Car-Parrinello Molecular Dynamics Investigation of H_2O Adsorption on α-Al_2O_3(0001)

W. F. Schneider and K. C. Hass
Ford Research Laboratory

W. Andreoni and A. Curioni
IBM Zurich

Density Functional Theory

- Hohenberg-Kohn theorems:
  - ❖ Ground state is a unique functional of $\rho(\mathbf{r})$
  - ❖ "True" $\rho(\mathbf{r})$ minimizes the system energy

$$\hat{H}\Psi(\vec{r}_1,\ldots,\vec{r}_n) = E\Psi(\vec{r}_1,\ldots,\vec{r}_n)$$

$$\updownarrow$$

$$E[\rho] = T[\rho] + V_{ee}[\rho] + \int \rho(\vec{r})\upsilon_{\text{ext}}(\vec{r})d\vec{r}$$

- Kohn-Sham construction:
  - ❖ Express $\rho(\mathbf{r})$ in terms of one-electron orbitals
  - ❖ Fold unknowns into "exchange-correlation" functional

$$\rho(\vec{r}) = \sum_i |\psi_i(\vec{r})|$$

$$\left[-\frac{1}{2}\nabla^2 + \upsilon_{\text{ext}}(\vec{r}) + \upsilon_{\text{Coul}}[\rho] + \upsilon_{XC}[\rho]\right]\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r})$$

$$\hat{h}_{KS}\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r})$$

Exact one-electron formulation

Approximate Kohn-Sham Theories

Ÿ Xα: $$\upsilon_{XC}[\rho] \approx \upsilon_{X,local} = -\frac{3}{2}\alpha\left(\frac{3\rho(1)}{\pi}\right)^{1/3}$$

Ÿ Hartree-Fock: $$\upsilon_{XC}[\rho] \approx \upsilon_X = -\sum_j K_j(1)$$

Ÿ Local Density Approximation:

$$\upsilon_{XC}[\rho] \approx \upsilon_{X,local}(1) + \upsilon_{C,local}(1)$$

"VWN" parameterization

Ÿ Generalized Gradient Approximation

$$\upsilon_{XC}[\rho] \approx f(\rho, \nabla\rho)$$

Becke ; Perdew-Wang; Lee-Yang-Parr

Ÿ "Hybrid" methods

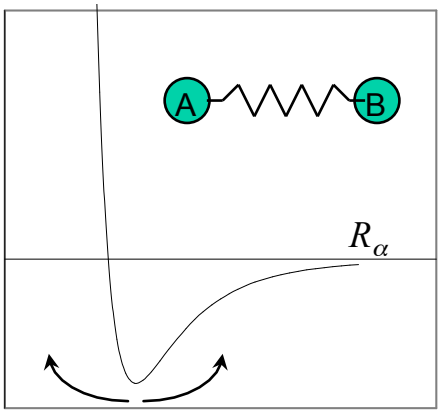
$$\upsilon_{XC}[\rho] \approx \alpha\upsilon_{X,HF} + \beta\upsilon_{XC,GGA}$$

"adiabatic connection formula"

Born-Oppenheimer Dynamics

"Ions move in potential instantaneously generated by electrons"

$$\Phi(\{R_\alpha\}) = E_{KS}(\{R_\alpha\}) + \sum_{\alpha>\beta} \frac{Z_\alpha Z_\beta}{|R_{\alpha\beta}|^2}$$



Lagrangian Formulation of Equations of Motion

$$L = T - V, \qquad \frac{d}{dt}\frac{\partial L}{\partial \dot{x}_i} - \frac{\partial L}{\partial x_i} = 0$$

$$x_i \rightarrow R_\alpha \qquad T = \frac{1}{2}\sum_\alpha M_\alpha \dot{R}_\alpha^2 \qquad V = \Phi(\{R_\alpha\})$$

$$\downarrow$$

$$M_\alpha \ddot{R}_\alpha = -\frac{\partial \Phi(\{R_\alpha\})}{\partial R_\alpha}$$

Newton's equation

Traditional Ab Initio Molecular Dynamics

- Choose initial ionic positions $\{\mathbf{R}_\alpha\}$
  - ❖ fixes external potential
- Expand $\psi_i(\mathbf{r})$ in basis
  - ❖ guess initial expansion coefficients
  - ❖ fixes electronic potential through $\rho(\mathbf{r})$
- Construct secular matrix and diagonalize
- Iterate to self-consistency

$$\psi_i(\vec{r}) = \sum_k c_{k,i}\phi_k(\vec{r})$$

$$\mathbf{HC} = \mathbf{SC}\varepsilon \,, H_{jk} = \left\langle \phi_j \middle| \hat{h}_{KS} \middle| \phi_k \right\rangle$$

- Calculate gradient of electronic energy
  - ❖ *Exact* forces required for energy conservation

$$\frac{\partial \Phi(\{R_\alpha\})}{\partial R_\alpha} =$$

$$\left\langle \frac{\partial \Psi_{KS}}{\partial R_\alpha} \middle| \hat{H}_{KS} \middle| \Psi_{KS} \right\rangle + \left\langle \Psi_{KS} \middle| \frac{\partial \hat{H}_{KS}}{\partial R_\alpha} \middle| \Psi_{KS} \right\rangle + \left\langle \Psi_{KS} \middle| \hat{H}_{KS} \middle| \frac{\partial \Psi_{KS}}{\partial R_\alpha} \right\rangle$$

- Propogate nuclear positions using Newton's equation
- Repeat

Car-Parrinello Dynamics

Treat both ionic positions and electronic coordinates as dynamical variables

$$T = \frac{1}{2}\sum_{\alpha} M_\alpha \dot{R}_\alpha^2 + \frac{1}{2}\mu\sum_i \dot{\psi}_i^2 \qquad V = \Phi(\{R_\alpha\},\{\psi_i\})$$

Ionic coordinates

$x_i \rightarrow R_\alpha$

$$M_\alpha \ddot{R}_\alpha = -\frac{\partial \Phi(\{R_\alpha\})}{\partial R_\alpha} = \left\langle \Psi_{KS} \left| \frac{\partial \hat{H}_{KS}}{\partial R_\alpha} \right| \Psi_{KS} \right\rangle$$

Error in Hellman-Feynman force oscillates, producing stable dynamics

Electronic coordinates

$x_i \rightarrow \psi_i$

$$\mu\ddot{\psi}_i = -\frac{\partial \Phi(\{R_\alpha\},\{\psi_i\})}{\partial \psi_i^*} + \sum_j \Lambda_{ij}\psi_j$$

Fictitious mass μ << M_α isolates ionic, electronic d.o.f.

Lagrange multipliers maintain wavefunction orthogonality

$$\int \psi_i(\vec{r})\psi_j^*(\vec{r})d\vec{r} = \delta_{ij}$$

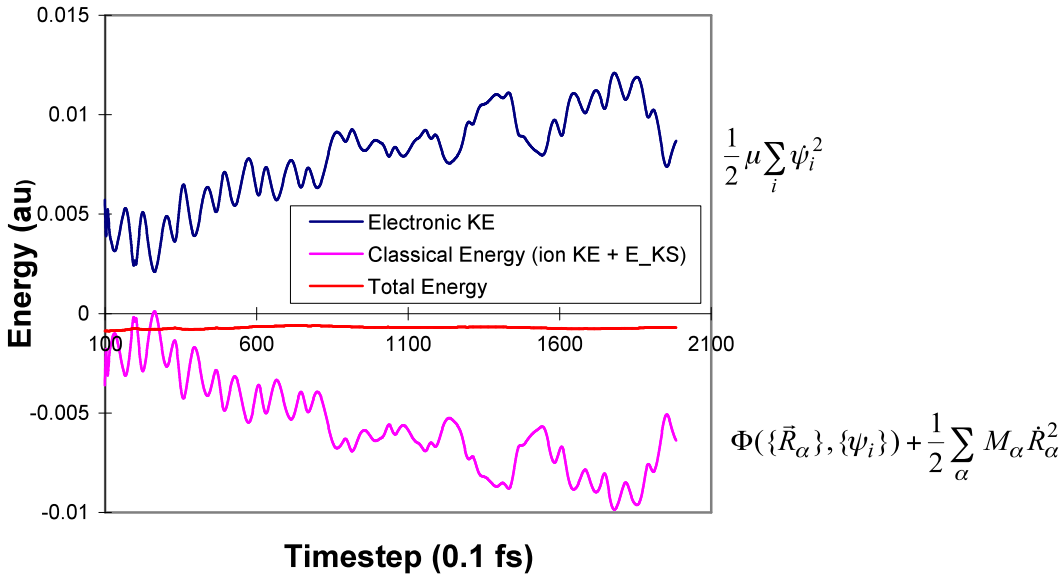
Potential derivative directly from Hamiltonian

$$\hat{h}_{KS}\psi_i = \frac{\partial E_{KS}}{\partial \psi_i^*} = \frac{\partial \Phi}{\partial \psi_i^*}$$

CPMD "Recipe"

- Choose initial ionic coordinates $\mathbf{R}_\alpha$ and electronic "mass" μ
- "Quench" wavefunction to B.O. surface
- Assign thermal energies to ionic and electronic coordinates
- Propogate ionic and electronic coordinates
  - ❖ Verlet integrator

large μ	⟶	longer timestep greater ion/electron coupling
small μ	⟶	shorter timestep lesser ion/electron coupling



Highly efficient algorithm for producing first-principles molecular dynamics trajectories

Technical Details

- Periodic supercell representation
- Plane wave basis set
  - ❖ Bloch's theorem

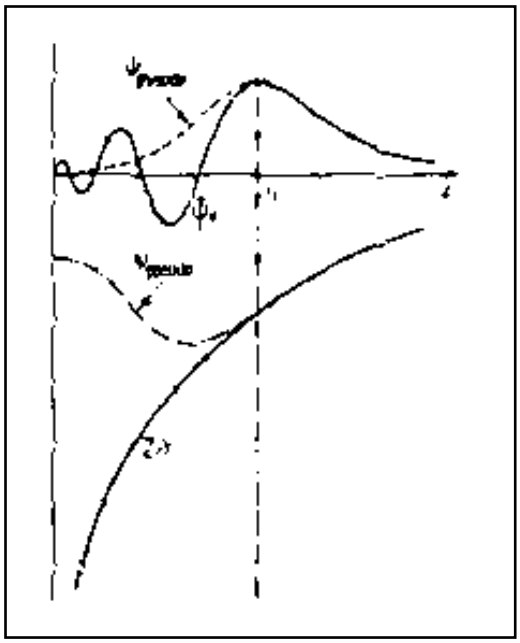
$$\psi_i(\vec{r}) = \sum_G c_{i,k+G} \exp[i(\vec{k}+\vec{G})\cdot\vec{r}]$$

$$\vec{G}\cdot\vec{l} = 2\pi m,\ \ m \in I$$

- Finite energy cutoff
  - ❖ produces finite basis set

$$\left(\hbar^2/2\right)\left|\vec{k}+\vec{G}\right|^2 < E_{cutoff}$$

- Single k point (Γ)
- Norm-conserving pseudopotentials
  - ❖ Kleinman-Bylander separtion



$$V_{\text{ion}} = V_{\text{local}} + \sum_{l,m} \frac{\left|\varphi^{\circ}_{lm}\delta V_l\right\rangle\left\langle\delta V_l\varphi^{\circ}_{lm}\right|}{\left\langle\varphi^{\circ}_{lm}\left|\delta V_l\right|\varphi^{\circ}_{lm}\right\rangle}$$