Intermolecular Interactions in Molecular Crystals

Mixed-Ligand Organophosphonates

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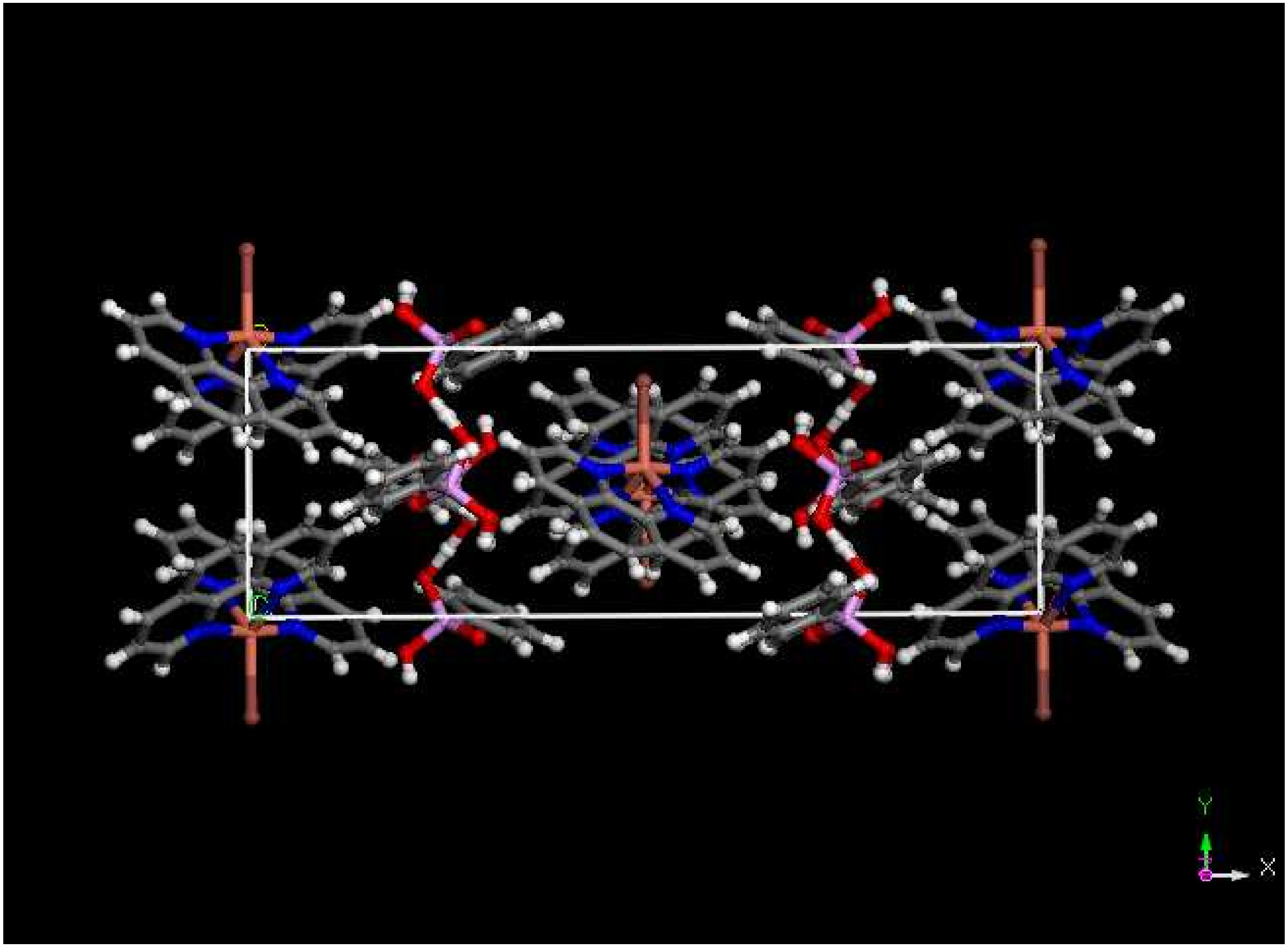
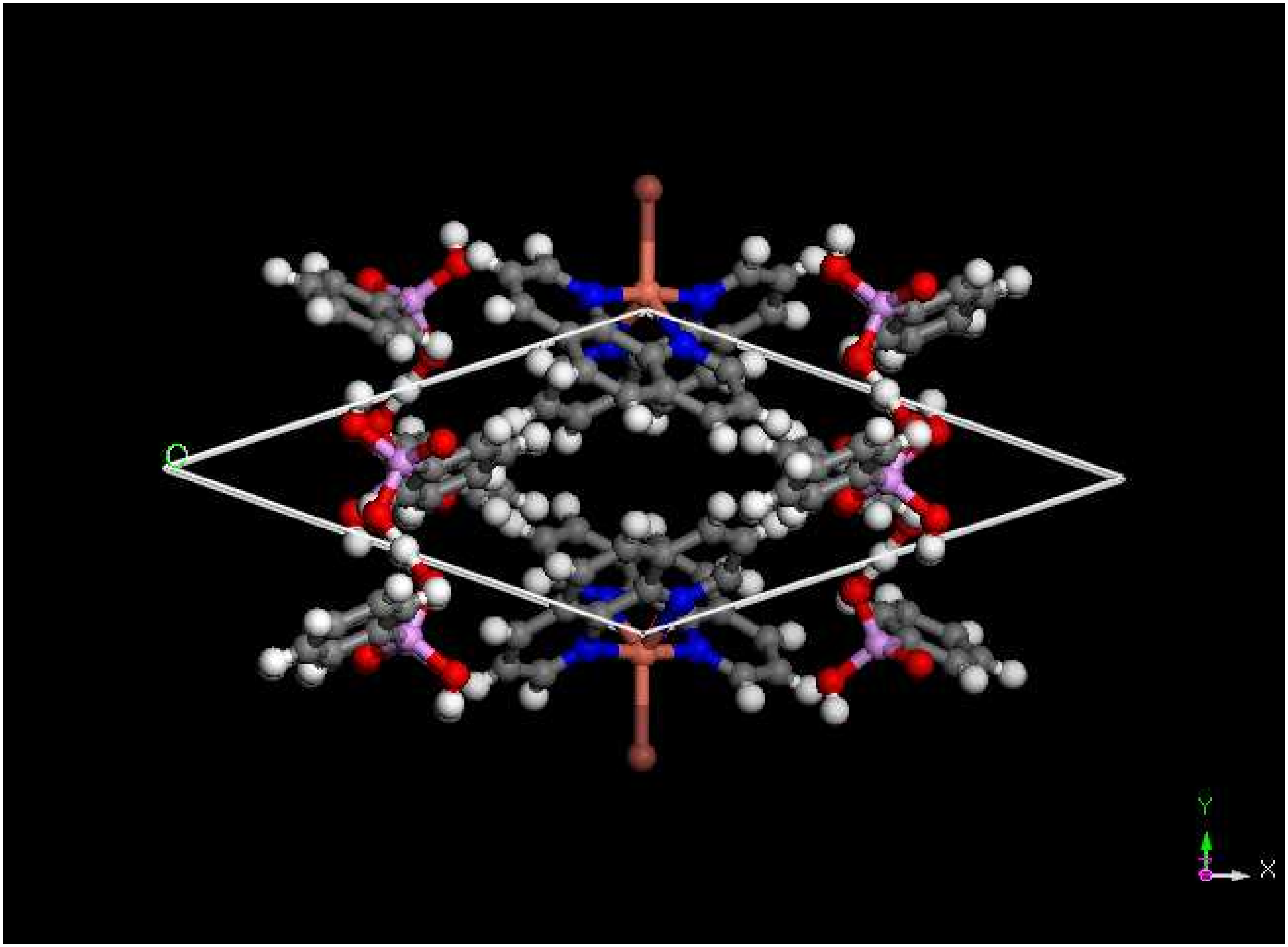
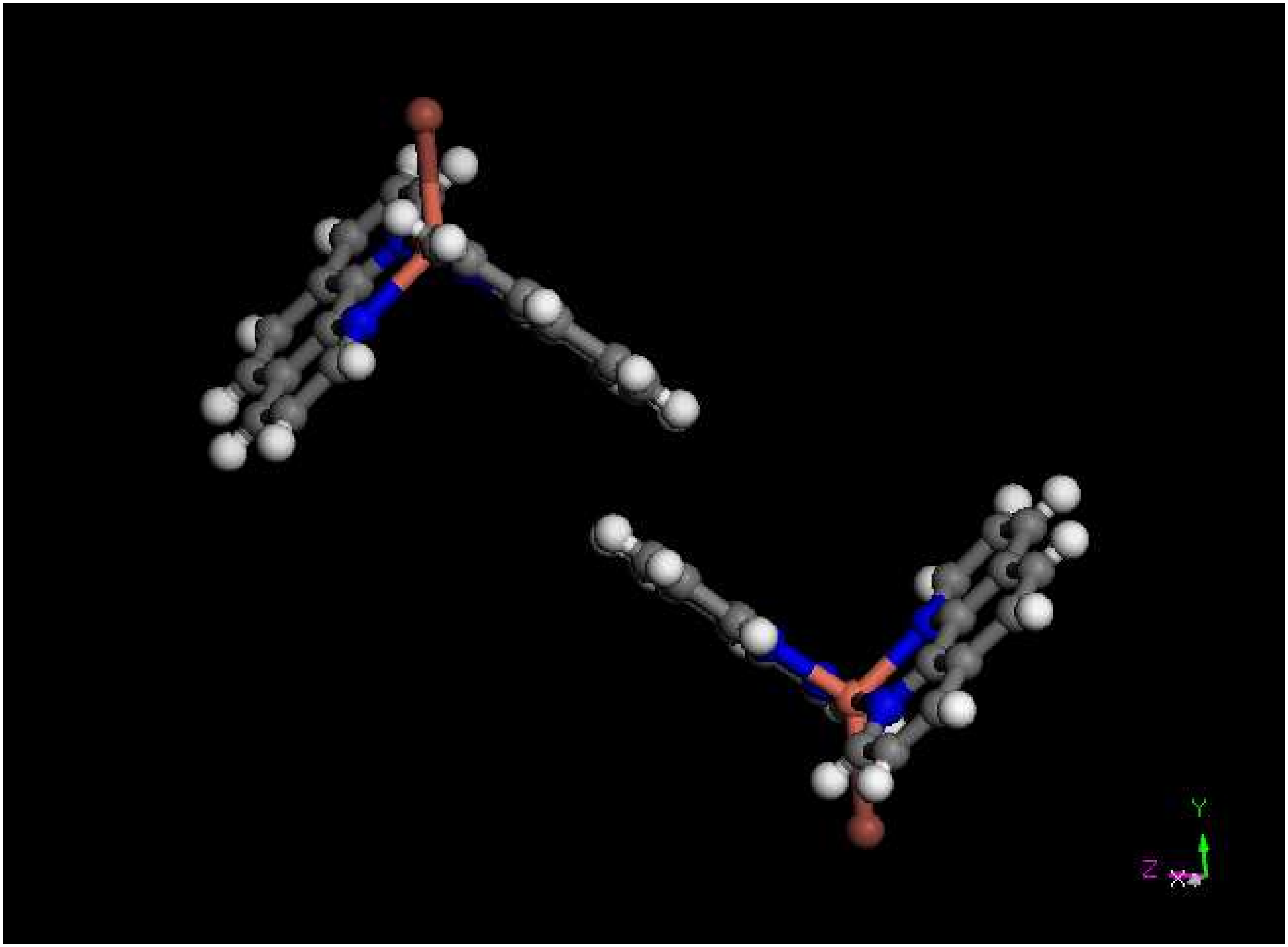
An Organophosphonate Complex



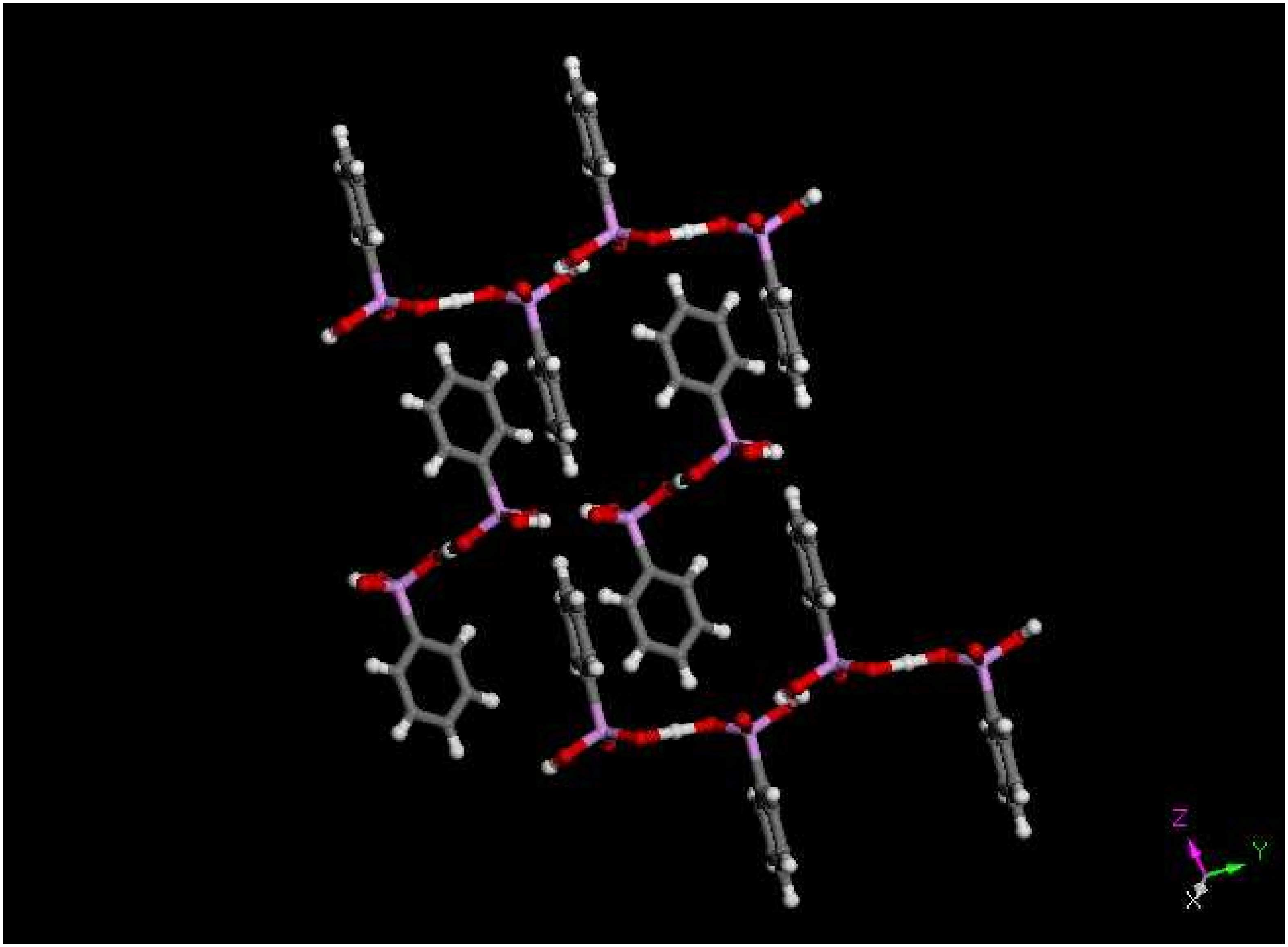
An Organophosphonate Complex



An Organophosphonate Complex



An Organosphosphonate Complex



Summary of Interactions

- Strong hydrogen bonds between individual phenylphosphonic acid molecules to form dimers.

- Weaker hydrogen bonds between phenylphosphonic acid dimers to form chains.

- Very weak (so-called) $\pi - \pi$ interactions between phenyl rings to form layers.

- Very weak $\pi - \pi$ interactions between copper complex molecules to form 'chains'.

- In general, interactions are numerous and variable!

Applications

- Gas sensors
- Ion-exchangers
- Catalysts
- Non-linear optical materials

The Problem...

- Many purported applications, comparitively few have actually been realised.
- The Ultimate Goal of synthetic chemists is to be able to manipulate intermolecular interactions to produce ’designer’ structures.
- If we want to manipulate these interactions, we need to understand them.
- More work is needed in the fundamentals.

Where to Start?

- Start by simulating simple models of each major interaction: water clusters for hydrogen bonds and benzene dimer for aromatic interactions.
- Next, move on to simulating clusters of component molecules.
- Finally, look at properties of the bulk molecular crystal.

Problems

- DFT can't describe dispersion forces. It is still unclear as to whether it can adequately (universally) handle hydrogen bonding.

- Conventional high-level techniques (Configuration Interaction and Coupled Cluster) scale very badly with system size.

All-Electron Calculations in QMC

- Large disparity in time and energy scales for core and valence electrons.

- The wavefunction varies rapidly in the core region so core electrons require the smallest time-steps.

- For very large systems, the simulation will take a really, really, really long time.

All-Electron Calculations in QMC: Some Solutions

- Don't simulate large systems (BORING!).
- Use pseudopotentials.
- Use an acceleration algorithm (VMC only, at present).

VMC Acceleration Scheme (Umrigar)

- The Metropolis algorithm is used to evaluate expectation values of various observables for a given many-particle trial wavefunction, $\Psi_T(\mathbf{R})$.

- A move from position $\mathbf{R} \rightarrow \mathbf{R}'$ is proposed according to some transition matrix, $T(\mathbf{R} \rightarrow \mathbf{R}')$, and accepted with probability

$$A(\mathbf{R} \rightarrow \mathbf{R}') = min\{\frac{|\Psi_T(\mathbf{R}')|^2 T(\mathbf{R}' \rightarrow \mathbf{R})}{|\Psi_T(\mathbf{R})|^2 T(\mathbf{R} \rightarrow \mathbf{R}')}, 1\}$$

- In the original formulation of the Metropolis method, the transition matrix is chosen to be symmetric, which is generally applicable but not very efficient.

- The transition matrix can be modified, provided detailed balance is satisfied.

- We can choose a transition matrix such that each electron will attempt moves that are proportional to its distance from the (nearest) nucleus. Working in spherical polar coordinates avoids derivative discontinuities in $\Psi(\mathbf{R})$.

In Summary

- Molecular crystals provide an interesting laboratory for the study of intermolecular interactions. If we want to manipulate them (intelligently) we need to be able to understand them.

- Computer simulations play a very important role in this area, where experimental data is either very expensive or inaccessible. Due to the nature of the interactions under study, we need a high-accuracy technique but one that also scales well with system size. QMC fits the bill!

- All-electron QMC calculations for big/heavy systems take large amounts of computer time. Methods exist to alleviate the problem but are currently only applicable to VMC. An acceleration scheme suitable for DMC would be desirable.