

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

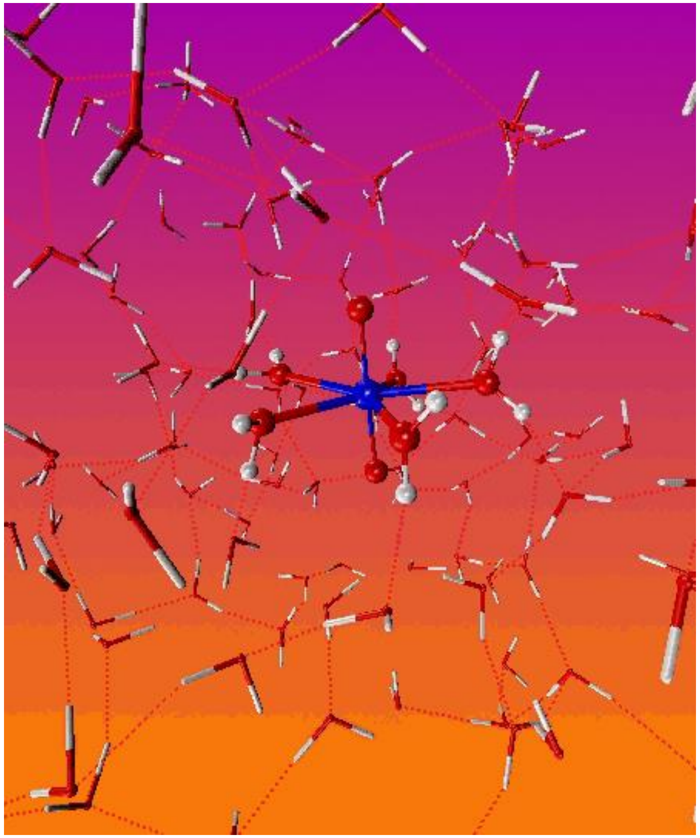
$$H\psi_i(\mathbf{r}) = \begin{pmatrix} -\frac{1}{2}\nabla^2 + V_l(\mathbf{r}) + \hat{V}_{NL} + V_H[\rho](\mathbf{r}) \\ +(1-\alpha)V_x[\rho](\mathbf{r}) + V_c[\rho](\mathbf{r}) \end{pmatrix} \psi_i(\mathbf{r}) - \alpha \sum_j K_{ij}(\mathbf{r})\psi_j(\mathbf{r})$$

CP dynamics: Ion and wavefunction motion coupled. Ground state energy μ=0

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

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

Want to do this in ~1second per step



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

Why do we need a second per step?

- Current *ab-initio* molecular dynamics simulations for 10 to 100 picoseconds can take several months to complete

- The step length in ab initio molecular dynamics simulation is on the order of 0.1…0.2 fs/step
  - 20 ps of simulation time → 200,000 steps
    - At 1 second per step → 2-3 days
    - At 10 seconds per step → 23 days
    - At 30 seconds per step →70 days

  - 1 ns of simulation time → 10,000,000 steps
    - at 1 second per step → 115 days of computing time
    - At 10 seconds per step → 3 years
    - At 30 seconds per step → 9 years

    - At 0.1 seconds per step → 11.5 days

Cost of AIMD step

$$(1/2)\,\Delta\Psi + V_{ext}\Psi + V_{H}\Psi + V_{xc}\Psi + V_{x,exact}\Psi = E\Psi$$

$$\langle \Psi_i | \Psi_j \rangle = \delta_{ij}$$

N_eN_g

$(N_aN_g + N_g\mathrm{Log}N_g + N_eN_g) + N_aN_eN_g$

$N_eN_g\mathrm{Log}N_g + N_eN_g + 2N_g\mathrm{Log}N_g + N_g + N_eN_g$

$N_eN_g\mathrm{Log}N_g + N_eN_g$

$N_e(N_e+1)N_g\mathrm{LogNg}$

$N_e^2N_g + N_e^3$

N_a - number of atoms
N_e - number of electrons
N_g - number of grid points

Remember we want to do this 100,000+ times

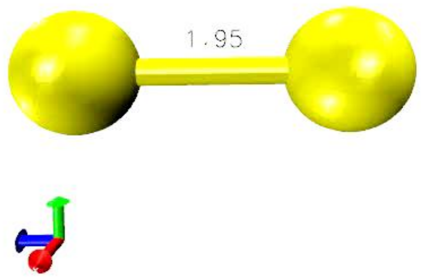
For hybrid-dft: A day of computation on the PNNL Chinook system
→ $16K/ε

- Na=500, Ne=500, Ng=256^3
  - Ne*Ng=8.4e9
  - Ne*Ng*Log(Ng)=2.0e11
  - Na*Ne*Ng=4.2e12, Ne*Ne*Ng=4.2e12
  - Hybrid-DFT: Ne*(Ne+1)*Ng*Log(Ng) = 1.0e14

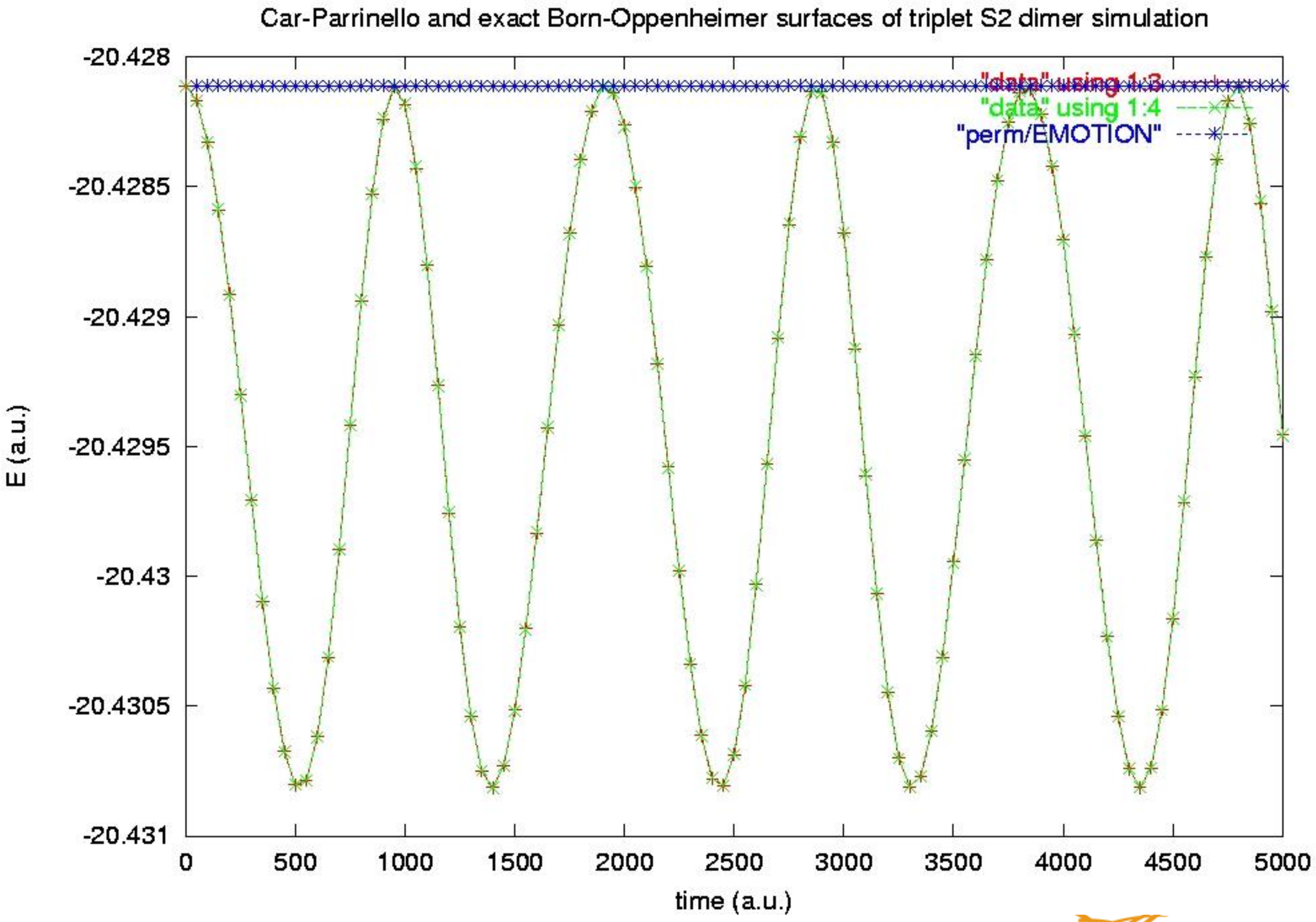
Critical path

Example: S_2 molecule LDA Car-Parrinello Simulation

```
title "S2 MD LDA/30Ry"
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
   cutoff 15.0
   mult 3
   lmbfgs
end
task pspw energy
task pspw car-parrinello
```



$^3\Sigma_g^-$ S_2 Energy Surface from Car-Parrinello Simulation



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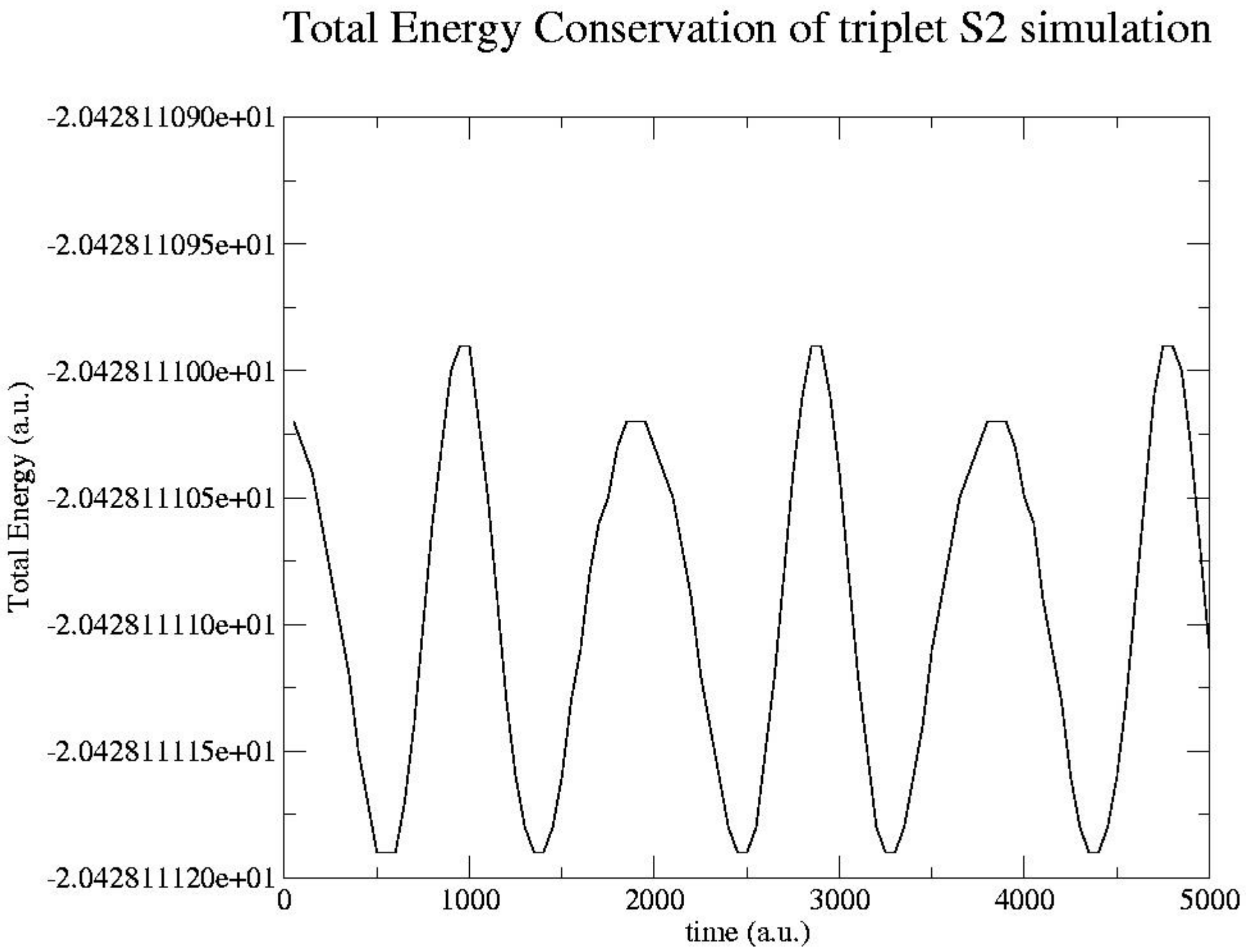
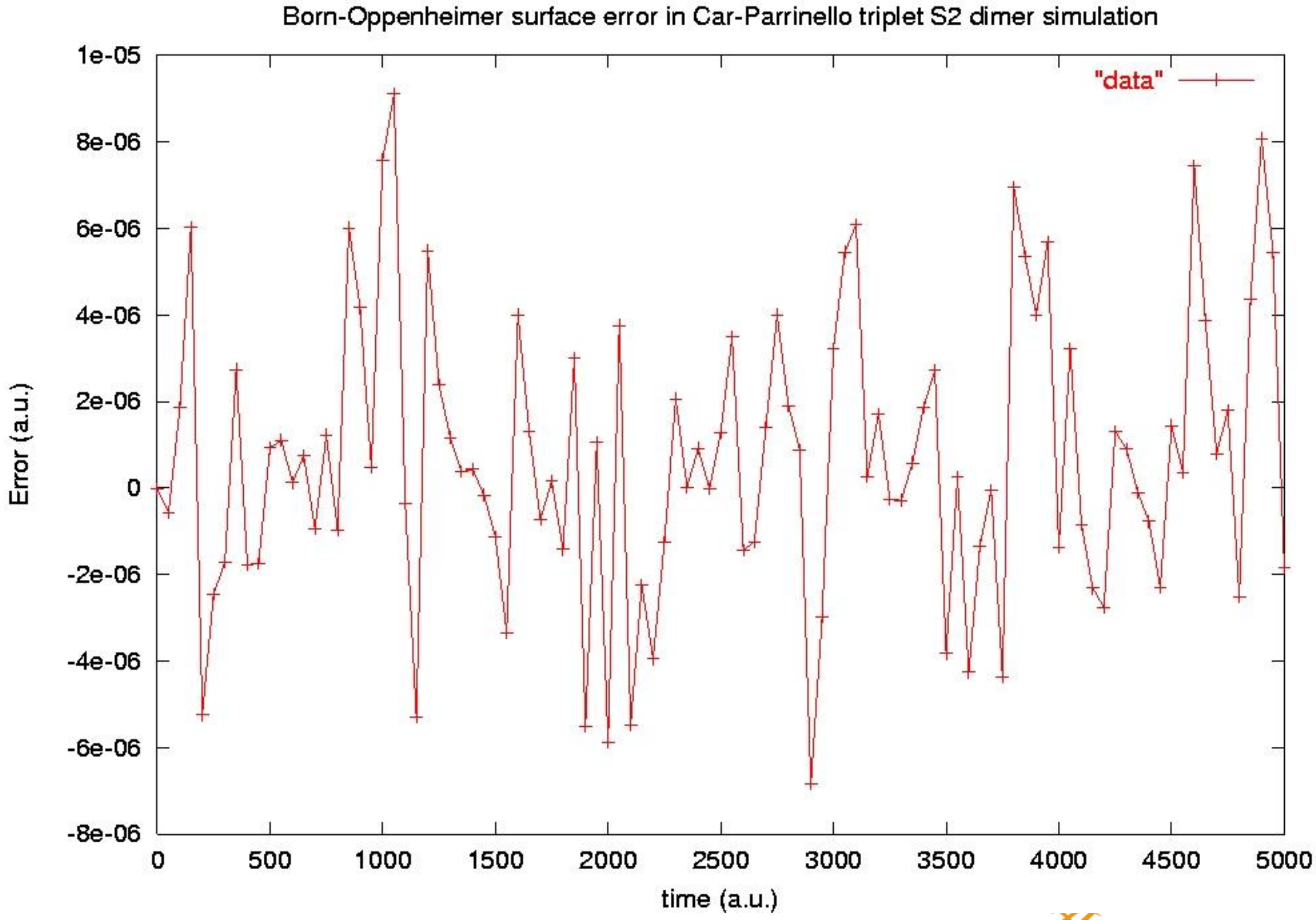
Energy Conservation



Born-Oppenheimer Error



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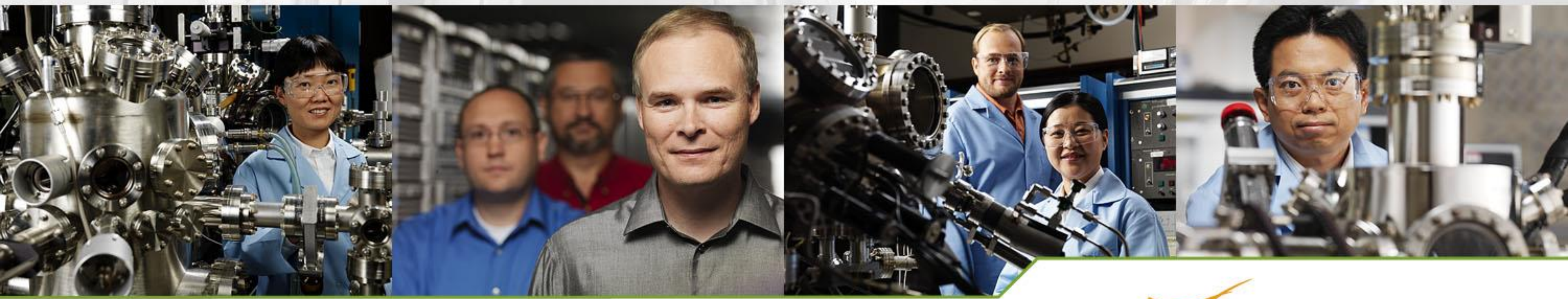
Questions?



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