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Quantum (Path Integral) Molecular Dynamics

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Overview of lecture

- Background Theory
- CASTEP details
- Examples

Background Theory

What is PIMD?

- Path-Integral
  - We use the Feynmann Path-Integral formulation of quantum mechanics to incorporate an approximate quantum treatment for the non-electronic part of the problem

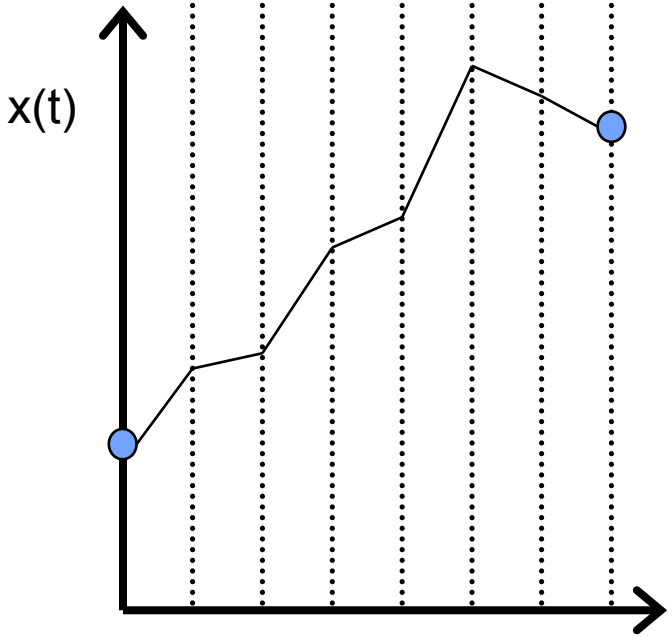
- Molecular Dynamics
  - We use standard CASTEP + extra contributions from PI to generate forces & energies and hence move the atoms
  - This motion is fictitious and does NOT represent the real dynamics of the system
  - BUT ensemble averages of the PIMD are equivalent to the QM expectation values at an appropriate temperature
  - Hence can use PIMD to incorporate the effects of finite temperature and QM properties of the nucleus into our calculation
  - Hence include effects of zero-point motion, tunnelling, etc.

PIMD Background Theory

- Statistical Mechanics
  - Partition Function
  - Expectation Values
  - Density Matrix
  - Time Evolution
- Quantum Mechanics
  - Density Matrix operator
  - Time evolution operator
  - Action

Path Integral view of QM

- The probability amplitude for a particle beings at some (x’,t’) is given by the probability of it coming from some starting point (x,t) and then summing over all possible starting points!



A possible path through space-time. The dotted lines indicate possible positions that a path could pass through at each time slice. The propagator integrates over all such possible positions, keeping the end points fixed.

The Path Integral

- Integration over all possible paths is done by *time slicing*, i.e. discretizing the path into a number of slices in time, performing the space integration at each slice, and then letting the number of slices go to infinity.
- Mathematically:

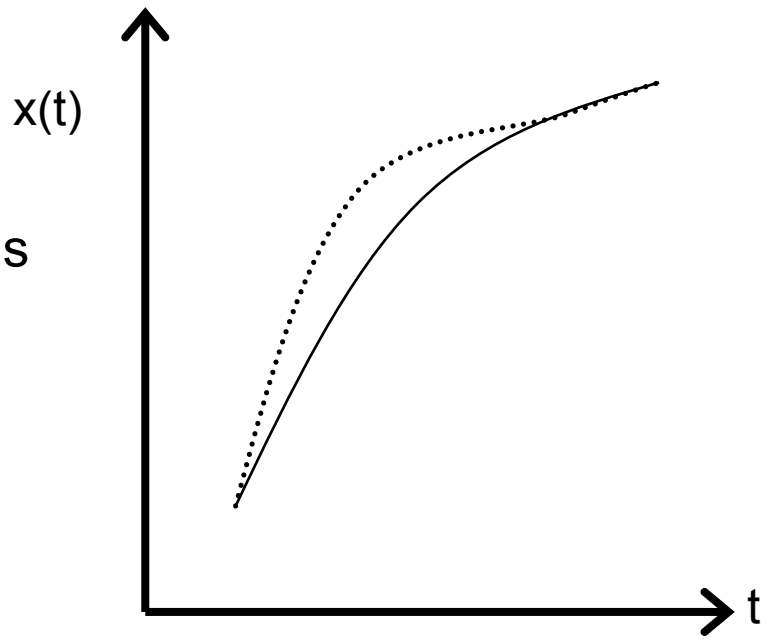
$$\int Dx \equiv \lim_{N\to\infty,\Delta t\to\infty} \int dx_{N-1} \int dx_{N-2} \ldots \int dx_1$$

Action and Classical Paths

- The *action* is defined as

$$S\left[x\left(t\right)\right] = \int_{t1}^{t2} dt\, L\left[x\left(t\right)\right]$$

  - where the Lagrangian is L=T-V
- The classical path is that for which the action is a *minimum*



A ball moving under gravity. The solid line is the classical path, whereas the broken line is a *close* path which has a greater action. The classical trajectory balances potential and kinetic energy to minimise the overall action.

Propagator

- Define

$$\Psi\left(x',t'\right) = \int dx\, \hat{u}\left(x',t';x,t\right)\Psi\left(x,t\right)$$

where û(x',t';x,t) is called the *propagator* and represents the probability of a particle arriving at (x',t') having started at (x,t)

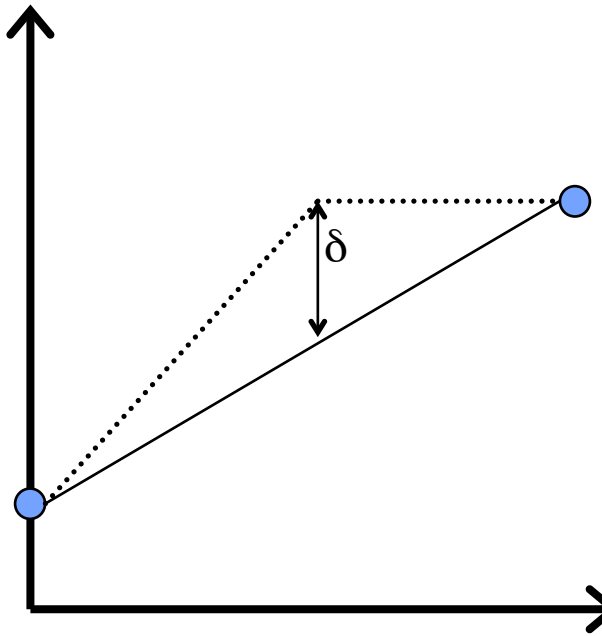
- With path integrals, can write propagator as

$$\hat{u}\left(x',t';x,t\right) = \int_{x(t)=x}^{x(t')=x'} \bar{D}x\left(t''\right)\exp\left(\frac{i}{\hbar}S\left[x\left(t''\right)\right]\right)$$

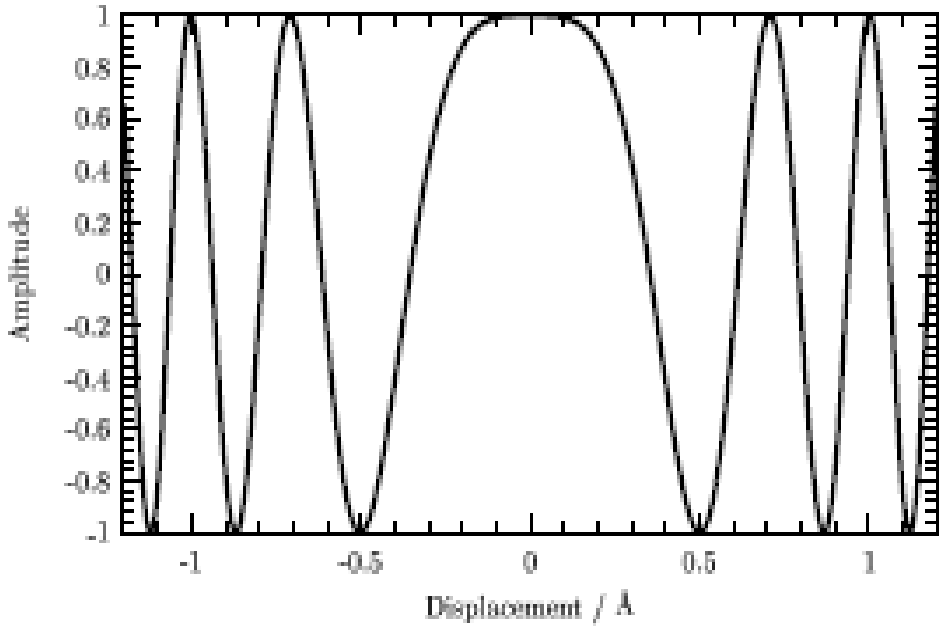
  - where Ďx denotes integration over all possible positions at each time slice and includes some simple numeric prefactors.

Phase Factors

- The action causes a complex phase factor which causes interference when adding neighbouring paths, e.g. H atom:



The deviation between two possible paths at a single time slice.



Classical-Quantum Crossover

- Oscillations very rapid for large path differences δ
  - For a classical 1 kg mass we see same shape shape as figure 4 but oscillation over ym scale!
- A system becomes quantum when action S~ħ
  - Oscillations add constructively over width of central peak, and then decohere
- Temperature also matters
  - see quantum effects when thermal wavelength ~ de Broglie wavelength

Link to Classical Stat Mech

- It can be shown that QM in imaginary time with Path Integrals is equivalent to classical statistical mechanics at finite temperature!
- If we want the properties of a particle at some (x,t) then the paths in the path integral begin and end on the same point which means that imaginary time is cyclic.
- In practice we discretise the path integral into *P* slices and converge w.r.t. *P*

Discretising

- Skipping details, we finally arrive at:

$$Z = Tr\left(\rho\right) = Tr\left(\exp\left(-\beta H\right)\right) = \lim_{P\to\infty} Tr\left(\exp\left(-\beta H / P\right)\right)^{P}$$

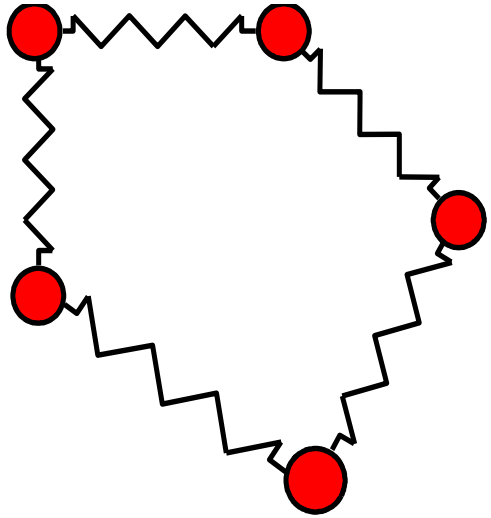
$$Z_P \sim \int dx_1 \ldots dx_P \exp\left(-\beta \sum_{s=1}^{P}\left(\frac{mP}{2\beta^2\hbar^2}\left(x_{s+1} - x_s\right)^2 + \frac{V\left(x_s\right)}{P}\right)\right)$$

where x_s is the position of at one value of the time slice in imaginary time, and $x_{P+1}=x_1$ due to cyclic nature.

- Hence the ‘beads on springs’ model :

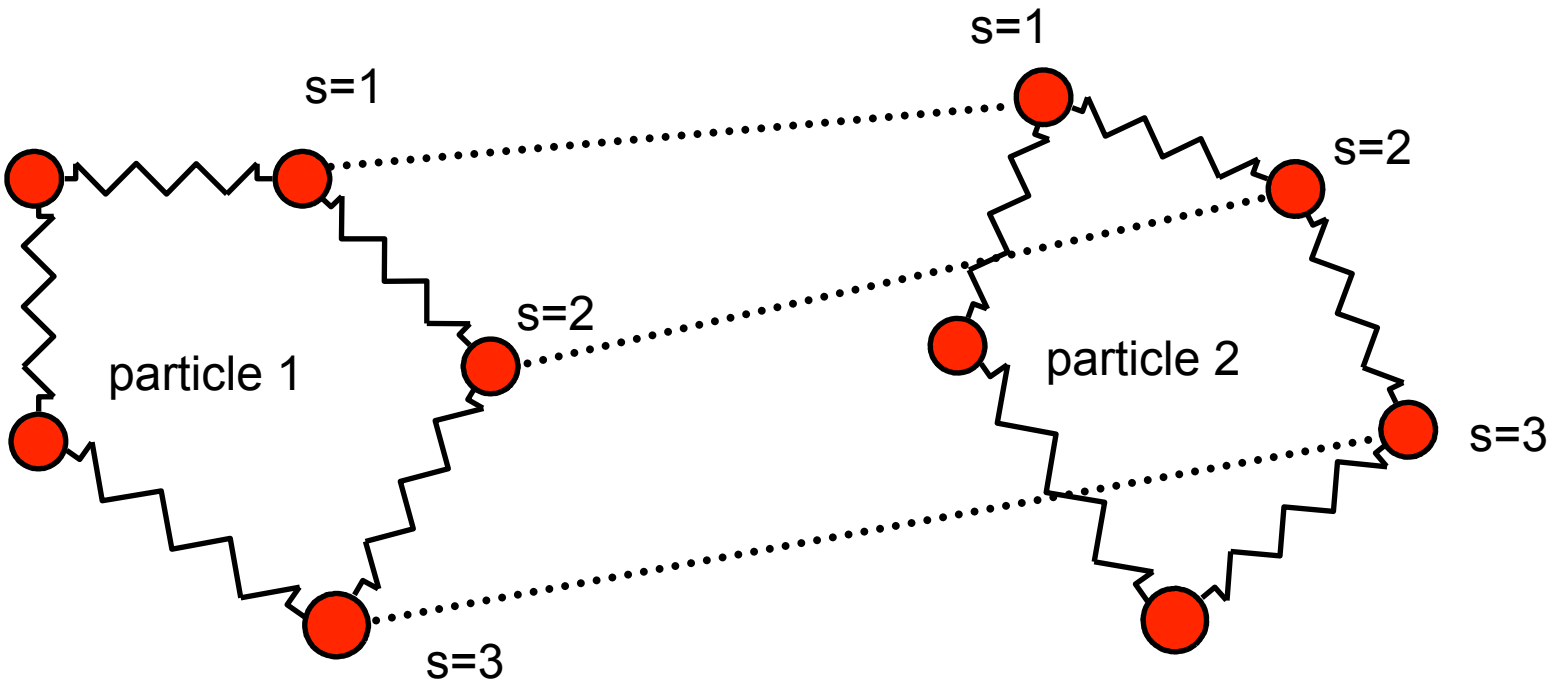
Beads on Springs

- Discretised Path Integral
- SHO interaction between nearest neighbours in imaginary time
- 1/P reduction in effect of potential
- Spring constant $k=mP/\beta^2\hbar^2$
- Hence springs get stiffer at high T
  - classical limit of a single bead
- Floppy springs at low T
  - QM delocalisation
- Centroid corresponds to classical position



Path integral view of a single quantum particle.

Multiple QM Particles



- Spring interaction only within a single particle
- Conventional V/P interaction at equivalent values of imaginary time between particles

Harmonic Issues

- The spring interaction has a fundamental frequency + harmonic modes
  - Need to integrate these accurately with MD to get proper ensemble distribution
  - Ergodicity problems => cannot use NVE or simple Nose-Hoover thermostat
  - Use N-H chain or Langevin
  - In CASTEP PIMD can only use Langevin at moment
- Also, k~P so frequency increases as converge number of beads
  - so must *reduce* MD timestep => more expensive
- Unless use *staging modes* transformation
  - Transform bead masses to compress the intra-bead spectrum and hence keep timestep constant as increase P

PIMD in CASTEP

CASTEP keywords

- Usual SCF & MD keywords PLUS

  `md_use_pathint=true`

  `md_num_beads=16`

  `num_farms=16`

  `md_pathint_staging=true`

  `md_num_stages=1`

- Restrictions
  - **`num_farms=1`** or **`md_num_beads`**
  - no constraints
  - only Langevin thermostat

Analysis

- Materials Studio does not support PIMD
- The `.castep` file gives a brief summary of what is happening in the user units …

```
          ======> Path integral bead no. 003 <=====

xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx
x                                                  MD Data:     x
x                                                               x
x              time :      0.001000                    ps       x
x                                                               x
x   Potential Energy:   -543.432706                    eV       x
x   Kinetic   Energy:      0.034494                    eV       x
x   Total     Energy:   -543.398212                    eV       x
x   Hamilt    Energy:   -543.397578                    eV       x
x                                                               x
x        Temperature:    266.854751                     K       x
xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx
```

Analysis

- More advanced analysis requires more data, for which we use the `.md` file.
- This contains a LOT of information, for each time step, always using atomic units:

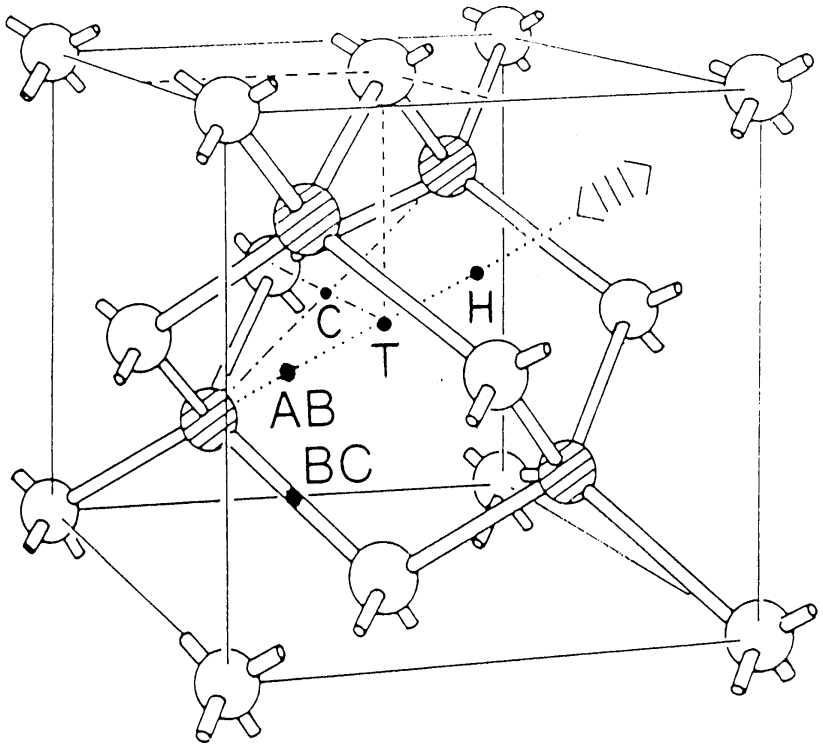
```
                  1.19476569E+004
          -1.99707968E+001     -1.99692125E+001      9.64993404E-004  <-- E
            6.43328936E-04                                           <-- T
           1.32280829E+001      0.00000000E+000      0.00000000E+000  <-- h
           0.00000000E+000      1.32280829E+001      0.00000000E+000  <-- h
           0.00000000E+000      0.00000000E+000      1.32280829E+001  <-- h
N      1    4.83250673E+000      3.95868000E+000     -3.95873877E+000  <-- R
N      2    4.61612393E+000      5.48995066E+000     -5.48989189E+000  <-- R
N      1    1.15732344E-004      1.10453835E-004     -1.10452023E-004  <-- V
N      2   -1.15732344E-004     -1.10453835E-004      1.10452023E-004  <-- V
N      1   -1.83347496E-004      1.53896599E-003     -1.53886170E-003  <-- F
N      2    1.83347496E-004     -1.53896599E-003      1.53886170E-003  <-- F
```

Visualisation

- PIMD produces usual CASTEP output PLUS
- `<seedname>_pimdXXX.md` file for each bead (1<= XXX <= P)
- These files are identical to normal `<seedname>.md` file but get 1 for all particles at same value of imaginary time.
- Can then use conventional CASTEP MD tools to analyse such as MDTEP
- Or use the `pi_merge` script to combine into a single file for visualisation (use md2xyz) ...

PIMD case studies

Hydrogen in Silicon



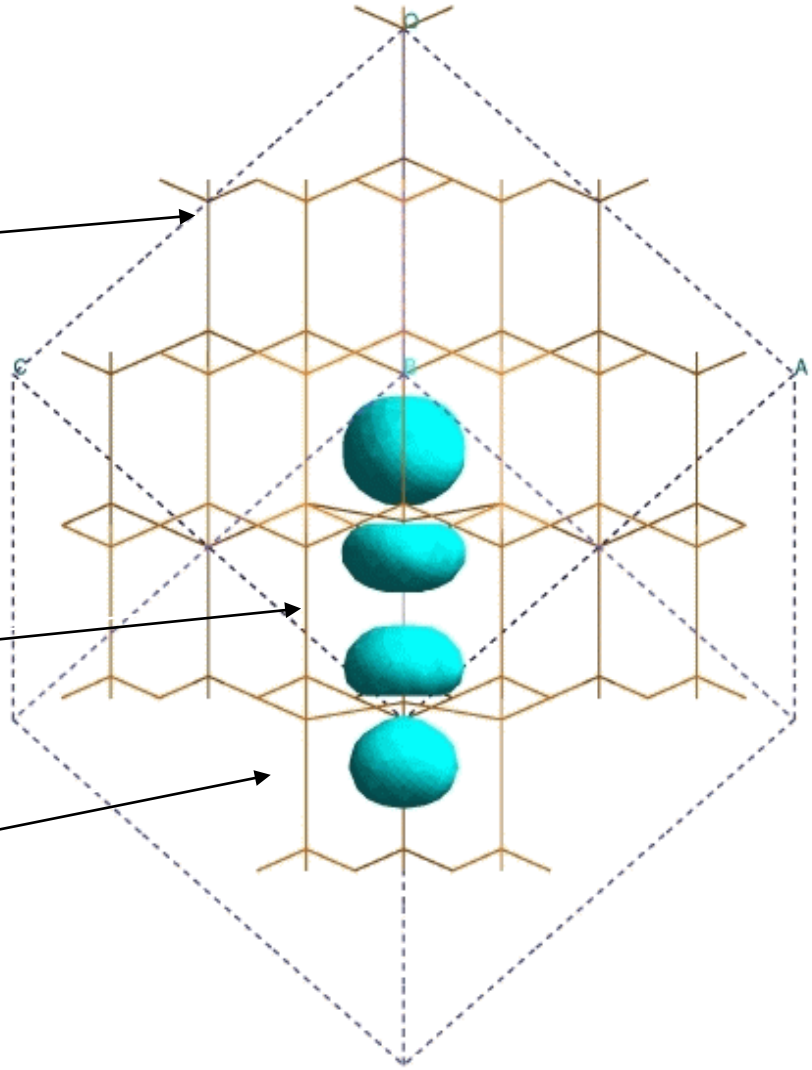
- Stable / Metastable sites
  - BC two-fold coordinated
  - T four-fold coordinated
- Possible saddlepoint sites
  - AB antibonding site
  - C half-way to T
  - H hexagonal (6-fold) site

Spin Density at BC site

Planes of silicon atoms seen "edge-on"

BC site

Spin density iso-surface due to single extra electron



T=0 Results

- Large lattice strain around BC site
- Small (inwards) relaxation around T
- Both sites stable with BC preferred to T
- Relative energy (BC–T) ~ -0.27eV

Bond	Length (Å)
Si-Si in bulk	2.351
Si-H in SiH4	1.480
Si-H at T	2.278 (-3%)
Si-H at BC	1.650 (+40%)

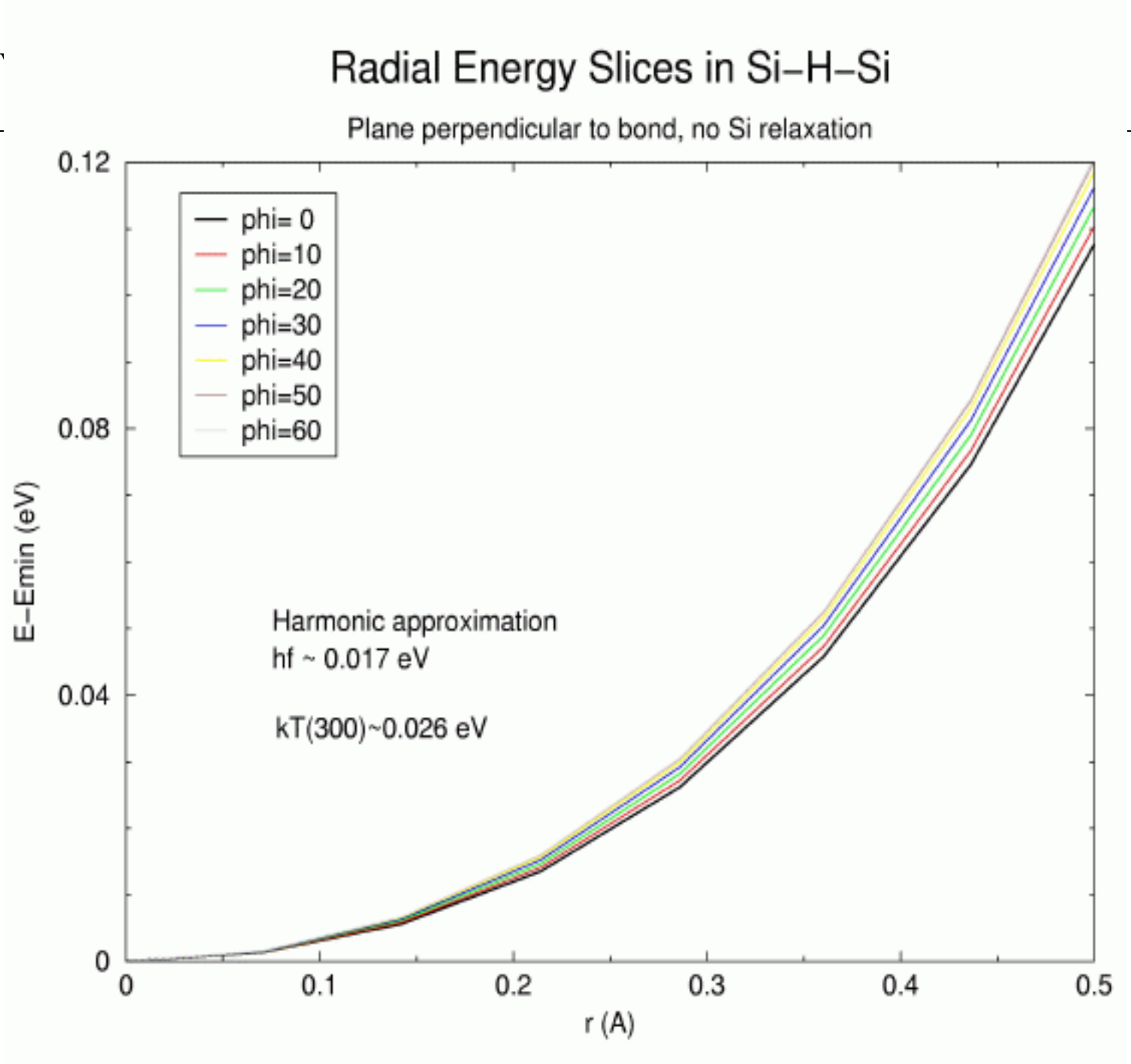
Site	Lattice Relaxation Energy (eV)
H at T	0.032
H at BC	1.662

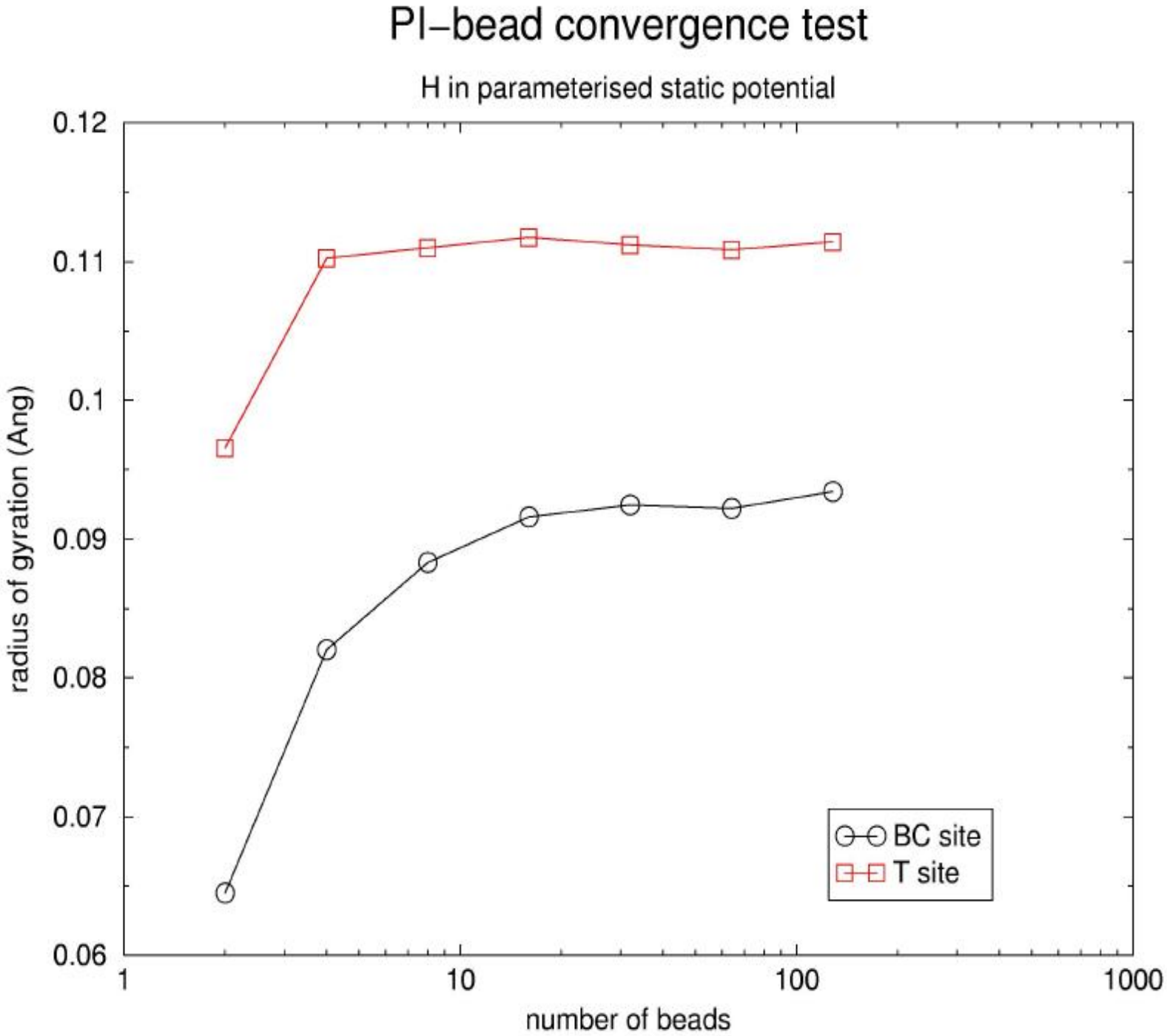
Site	Binding Energy (eV)
H at T	0.284
H at BC	0.554

Awkward Experimental Fact

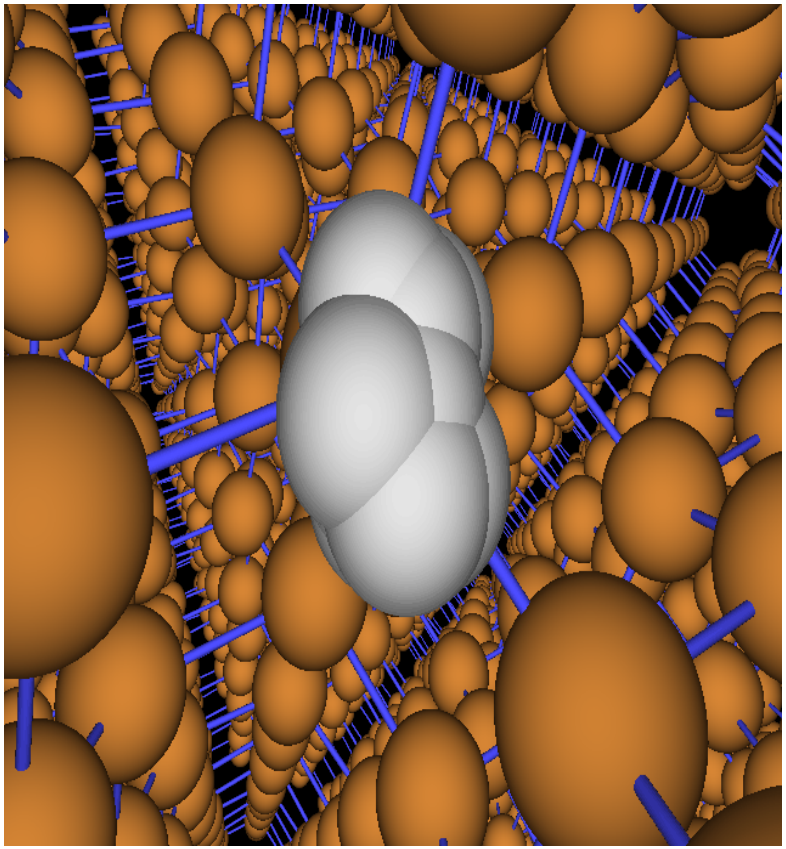
μSR → 1:2 population of BC:T sites …

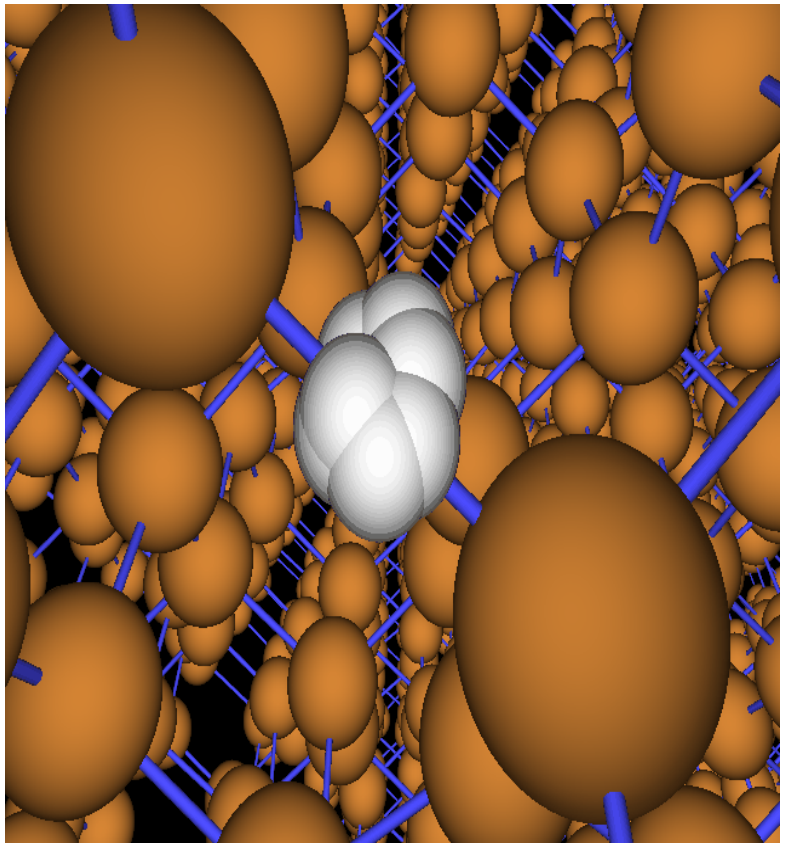
- BUT we see BC<T and there are 8 BC sites for every T site!
- Is it a thermal effect?
  - *Ab initio* MD suggests no significant energy changes
- Non-equilibrium effect?
  - need barrier heights → saddlepoints → yet to be tackled
- Is it a quantum effect?
  - Mass Mu ~ $^1/_9$ Mass H and ZPM ~ 1/sqrt(mass) …


Radial Energy Slices in Si–H–Si
Plane perpendicular to bond, no Si relaxation
phi= 0
phi=10
phi=20
phi=30
phi=40
phi=50
phi=60
Harmonic approximation
hf ~ 0.017 eV
kT(300)~0.026 eV
E–Emin (eV)
r (A)
0
0.04
0.08
0.12
0.1
0.2
0.3
0.4
0.5


PI–bead convergence test
H in parameterised static potential
radius of gyration (Ang)
number of beads
0.12
0.11
0.1
0.09
0.08
0.07
0.06
1
10
100
1000
BC site
T site

Visualisations





Superimposing all beads at same value of imaginary time
at a single instance of MD time (T=300 K, P=16).

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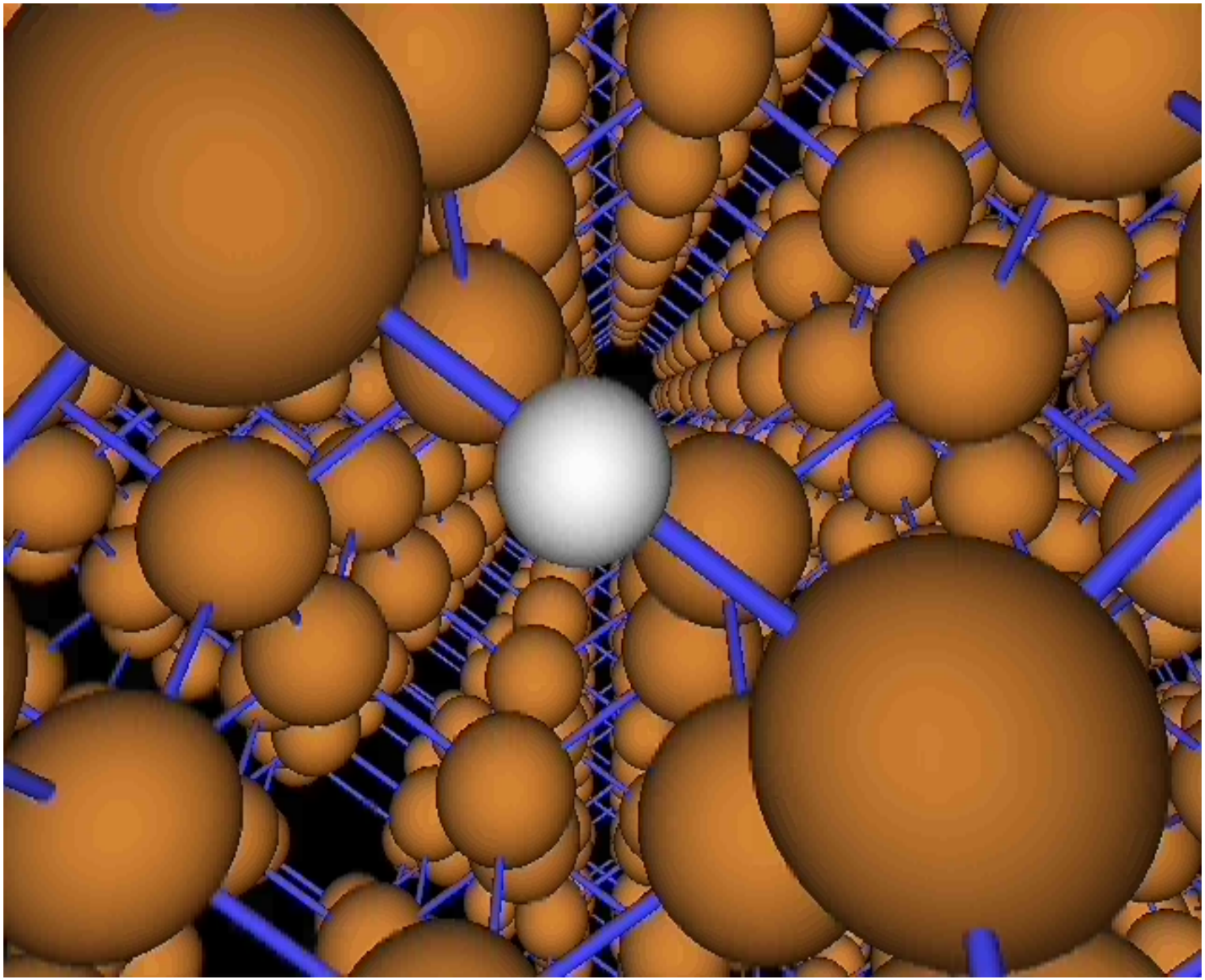
H-Defect at BC Site in Silicon



Energy Results

- PI is indeed capturing the quantum effects
  - big difference in energies when turn PI on
  - now get relative energy (BC-T) ~ -0.08 eV
- Still have conventional view BC<T
- Adding ZPM increases energy at both sites
  - bigger effect at BC than T due to confinement
  - enhanced effect for Mu expected

Implications

- Hydrogen
  - BC is still confined BUT T may not be, *i.e.* no longer fixed but mobile/delocalized
  - need definitive saddlepoints
- Muonium
  - probable cross-over in ordering of sites
  - probably BC confined but T highly mobile
  - no longer a good analogue for Hydrogen?

Water-Hydroxyl Overlayers on Metal Surfaces

Phys. Rev. Lett. **104**, 066102 (2010)

Xin-Zheng Li, Matt Probert, Ali Alavi, and Angelos Michaelides

Water-hydroxyl layers

- In many systems, the initial wetting layer is not pure water, but a water-hydroxyl mix
  - Bond lengths/angles unusual due to “pinning” with hydrogen-bonds formed to surface atoms
- Transition metal surfaces have been well-characterised
  - Pt(111) has large lattice constant and so inter-molecule distance ~ 2.83 Å
  - Ni(111) has much smaller distance ~2.50 Å

Water problem

- In bulk ice have typical O-O distance ~ 2.8Å
- At high pressures (>70 GPa) ice has typical O-O distance of ~2.3 Å
  - No longer a molecular crystal
  - Have delocalised protons between O nuclei
- Low T (160 K) measurements of hydrogen diffusion on metal surfaces suggests that quantum tunnelling important
  - Hence need full QM treatment for hydrogen!
  - Short cut to converge number of beads …

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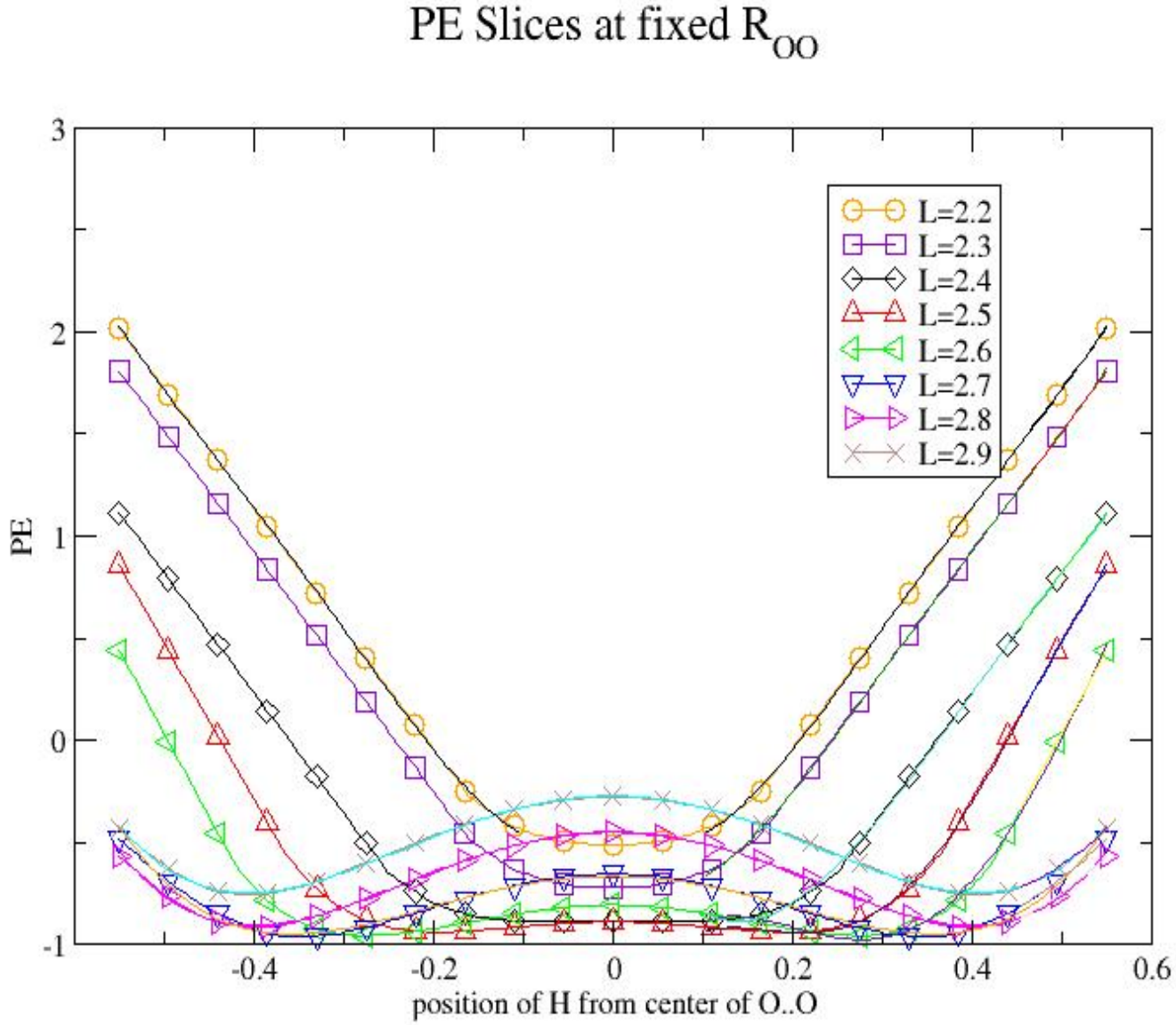
Static H_2O/OH on Ni PES



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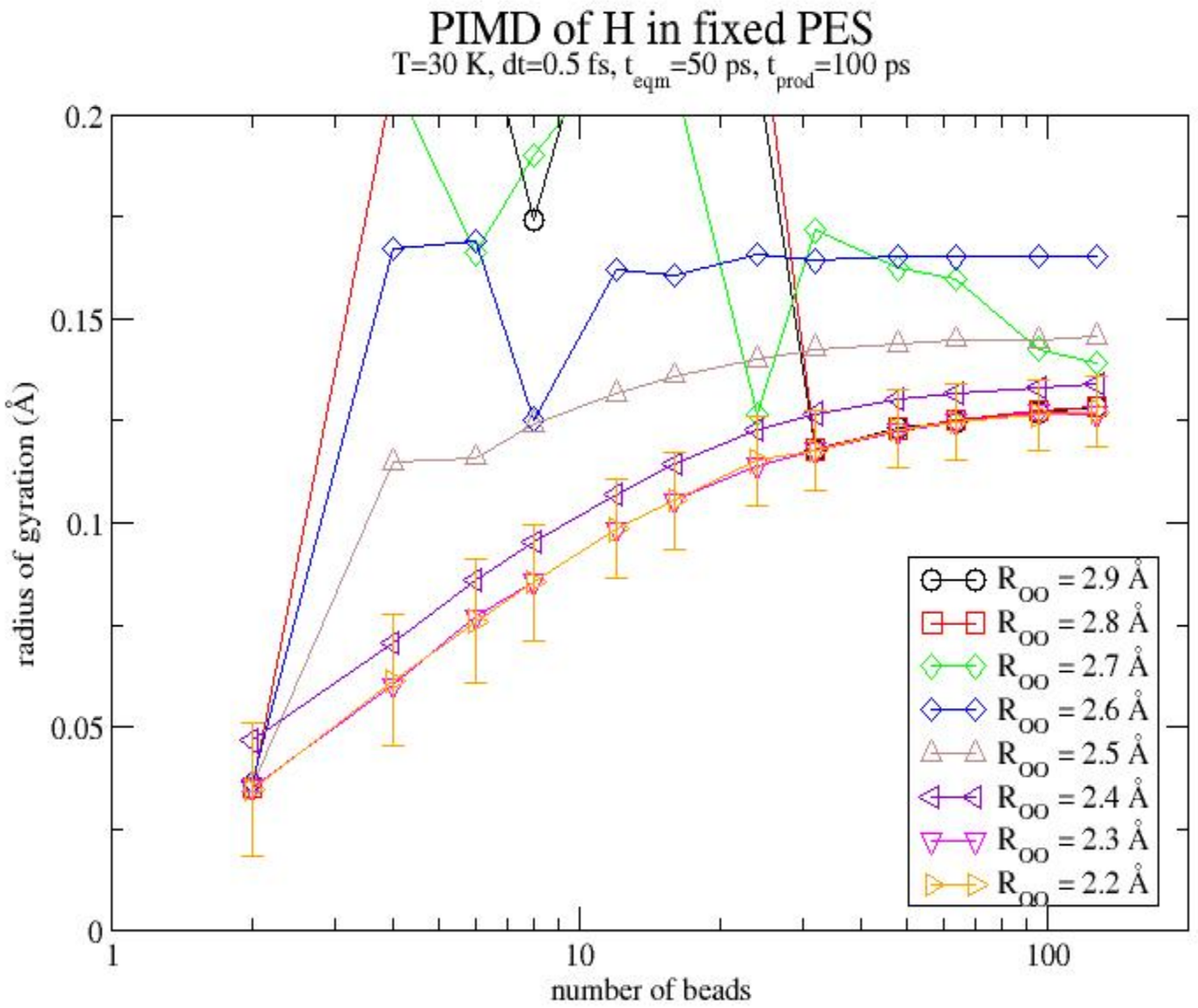
Bead Convergence in static PES



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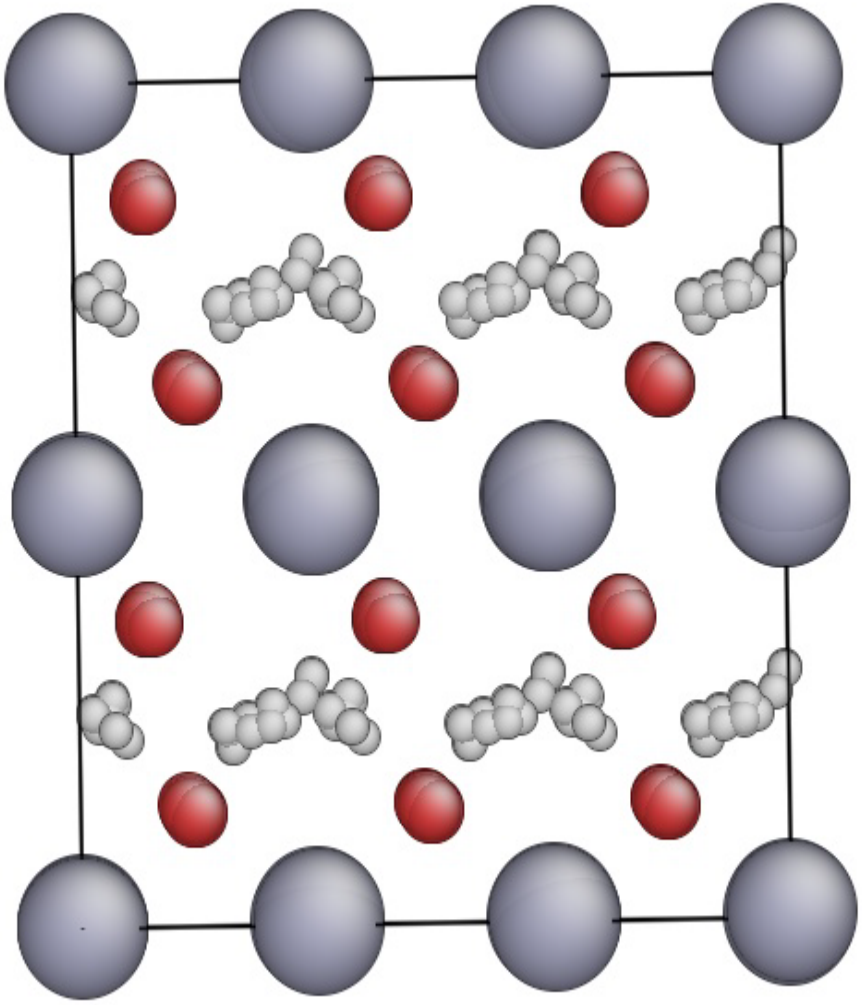
Hydrogen in Minerals



Hydrogen is a common component of many minerals but position very hard to locate by traditional techniques

Brucite - $Mg(OH)_2$ – is a simple mineral but location of H unclear

PIMD shows why …

Other examples

- Recent paper on high-pressure hydrogen phase diagram
  - Correcting previous paper on structure search to include ZPE and finite T
- Recent paper on high-pressure melting of hydrogen – two-phase coexistence with PIMD
- Paper under review – diffusion of H on Ru – looking at quantum vs classical diffusion vs T
- Current project – diffusion of H on Ni and isotope effects

Summary

Summary

- PIMD as a way of going beyond BOMD
  - Quantum treatment of ions but expensive!
- Usual MD caveats
  - Beware equilibration, not all configurations are equal, consider sampling and correlation, etc.
- Apply basic physics to the results
  - conservation laws, equipartition, etc
- Additional concern
  - need to converge w.r.t. number of beads
- BEWARE:
  - the dynamics ARE FICTITIOUS and only the ensemble average is meaningful …
  - some recent theoretical developments (e.g. centroid PIMD, ring-polymer PIMD) can do this – being actively developed – hope to get into CASTEP soon!

References

- R.P. Feynman, Rev. Mod. Phys **20**(2) 367 (1948)
  - The original paper
- "*Quantum Mechanics and Path Integrals*"
  - R.P. Feynman and A.R. Hibbs (McGraw-Hill) (1965). Definitive Text.
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- M.J. Gillan, Phil. Mag. A **58**(1) 257 (1988)
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- M. E. Tuckerman, D. Marx, M. L. Klein, and M. Parrinello, J. Chem. Phys. **104**, 5579 (1996)
  - Efficiency improvements such as staging modes
- **www.castep.org** web site
  - Useful MD and geometry optimisation tutorials, plus FAQs, on-line keyword listing, MDTEP download, etc.