QM/MM approaches in *ab initio* molecular dynamics

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Outline

- Overview of the QM/MM methodology
- Available QM/MM Electrostatic Schemes
- GEEP: CP2K QM/MM driver
- Charged Oxygen Vacancies in SiO2

Nobel Prize in Chemistry 2013

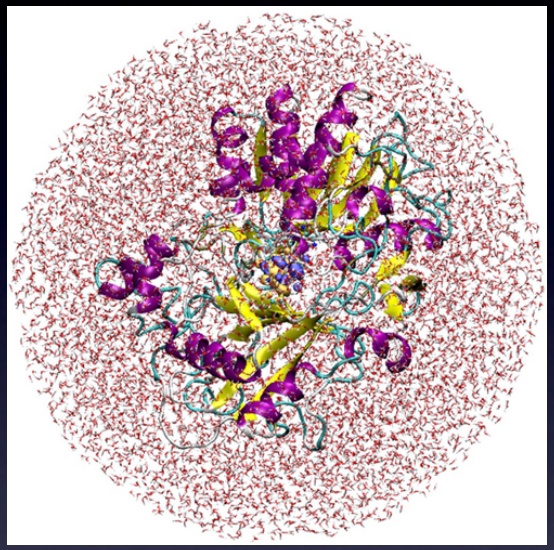
Martin Karplus, Harvard U., Cambridge, MA, USA

Micheal Levitt, Stanford U., Stanford, CA, USA

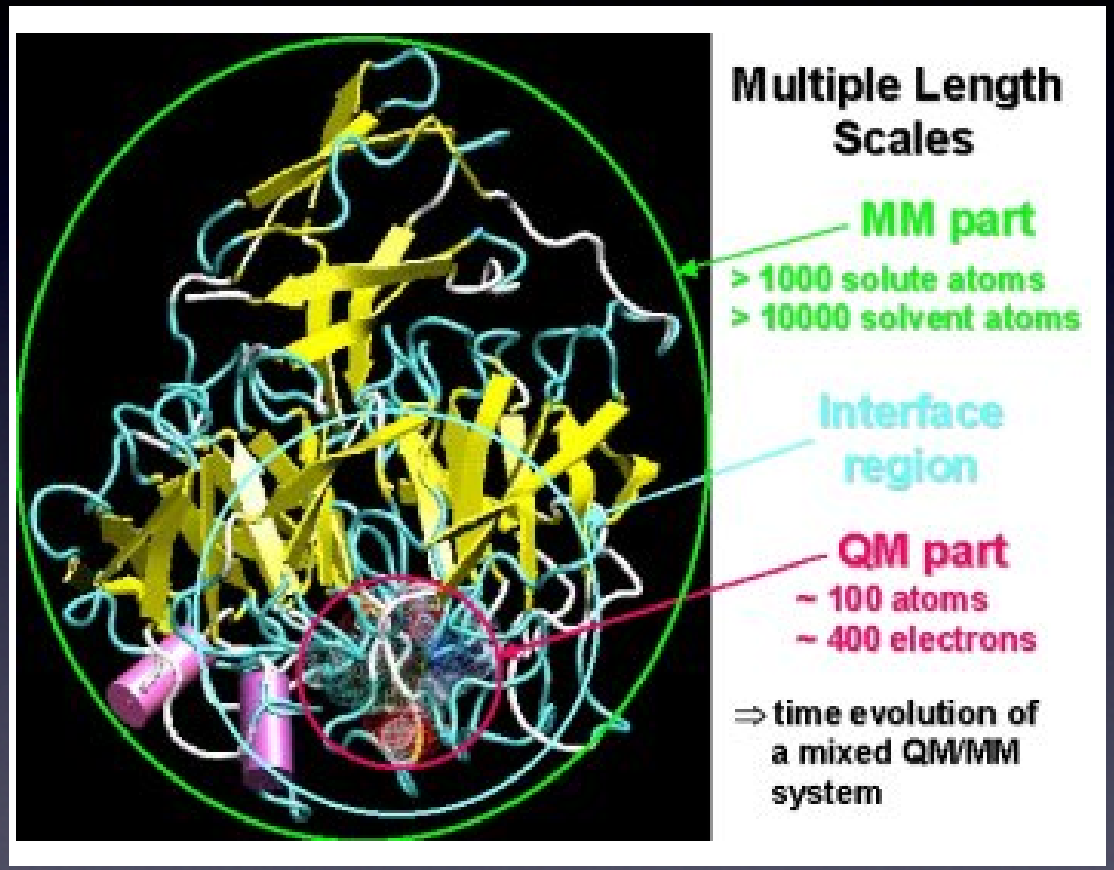
Arieh Warshel, U. Southern Ca., Los Angeles, CA, USA

Development of Multiscale Models of Complex Chemical Systems

Combine QM and MM

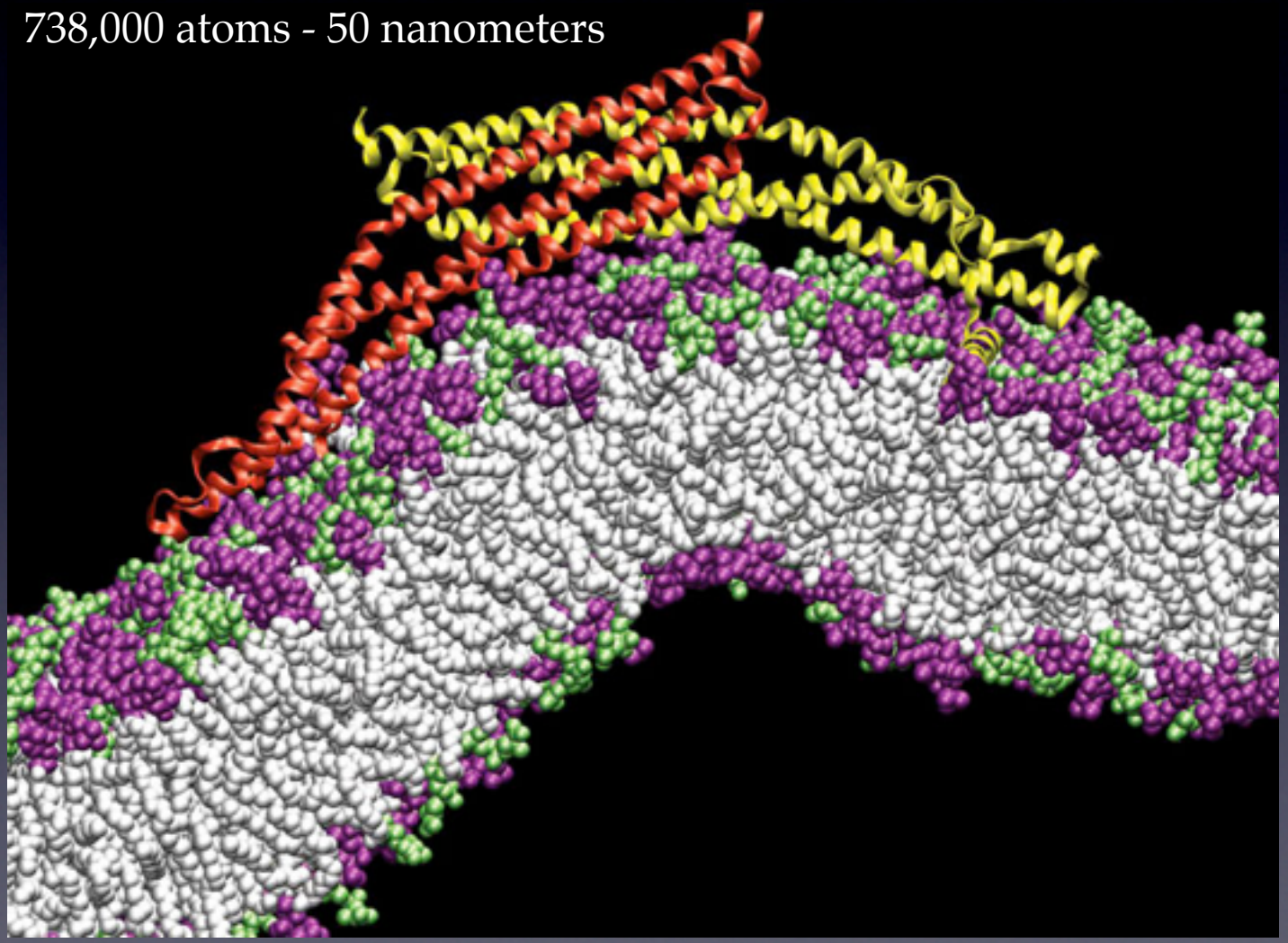


full atomistic by classical FF



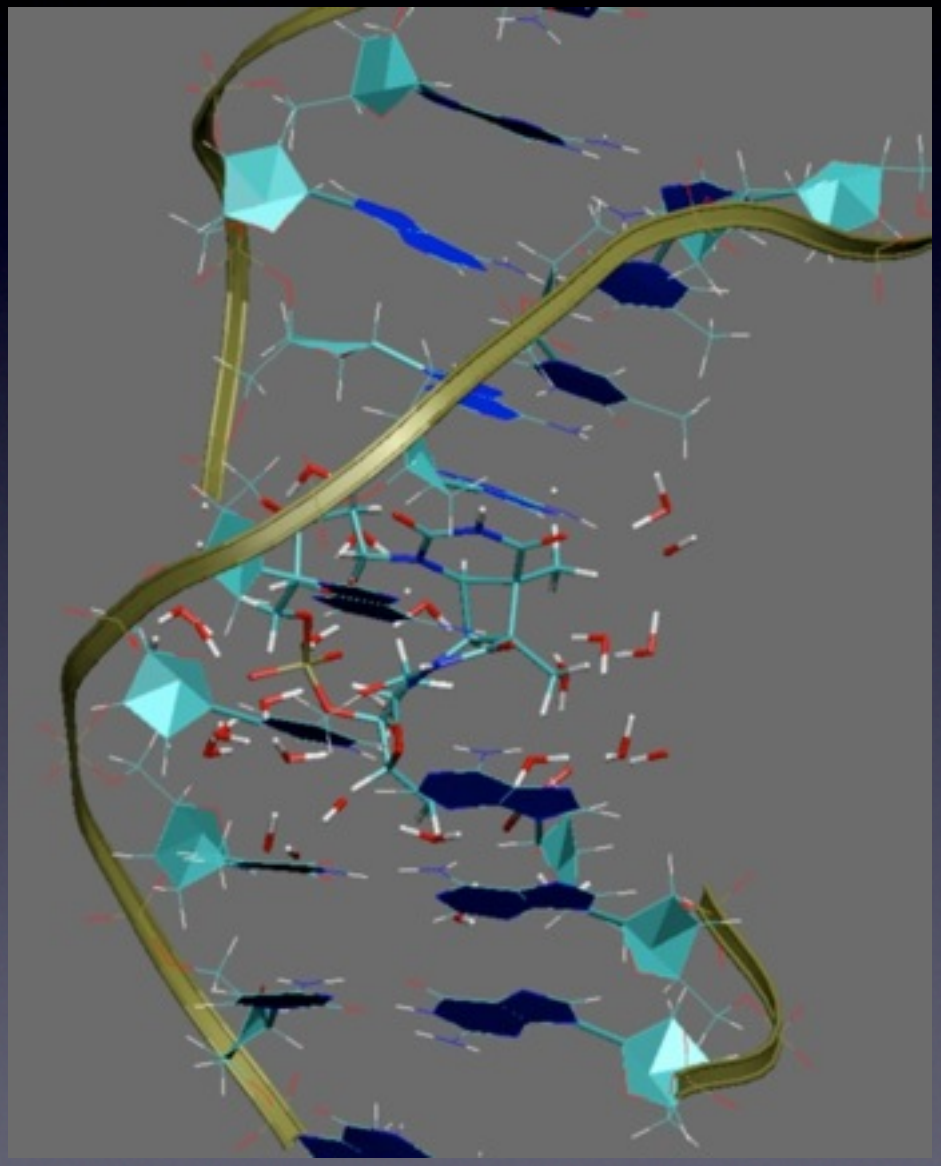
$$V(\mathbf{R}) = V_{\mathrm{QM}}(\mathbf{R}) + V_{\mathrm{MM}}(\mathbf{R}) + V_{\mathrm{int}}(\mathbf{R})$$

QMMM: overview



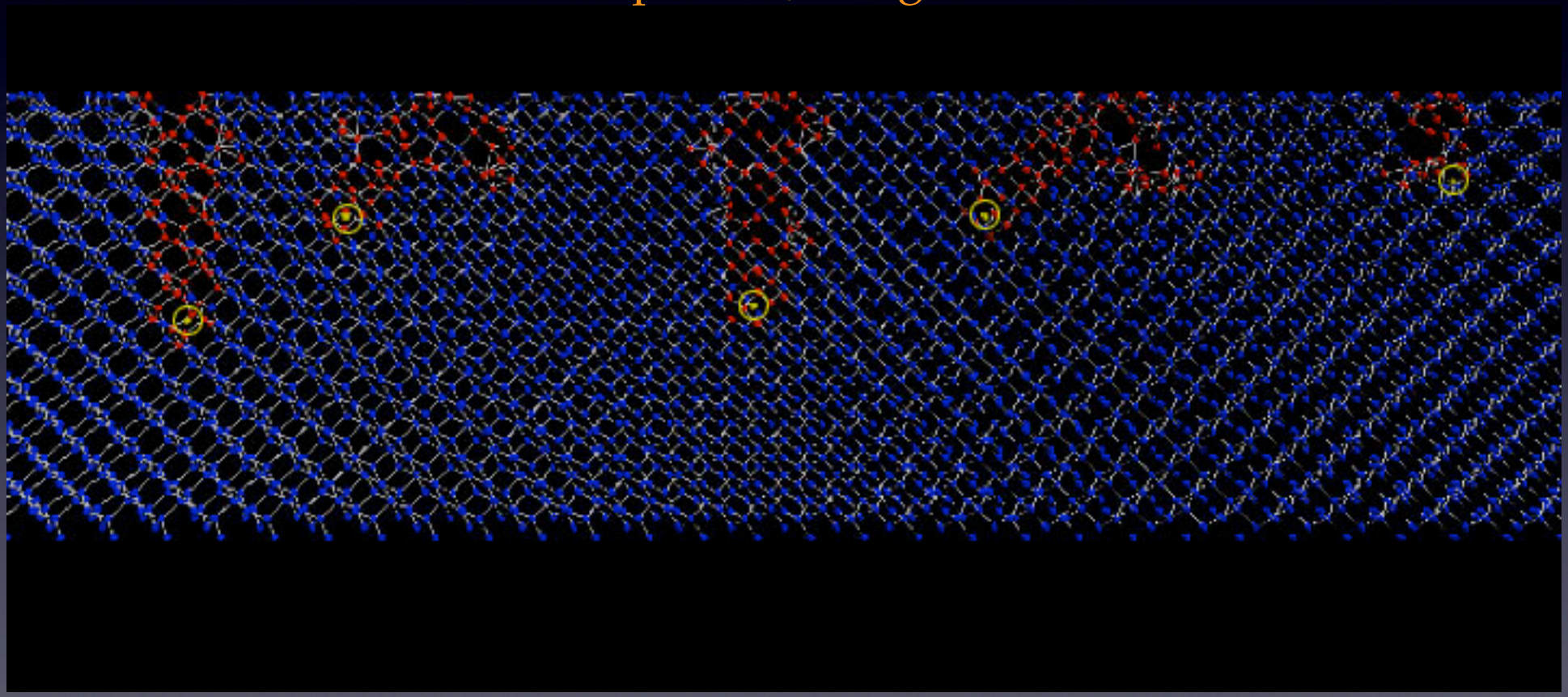
P.D. Blood and G.A. Voth, *PNAS*, 103, **2006**, pp. 15068-15072

QMMM: overview



QMMM: overview

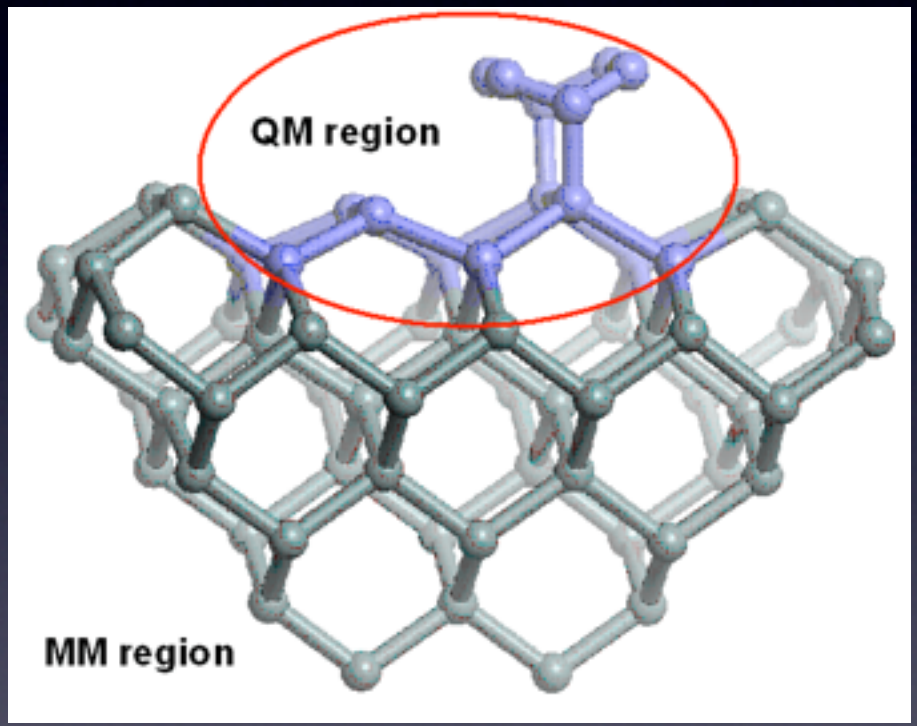
0.11 million atoms
5 QM regions: effects of O implantation into Si
adaptive QM regions



simoX technology

Yoshio Tanaka (AIST) and Aiichiro Nakano (USC)

QMMM: overview



$$E_{QM/MM} = \int d\vec{r} \rho_{tot}^{QM}(\vec{r}) \cdot V^{MM}(\vec{r})$$

Computing $V^{MM}(\vec{r})$ on the same cell on which is defined $\rho_{tot}^{QM}(\vec{r})$

T. Laino et al, J. Chem. Theory Comput., 1, **2005**, pp. 1176-1184
T. Laino et al, J. Chem. Theory Comput., 2, **2006**, pp. 1370-1378

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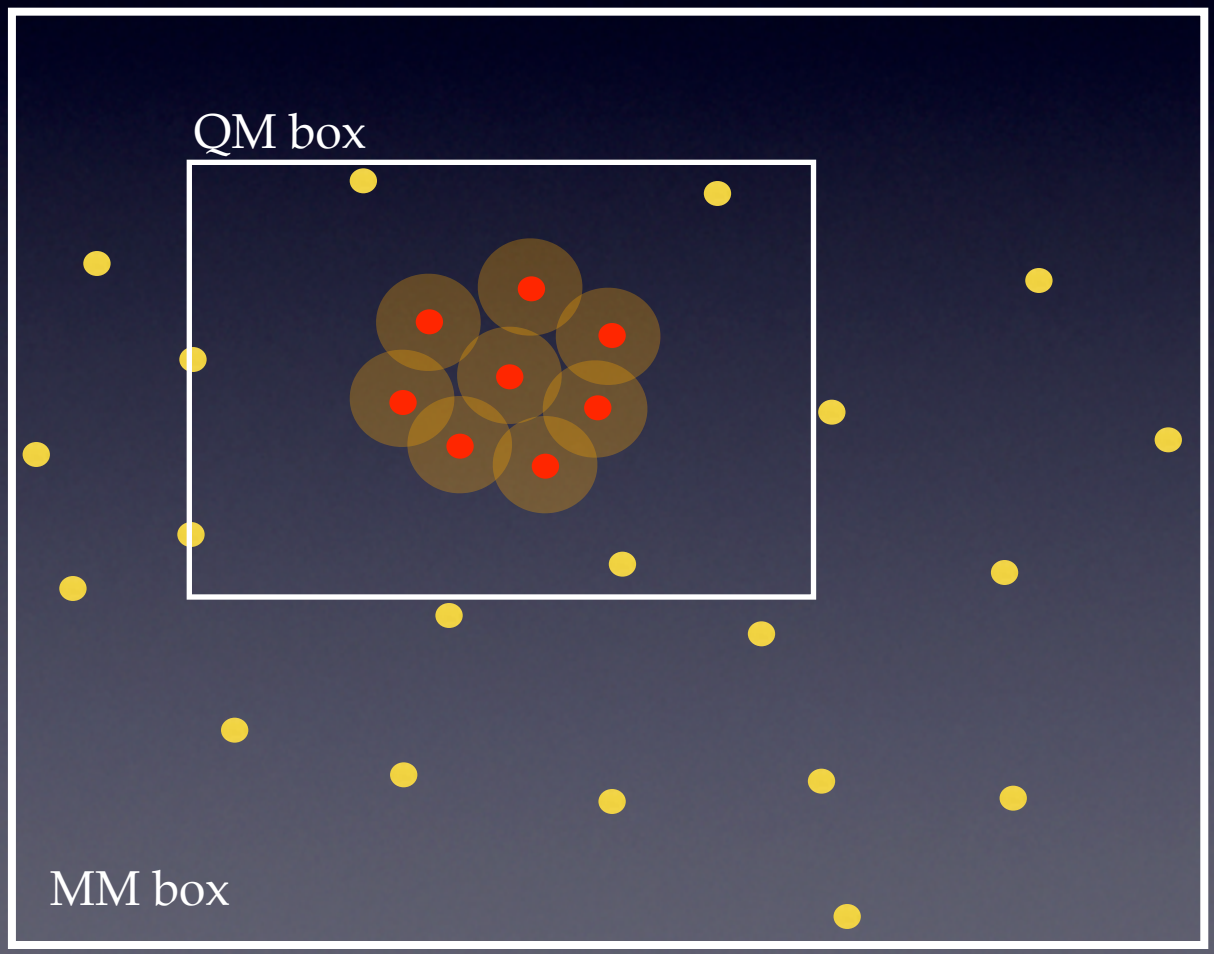
Available QM/MM Electrostatic Schemes

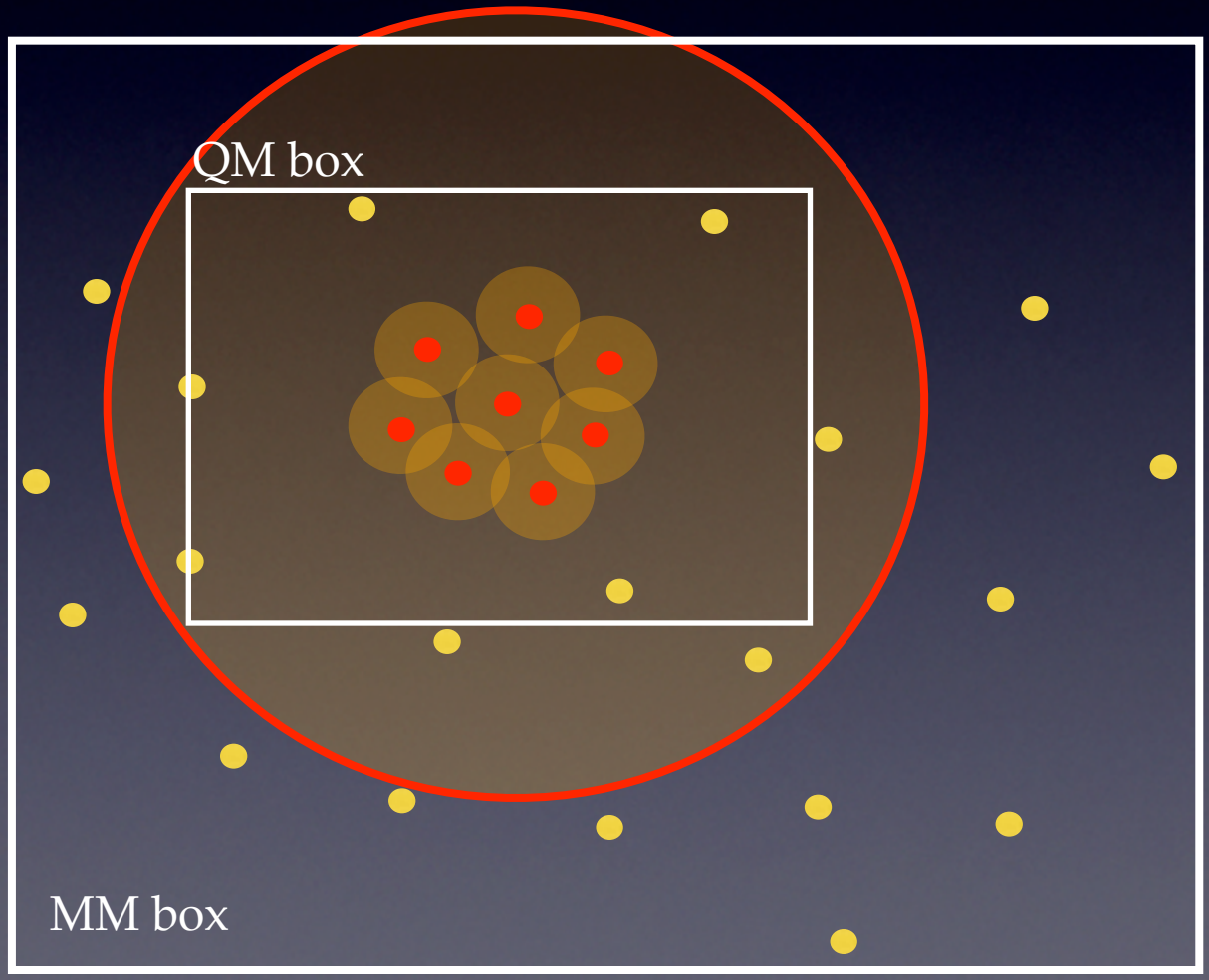
$$\text{Cost} \approx N_{MM} * P^1$$



Available QM/MM Electrostatic Schemes

Spherical Cutoff

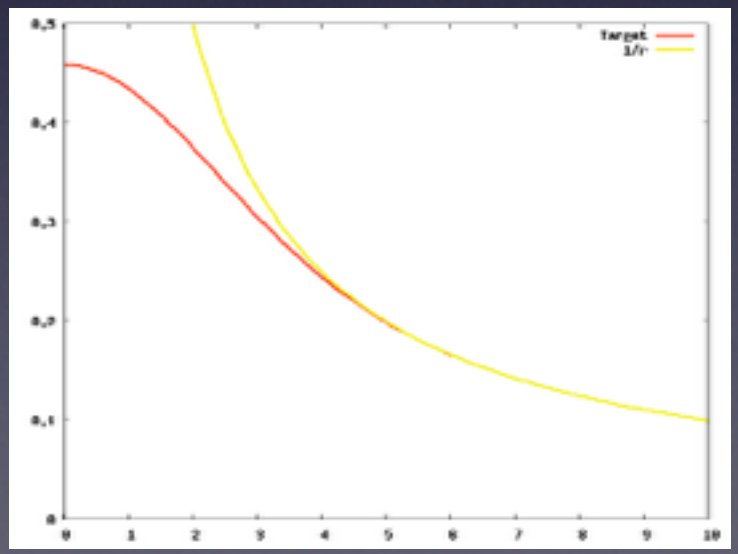
Cost ≈ N^{c}_{MM} * P^{1}

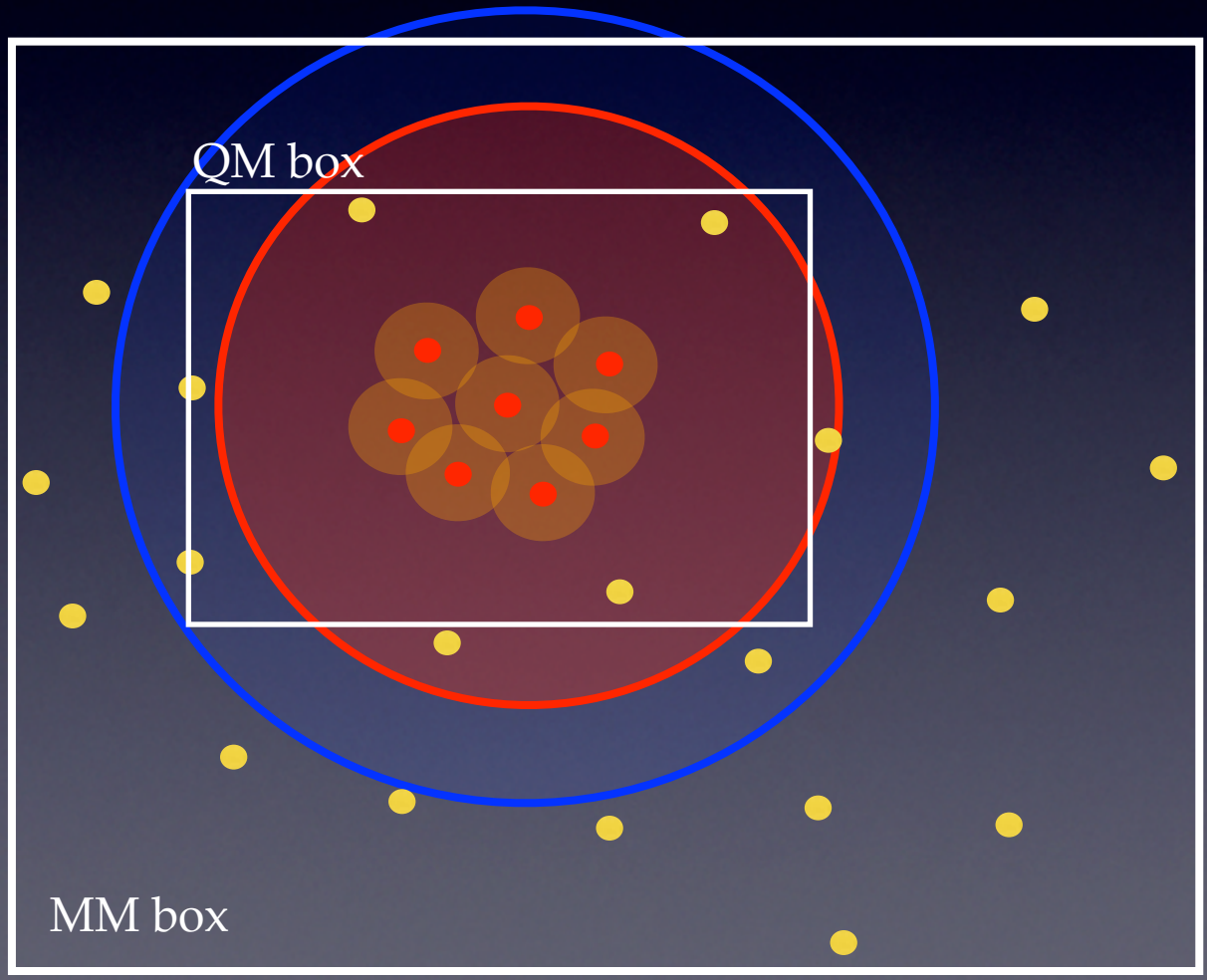


Available QM/MM Electrostatic Schemes

Multi-pole

Expansion





A. Laio, J. VandeVondele, U. Rothlisberger , *J. Chem. Phys.*, 116, **2002**, pp. 6941

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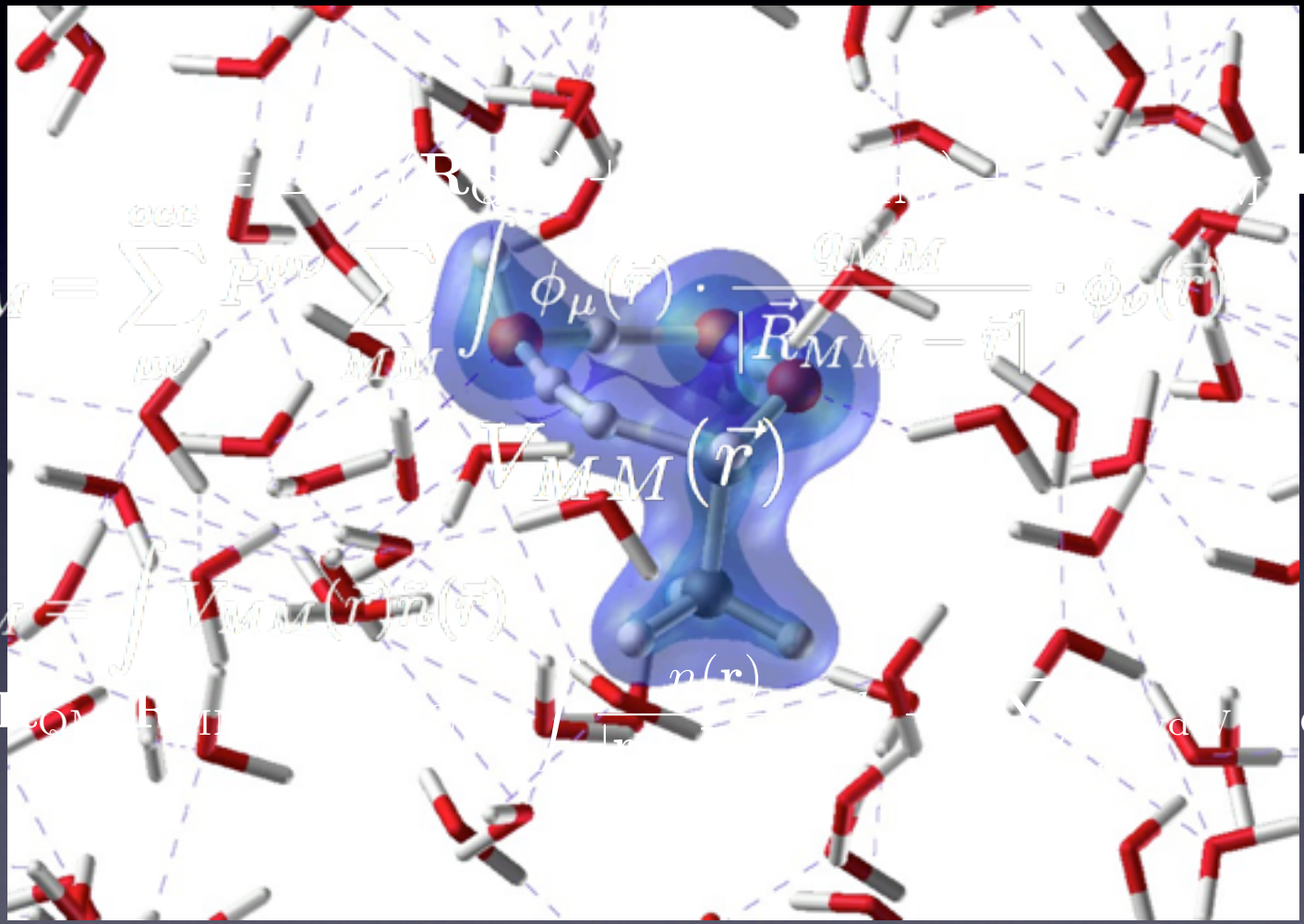
QM/MM

$E_{\mathrm{TOT}}(\mathbf{R}_{\mathrm{QM}}$ $\mathbf{R}_{\mathrm{QM}}, \mathbf{R}_{\mathrm{MM}})$

$H_{QM/MM}$ Gaussians

$H_{QM/MM}$ Plane Waves

$E_{\mathrm{QM/MM}}$($\mathbf{R}_{\mathrm{QM}}, \mathbf{R}_{\mathrm{MM}})$



Gaussian charge distribution

$$n(\mathbf{r}, \mathbf{R}_{\mathrm{MM}}) = \left(\frac{r_{c,\mathrm{MM}}}{\sqrt{\pi}} \right)^3 e^{-(|\mathbf{r}-\mathbf{R}_{\mathrm{MM}}|/r_{c,\mathrm{MM}})^2}$$

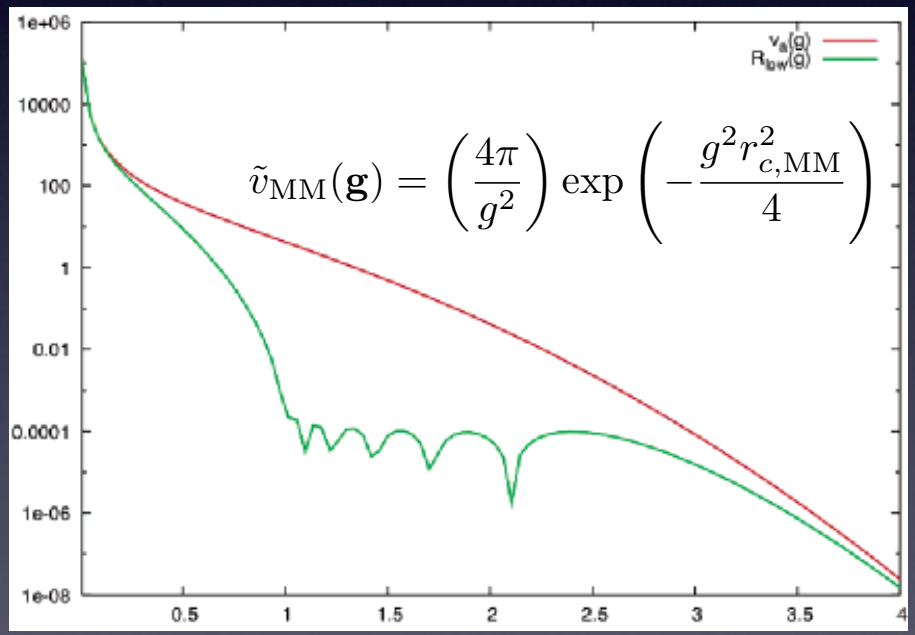
$$v_{\mathrm{MM}}(\mathbf{r}, \mathbf{R}_{\mathrm{MM}}) = \frac{\mathrm{Erf}\left(\frac{|\mathbf{r}-\mathbf{R}_{\mathrm{MM}}|}{r_{c,\mathrm{MM}}} \right)}{|\mathbf{r} - \mathbf{R}_{\mathrm{MM}}|}$$

prevent spill out problem
accelerate calculations of electrostatics

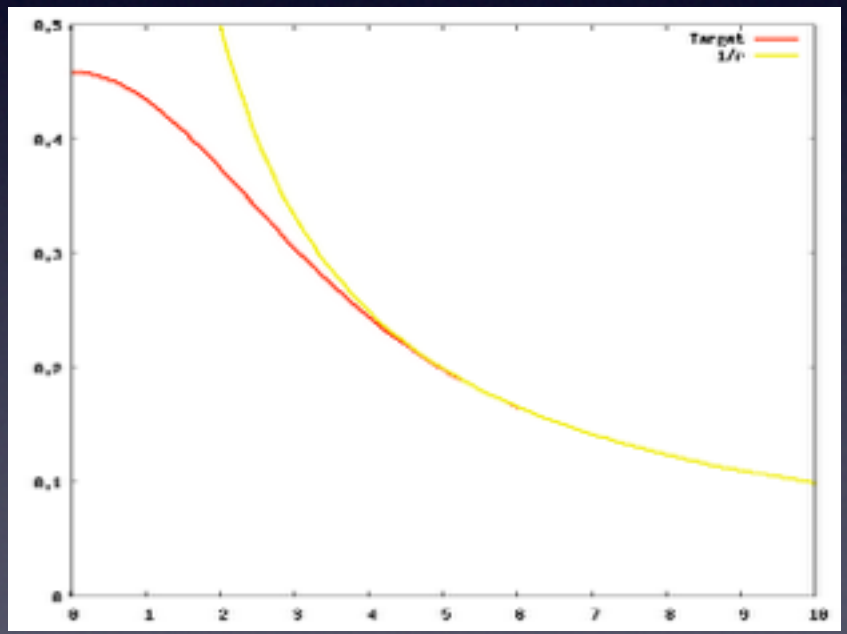
GEEP

$$\frac{\mathrm{Erf}(\frac{r}{r_c})}{r} = \sum_{N_g} A_g \exp^{-(\frac{r}{G_g})^2} + R_{low}(r)$$

$$\frac{\mathrm{Erf}(\frac{r}{r_c})}{r}$$



G vectors

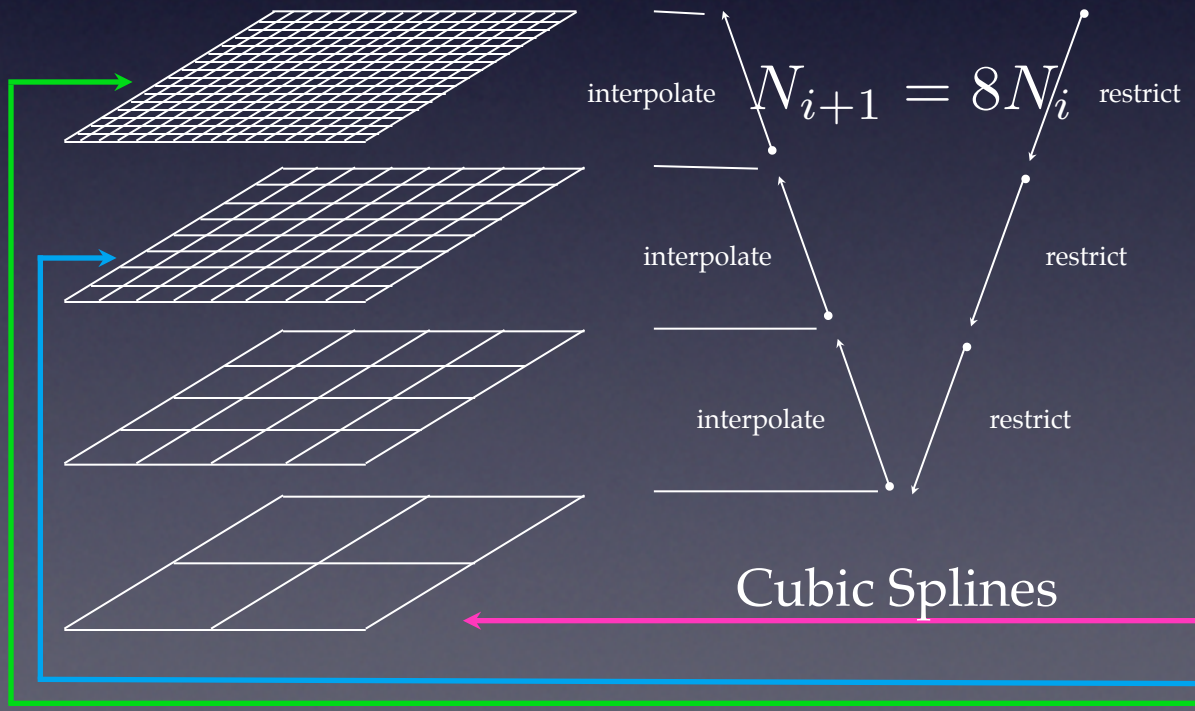


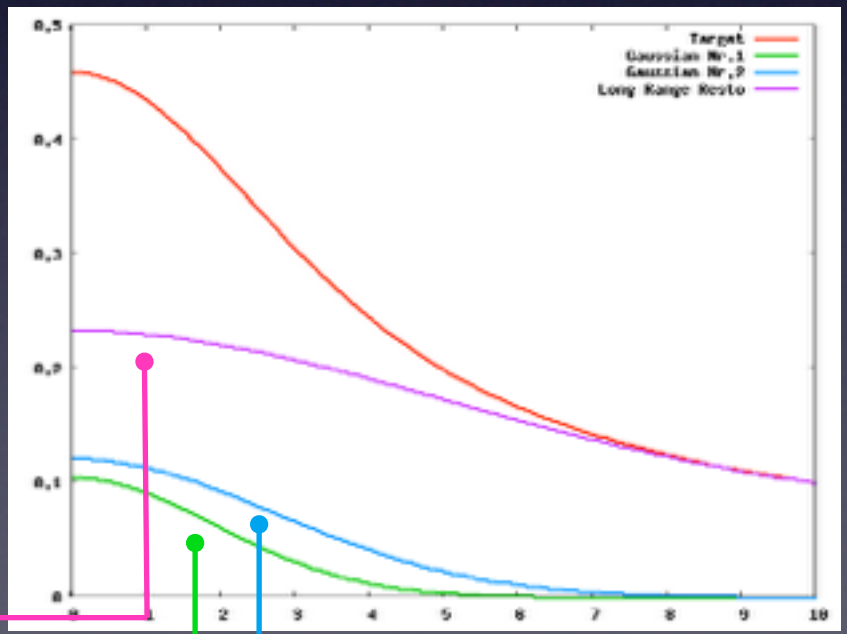
Distance

T. Laino, F. Mohamed, A. Laio and M. Parrinello, *J. Chem. Th. Comp.*, 1, **2005**, pp. 1176-1184

Multigrid Framework

$$\frac{\mathrm{Erf}(\frac{r}{r_c})}{r} = \sum_{N_g} A_g \exp^{-(\frac{r}{G_g})^2} + R_{low}(r)$$



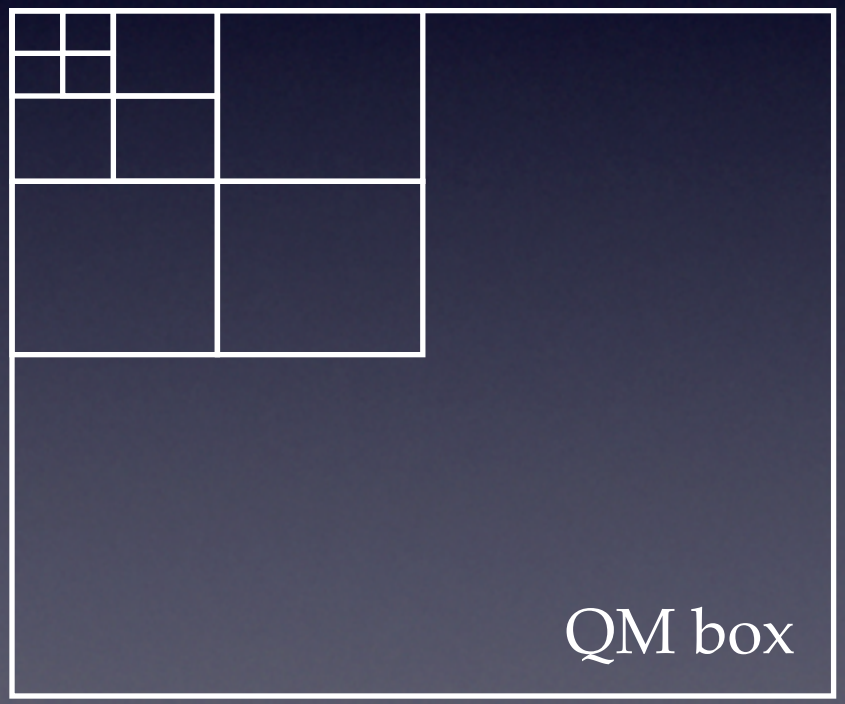


T. Laino, F. Mohamed, A. Laio and M. Parrinello, *J. Chem. Th. Comp.*, 1, **2005**, pp. 1176-1184

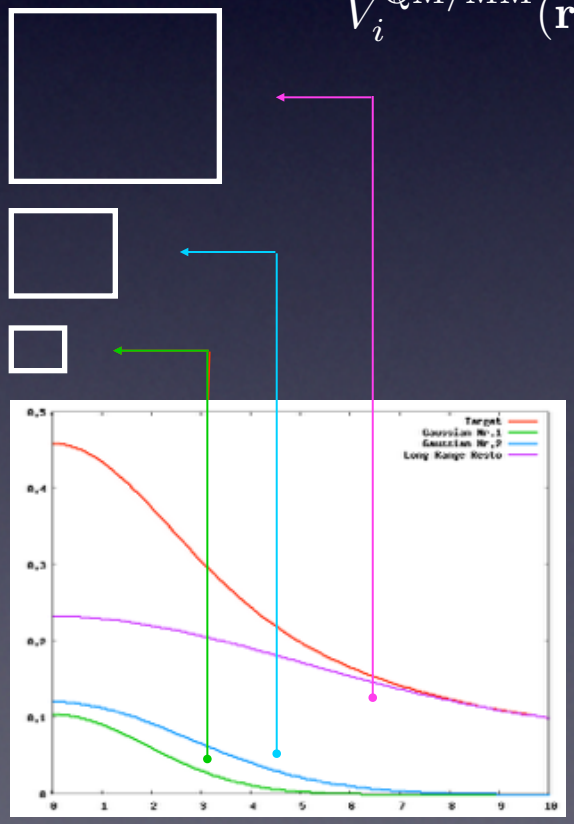
Collocation in the QM Box

$$E_{\mathrm{QM/MM}}(\mathbf{R}_{\mathrm{QM}}, \mathbf{R}_{\mathrm{MM}}) = \int n(\mathbf{r}, \mathbf{R}_{\mathrm{QM}}) V^{\mathrm{QM/MM}}(\mathbf{r}, \mathbf{R}_{\mathrm{MM}}) d\mathbf{r}$$

potential on the finest QM grid



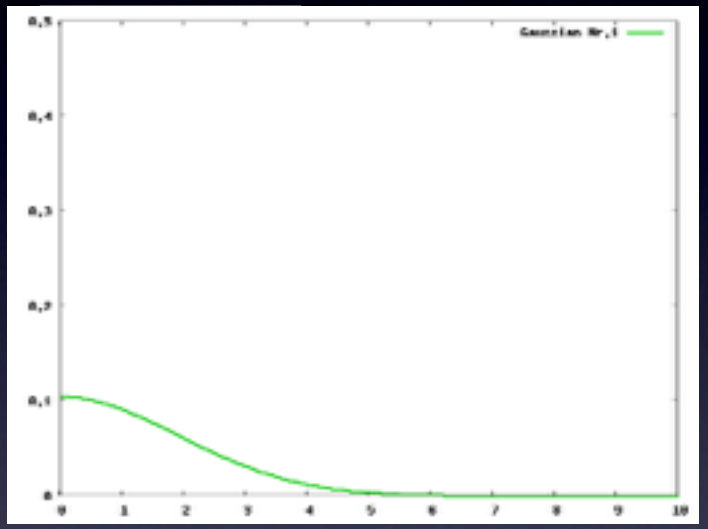
$$V_i^{\mathrm{QM/MM}}(\mathbf{r}, \mathbf{R}_{\mathrm{MM}}) = \sum_{\mathrm{MM}} v_{\mathrm{MM}}^i(\mathbf{r}, \mathbf{R}_{\mathrm{MM}})$$

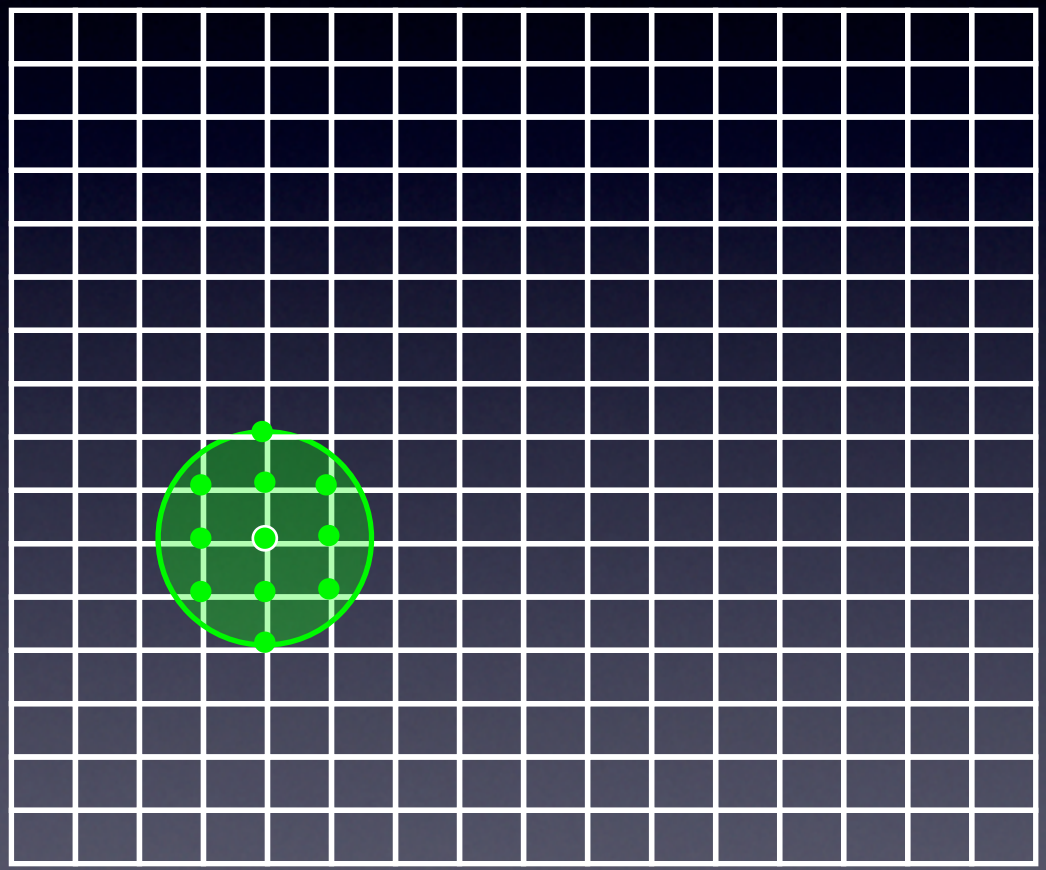


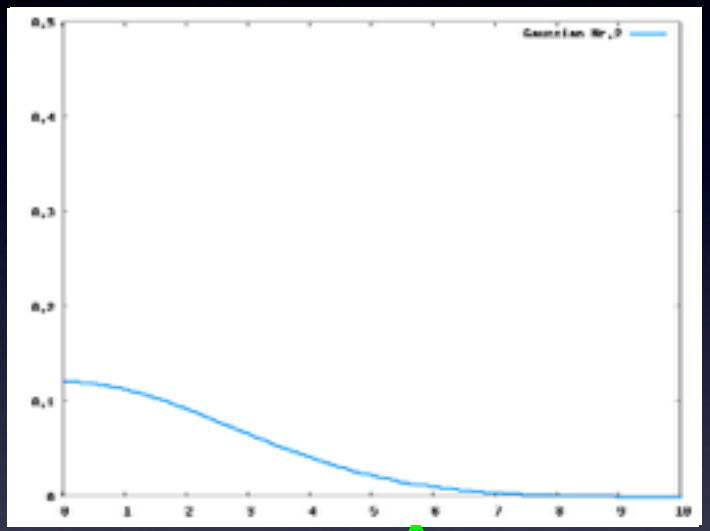
optimal grid levels

60-80% of time

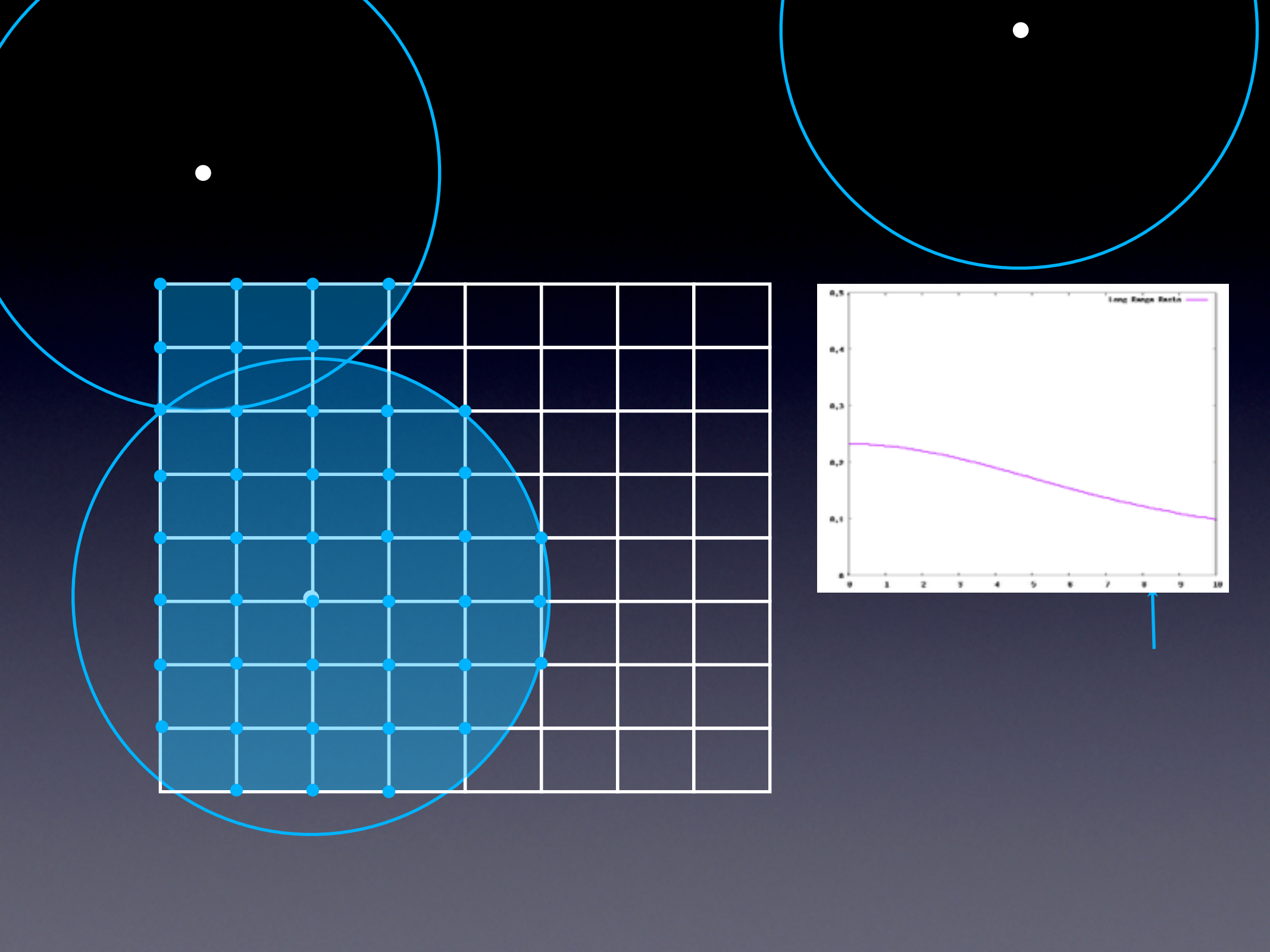
QM box







compact Gaussian functions


Long Range Rate
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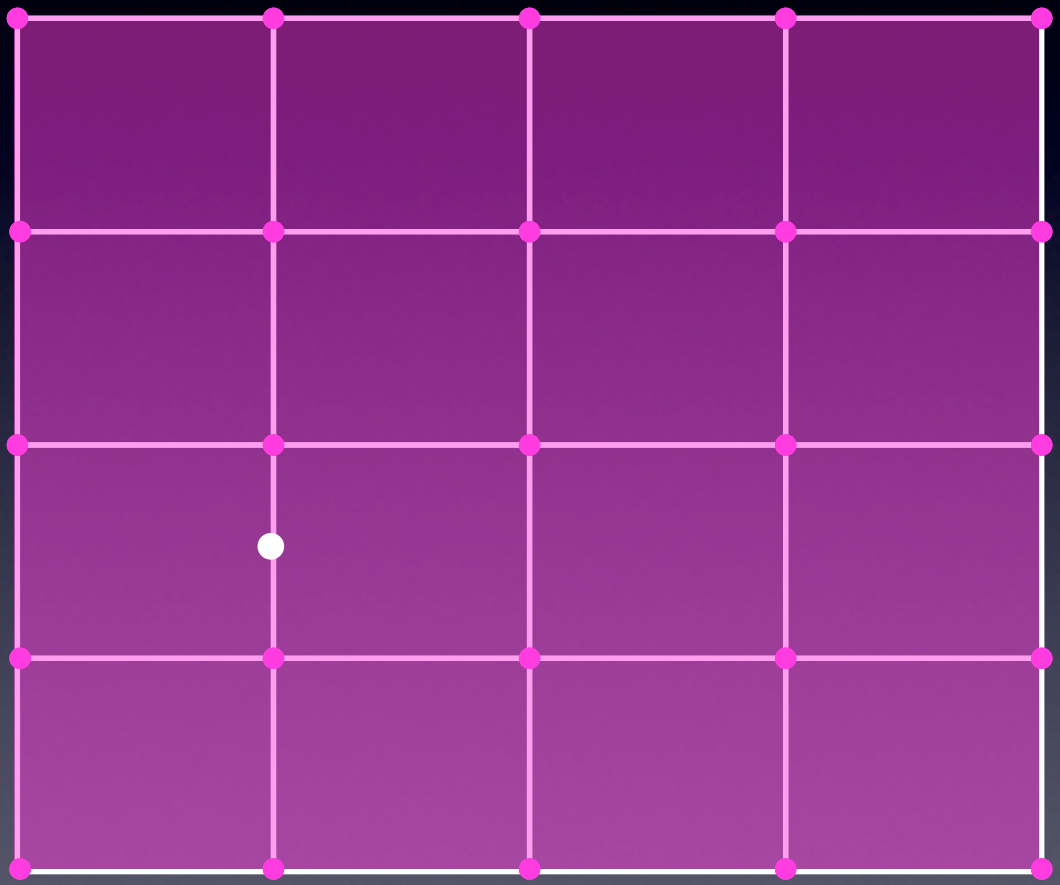

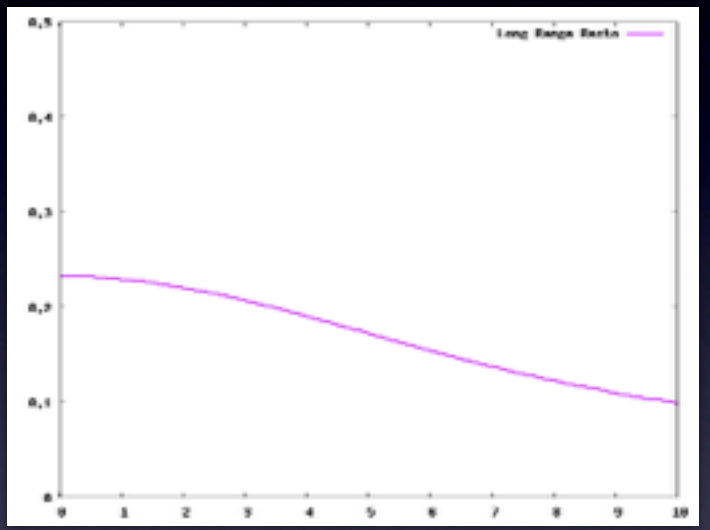
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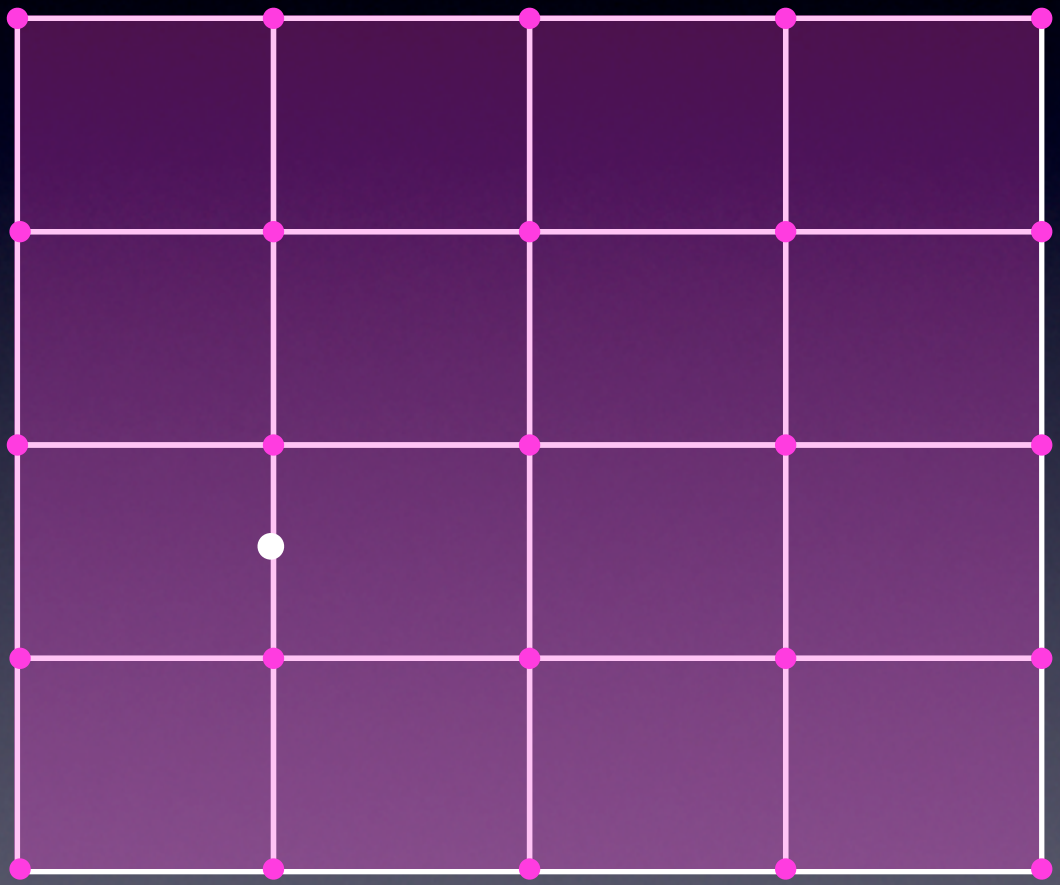
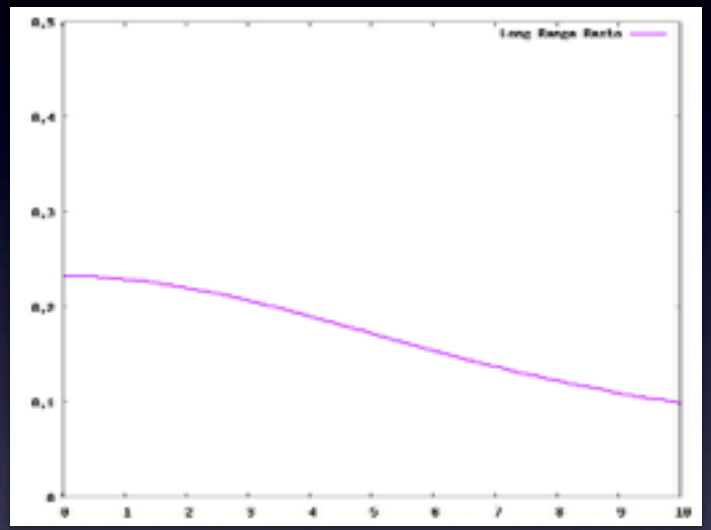
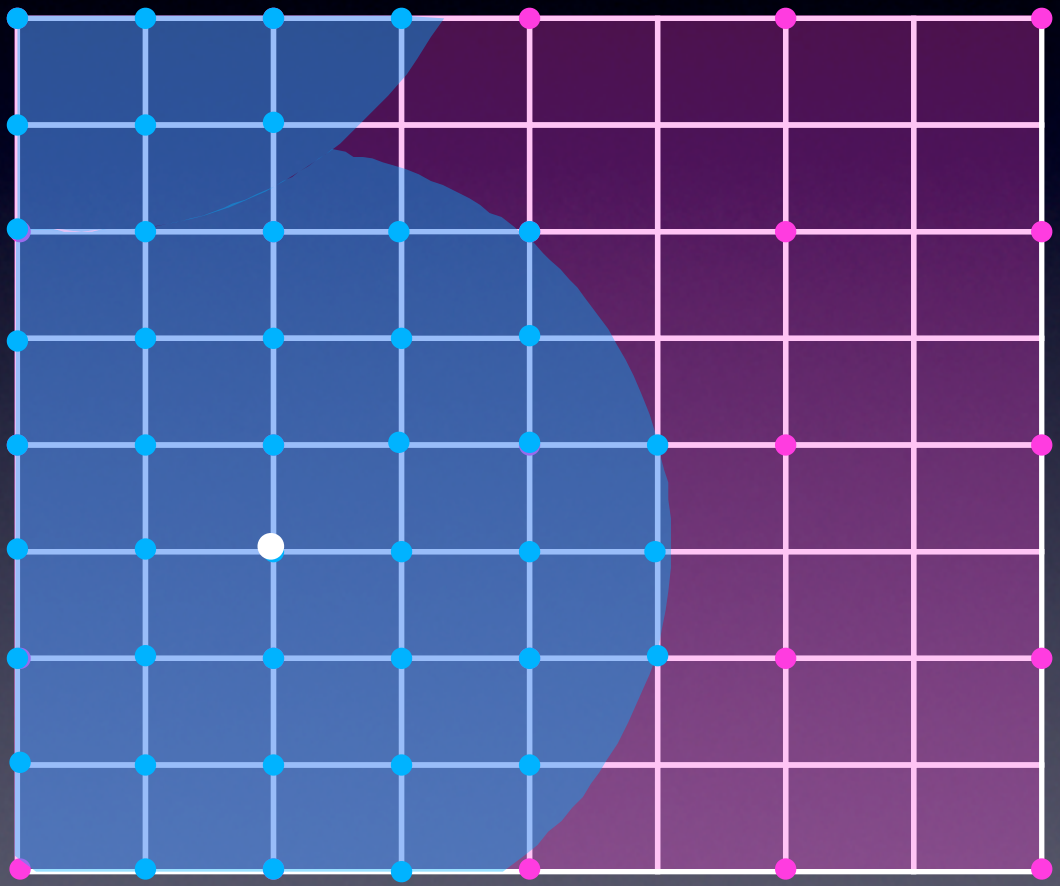
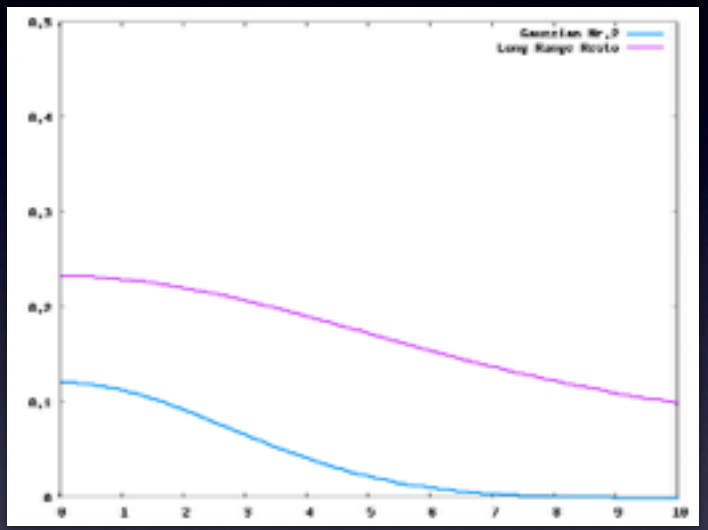




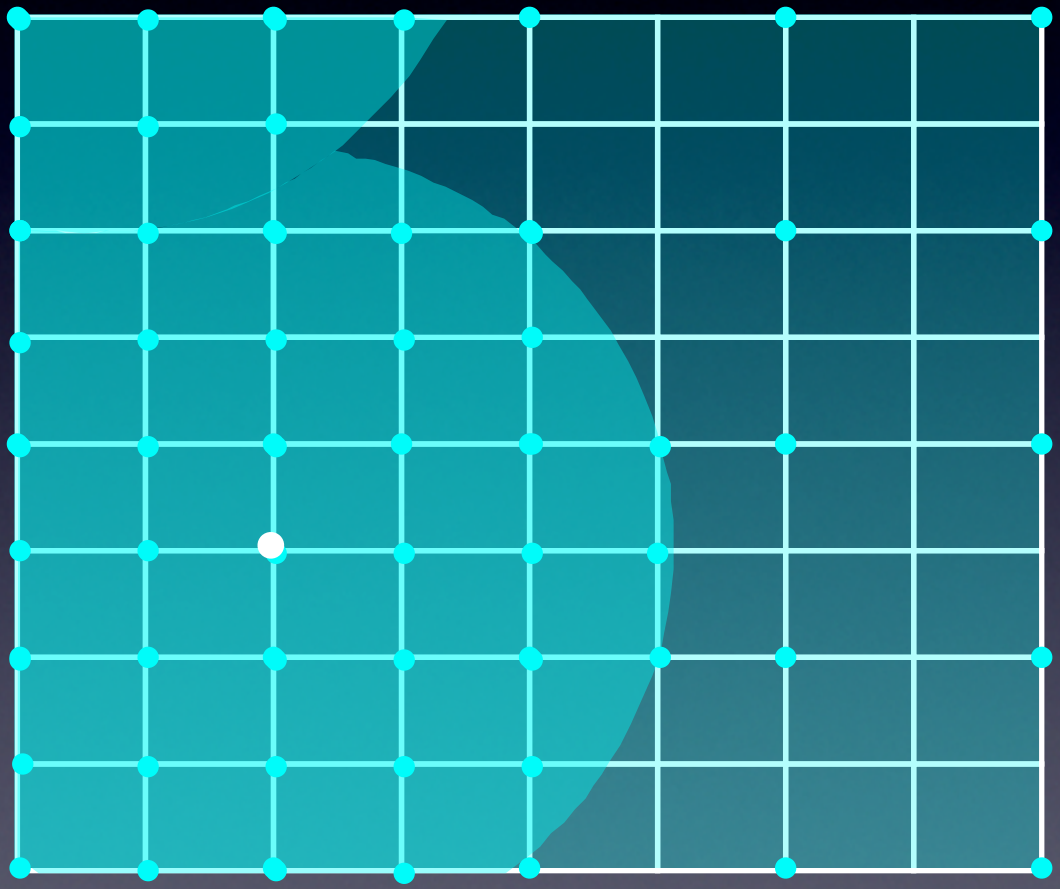
Scaling ~ Nc^3

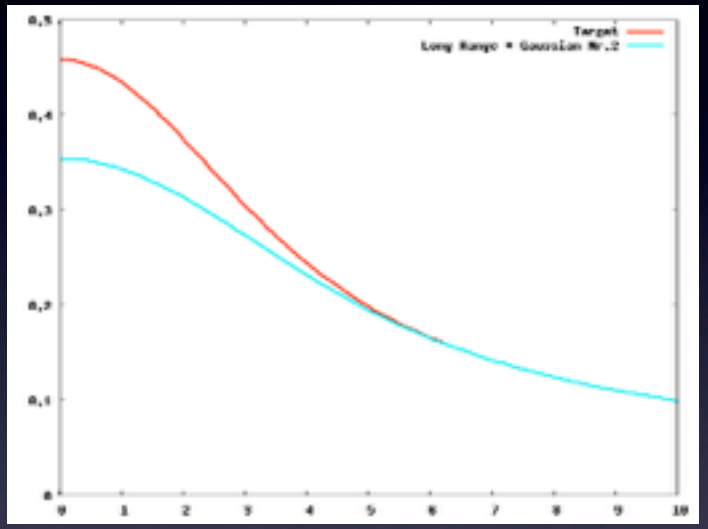




real space interpolation from coarsest to finest

$$V^{\mathrm{QM/MM}}(\mathbf{r}, \mathbf{R}_{\mathrm{MM}}) = \sum_{i=\mathrm{coarse}}^{\mathrm{fine}} \prod_{k=i}^{\mathrm{fine}-1} I_{k-1}^{k} V_i^{\mathrm{QM/MM}}(\mathbf{r}, \mathbf{R}_{\mathrm{MM}})$$





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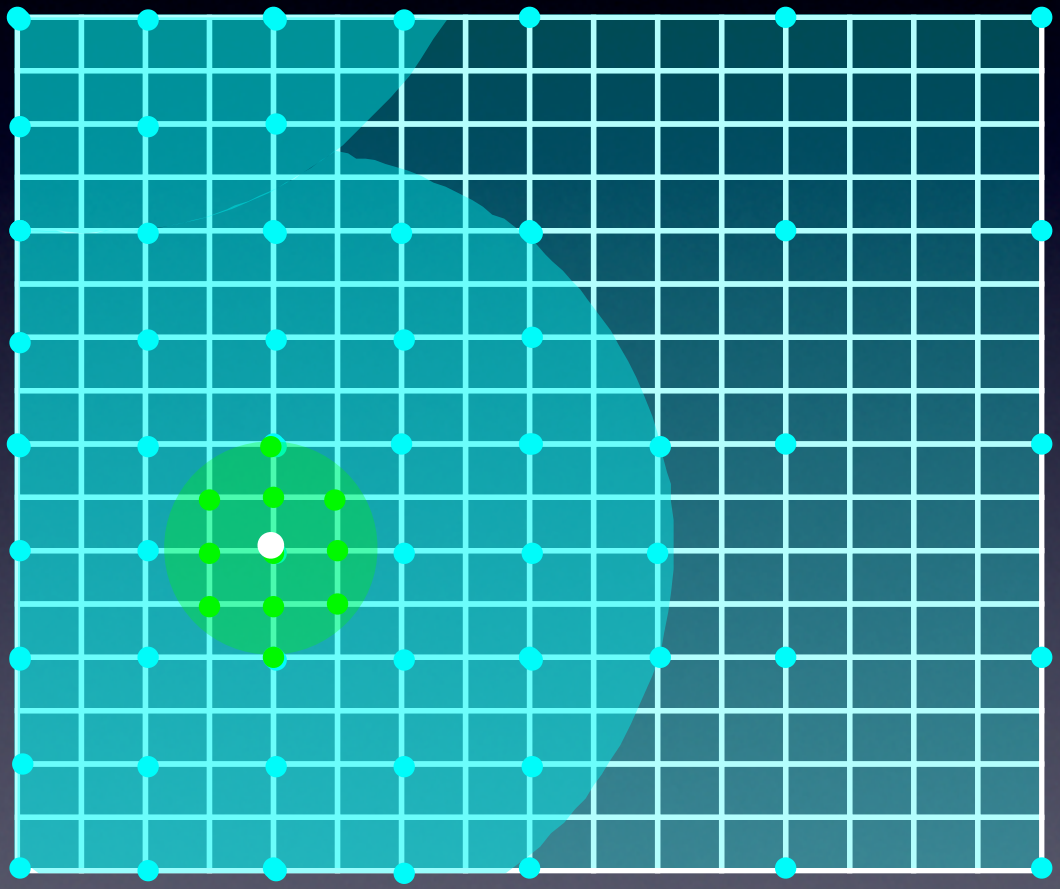
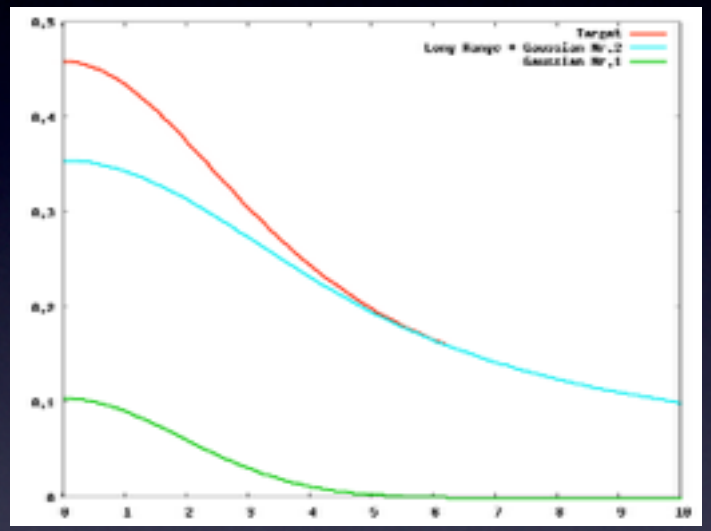
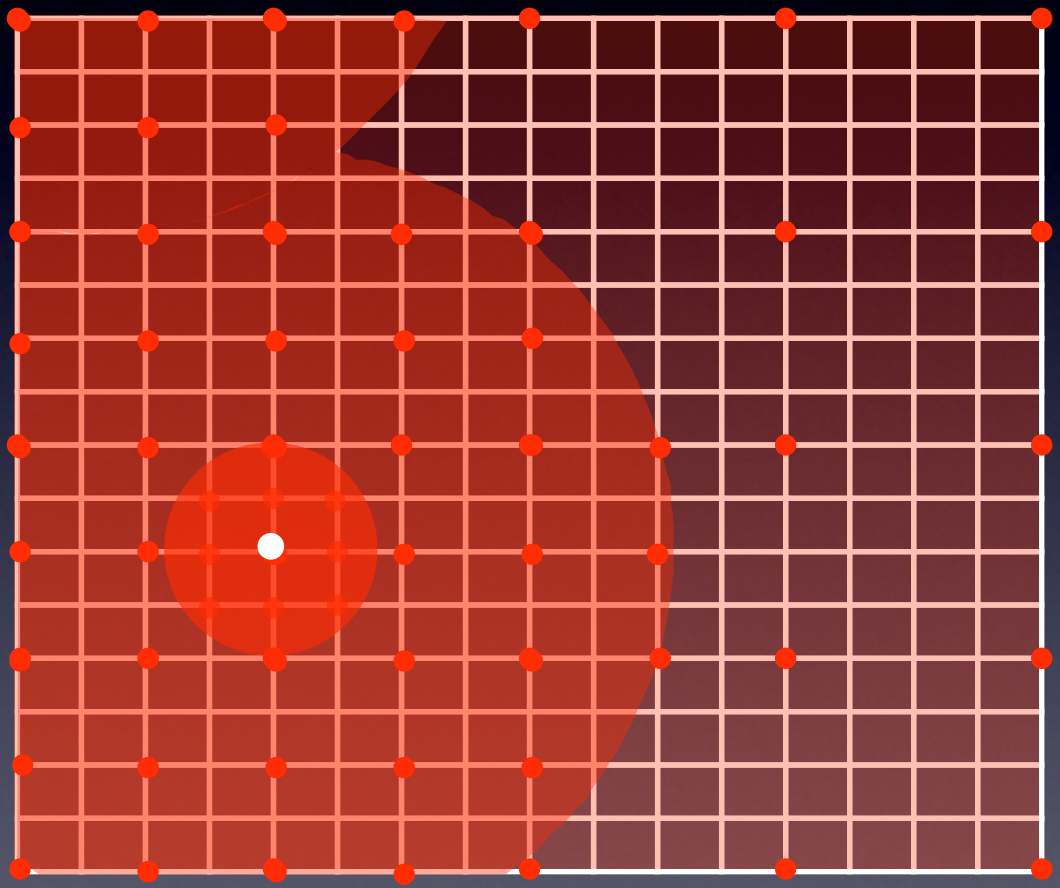
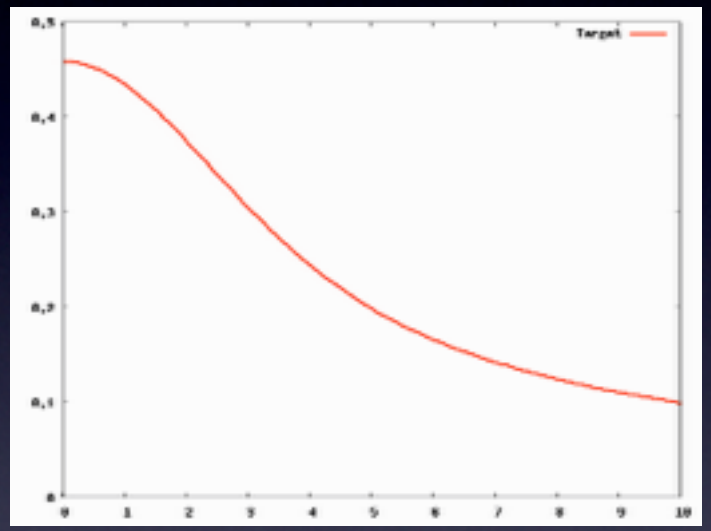




$$V^{\mathrm{QM/MM}}(\mathbf{r}, \mathbf{R}_{\mathrm{MM}}) = \sum_{i=\mathrm{coarse}}^{\mathrm{fine}} \prod_{k=i}^{\mathrm{fine}-1} I_{k-1}^{k} V_i^{\mathrm{QM/MM}}(\mathbf{r}, \mathbf{R}_{\mathrm{MM}})$$

Electrostatic Potential





interpolation
20-40% of time

```
&QMMM

  &CELL
    ABC 6.0 6.0 6.0
  &END CELL
  USE_GEEP_LIB 9
  ECOUPL GAUSS

  &MM_KIND H
    RADIUS 0.44
  &END MM_KIND
  &MM_KIND O
    RADIUS 0.78
  &END MM_KIND

  &QM_KIND H
    MM_INDEX 8 9
  &END QM_KIND
  &QM_KIND O
    MM_INDEX 7
  &END QM_KIND

&END QMMM
```

Extension to PBC

How to handle the electrostatic potential in presence of periodic boundary conditions (PBC)?

Ewald Summation scheme:

$$V(\vec{r}) = \sum_{MM} q_{MM} \frac{1}{|\vec{r} - \vec{r}_{MM}|}$$

$$V_{rec}(\vec{r}) = \frac{4\pi}{\Omega} \sum_{\vec{k} \neq 0} \frac{e^{\frac{|\vec{k}|^2}{4\kappa}}}{|\vec{k}|^2} \cdot \sum_{MM} q_{MM} e^{-i\vec{k}\cdot\vec{r}}$$

$$V_{real}(\vec{r}) = \sum_{MM} \sum_{\vec{n}} q_{MM} \frac{Erfc(\kappa * |\vec{r} + \vec{n}|)}{|\vec{r} + \vec{n}|}$$

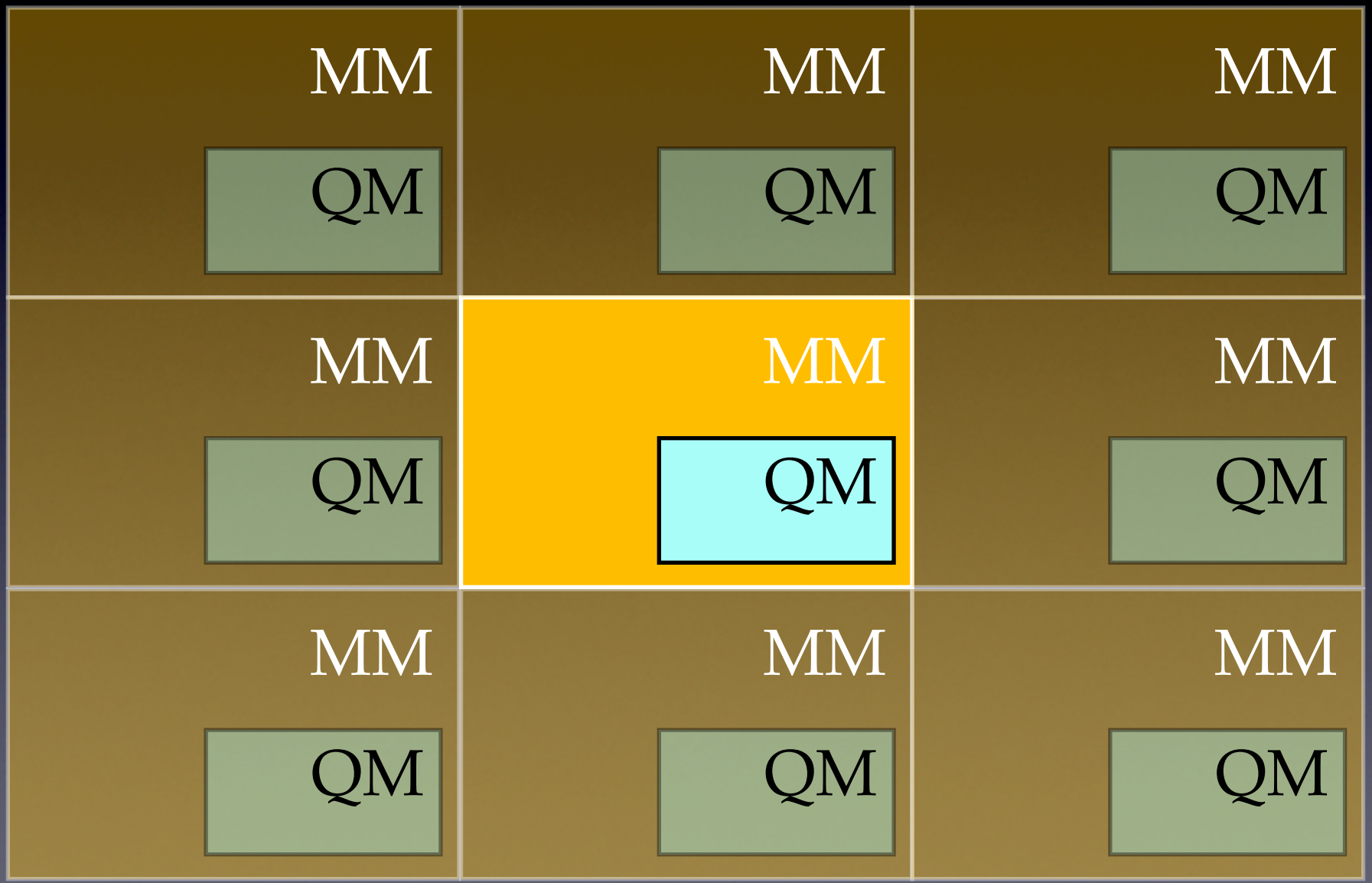
$$V(\vec{r}) = V_{rec}(\vec{r}) + V_{real}(\vec{r})$$

$$\sum_{MM} q_{MM} \frac{Erf(\vec{r}\kappa) + Erfc(\vec{r}\kappa)}{|\vec{r} - \vec{r}_{MM}|}$$

Reciprocal space

Real space

QM/MM fully periodic



T. Laino, F. Mohamed, A. Laio and M. Parrinello, *J. Chem. Th. Comp.*, 2 (5), **2006**, pp.1370-1378

Total ES Energy

$$n(\mathbf{r}) = n^{\mathrm{QM}}(\mathbf{r}) + n^{\mathrm{MM}}(\mathbf{r}) \qquad \pm n^{B}$$

background charge

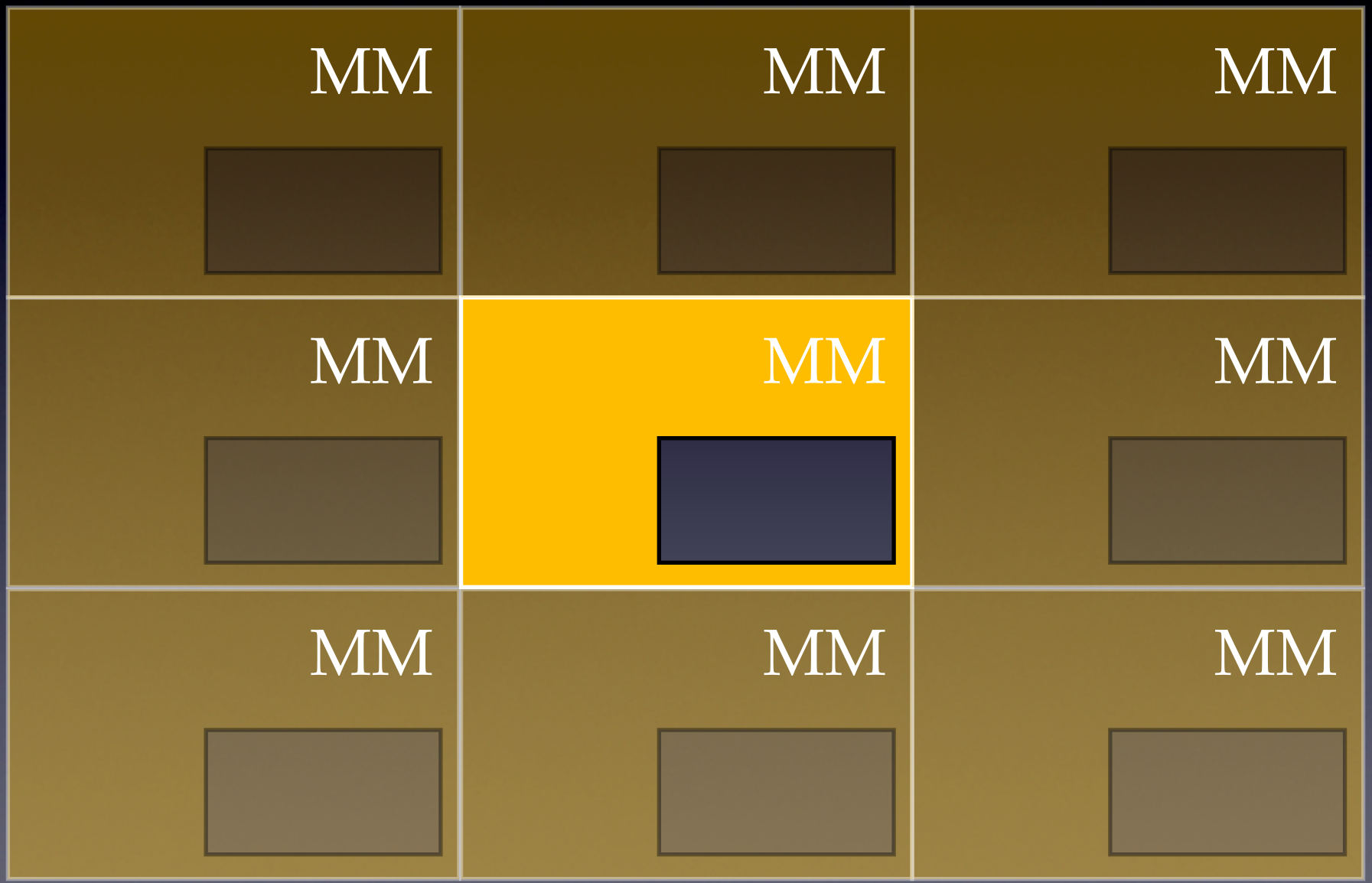
$$E^{\mathrm{TOT}} = \frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$E^{\mathrm{MM}} = \frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}' \frac{(n^{\mathrm{MM}}(\mathbf{r}) + n^{B,\mathrm{MM}})(n^{\mathrm{MM}}(\mathbf{r}') + n^{B,\mathrm{MM}})}{|\mathbf{r}-\mathbf{r}'|}$$

$$E^{\mathrm{QM}} = \frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}' \frac{(n^{\mathrm{QM}}(\mathbf{r}) + n^{B,\mathrm{QM}})(n^{\mathrm{QM}}(\mathbf{r}') + n^{B,\mathrm{QM}})}{|\mathbf{r}-\mathbf{r}'|}$$

$$E^{\mathrm{QM/MM}} = \int\int d\mathbf{r}d\mathbf{r}' \frac{(n^{\mathrm{QM}}(\mathbf{r}) + n^{B,\mathrm{QM}})(n^{\mathrm{MM}}(\mathbf{r}') + n^{B,\mathrm{MM}})}{|\mathbf{r}-\mathbf{r}'|}$$

MM/MM fully periodic



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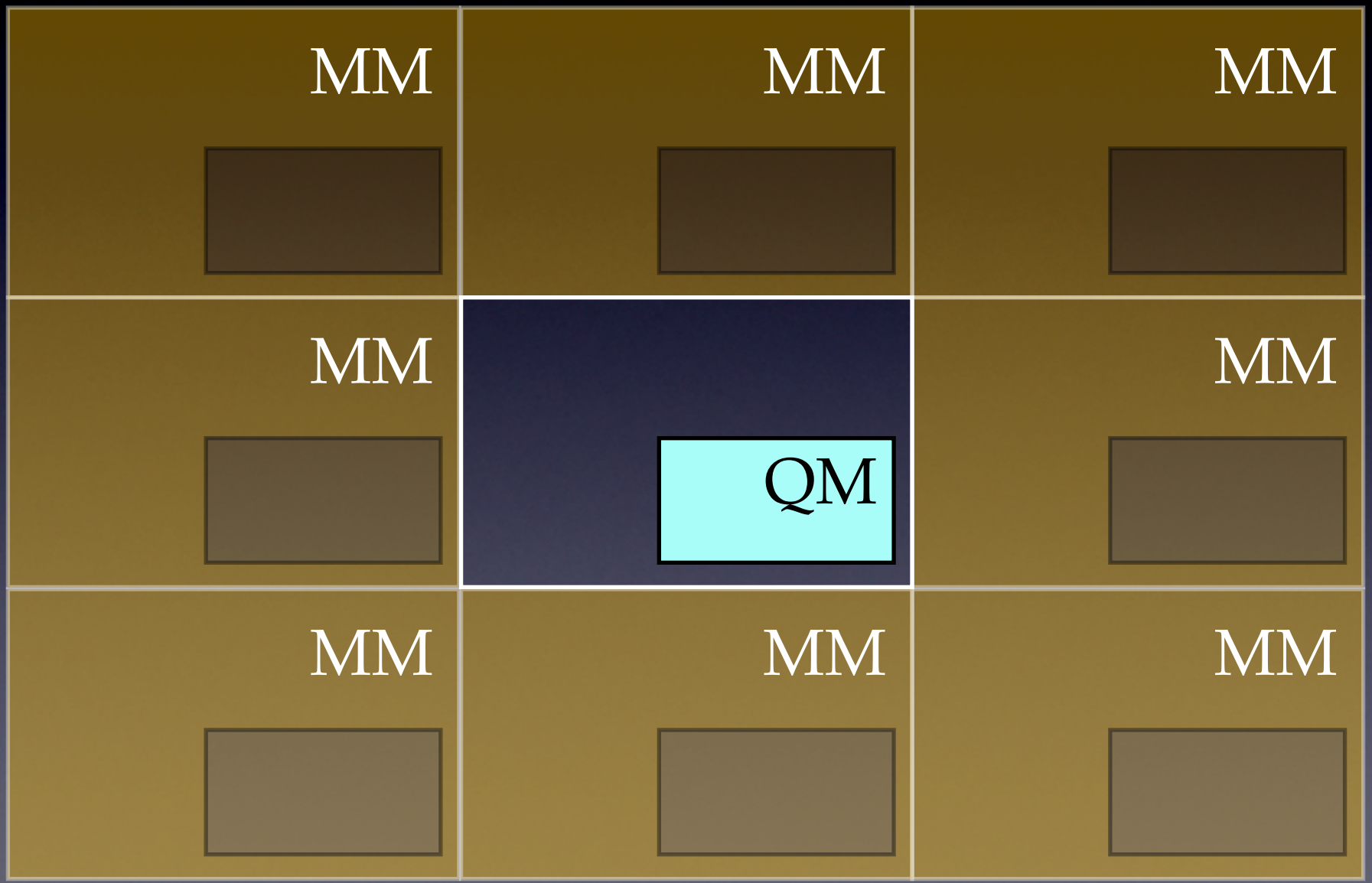
QM/MM fully periodic



T. Laino, F. Mohamed, A. Laio and M. Parrinello, *J. Chem. Th. Comp.*, 2 (5), **2006**, pp.1370-1378

GEEP with PBC

$$\frac{\mathrm{Erf}(\frac{r}{r_c})}{r} = \sum_{N_g} A_g \exp^{-(\frac{r}{G_g})^2} + R_{low}(r)$$

$$V(r)_{real} = \sum_{N_g} A_g \exp^{-(\frac{r}{G_g})^2}$$

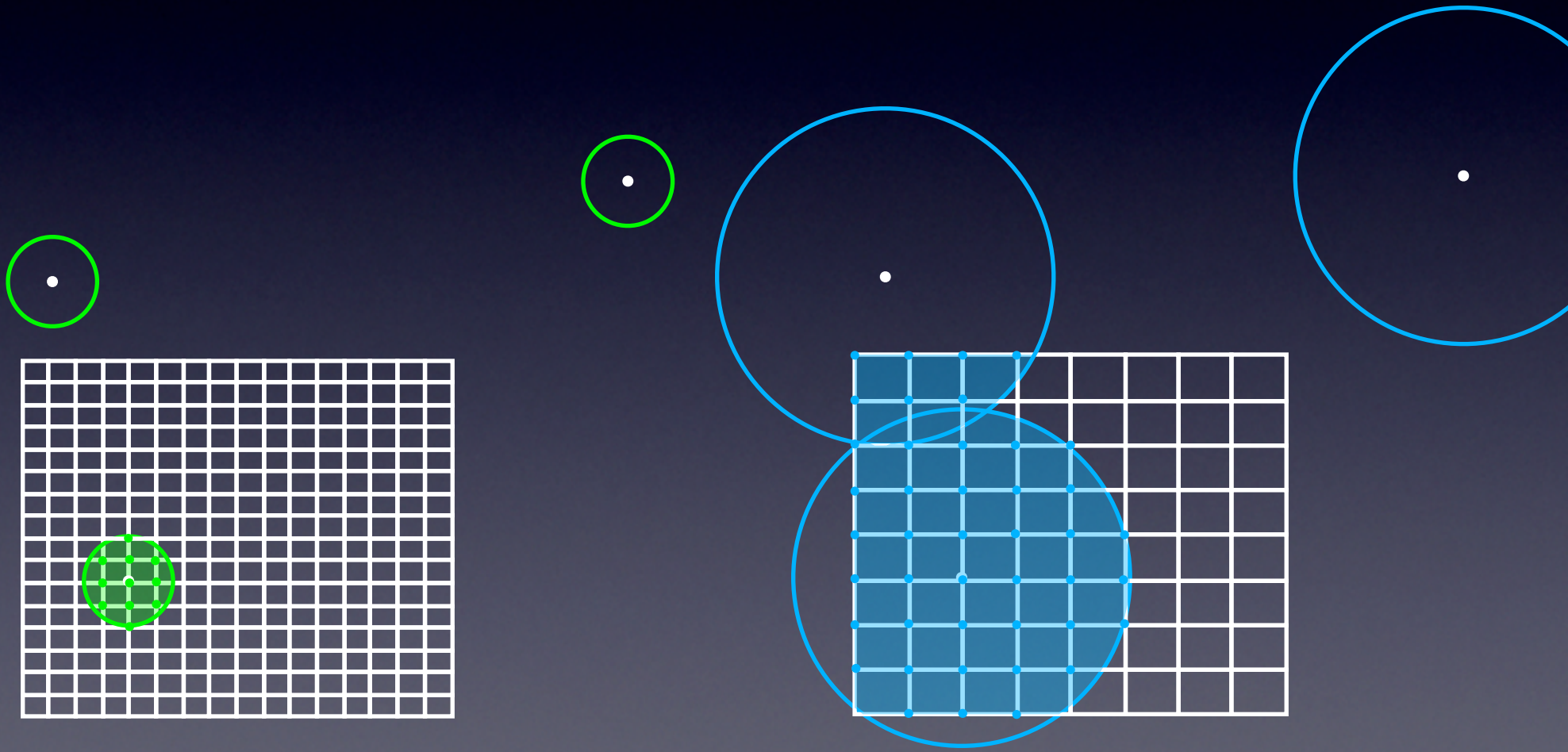
$$V(r)_{rec} = \frac{1}{\Omega} \sum_{k}^{k_{cut}} R_{low}(r) \tilde{R}_{low}(k) e^{i\vec{k}\cdot\vec{r}}$$

smooth
coarsest grid

T. Laino, F. Mohamed, A. Laio and M. Parrinello, *J. Chem. Th. Comp.*, 2 (5), **2006**, pp.1370-1378

QM/MM real space term

$$V_{\mathrm{rs}}^{\mathrm{QM/MM}}(\mathbf{r},\mathbf{R}_{\mathrm{MM}}) = \sum_{|\mathbf{L}\leq L_{\mathrm{cut}}} \sum_{\mathrm{MM}} \left[\sum_{N_g} A_g \exp\left(-\frac{|\mathbf{r}-\mathbf{R}_{\mathrm{MM}}+\mathbf{L}|^2}{G_g^2} \right) \right]$$



T. Laino, F. Mohamed, A. Laio and M. Parrinello, *J. Chem. Th. Comp.*, 2 (5), **2006**, pp.1370-1378

QM/MM reciprocal space term

$$V(r)_{rec} = \frac{1}{\Omega} \sum_{k}^{k_{cut}} \tilde{R}_{low}(k) e^{\imath \vec{k} \cdot \vec{r}}$$

$$\tilde{R}_{low}(k) = \left[\frac{4\pi}{|\vec{k}|^2} \right] e^{-\frac{|\vec{k}|^2 r_c^2}{4}} - \sum_{N_g} \hat{A}_g(\pi)^{\frac{3}{2}} G_g^3 e^{-\frac{|\vec{k}|^2 G_g^2}{4}}$$

low cutoff function
only few k vectors
needed

T. Laino, F. Mohamed, A. Laio and M. Parrinello, *J. Chem. Th. Comp.*, 2 (5), **2006**, pp.1370-1378

```
&QMMM

 &CELL
  ABC 17.320500 17.320500 17.320500
 &END CELL

 ECOUPL GAUSS
 USE_GEEP_LIB 6

 &MM_KIND NA
  RADIUS 1.5875316249000
 &END MM_KIND
 &MM_KIND CL
  RADIUS 1.5875316249000
 &END MM_KIND

 &PERIODIC
  GMAX 0.5
  &MULTIPOLE
   EWALD_PRECISION 0.00000001
   RCUT 8.0
   ANALYTICAL_GTERM
  &END MULTIPOLE
 &END PERIODIC

&END QMMM
```

GEEP Summary

- GEEP is a technique to speed up the evaluation of a function on a grid
- The speed up factor is ~ $(Nf/Nc)^3 = 2^{3(Ngrid-1)}$
- Usually 3-4 grid levels are used corresponding to a speed up of 64-512 ~ 10^2 times faster than the simple collocation algorithm (Interpolations and Restrictions account for a negligible amount of time)

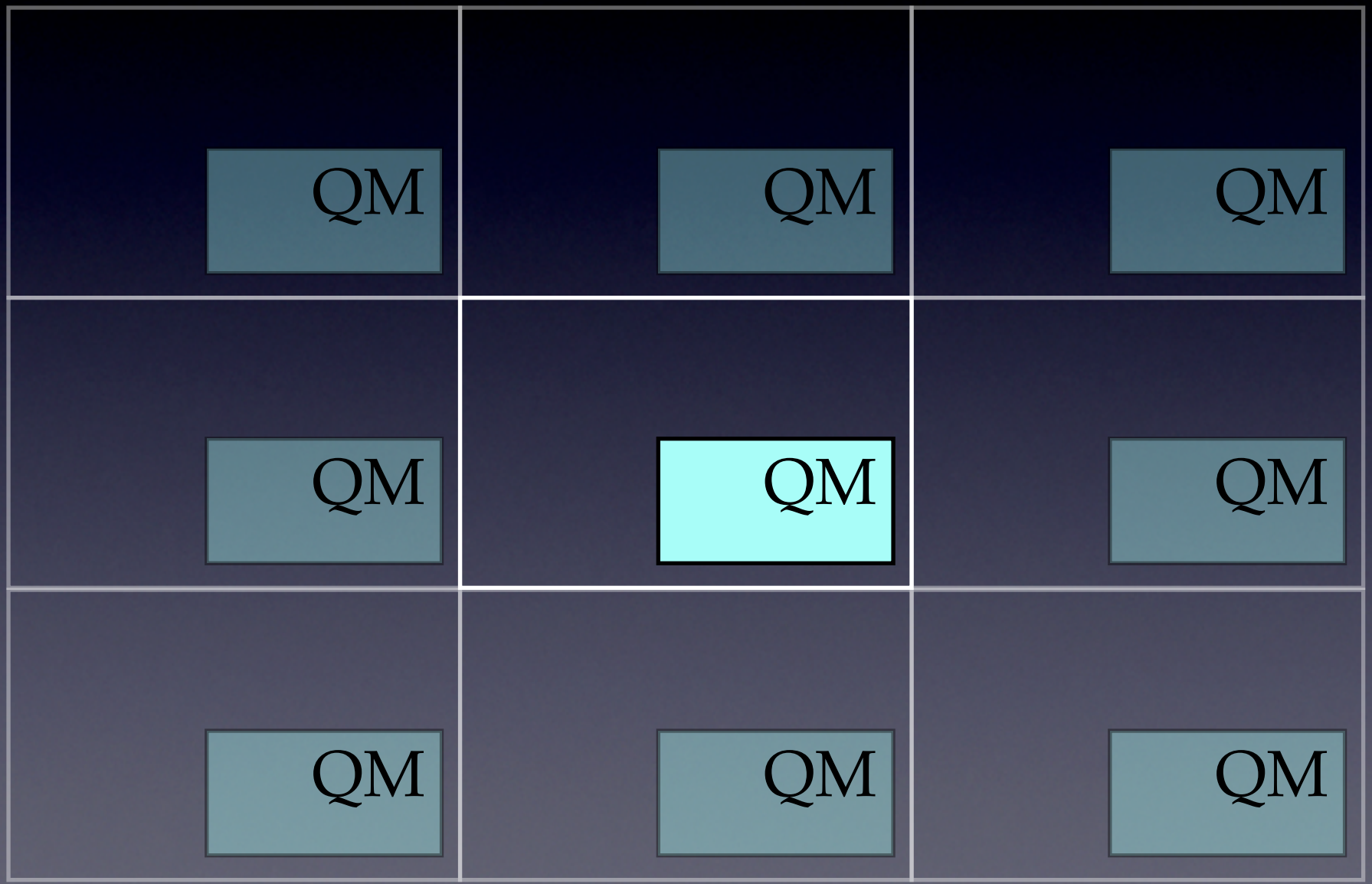
GEEP Summary

- Since the residual function is different from zero only for few k vectors, the sum in reciprocal space is restrained to few points.
- Small computational overhead between the fully periodic and non-periodic

Sources of Errors

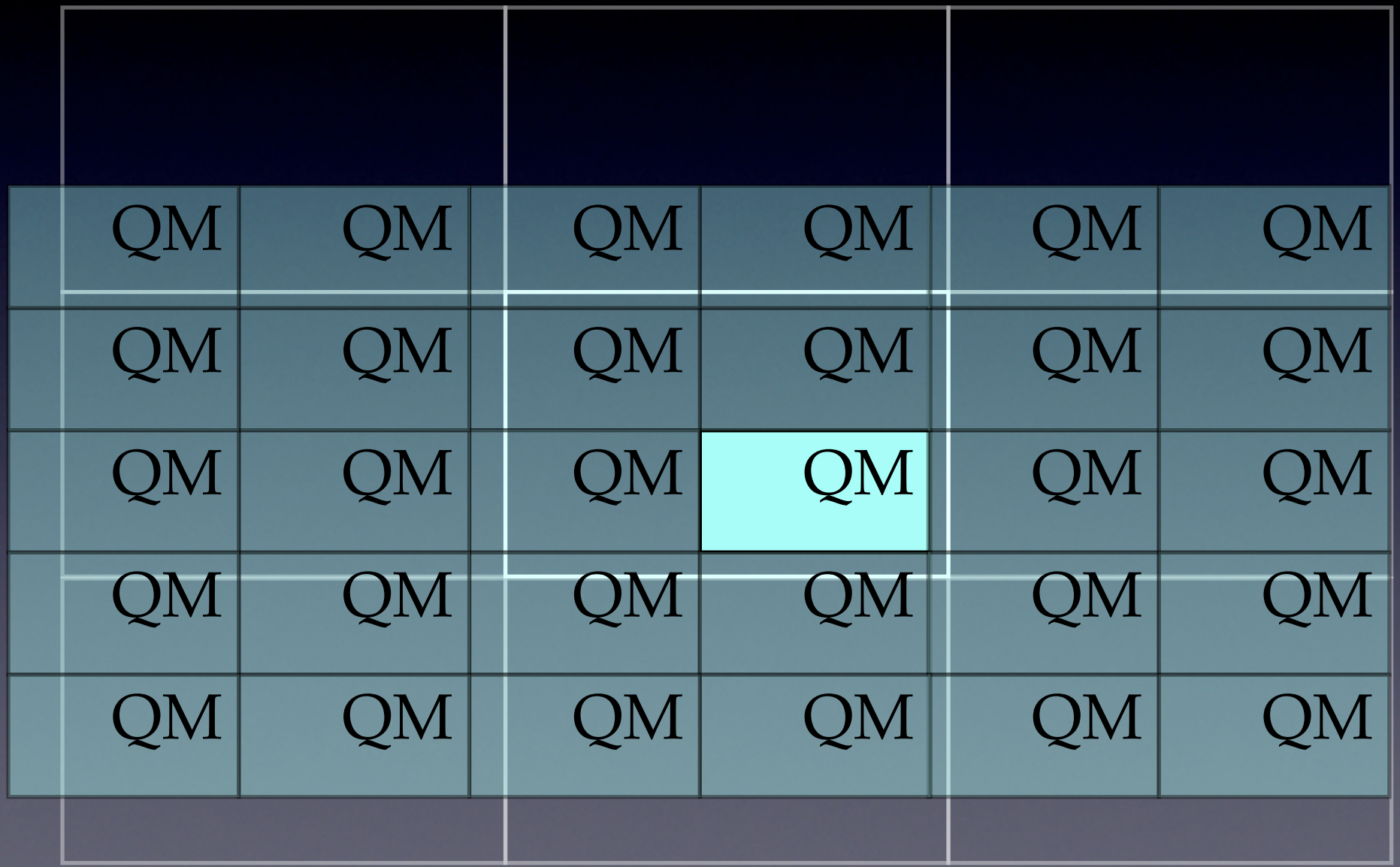
- Cutoff of grid level appropriate to the cutoff of the mapped Gaussian (~ 20-25 points per linear direction)
- Error in Cubic Spline interpolation
- Cutoff of the coarse grid level comparable to the cutoff of the long range function.

QM fully periodic



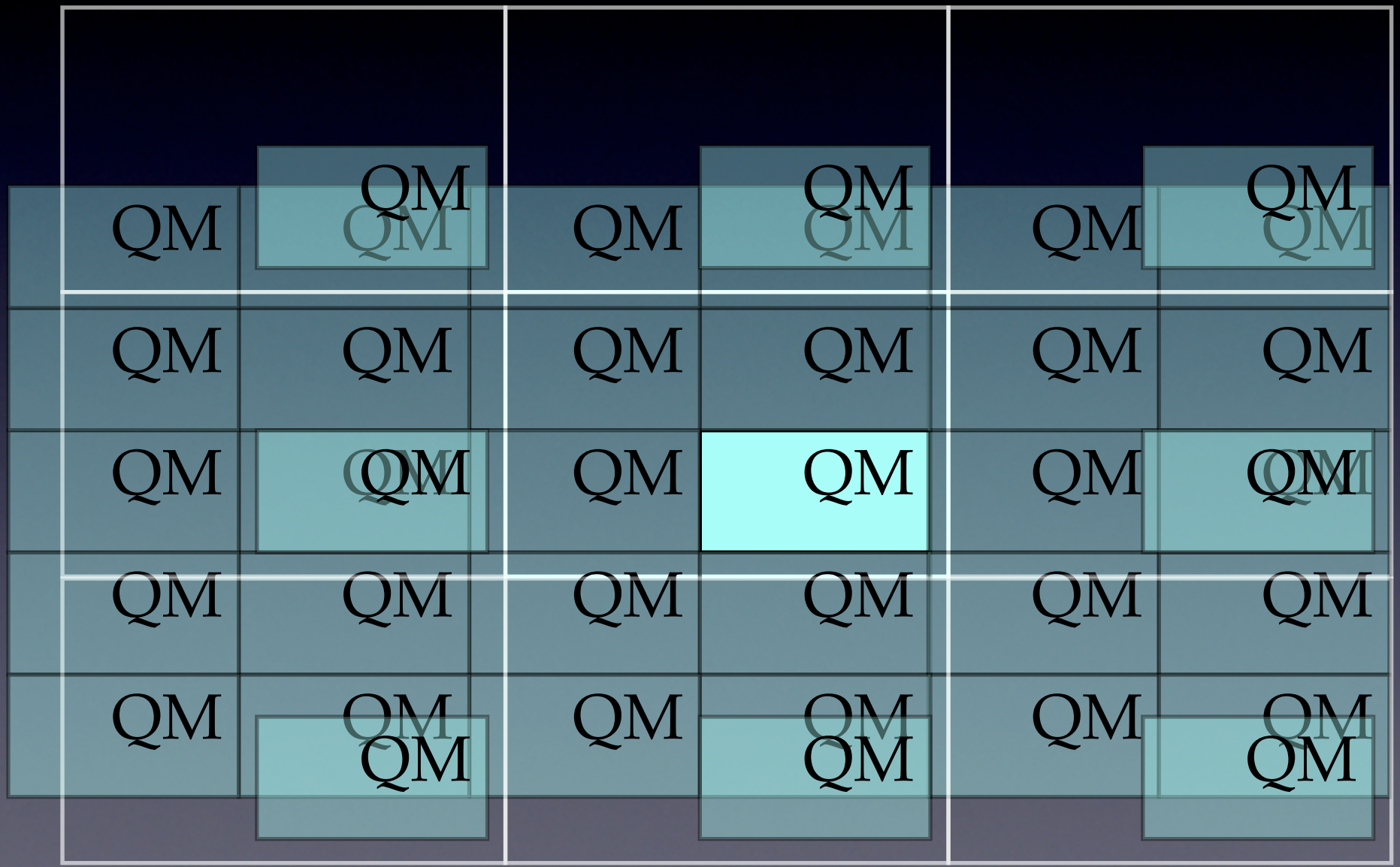
T. Laino, F. Mohamed, A. Laio and M. Parrinello, *J. Chem. Th. Comp.*, 2 (5), **2006**, pp.1370-1378

QM fully periodic



T. Laino, F. Mohamed, A. Laio and M. Parrinello, *J. Chem. Th. Comp.*, 2 (5), **2006**, pp.1370-1378

De-coupling and re-coupling



T. Laino, F. Mohamed, A. Laio and M. Parrinello, *J. Chem. Th. Comp.*, 2 (5), **2006**, pp.1370-1378

Bloechl Scheme

- Density fitting in g-space of the total density

$$\hat{n}(\mathbf{r}, \mathbf{R}_{\mathrm{QM}}) = \sum_{\mathrm{QM}} q_{\mathrm{QM}} g_{\mathrm{QM}}(\mathbf{r}, \mathbf{R}_{\mathrm{QM}})$$

- Reproduce the correct Long-Range electrostatics

$$\Delta Q_l = \left| \int d\mathbf{r}\, \mathbf{r}^l \mathcal{Y}_l \left(n(\mathbf{r}, \mathbf{R}_{\mathrm{QM}}) - \hat{n}(\mathbf{r}, \mathbf{R}_{\mathrm{QM}}) \right) \right|$$

$$\Delta W = \left| \int d\mathbf{r}\, \mathbf{r}^2 \left(n(\mathbf{r}, \mathbf{R}_{\mathrm{QM}}) - \hat{n}(\mathbf{r}, \mathbf{R}_{\mathrm{QM}}) \right) \right|$$

minimise

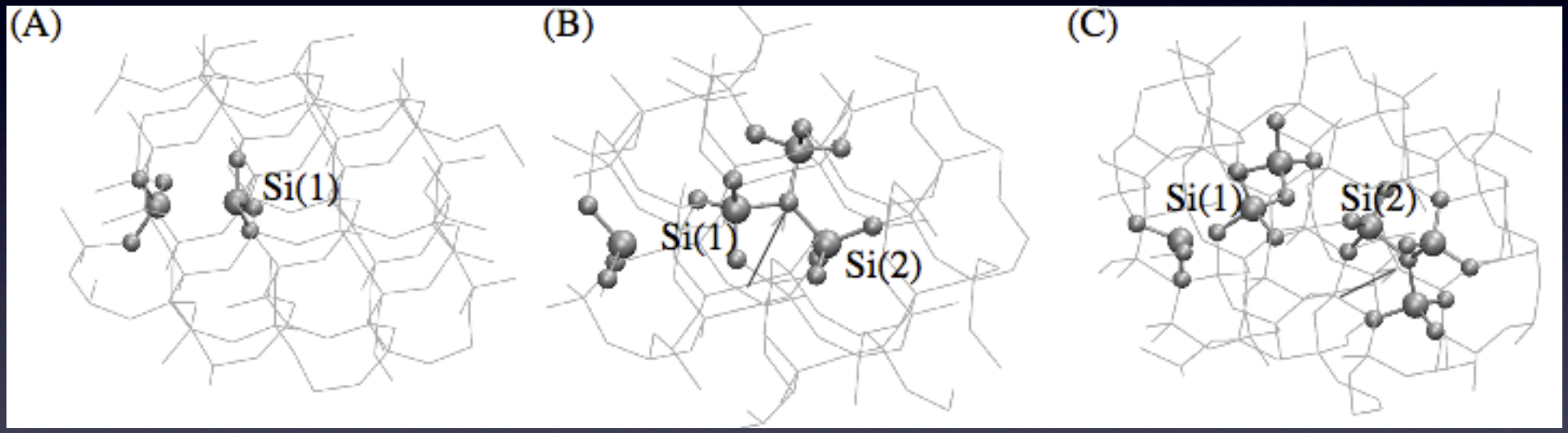
- Decoupling and Recoupling using these charges

P. E. Bloechl, *J. Chem. Phys.*, 103 (17), **1995**, pp.7422-7428

T. Laino, F. Mohamed, A. Laio and M. Parrinello, *J. Chem. Th. Comp.*, 2 (5), **2006**, pp.1370-1378

Charged OV

Migration of charged oxygen vacancy defects in silica

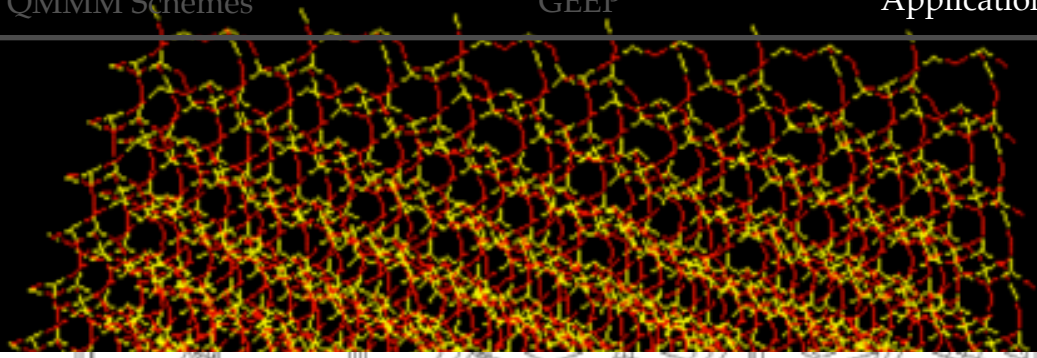


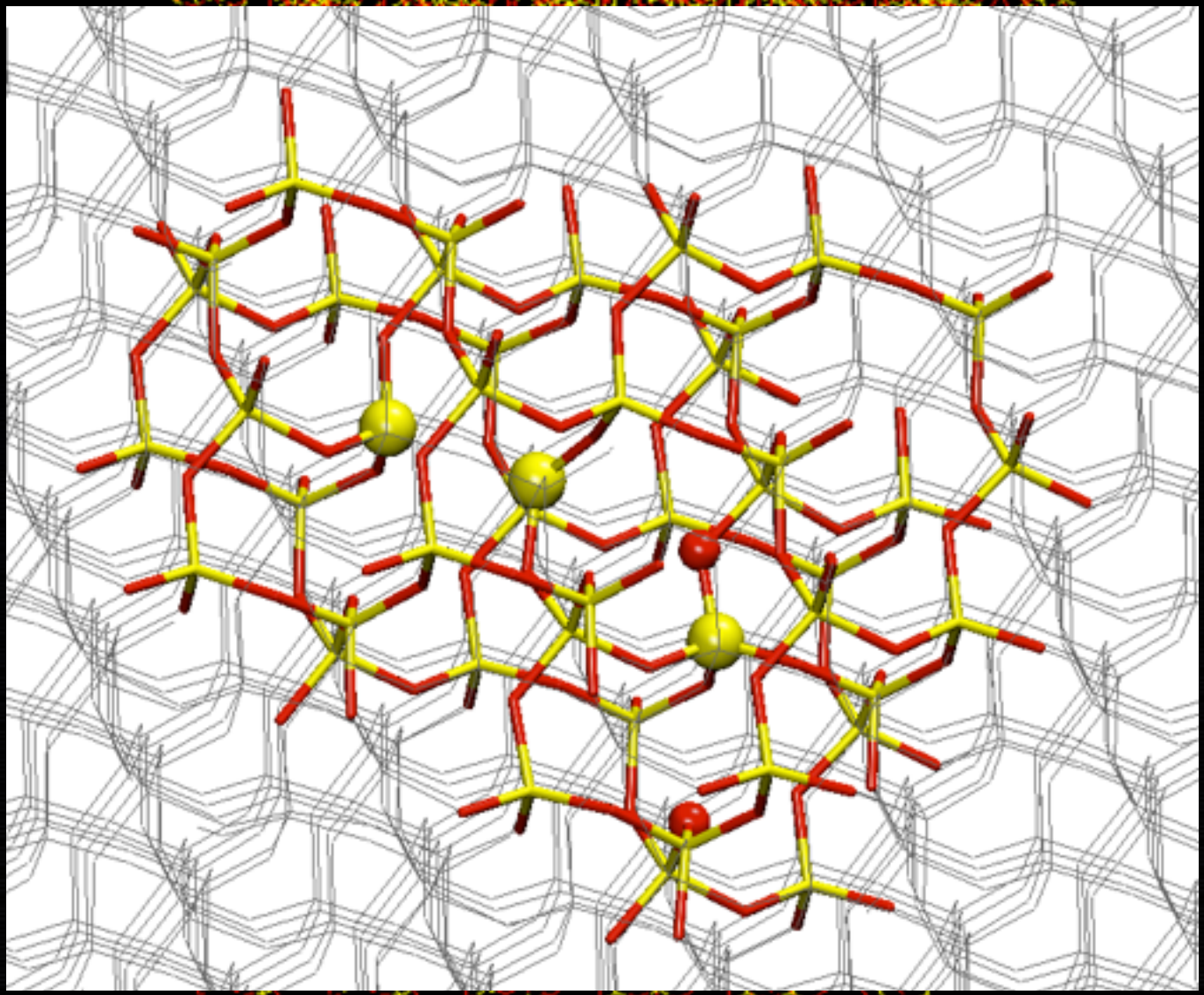
dimer

deloc. el.

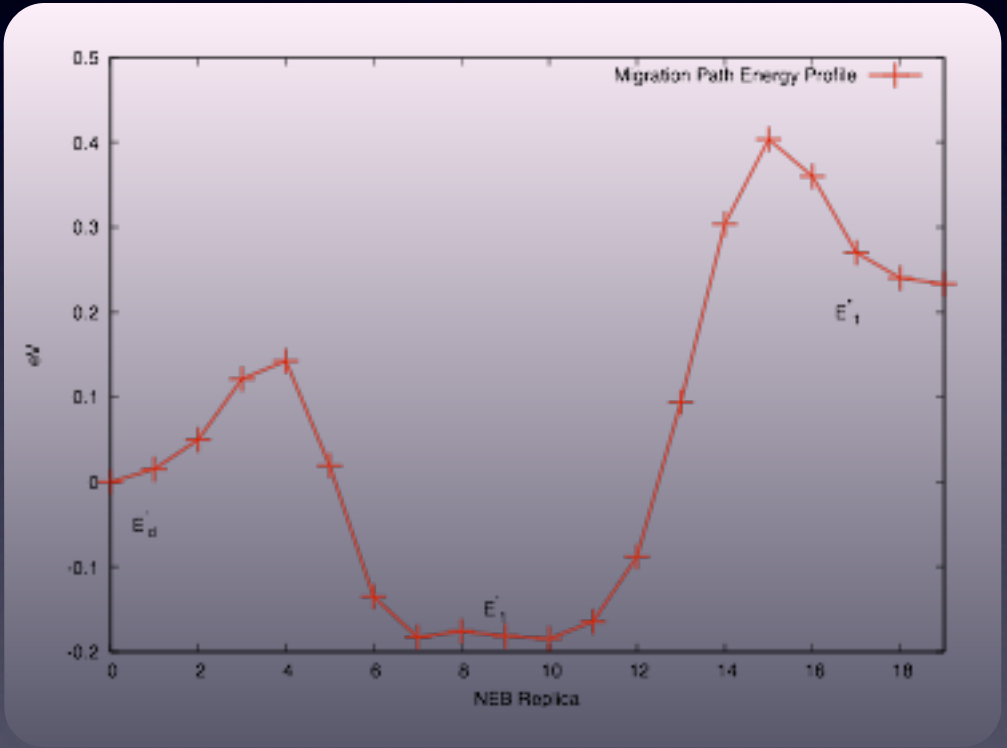
E'_δ E'_1 E^*_1

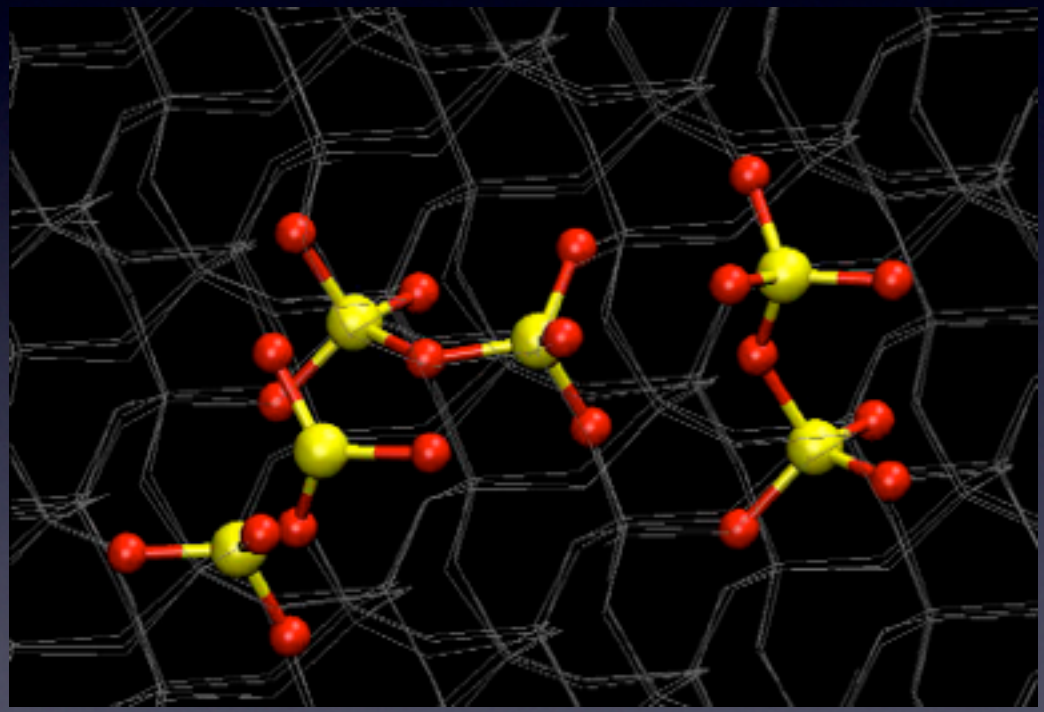
T. Laino, D. Donadio, I-Feng W. Kuo, *Phys. Rev. B*, 2007





NEB: Minimum Energy Path



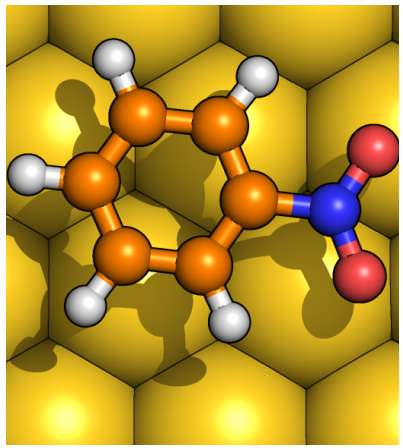


T. Laino, D. Donadio, I-Feng W. Kuo, *Phys. Rev. B*, 2007

Image Charge & QMMM

QM molecule + EAM metal

nitrobenzene/Au(111)



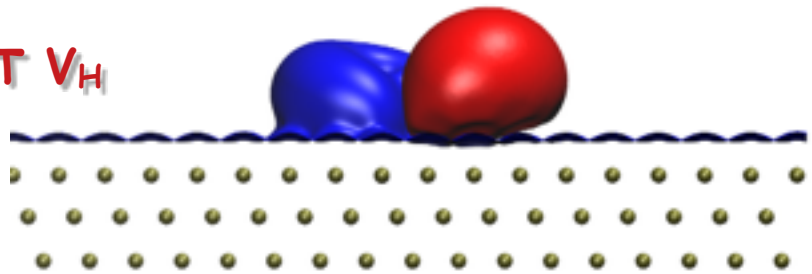
$$\rho_{\rm IC}(\mathbf{r}) = \sum_{I_{\rm met}} C_{I_{\rm met}} \exp\left[-\alpha|\mathbf{r} - \mathbf{R}_{I_{\rm met}}|^2\right]$$

$$V_H(\mathbf{r}) + V_{\rm IC}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}') + \rho_{\rm IC}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = V_0$$

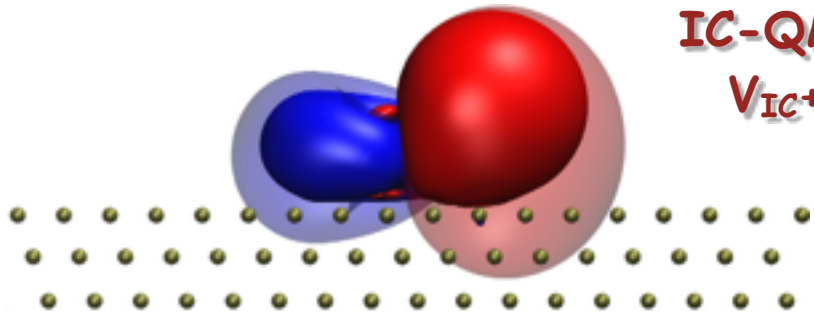
IC induce polarization, solved selfconsistently

Siepmann Sprik., JCP (1995) **102**
Golze Iannuzzi Passerone Hutter, JCTC (2013)

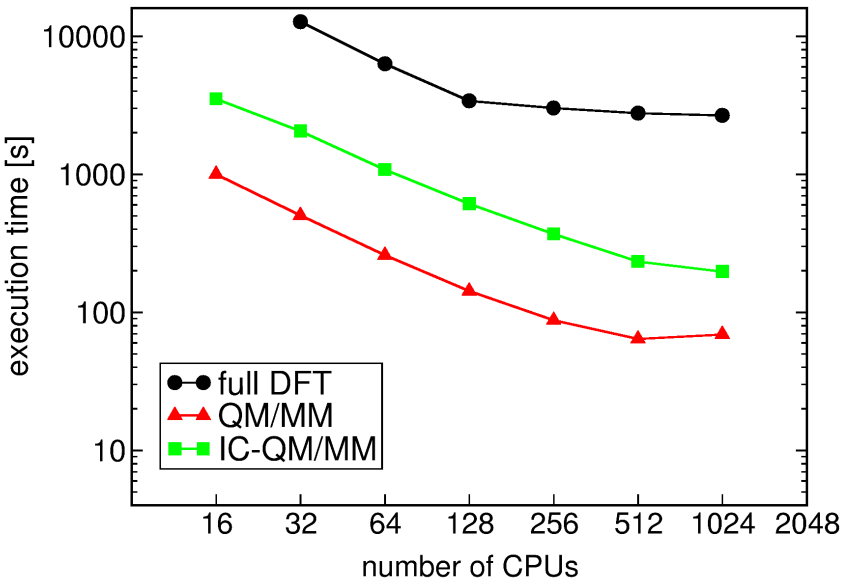
DFT V_H



IC-QMMM
$V_{IC}+V_H$



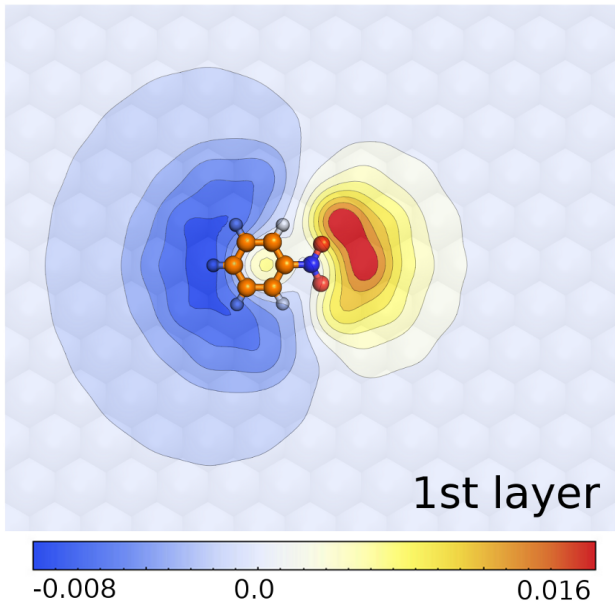
IC distribution

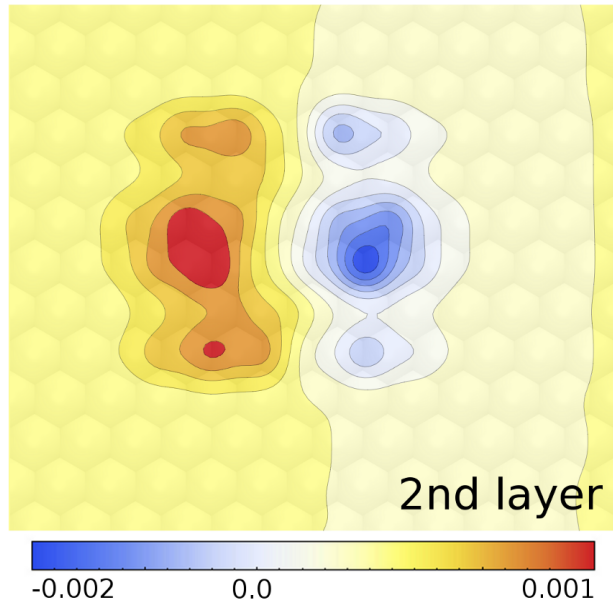


$$\int \left(V_H(\mathbf{r}) + V_{\mathrm{IC}}(\mathbf{r}) - V_0\right) g_I(\mathbf{r}) =$$

$$\int \left(V_H(\mathbf{r}) - V_0\right) g_I(\mathbf{r}) + \sum_J C_J \int\int \frac{g_J(\mathbf{r}')g_I(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$$

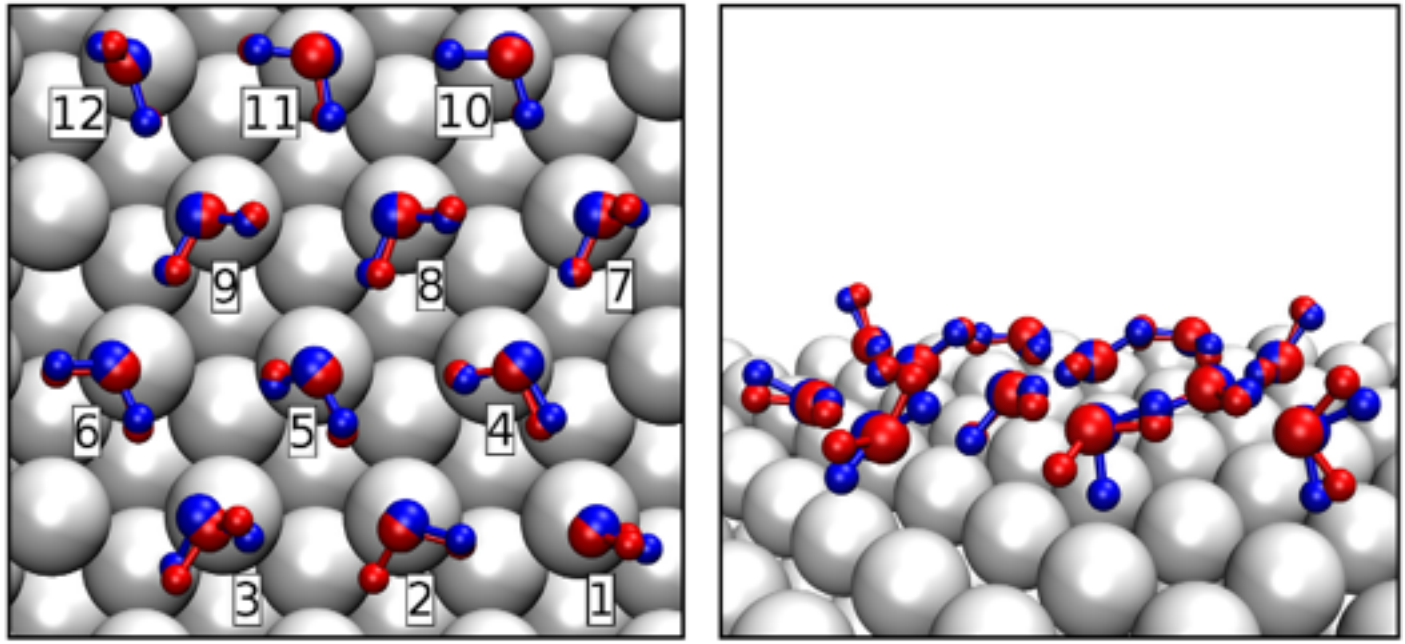
linear set of eq. (CG iterative scheme)





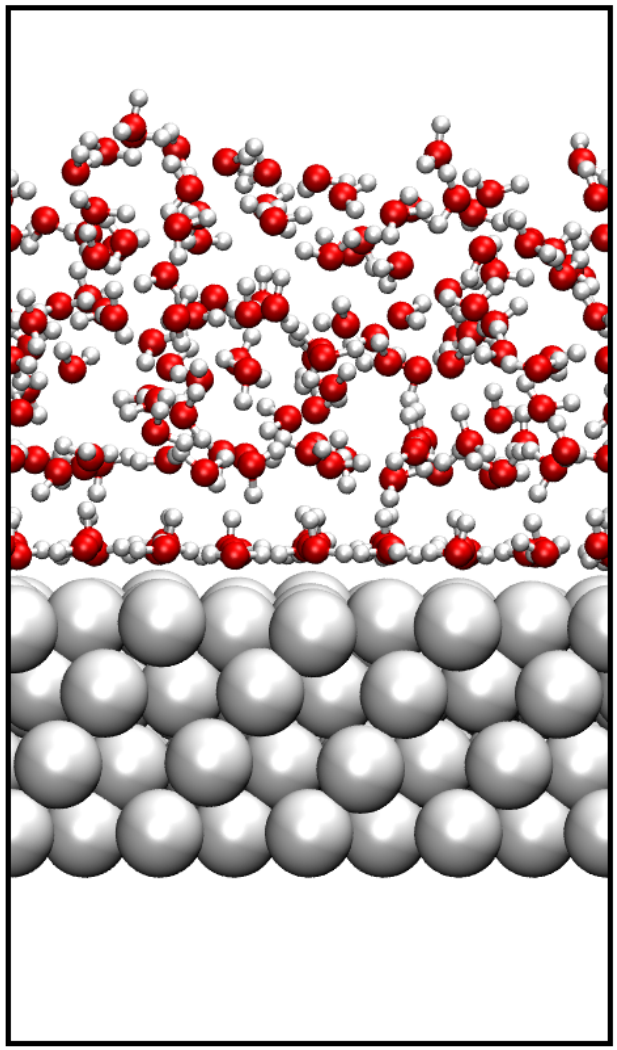
H_2O cluster on Pt(1 1 1)

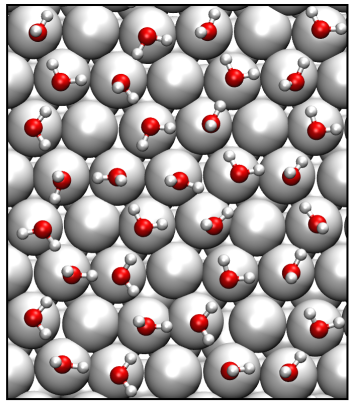
H_2O QM, Pt EAM, H_2O-Pt Siepmann-Sprik + IC



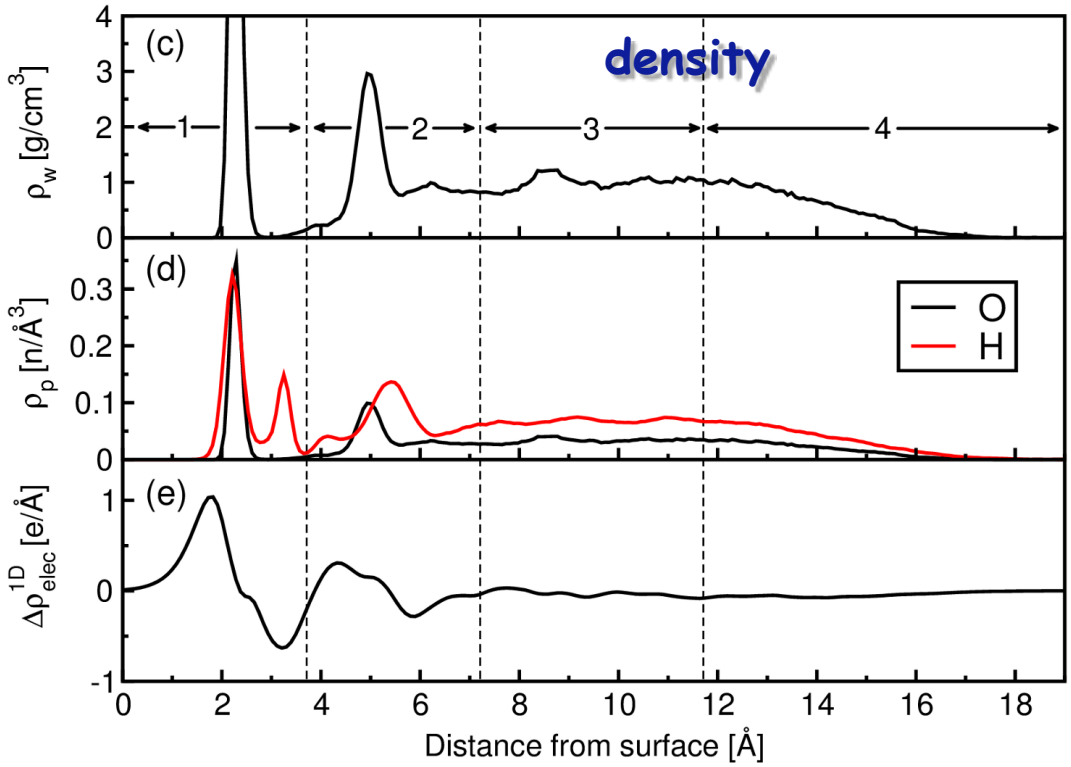
kJ/mol	1 H_2O		2H_2O			12H_2O		
	E_{int}	E_{ads}	E_{int}	E_{ads}	E_{H-bond}	E_{int}	E_{ads}	E_{H-bond}
QM/MM	−41.6	−37.3	−40.9	−49.2	−10.6	−36.4	−61.9	−26.0
IC-QM/MM	−44.2	−43.6	−43.7	−52.9	−10.5	−42.8	−66.6	−24.4
full DFT	−44.9	−43.5	−50.6	−56.8	−7.0	−44.2	−63.0	−19.7

Liquid Water at Pt(1 1 1)





honeycomb arrangement
70% on-top site occupied



H-bond distribution