Zen and the art of computer simulation

An inquiry into values

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The modes of science

- Problem driven: choose the method(s) that can solve your problem (not just address it)
- Method driven: choose a problem that can be solved by your method (not just be addressed by it)
- Quality driven: choose a challenging problem you can understand and a suitable scientific method you can master. Don't aim at "being the first" to tackle a problem, but rather at "being the last"

The quest of quality

- Know the problem so that you can ask meaninigful questions
- Know the method so that you can give meaningful answers
- Be ready to work hard on the method if it cannot (yet) provide the answers you ask*

(*) Because "the knowledge that quality counts makes even routine tasks rewarding" [Freeman J. Dyson]

The scope of computer simulation

- Measure theories. Solve equations which could not be solved otherwise. "Get numbers out of theories" much in the same way as experiments "get numbers out of a natural process"
- Do virtual experiments where experimental conditions can be controlled down to the atomic scale in ways which would not be possible in the lab

Ab initio simulations

$$i\hbar \frac{\partial \Phi(r,R;t)}{\partial t} = \left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R_I^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial r_i^2} + V(r,R) \right) \Phi(r,R;t)$$

The Born-Oppenheimer approximation (M>>m)

$$M\ddot{R}_I = -\frac{\partial E(R)}{\partial R_I}$$

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r_i^2} + V(r,R) \right) \Psi(r|R) = E(R)\Psi(r|R)$$

Density functional theory

$$V(r,R) = \frac{e^2}{2}\frac{Z_I Z_J}{|R_I - R_J|} - \frac{Z_I e^2}{|r_i - R_I|} + \frac{e^2}{2}\frac{1}{|r_i - r_j|}$$

⬇

$$V(r,R) \rightarrow \frac{e^2}{2}\frac{Z_I Z_J}{|R_I - R_J|} + v_{[n(r)]}(r)$$

Kohn-Sham Hamiltonian

$$n(r) = \sum_v |\phi_v(r)|^2$$

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + v_{[n(r)]}(r)\right)\phi_v(r) = \epsilon_v \phi_v(r)$$

Kohn-Sham equations from functional minimization

$$E[\{\phi\}, R] = -\frac{\hbar^2}{2m}\sum_v \int \phi_v(r)\frac{\partial^2 \phi_v(r)}{\partial^2 r}dr + \int v(r,R)n(r)dr +$$

$$+\frac{e^2}{2}\int \frac{n(r)n(r')}{|r-r'|}drdr' + E_{xc}[n(r)]$$

$$E(R) = \min\big(E[\{\psi\}, R]\big)$$

$$\int \phi_v^*(r)\phi_u(r)dr = \delta_{uv}$$

Kohn & Sham

$$H_{KS}\phi_v = \epsilon_v \phi_v$$

Helmann & Feynman

$$\frac{\partial E(R)}{\partial R_I} = \int \frac{\partial v(r,R)}{\partial R_I} n(r)dr$$

The tricks of the trade

- Expanding the Kohn-Sham orbitals into a suitable basis set turns DFT into a multi-variate minimization problem, and the KS equation into a non-linear matrix eigenvalue problem

- The use of pseudo-potentials allows to ignore chemically inert core states and to use plane waves (the name of the game!)

The tricks of the trade (II)

- Plane waves are orthogonal and the matrix elements are usually easy to calculate; the effective completeness of the basis is easy to check

- Plane-waves allow to calculate efficiently matrix-vector products and to solve the Poisson equation using FFT's

- Supercells for treating finite (or semi-infinite) systems

- Iterative diagonalization vs. global minimization

The tricks of the trade (III)

- Summing over occupied states: special-point and Gaussian-smearing techniques
- Non-linear extrapolation for SCF acceleration and density prediction in MD
- Choice of fictitious masses in CP dynamics

Numbers do matter

Scientific insight roots in our ability to compare quantitatively the behavior of natural processes with the predictions of theories

- Know how accurately a natural process is measured in the lab
- Know how accurately a theory is measured (its equations are solved)
- Know how the accuracy can be estimated and improved (when needed)
- Know how to estimate the resources needed to achieve the required accuracy

Accuracy vs. approximations

- Theoretical approximations / limitations
  - The Born-Oppenheimer approximation
  - DFT functionals (LDA, GGA ...)
  - Pseudopotentials
  - No easy access to electronic excited states and/or quantum dynamics
- Numerical approximations / limitations
  - Finite/limited size/time
  - Finite basis set
  - Differentiation / integration / interpolation

What do I (can't I) calculate today?

- Strong covalent and metallic bonds
- Weak e-e correlations
- Structural optimization, lattice vibrations, adiabatic dynamics, static response functions
- ☐ Strong correlations / Mott-Hubbard insulators
- ☐ Dispersion forces / weak chemical bond
- ☐ Optical properties / excitation energies

Which algorithm shall I use?

- Electronic structure: SCF diagonalization vs. energy minimization
- Geometry optimization: standard DFT
- Lattice vibrations, static response functions: DF perturbation theory
- Dynamics: Car-Parrinello vs. Born-Oppenheimer
- Slow kinetics and rare events: path sampling vs. Parrinello-Laio metadynamics
- Optical properties, excited states: Time-dependent DFT & many-body perturbation theory

What should I care today?

- Finite-size effects:
    - Finite systems → supercells
    - Infinite systems → k-point sampling (+ Gaussian smearing)
- Finite-basis effects:
    - Choice of the basis set (PW's, LCAO, augmented PW's, LMTO, ...)
    - Size of the basis set
- Pseudo-potentials:
    - "Hard" node-less orbitals (2p, 3d ...)
    - Semi-core states + NL XC core correction

What else should I care?

- Choice of the diagonalization / minimization algorithms
- MD time steps & CP fictitious masses
- Numerical and algorithmic details of the implementation
  - Integration & FFT meshes (1D/3D)
  - Differentiation and interpolation schemes
  - Parallelization issues
    (by band / by k-point / by G-vector)
  - ...
- ...

PWscf
is a community enterprise

Don't ask what PWscf can do for you,
but rather what you can do for PWscf

- Be part of the community
- Do great science with it
- Report bugs and suggest improvements
- Even better, fix the bugs and implement the improvements
- Write some documentation
- Help integrate it with other OS software
- ...

To start with ...

Enjoy this course!