Summary of Day I

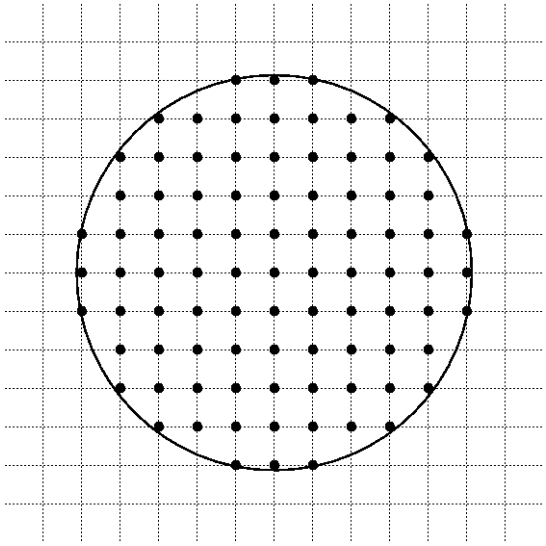
Plane wave basis set

Summary

- ONE parametre defines the basis set (for a given unit cell), and the convergence is *variational* with respect to it

Cutoff: Finite basis set

$$\frac{1}{2} G^2 \leq E_{\text{cut}}$$



$$N_{\text{PW}} \approx \frac{1}{2\pi^2} \Omega E_{\text{cut}}^{3/2} [a.u.]$$

Basis set size depends on volume of box and cutoff only

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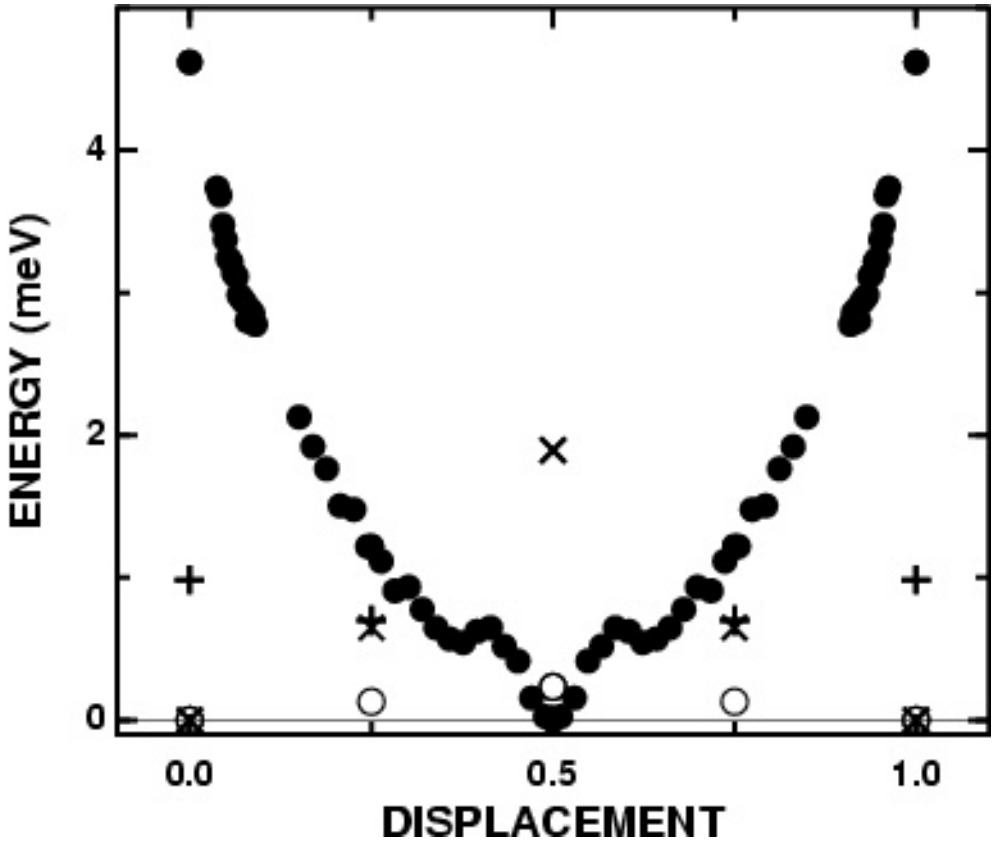
Energy of oxygen atom

Oxygen atom



PW'91: 40 / 3.2 Ry •
PW'91: 70 / 4.0 Ry +
PW'91: 50 / 3.85 Ry ×
PBE: 50 / 3.85 ∘

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- Exchange-correlation on the real-space grid causes discontinuities
- The resulting formulas easy to evaluate

Plane wave expansion: Examples

$$E_{\text{kin}} = \frac{\Omega}{2} \sum_i \sum_{\mathbf{G}} \mathbf{G}^2 |c_i(\mathbf{G})|^2$$

$$E_{\text{ES}} = \frac{1}{2} 2\pi\,\Omega \sum_{\mathbf{G}\neq 0} \frac{|n_{\text{tot}}(\mathbf{G})|^2}{G^2}$$
$$+ \frac{1}{2} \sum_{I\neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \text{erfc}\left[\frac{|\mathbf{R}_I - \mathbf{R}_J|}{\sqrt{\text{R}_I^{\text{c}2} + \text{R}_J^{\text{c}2}}}\right] - \sum_I \frac{1}{\sqrt{2\pi}} \frac{Z_I^2}{R_I^{\text{c}}}$$

Poisson's equation for periodic boundary conditions

$$V_{\text{H}}(\mathbf{G}) = 4\pi \frac{n_{\text{tot}}(\mathbf{G})}{G^2}$$

Pseudo potentials

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- They replace the action of core electrons on the valence electrons
- Replace the equation for the (valence) electrons with an equivalent one for the *pseudo* valence electrons only
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Kleinman–Bylander form

$$E_{\mathsf{PS}} = \sum_i f_i \sum_L \langle \Phi_i \mid \Delta V_L \varphi_L Y_L \rangle \, \omega_L \, \langle \Delta V_L \varphi_L Y_L \mid \Phi_i \rangle + V_{\mathsf{loc}}$$

where

$$\omega_L = \langle \varphi_L \mid \Delta V_L \mid \varphi_L \rangle$$

$$\Delta V_L = V_L - V_{\mathsf{loc}}$$

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- The pseudo potential is different for different $L = \{l, m\}$
- Kleinman-Bylander form is numerically efficient
- Once created, a pseudo potential must be **tested, tested, tested!!!**

Molecular Dynamics

Summary

- One can simulate a system in real time
- Reactions, thermodynamic averages, . . .

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Velocity Verlet

Derivation

- Taylor expansion for ionic positions $\mathbf{R}_I(t)$

$$\begin{aligned}\mathbf{R}_I(t+\Delta t) &= \mathbf{R}_I(t) + \Delta t\ \dot{\mathbf{R}}_I(t) + \frac{(\Delta t)^2}{2}\ \ddot{\mathbf{R}}_I(t) + \ldots \\ &= \mathbf{R}_I(t) + \Delta t\ \mathbf{v}_I(t) + \frac{(\Delta t)^2}{2M_I}\ \mathbf{F}_I(t) + \ldots\end{aligned}$$

- Backward Taylor expansion for ionic positions $\mathbf{R}_I(t)$

$$\mathbf{R}_I(t+\Delta t) = \mathbf{R}_I(t) - \Delta t\ \mathbf{v}_I(t+\Delta t) + \frac{(\Delta t)^2}{2M_I}\mathbf{F}_I(t+\Delta t) + \ldots$$

- Add up:

$$\mathbf{R}_I(t+\Delta t)+\mathbf{R}_I(t) = \mathbf{R}_I(t+\Delta t)+\mathbf{R}_I(t)+\Delta t\,[\mathbf{v}_I(t) - \mathbf{v}_I(t+\Delta t)]+\frac{(\Delta t)^2}{2M_I}\,[\mathbf{F}_I(t) + \mathbf{F}_I(t+\Delta t)]$$

- Yields velocities

$$\mathbf{v}_I(t+\Delta t) = \mathbf{v}_I(t) + \frac{\Delta t}{2M_I}\,[\mathbf{F}_I(t) + \mathbf{F}_I(t+\Delta t)]$$

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- (velocity) Verlet algorithm is efficient
- $\Delta t \approx 0.5$ fs (BO-MD) and 0.1 fs (CP-MD)
- Simulated annealing is an efficient tools to relax large, complex geometries (choose artificial masses on ions)

Car-Parrinello Molecular Dynamics

Summary

- Fictitious dynamics for the electrons
- Simultaneous dynamics for the ions and electrons

Car-Parrinello method

Equations of motion

- Euler-Lagrange equations

$$\frac{d}{dt}\frac{\partial \mathcal{L}_{\mathsf{CP}}}{\partial \langle \dot{\psi}_i|} = \frac{\partial \mathcal{L}_{\mathsf{CP}}}{\partial \langle \psi_i|}$$
$$\frac{d}{dt}\frac{\partial \mathcal{L}_{\mathsf{CP}}}{\partial \langle \dot{\mathbf{R}}_I|} = \frac{\partial \mathcal{L}_{\mathsf{CP}}}{\partial \langle \mathbf{R}_I|}$$

- equations of motion

$$\mu\ddot{\psi}_i = -\frac{\partial E_{\mathsf{KS}}}{\partial \langle \psi_i|} + \sum_j \Lambda_{ij} |\psi_j\rangle$$
$$M_I\ddot{\mathbf{R}}_I = -\frac{\partial E_{\mathsf{KS}}}{\partial \mathbf{R}_I} + \sum_{ij} \Lambda_{ij} \frac{\partial}{\partial \mathbf{R}_I} \langle \psi_i | \psi_j \rangle$$

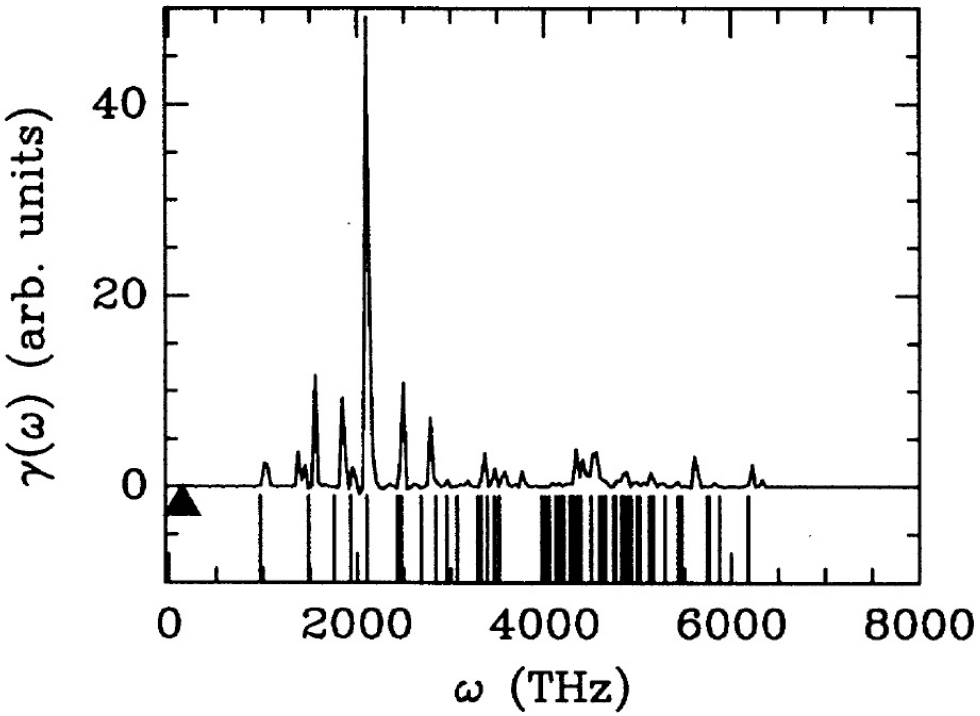
Car-Parrinello Molecular Dynamics

Summary

- Fictitious dynamics for the electrons
- Simultaneous dynamics for the ions and electrons
- Works best for insulating/semi-conducting materials; metals with care (thermostat on the electrons)
- Relies on the adiabatic separation between the dynamics of electrons and ions

Adiabatic separation

- Thus there's no efficient mechanism for exchange of energies: The two subsystems are adiabatically decoupled



Triangle = highest ionic frequency

$$f^e(\omega) = \int_{t=0}^{\infty} \cos(\omega t) \sum_i \left\langle \dot{\psi}_i(t) \middle| \dot{\psi}_i(0) \right\rangle \, dt$$

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- New constant of motion

Constant of motion

Conservation of energy

- Physical and conserved energy:

$$E_{\text{physical}} = E_{\text{KS}}\left(\{\psi_i\}, \mathbf{R}^N\right) + \sum_{I=1}^{N} \frac{1}{2} M_I \dot{\mathbf{R}}_I^2$$

$$E_{\text{conserved}} = \sum_{i=1}^{M} \frac{1}{2} \mu \left\langle \dot{\psi}_i \middle| \psi_i \right\rangle + E_{\text{KS}}\left(\{\psi_i\}, \mathbf{R}^N\right) + \sum_{I=1}^{N} \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 = E_{\text{kin,fict}} + E_{\text{physical}}$$

- The difference, $E_{\text{kin,fict}} = \sum_{i=1}^{M} \frac{1}{2} \mu \left\langle \dot{\psi}_i \middle| \psi_i \right\rangle$, must thus correlate with the changes in the physical energy

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- Control of adiabacity via μ, fictitious electron mass

Control of adiabacity

- Lowest frequency has to be well above ionic frequencies

$$\omega^e_{\mathsf{min}} \propto \sqrt{\frac{E_{\mathsf{gap}}}{\mu}}$$

- Highest frequency limits the maximum possible time step

$$\omega^e_{\mathsf{max}} \propto \sqrt{\frac{E_{\mathsf{cut}}}{\mu}} \qquad\qquad (\Delta t^e)_{\mathsf{max}} \propto \sqrt{\frac{\mu}{E_{\mathsf{cut}}}}$$

- If Δt fixed and μ chosen
  - too small: Electrons too light and adiabacity will be lost
  - too large: Time step eventually large and electronic degrees of freedom evolve too fast for the Verlet algorithm

Car-Parrinello Molecular Dynamics

What is possible/typical?

- One needs parallel computers with fast inter-connect; depending on the size of system 8. . . 2048+ processors can be employed efficiently
- Still the simulations take weeks/months (if one wants/needs 10-20 ps to get statistical averages)
- Example: Wall-clock time 30 s/molecular step, typical time step 0.12 fs: 14.4 fs/hour, 340 fs/day $\Rightarrow$ two months for 20 ps (running 24/7!)
- The size of system (elements from $2p$ row):
  - 8 processors: 30-60 atoms
  - 32 processors: 50-100..150 atoms

Car-Parrinello & Born-Oppenheimer Molecular Dynamics

Which one to choose?

- It depends
- For metallic systems usually BO-MD

Questions?