10.675 LECTURE 16

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1. Today

MD and Car-Parrinellow
Summary of Localized BS vs Non-Localized
MD
Simulated Annealing
CPMD

2. Localized:Advantages

Can treat only one molecule
Integration is expensive
Can incorporate exchange
No correlation methods
Can or don't have to use pseudopotentials

3. Localized:Disadvantages

Can't use HF forces (expensive otherwise)
FFT (finite fourier transform) is harder
More doesn't lead to better results
BSSE issue

4. Non-localized:Advantages

Use HF forces (cheap)
Easier Integration
FFT easy
No Exchange terms
No Correlation Methods
More accurate w/more computation
BSSE is not an issue

5. Non-localized:Disadvantages

Must treat empty space
Must use pseudo potentials

Date: Fall 2004.

6. MD - Molecular Dynamics

Integrate numerically Newton's equations of motion along a trajectory.
1) Choose system and initial temperature and positions
2) Computer other forces
3) Integrate Newton's equations of motion using finite differences and store important properties
4) Analyze important properties

7. Integration Methods

Velocity Verlet
Leap
Gear
Choice of Δt is of extreme importance.
Velocity Verlet Algorhythm $x_{k+1}(t_\Delta t) = x_k(t) + v_x(t)\Delta t + \frac{f_k(t)(\Delta t)^2}{2\mu_k}$
$v_{k+1}(t+\Delta t) = v_k(t) + \frac{f_k(t+\Delta t)+f_k(t)}{2\mu_k}\Delta t$
$E^{elec} \rightarrow V^{potential}, T^{nuclear}$

8. Simulated Annealing

Typically want 1fs for Δt
Start out with high temperature and then "cool" slowly by decreasing T.
Designed by Kirpatrick, Gelati, Vecchi (Science 220 671 1983)
Optimizing highly non-linear complicated functions.
Essentially, anneal slowly and thus lower the system to minimums.

9. CPMD

CP is the method
MD is the method

10. Lagrangian Formulation of Mechanics

$L = T(\dot{q}'s) - V(q's)$ Where T is KE, $\dot{q}$'s are velocity, V is potential, q's are position
Lagrange's equations of motion
$\frac{d}{dt}(\frac{\delta L}{\delta q_i}) - \frac{\delta L}{\delta q_i} = 0$
Combined with simulated annealing
$L = \sum_i 1/2\mu_i \int dr|\Psi ki|^2$ (which is a CP trick to add the fictitious mass.)
$+\sum_i \frac{1}{2} M \dot{R}_I^2 - E\{\Psi_{ki}\}\{R_I\}$
$+\sum \Lambda_{ij}(\int dr \Psi^*_{ki}(r)\Psi_k(r) - \delta_{ij})$
The last term ensure orthogonality.
Solve for Ψ_k's and R's simultaneously using simulated annealing.
Main Issue: This approach assume BO approximation always
⇒ No exchange between fictitious and nuclear DOF

11. Misc

$\mu\ddot{\Psi}_i = \frac{-\delta E}{\delta \Psi_i^*} + \sum_p \Lambda_{ip}\Psi_p$

$M_I\ddot{R}_I = -\nabla_R E^{elec}$

Think of Characteristic frequencies of $\dot{\Psi}$ and $\dot{R}$

$\dot{\Psi} : w_{ij}(\frac{2(\epsilon_j - \epsilon_i)}{\mu})^{\frac{1}{2}}$

$\epsilon_j - \epsilon_i \Rightarrow$ Band Gap

Δ 0.1 fs

$\approx 1010TH_z$

$\mu = 300au$ for $E_g = 2.24eV$

$\dot{R}, \Omega$ $4000cm^{-1}$ $100TH_z$ Enough to practically prevent change

Method VERY problematic for metals.

CP Irony: No one actually used it for it's designed purpose! BUT, heavily used for computing the dynamics of systems for which QM is needed to describe well.