CP2K UK Workshop 2014
27-28 August, Imperial College, London

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

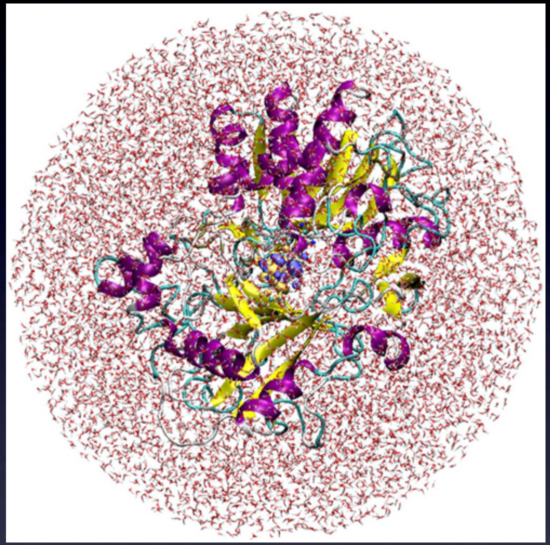
Martin Karplus, Harvard U., Cambridge, MA, USA

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

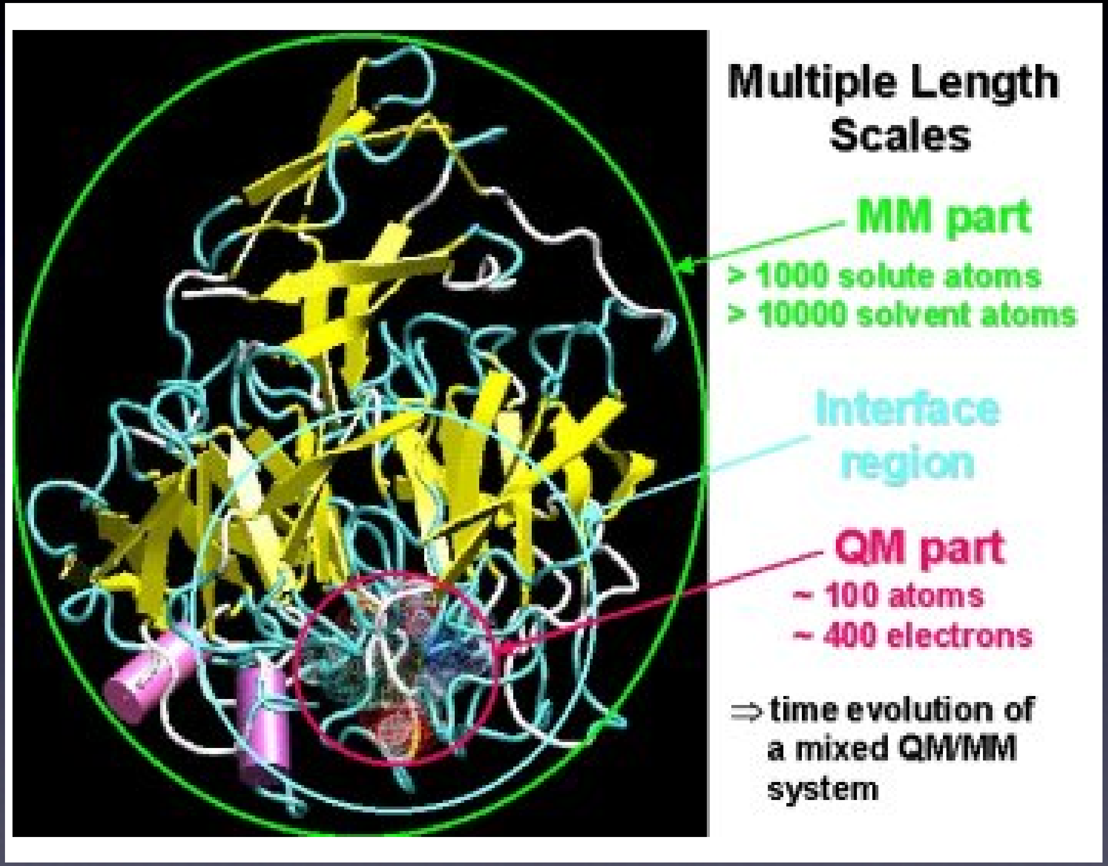
Arieh Warshel, U. Southern Ca., Los Angeles, CA, USA

Development of Multiscale Models of Complex Chemical Systems

Combine QM and MM



full atomistic by
classical FF

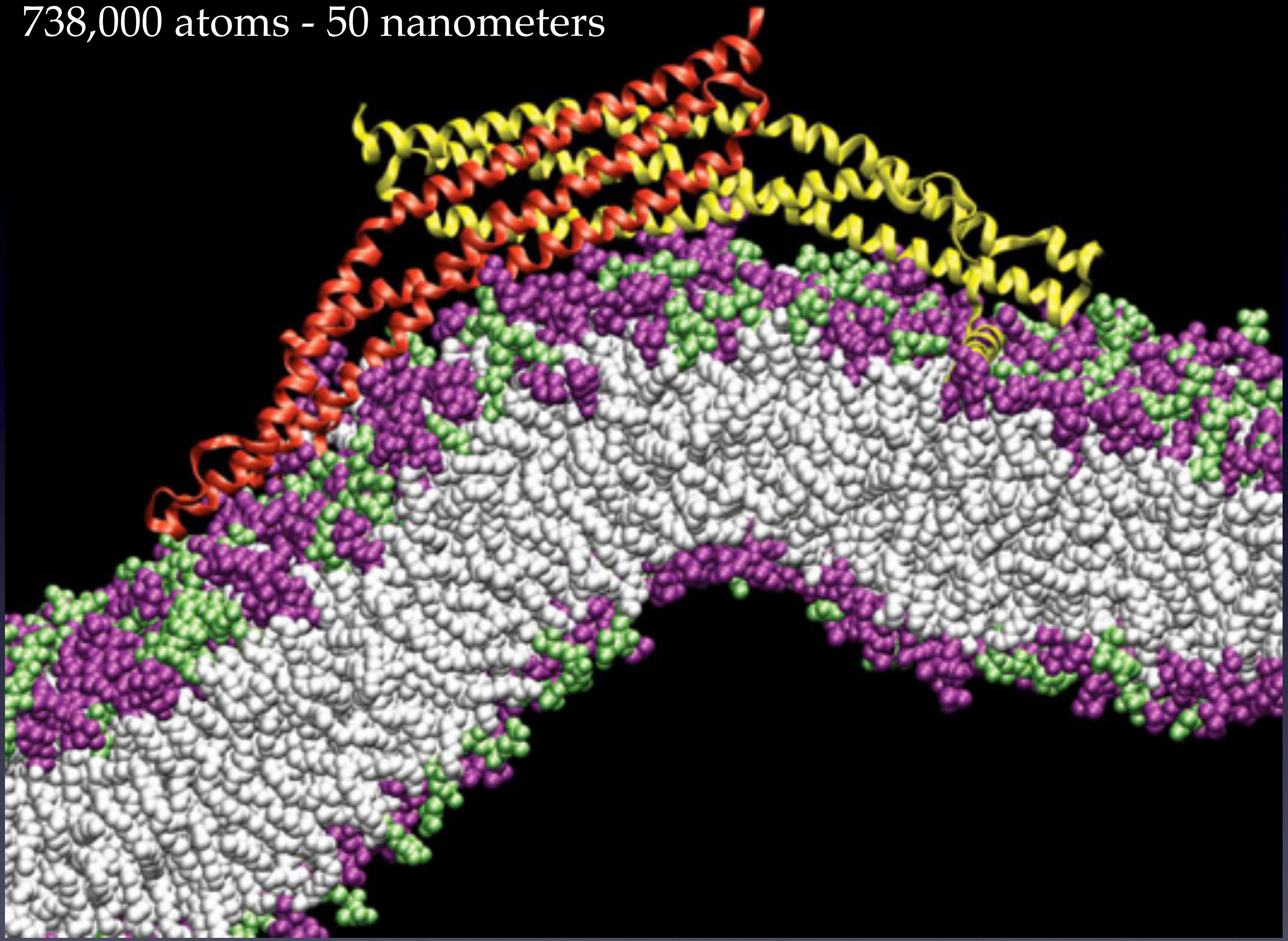


$$V(\mathbf{R}) = V_{\mathrm{QM}}(\mathbf{R}) + V_{\mathrm{MM}}(\mathbf{R}) + V_{\mathrm{int}}(\mathbf{R})$$

Combine QM and MM

- QM: modelling of electronic rearrangements
- MM: efficient inclusion of wider environment
- Choice of QM method (semi empirical, DFT, QC)
- Choice of the force field
- Partitioning and treatment of the boundary

738,000 atoms - 50 nanometers

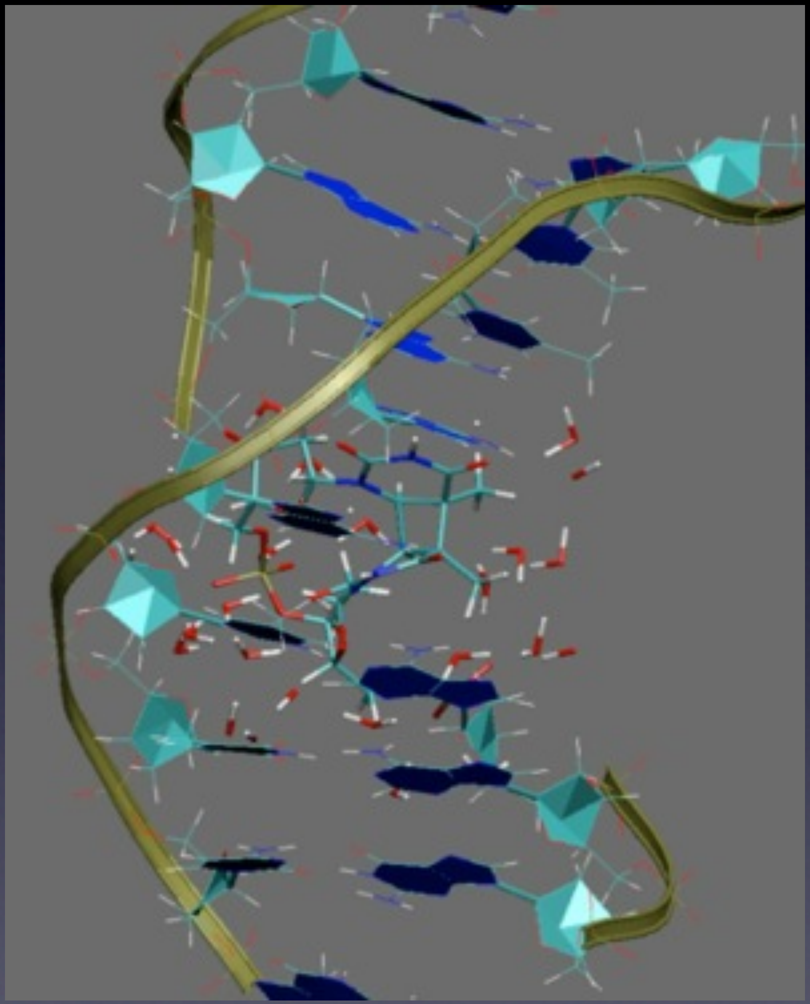


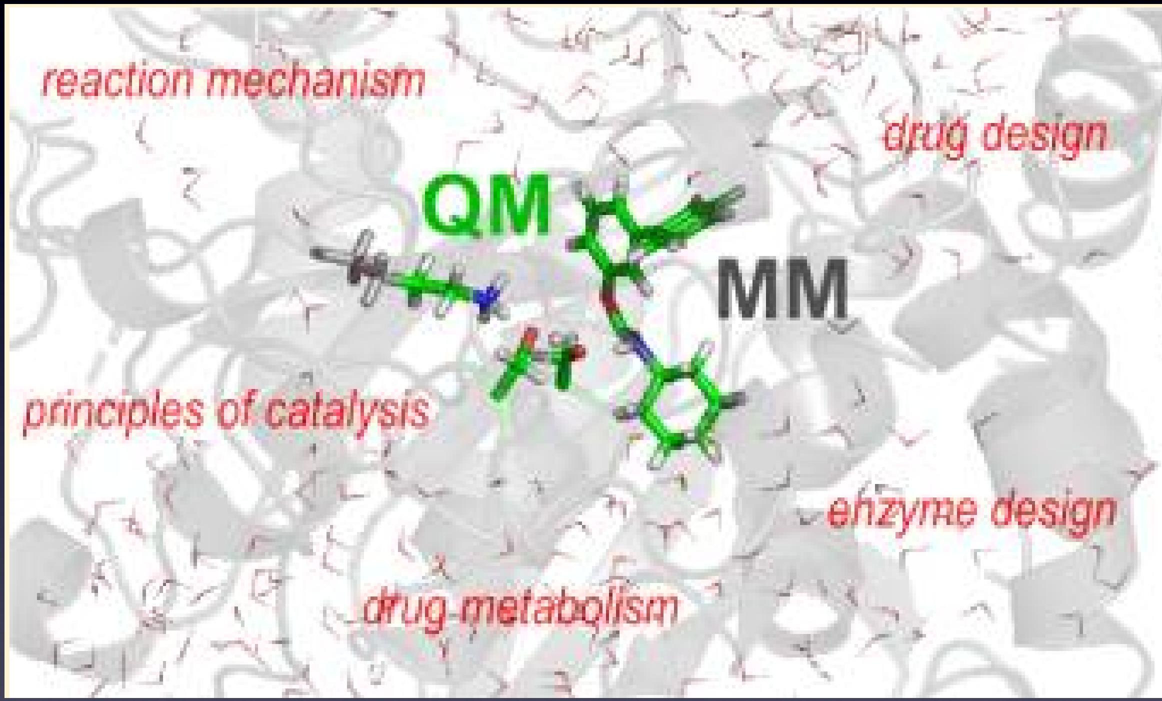
Ligand binding affinity in docking

Free energy simulations

Complex biomolecular structures

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

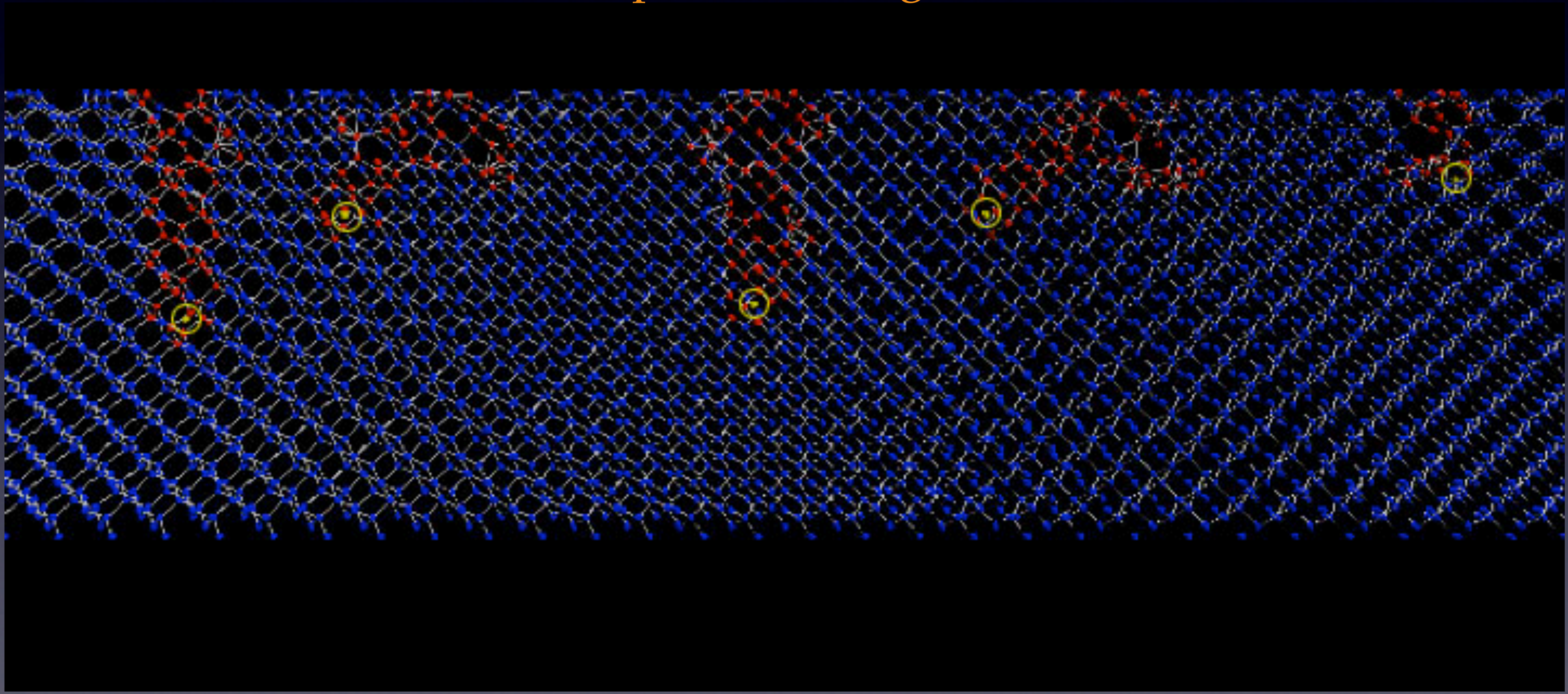




Environment effects on reaction energetics

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)

MM Environment

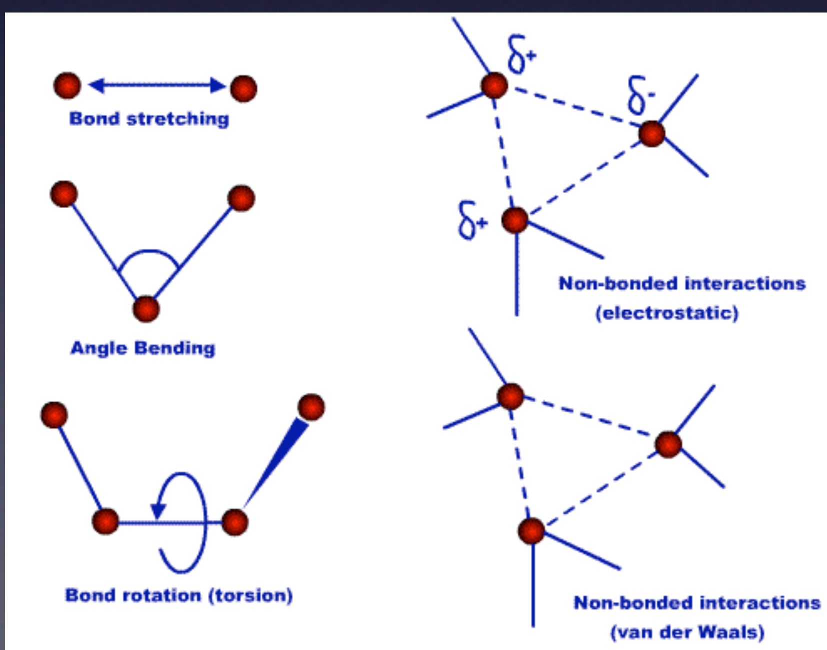
$$\mathcal{U}(\mathbf{R}^N) = \sum_i \mathcal{U}_1(\mathbf{R}_i) + \sum_i \sum_{j>i} \mathcal{U}_2(\mathbf{R}_i, \mathbf{R}_j) + \sum_i \sum_{j>i} \sum_{k>j} \mathcal{U}_3(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_k) + ...$$

$$\mathcal{U}(\mathbf{R}^N, \boldsymbol{\lambda}^{n_p})$$

MM Environment

$$\mathcal{U}(\mathbf{R}^N) = \sum_i \mathcal{U}_1(\mathbf{R}_i) + \sum_i \sum_{j>i} \mathcal{U}_2(\mathbf{R}_i, \mathbf{R}_j) + \sum_i \sum_{j>i} \sum_{k>j} \mathcal{U}_3(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_k) + \ldots$$

$$\mathcal{U}(\mathbf{R}^N, \boldsymbol{\lambda}^{n_p})$$



$$\begin{aligned}
\mathcal{U}(\mathbf{R}^N) \quad &= \quad \sum_{i \in \text{bonds}} \frac{k_i^{(b)}}{2}(l_i - l_{i,0})^2 + \sum_{j \in \text{angles}} \frac{k_j^{(a)}}{2}(\theta_j - \theta_{j,0})^2 \\
&+ \quad \sum_{s \in \text{torsion}} \frac{\mathcal{V}_s}{2}(1 + \cos(n_s \omega - \gamma_s)) \\
&+ \quad \sum_{j>i} \left(4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{R_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{R_{ij}} \right)^{6} \right] + \frac{q_i q_j}{|4\varepsilon_0 R_{ij}|} \right)
\end{aligned}$$

$$\boldsymbol{\lambda} : [(k^{(b)}, l_0)^{\text{bon}}; (k^{(a)}, \theta_0)^{\text{ang}}; (\mathcal{V}_s, \gamma_s)^{\text{tor}}; (\varepsilon, \sigma)^{\text{pair}}; q^{\text{at}}]$$

Topology

```
RESI ALA          0.00
GROUP
ATOM N    NH1    -0.47  !     |
ATOM HN   H       0.31  !  HN-N
ATOM CA   CT1     0.07  !     |     HB1
ATOM HA   HB      0.09  !     |    /
GROUP                   !  HA-CA--CB-HB2
ATOM CB   CT3    -0.27  !     |    \
ATOM HB1  HA      0.09  !     |     HB3
ATOM HB2  HA      0.09  !   O=C
ATOM HB3  HA      0.09  !     |
GROUP                   !
ATOM C    C       0.51
ATOM O    O      -0.51
BOND CB CA  N  HN  N  CA
BOND C  CA  C  +N  CA HA  CB HB1  CB HB2  CB HB3
DOUBLE O  C
IMPR N -C CA HN  C CA +N O
DONOR HN N
ACCEPTOR O C
IC -C   CA   *N   HN    1.3551 126.4900  180.0000 115.4200  0.9996
IC -C   N    CA   C     1.3551 126.4900  180.0000 114.4400  1.5390
IC N    CA   C    +N    1.4592 114.4400  180.0000 116.8400  1.3558
IC +N   CA   *C   O     1.3558 116.8400  180.0000 122.5200  1.2297
IC CA   C    +N   +CA   1.5390 116.8400  180.0000 126.7700  1.4613
IC N    C    *CA  CB    1.4592 114.4400  123.2300 111.0900  1.5461
IC N    C    *CA  HA    1.4592 114.4400 -120.4500 106.3900  1.0840
IC C    CA   CB   HB1   1.5390 111.0900  177.2500 109.6000  1.1109
IC HB1  CA   *CB  HB2   1.1109 109.6000  119.1300 111.0500  1.1119
IC HB1  CA   *CB  HB3   1.1109 109.6000 -119.5800 111.6100  1.1114
```

MM CP2K input

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       &END CHARGE
       &CHARGE
        ATOM YN
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       &CHARGE
        ATOM HC
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      &EWALD
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  &END MM

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&END FORCE_EVAL
```

Subtractive QM/MM

$$E_{\mathrm{total}} = E_{\mathrm{MM,tot}} + E_{\mathrm{QM(QM)}} - E_{\mathrm{MM(QM)}}$$

- MM FF also for active region
- QM density not polarised

Subtractive QM/MM

$$E_{\text{total}} = E_{\text{MM,tot}} + E_{\text{QM(QM)}} - E_{\text{MM(QM)}}$$

- MM FF also for active region
- QM density not polarised

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 &END FORCE_EVAL
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  &END SUBSYS
 &END FORCE_EVAL
```
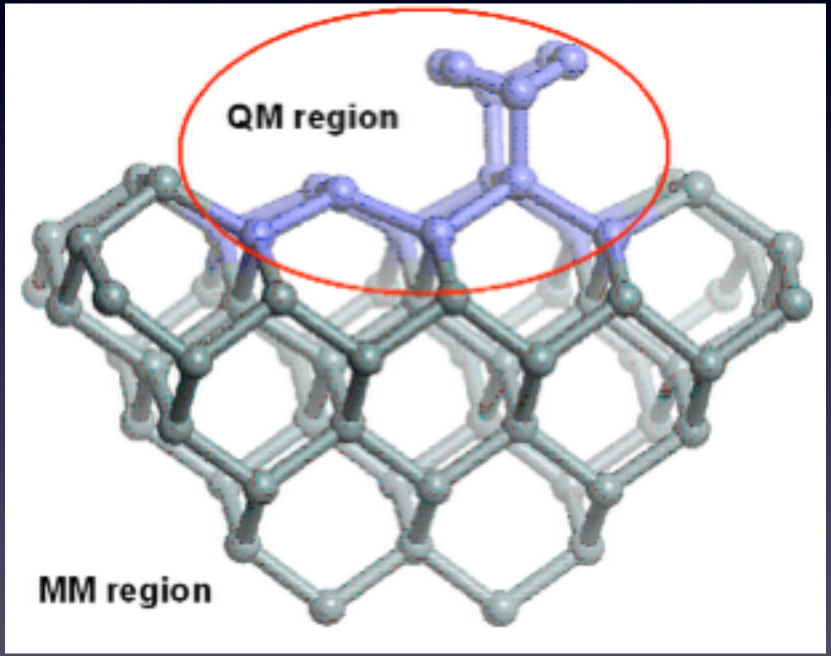

Additive QM / MM

$$E_{\text{total}} = E_{\text{MM,tot}} + E_{\text{QM(QM)}} + E_{\text{QM/MM}}$$



$$E_{\text{MM(QM)}} = E^{\text{el}}_{\text{MM(QM)}} + E^{\text{vdw}}_{\text{MM(QM)}} + E^{\text{b}}_{\text{MM(QM)}}$$

- Electrostatic coupling is the most involved term
- Mechanical embedding possible
- Linked atom scheme
- vdW might need ad hoc parameterisation

Outline

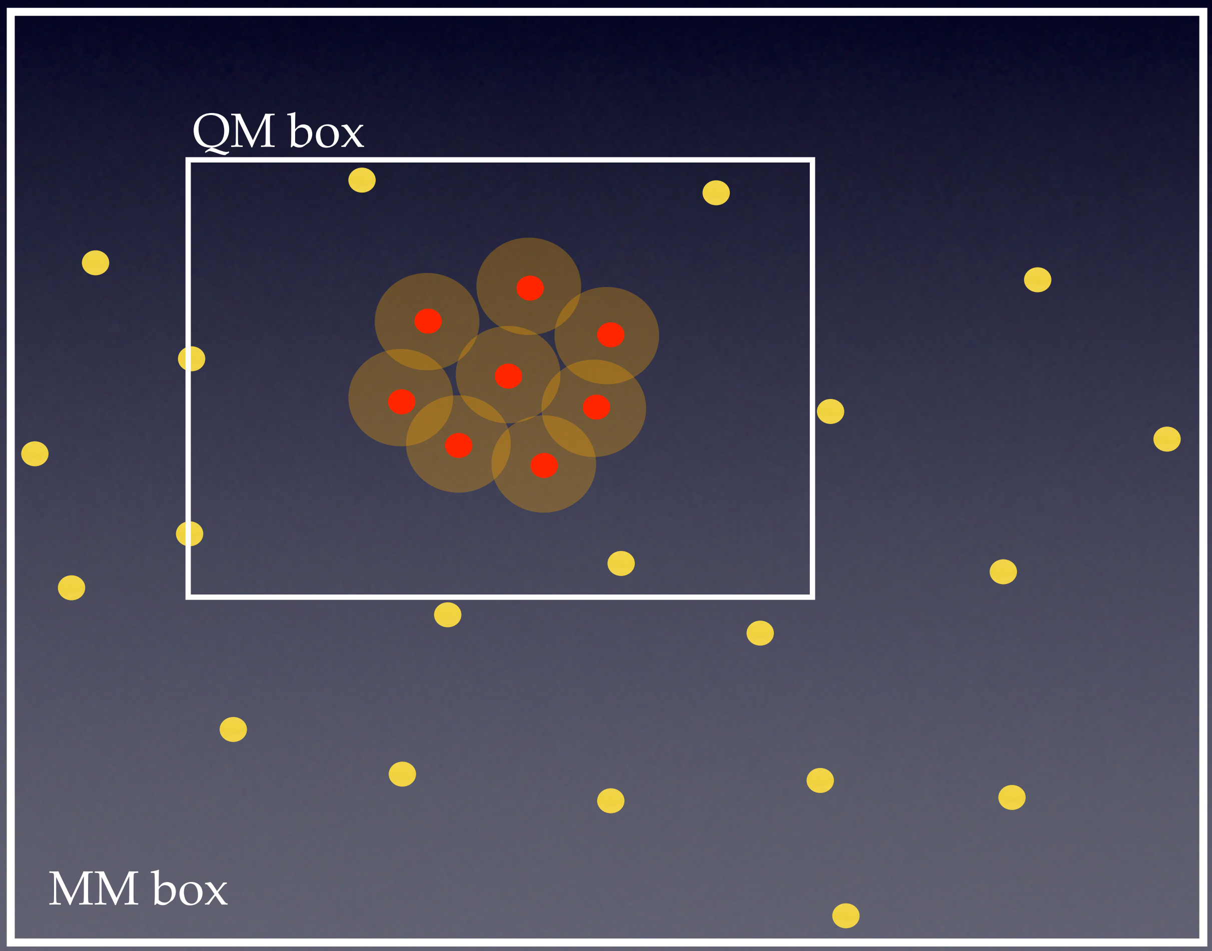
- Overview of the QM/MM methodology
- **Available QM/MM Electrostatic Schemes**
- GEEP: CP2K QM/MM driver
- Charged Oxygen Vacancies in SiO2

Available Electrostatic Schemes

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

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

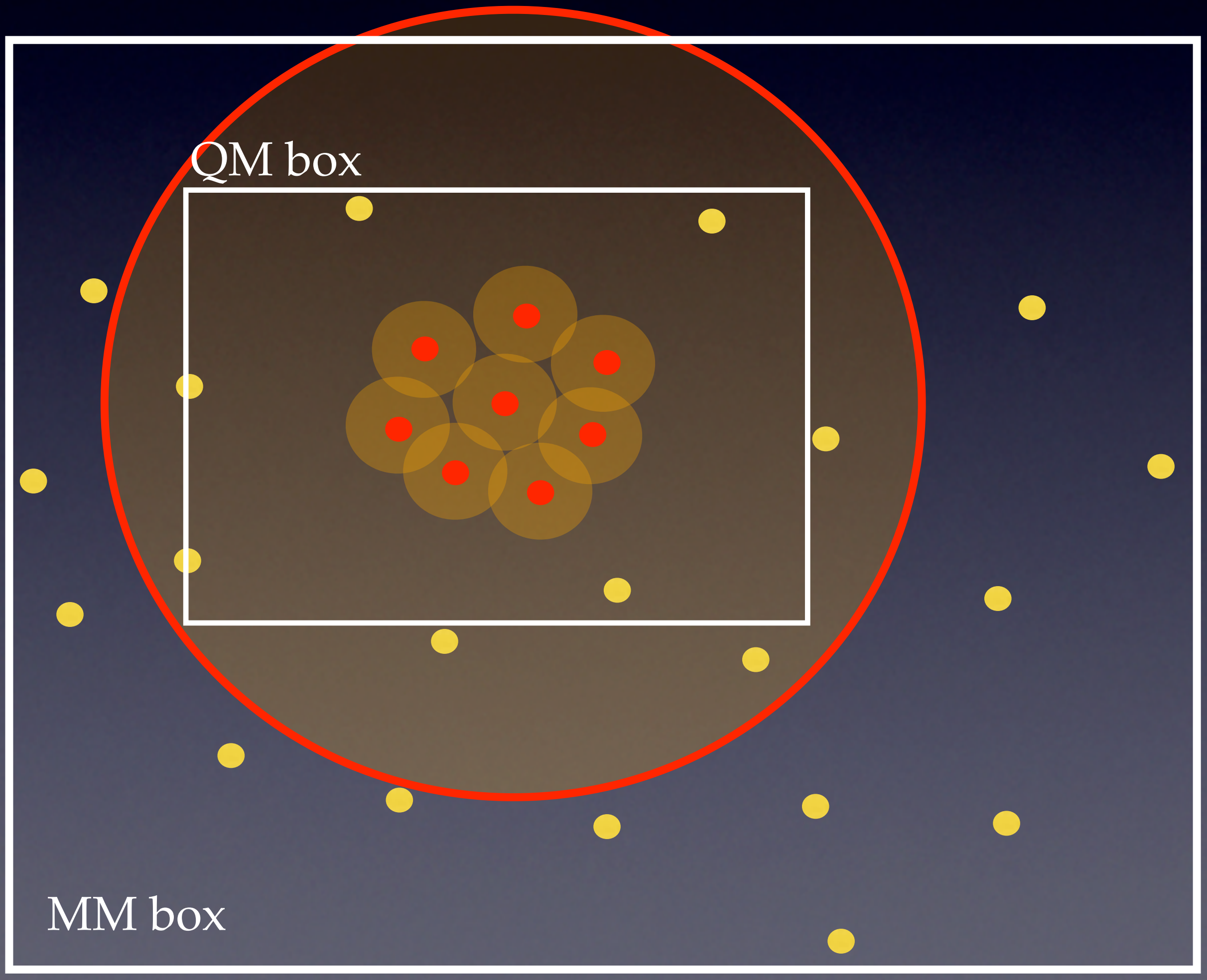
Cost ≈ $N_{MM} * P^1$



Available Electrostatic Schemes

Spherical Cutoff

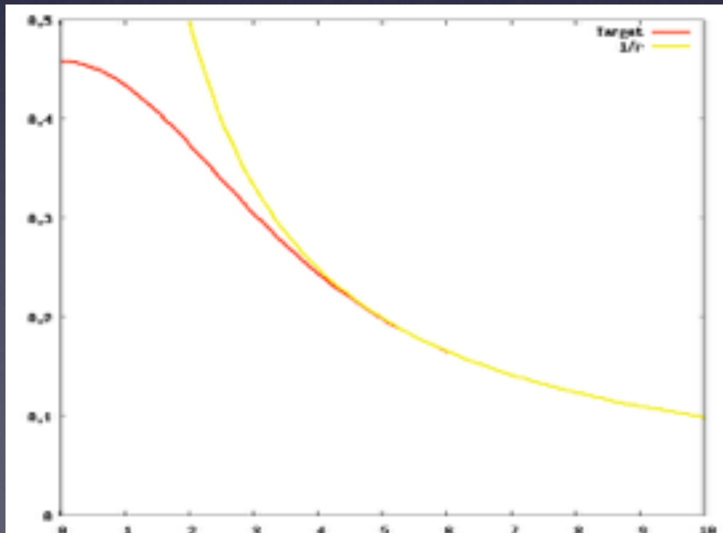
$$\text{Cost} \approx N^{c}_{MM} * P^{1}$$

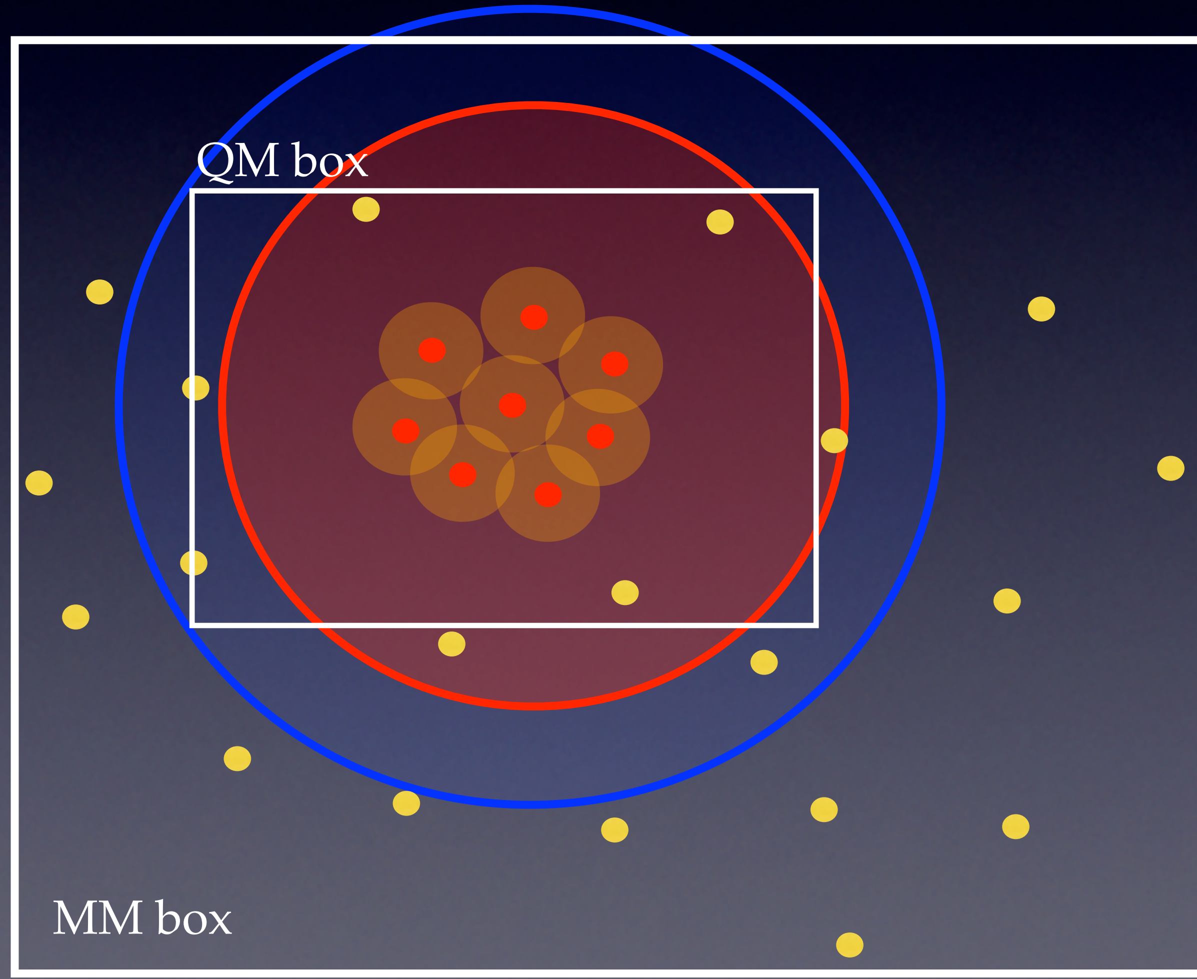


Available Electrostatic Schemes

Multi-pole

Expansion





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

Outline

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- Available QM / MM Electrostatic Schemes
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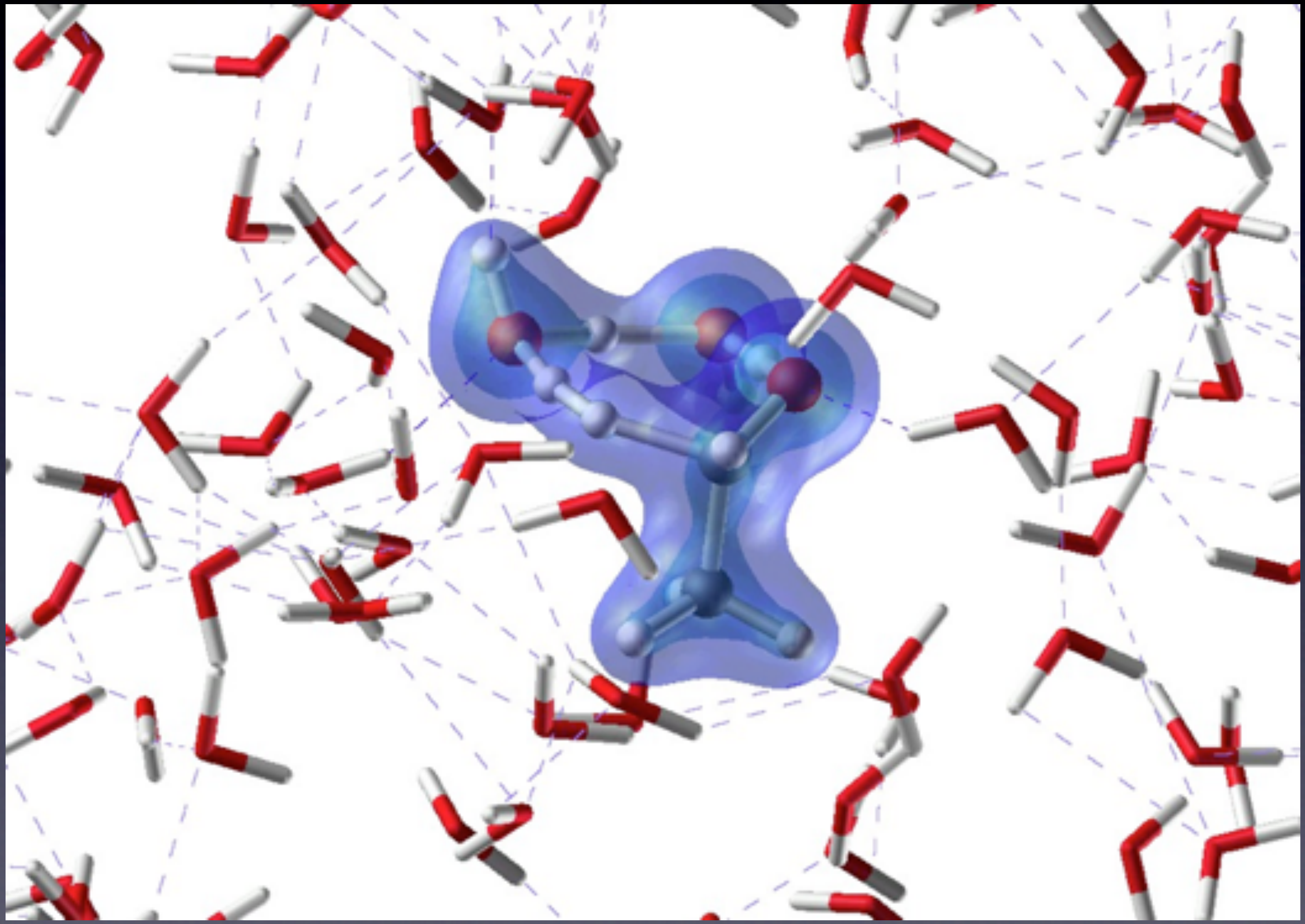
- Charged Oxygen Vacancies in SiO2

QM / MM



QM/MM

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

$$V_{MM}(\vec{r})$$

$$E_{\mathrm{QM/MM}}(\mathbf{R}_{\mathrm{QM}}, \mathbf{R}_{\mathrm{MM}}) = \sum_{\mathrm{MM}} q_{\mathrm{MM}} \int \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_{\mathrm{MM}}|} d\mathbf{r} + \sum_{\mathrm{QM,MM}} u_{\mathrm{vdW}}(\mathbf{R}_{\mathrm{QM}}, \mathbf{R}_{\mathrm{MM}})$$

QM / MM

$$H_{QM/MM} = \sum_{\mu\nu}^{occ} P^{\mu\nu} \sum_{MM} \int \phi_\mu(\vec{r}) \cdot \frac{q_{MM}}{|\vec{R}_{MM} - \vec{r}|} \cdot \phi_\nu(\vec{r})$$

Gaussians

$$H_{QM/MM} = \int V_{MM}(\vec{r})\tilde{n}(\vec{r})$$

Plane Waves

Gaussian charge distribution

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

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

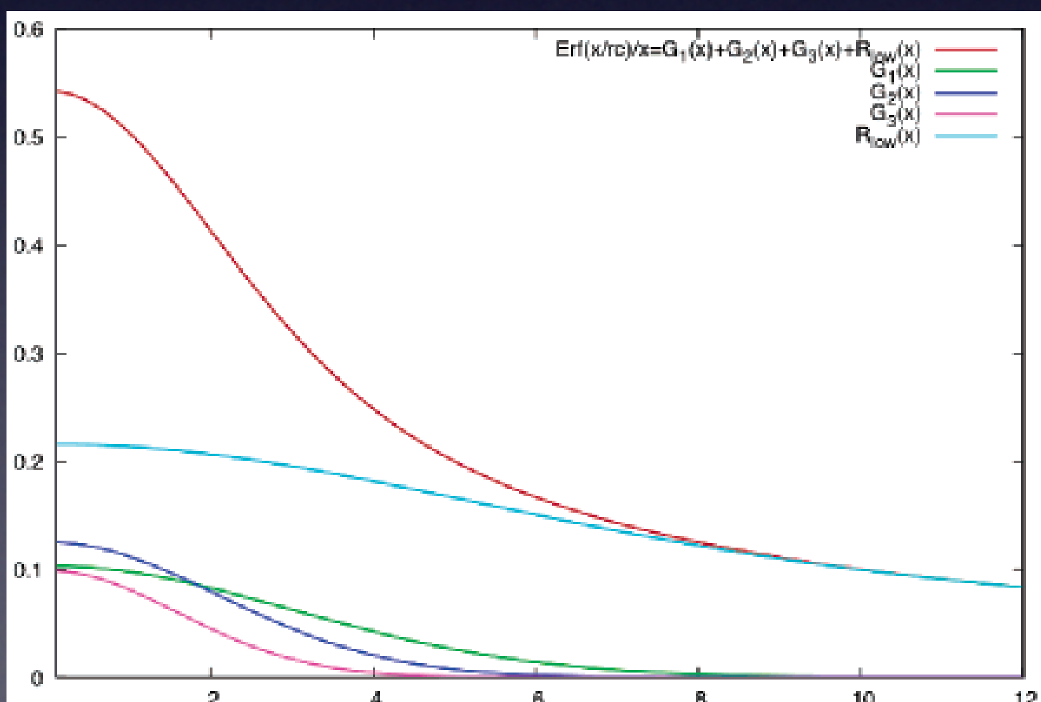
prevent spill out problem
accelerate calculations of electrostatics

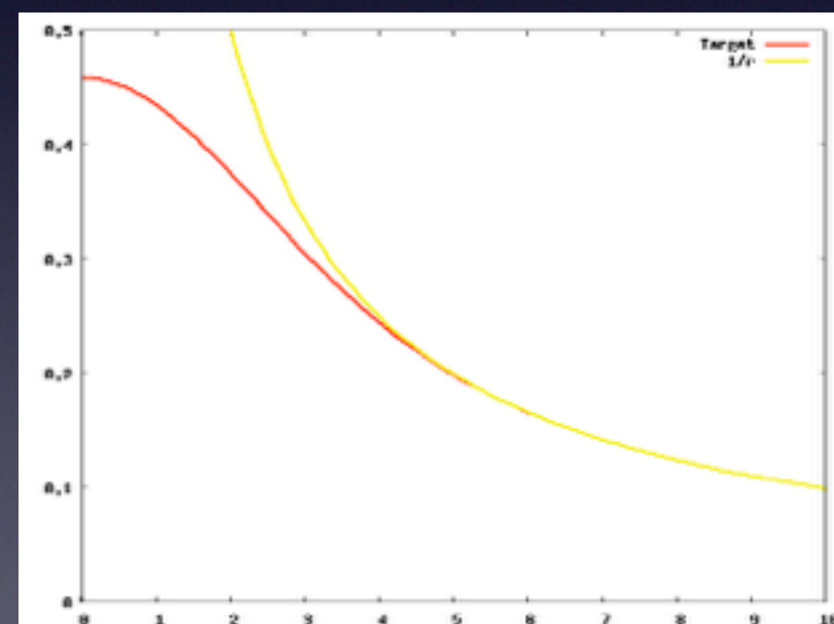
GEEP

Sum of functions with different cutoffs, derived from the new Gaussian expansion of the electrostatic potential

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

Energy [a.u.]



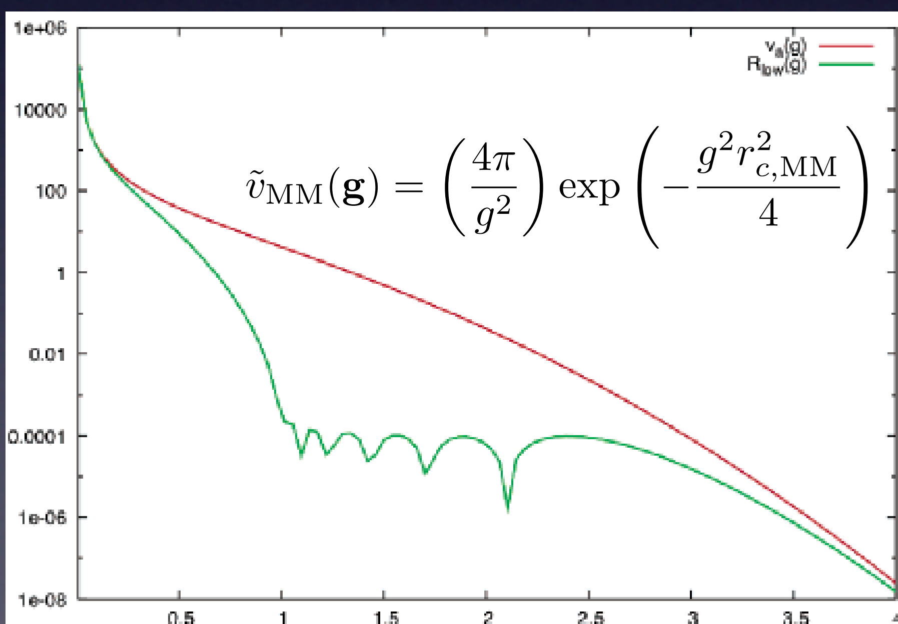


Distance

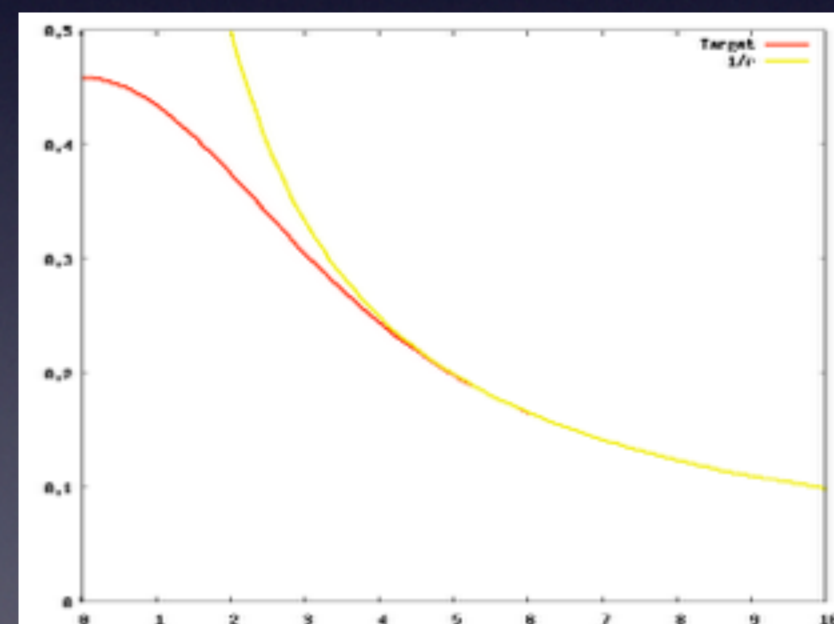
GEEP

Sum of functions with different cutoffs, derived from the new Gaussian expansion of the electrostatic potential

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



G vectors



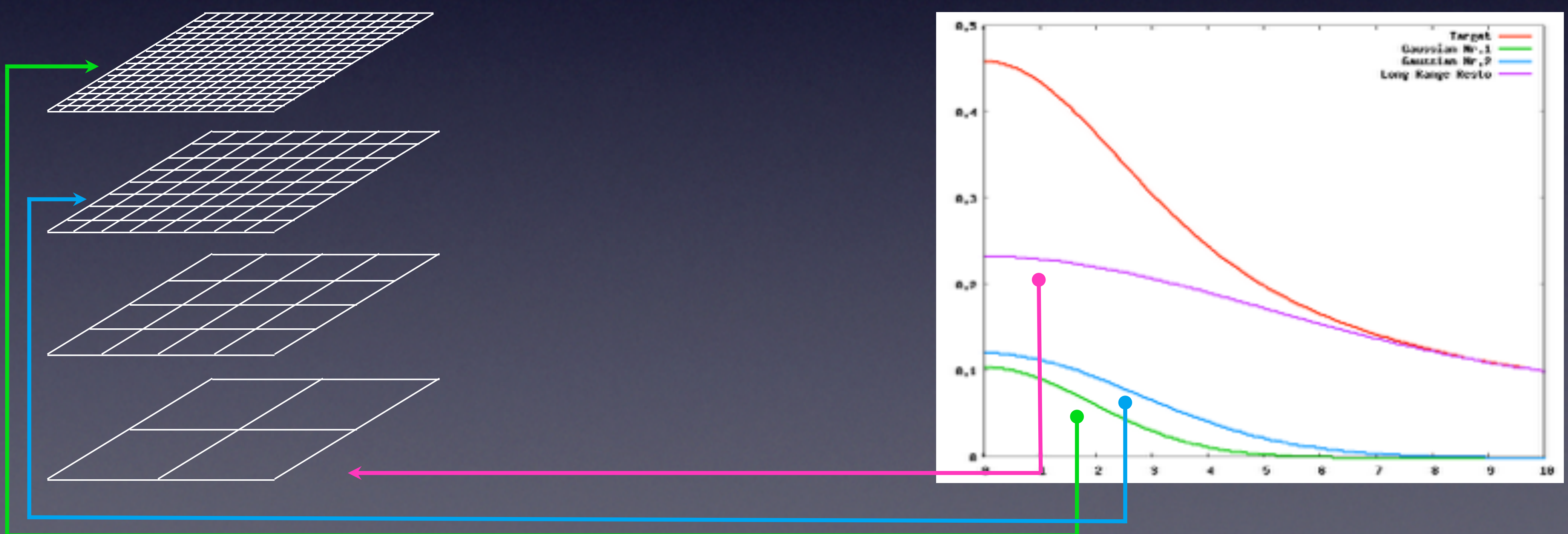
Distance

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

Multigrid Framework

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

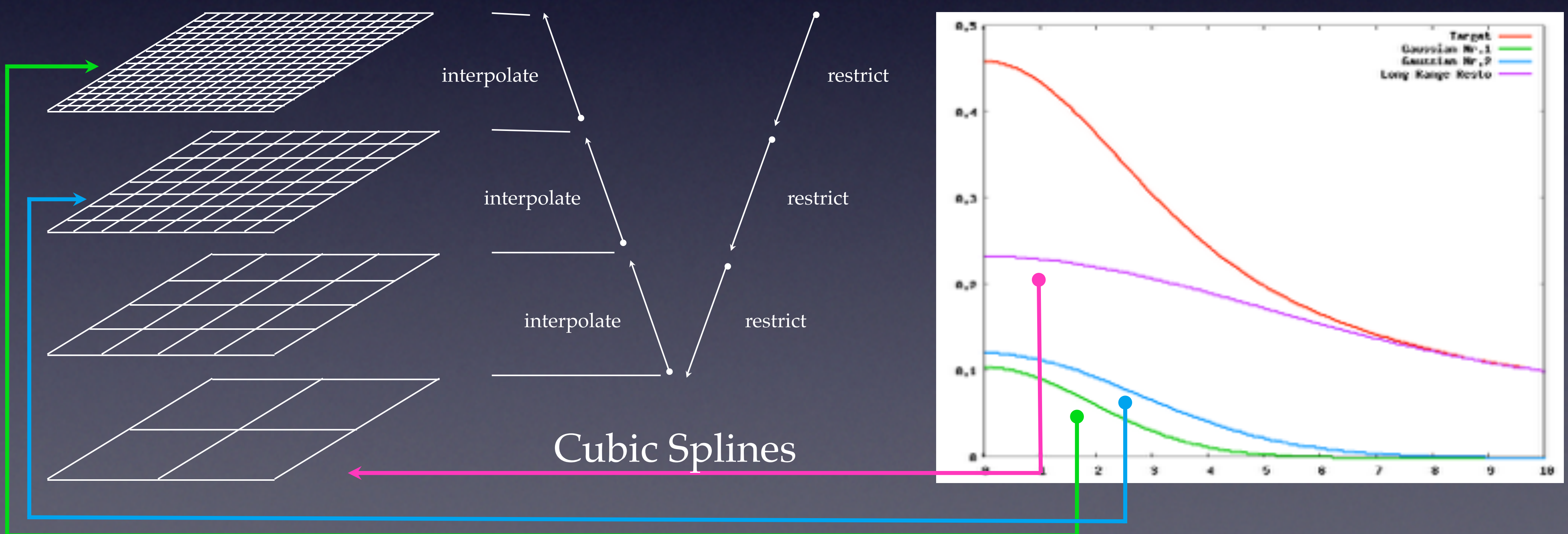
$$N_{i+1} = 8N_i$$



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

Multigrid Framework

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

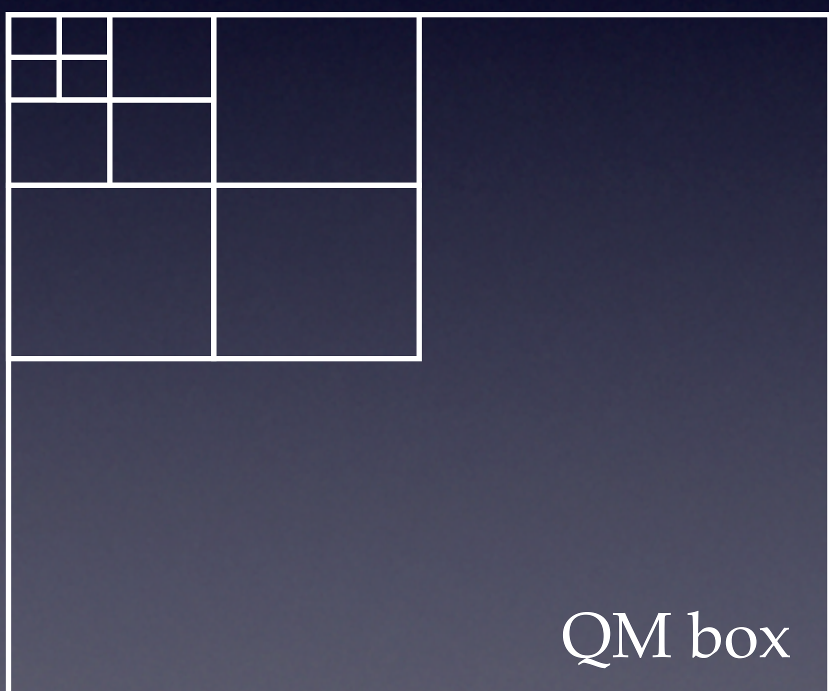


T. Laino, F. Mohamed, A. Laio and M. Parrinello, *J. Chem. Th. Comp.*, 1, **2005**, pp. 1176-1184

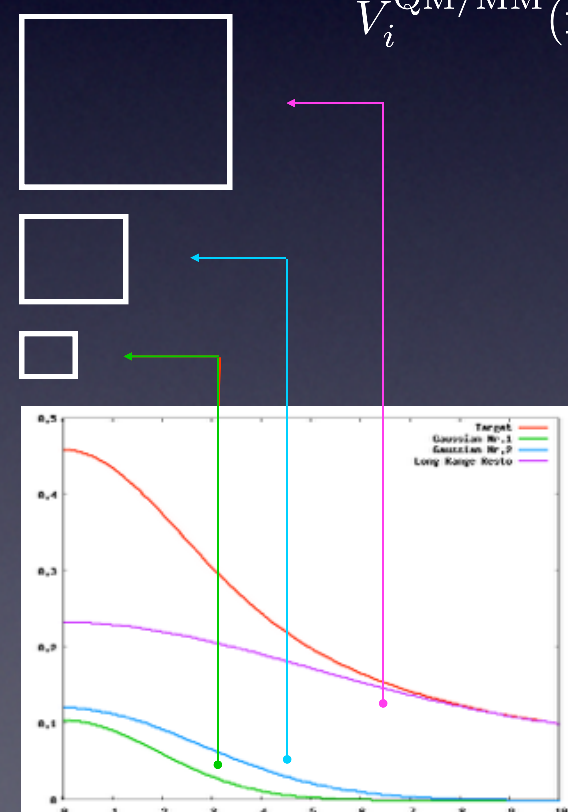
Collocation in the QM Box

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

potential on the finest QM grid

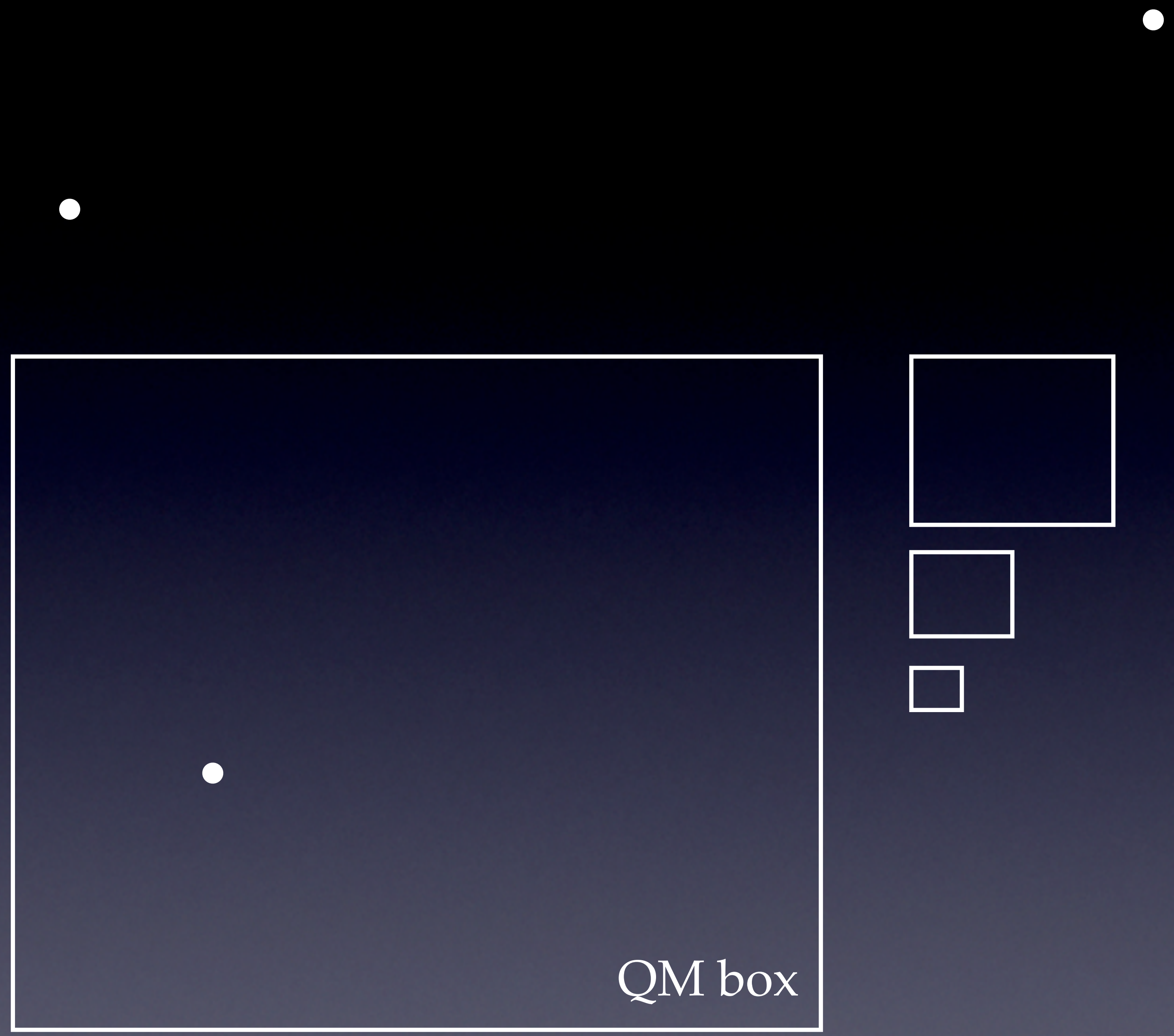


$$V_i^{\mathrm{QM/MM}}(\mathbf{r}, \mathbf{R}_{\mathrm{MM}}) = \sum_{\mathrm{MM}} v_{\mathrm{MM}}^i(\mathbf{r}, \mathbf{R}_{\mathrm{MM}})$$

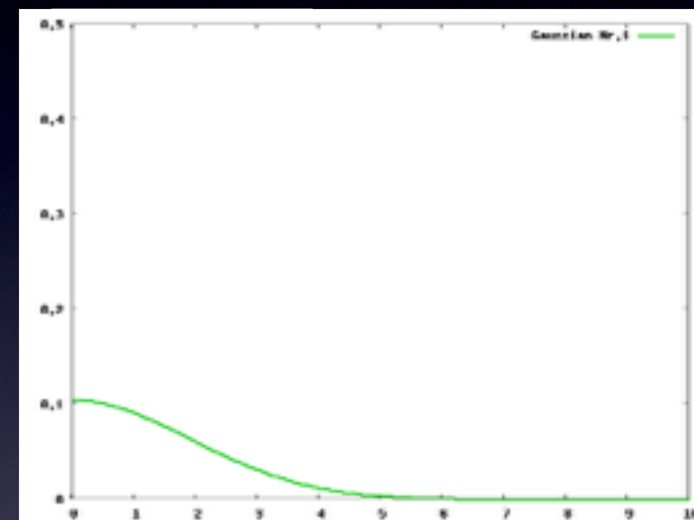


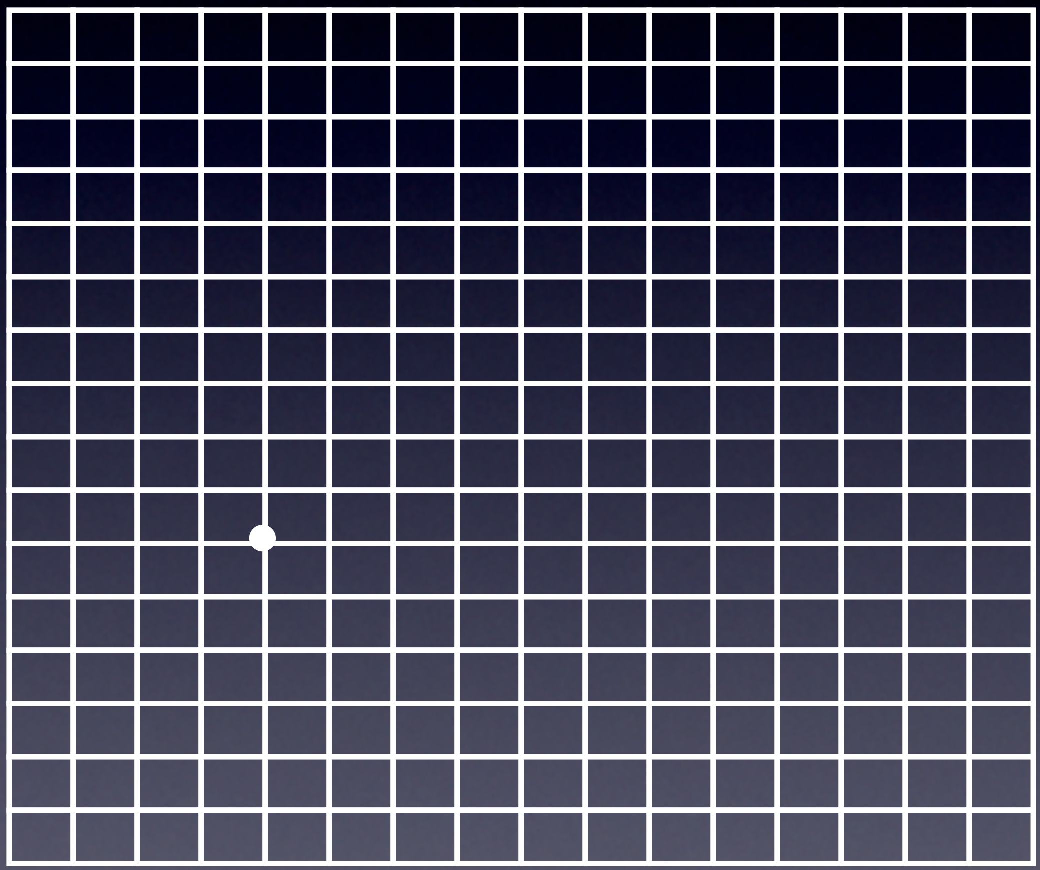
optimal grid levels

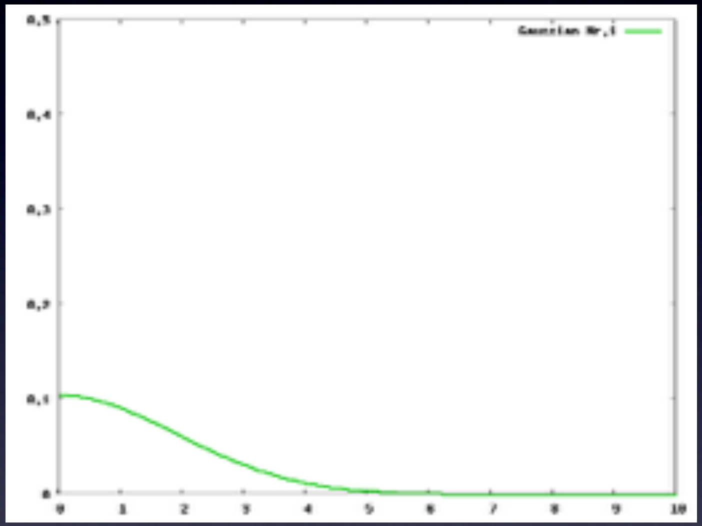
60-80% of time


QM box

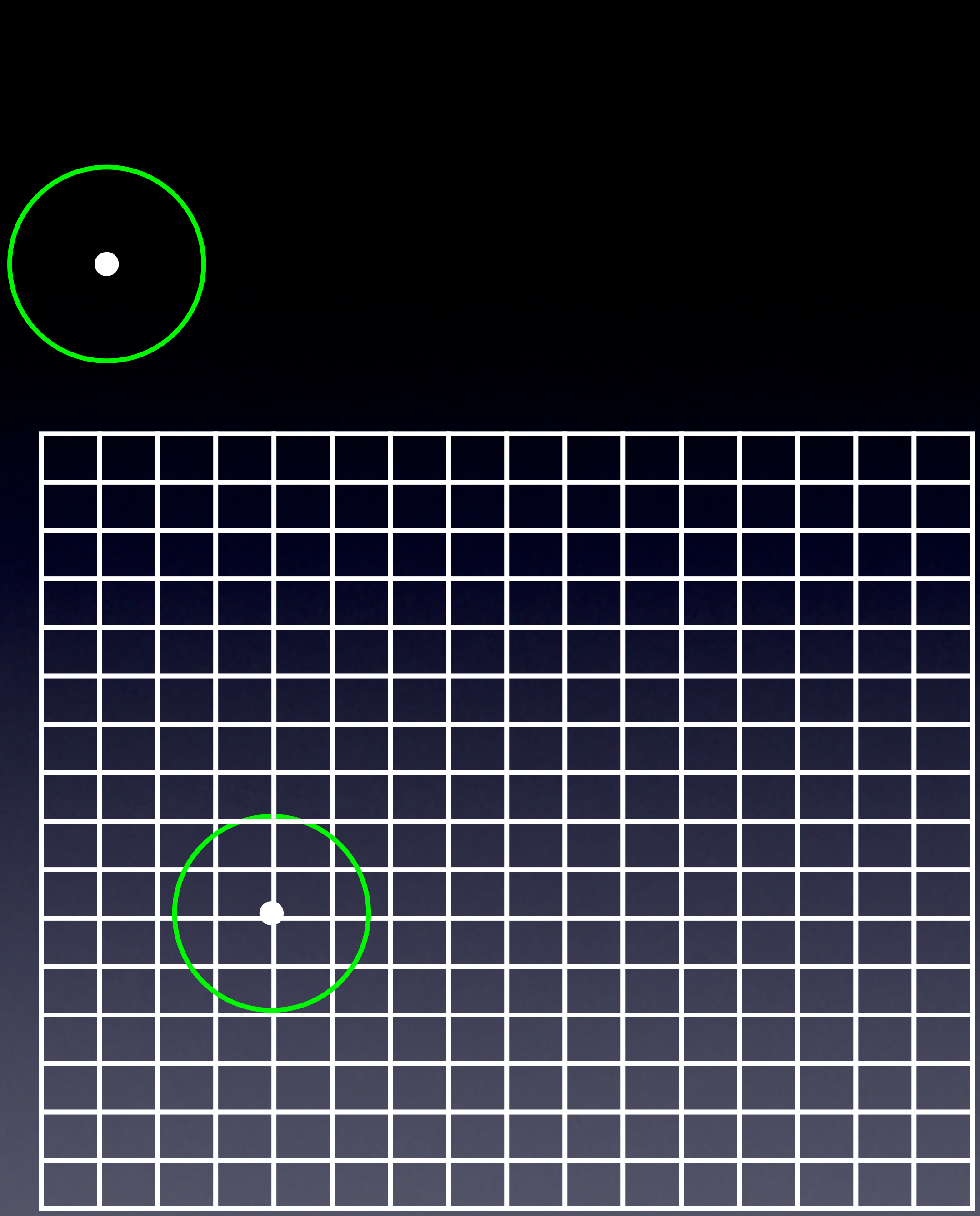

QM box

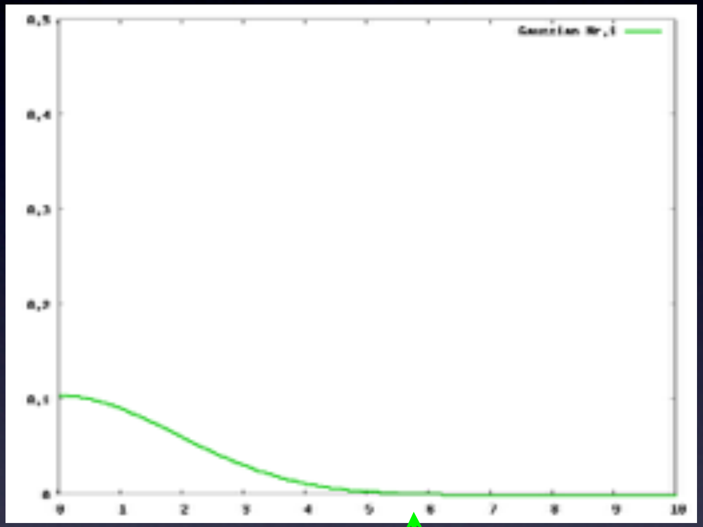




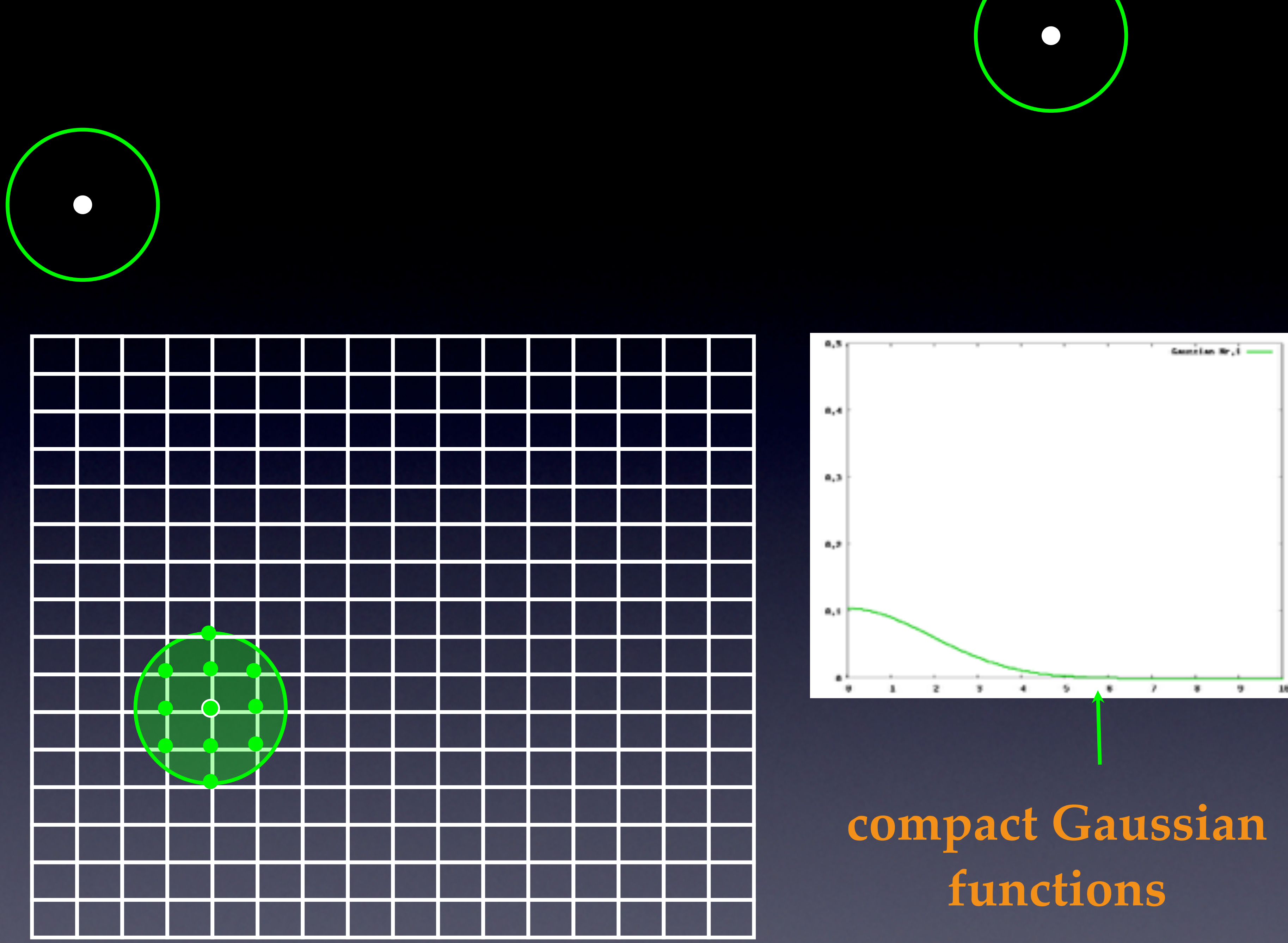


compact Gaussian functions

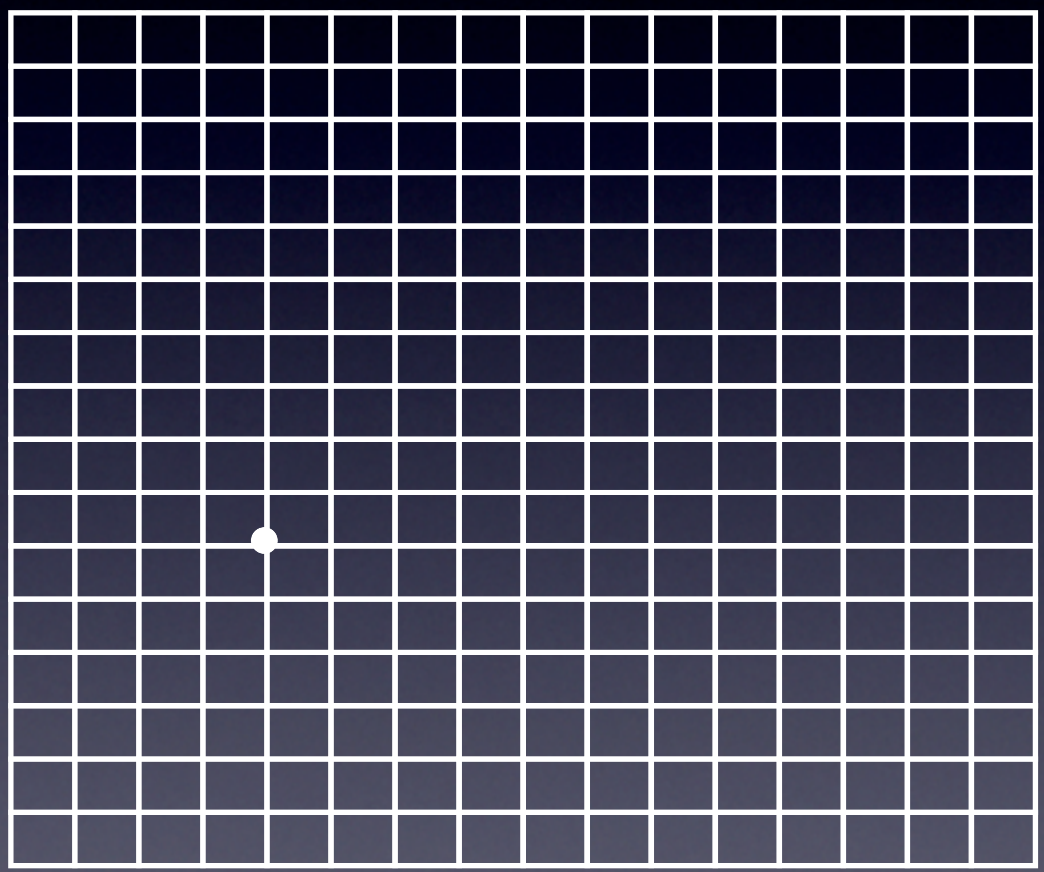


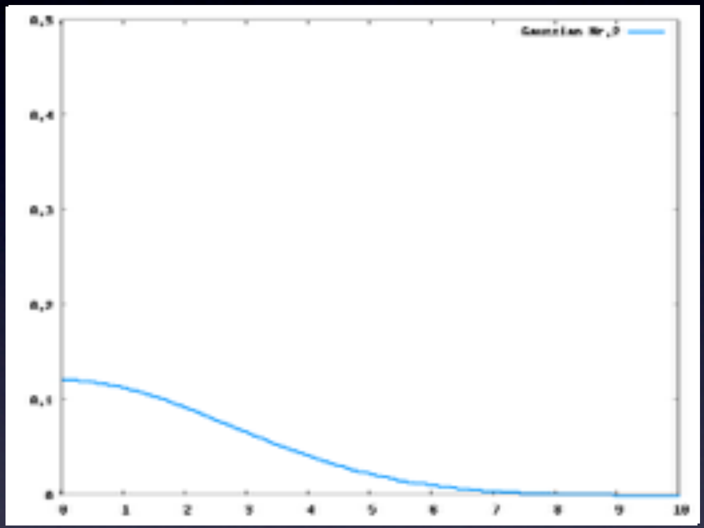


compact Gaussian functions

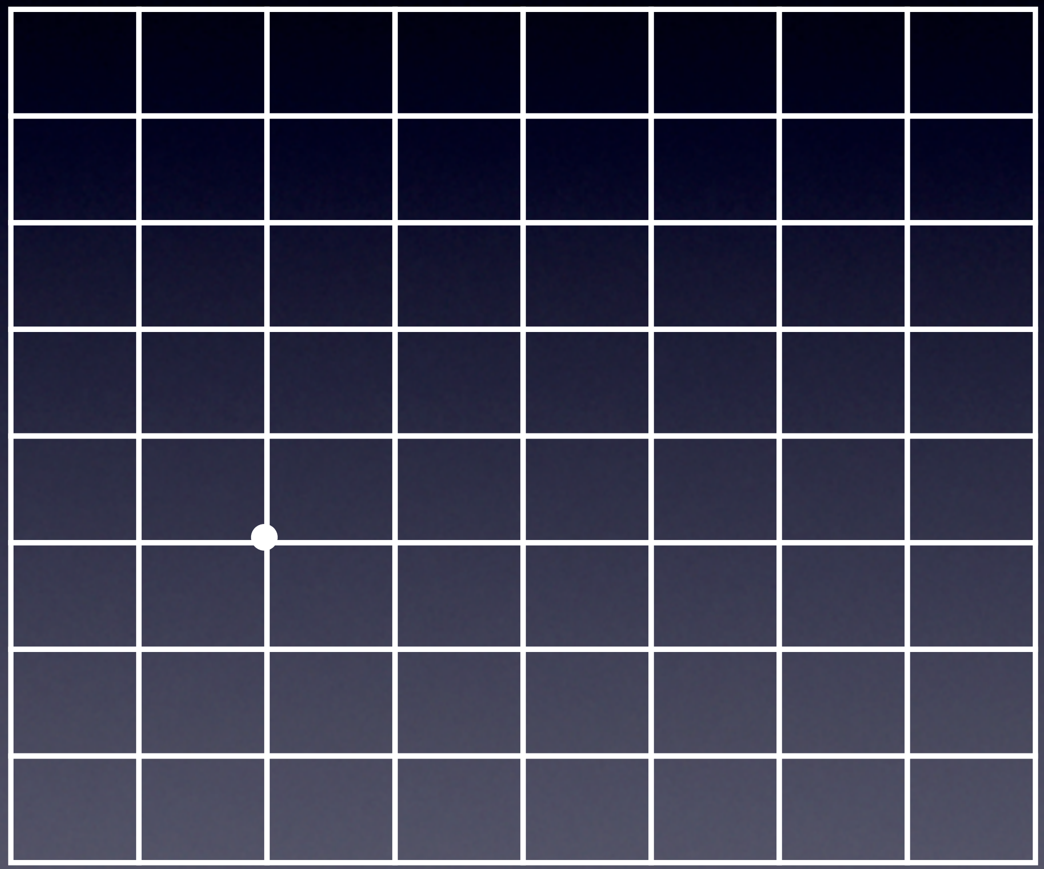


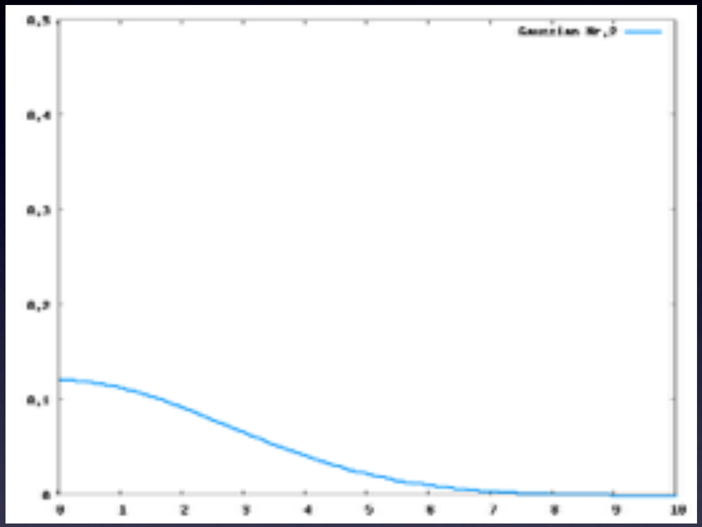
compact Gaussian functions





compact Gaussian functions

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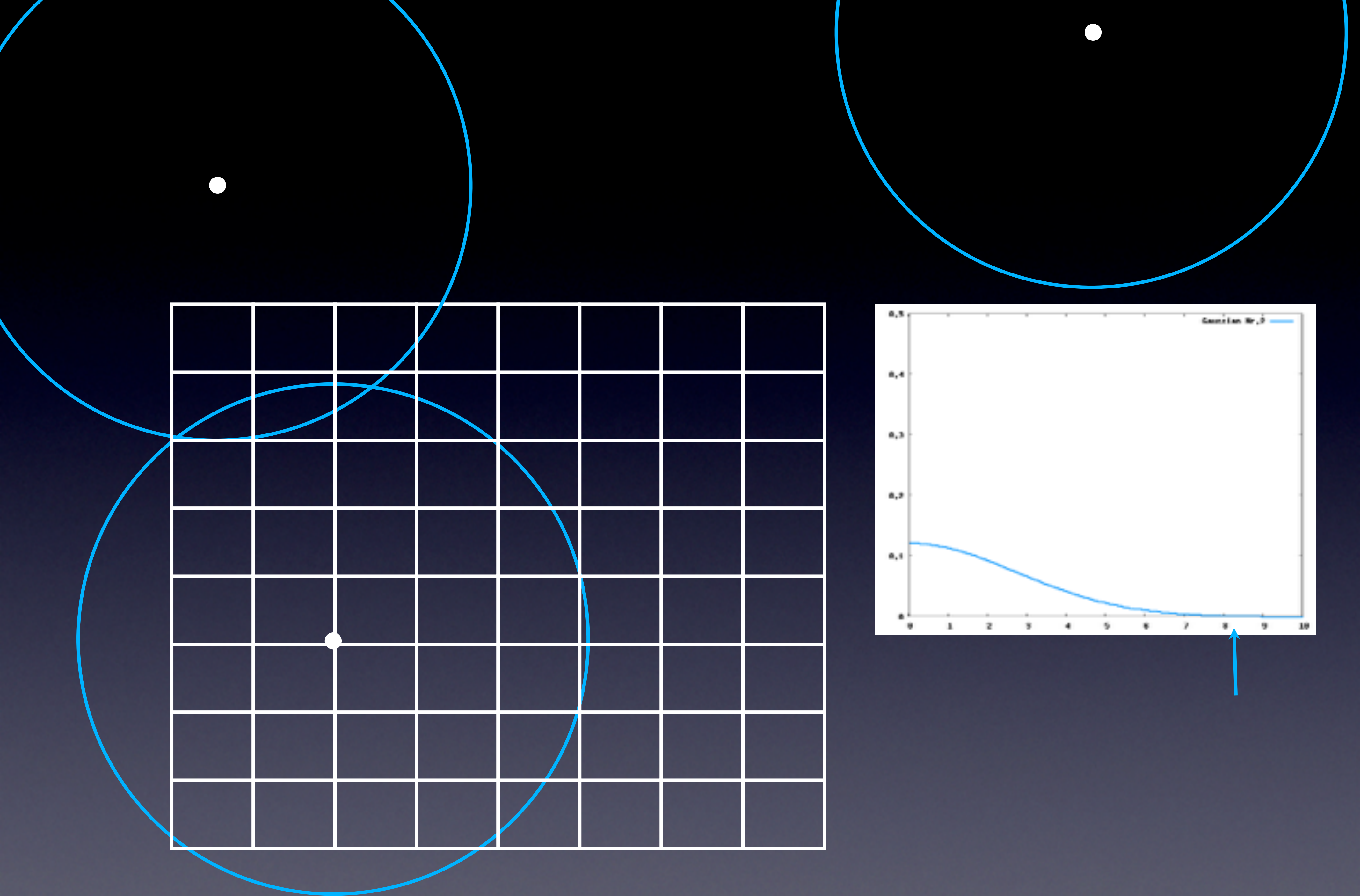
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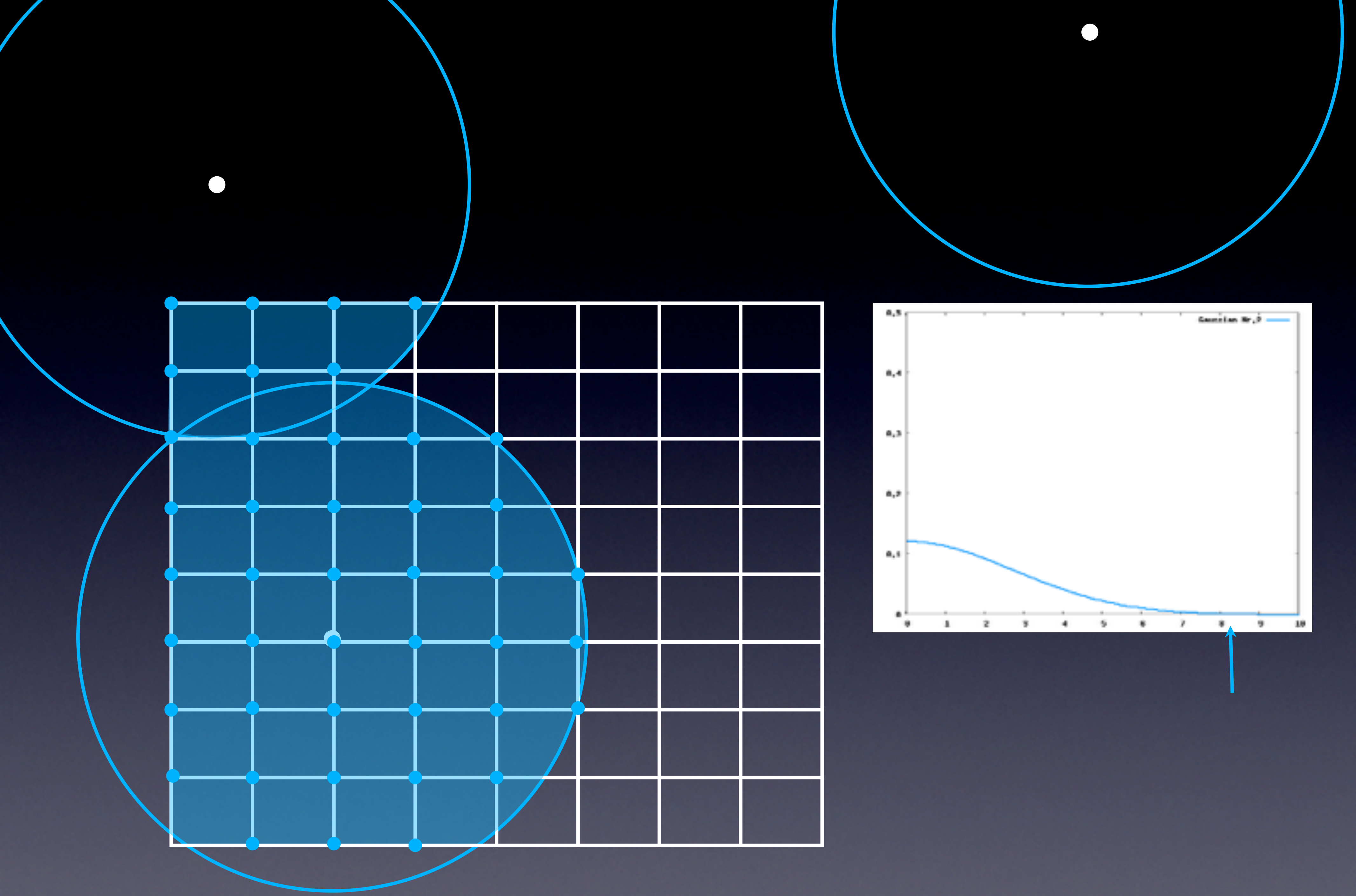

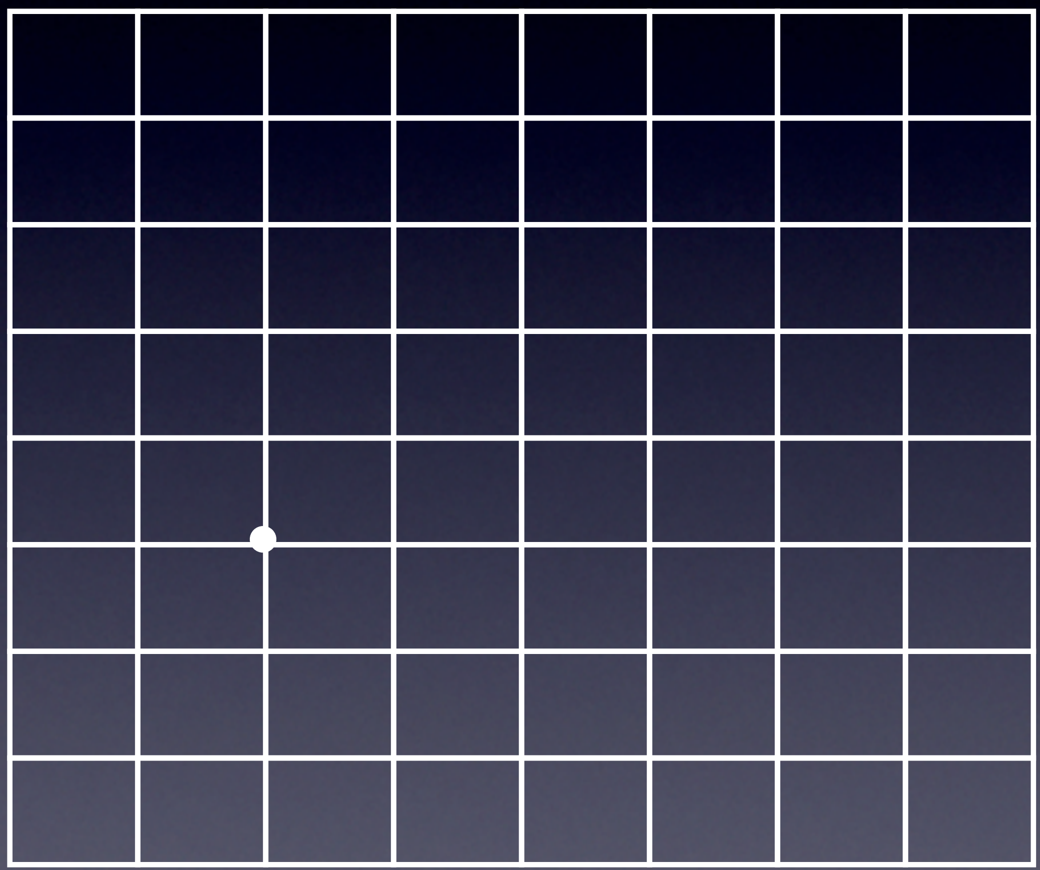

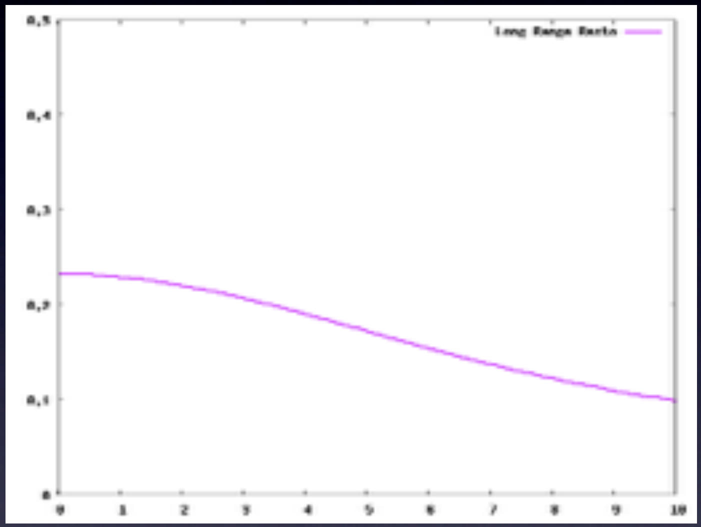
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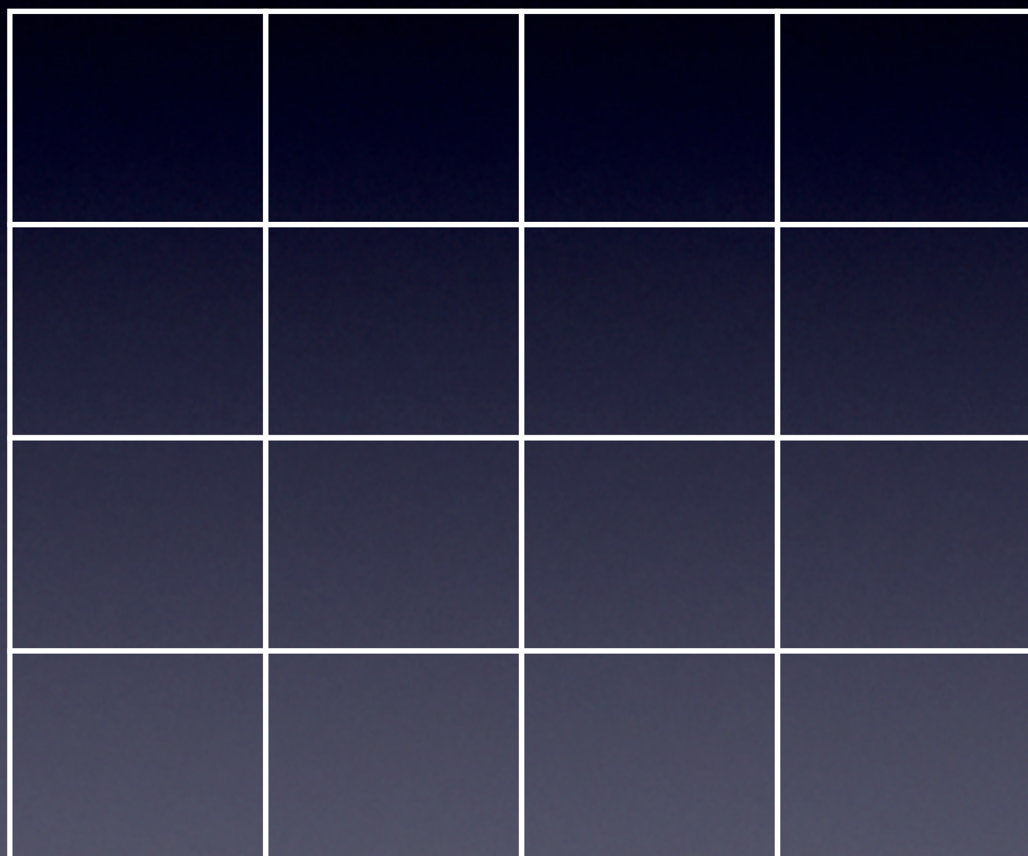

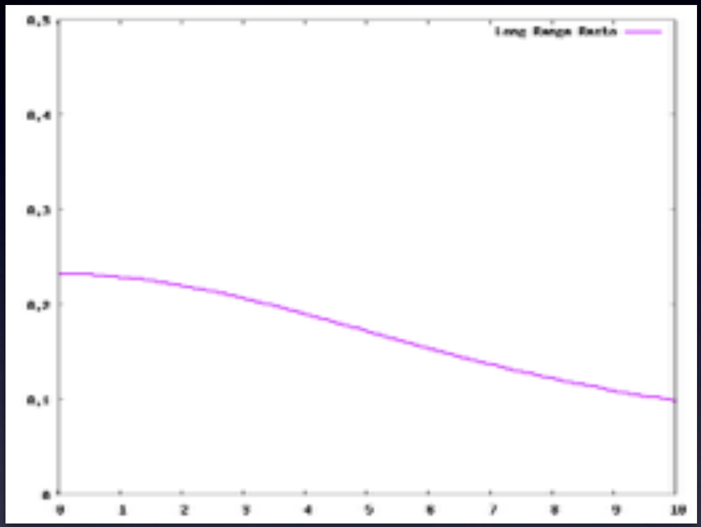
Long Range Ratio
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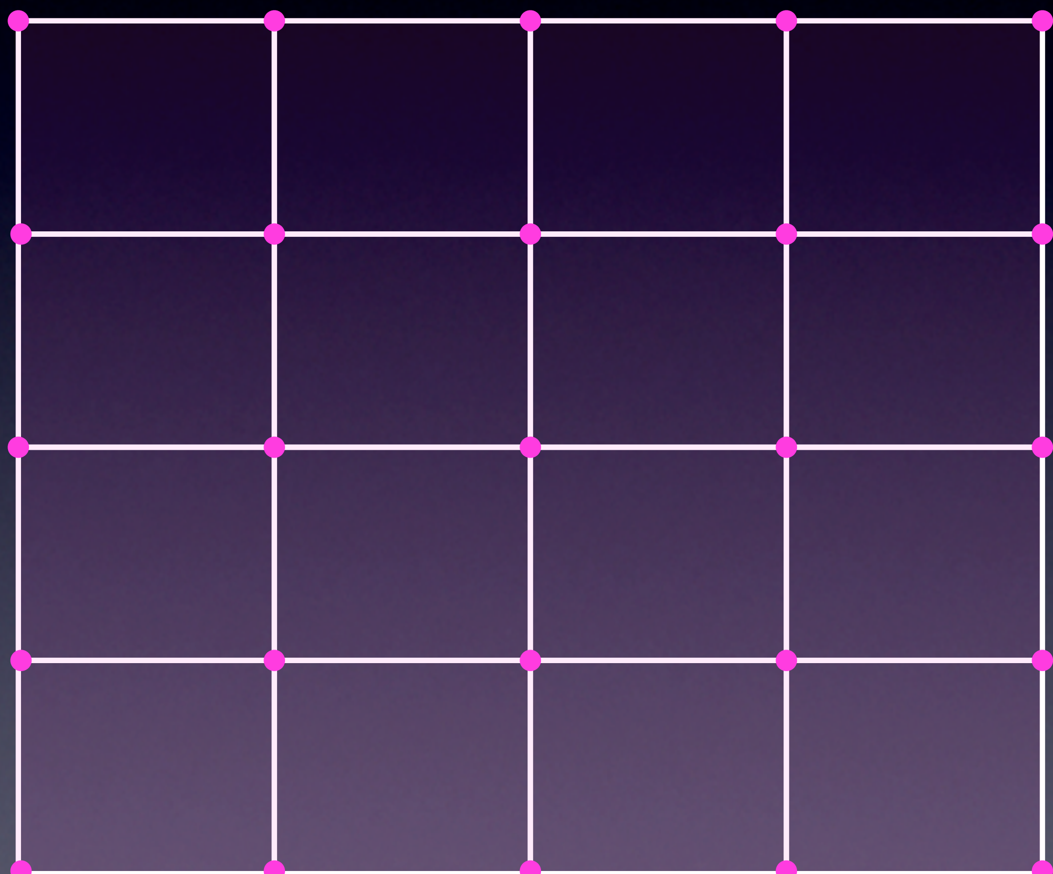

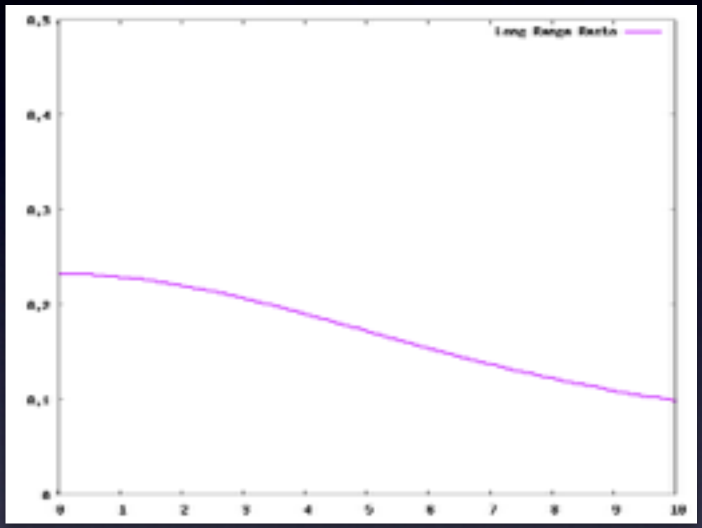

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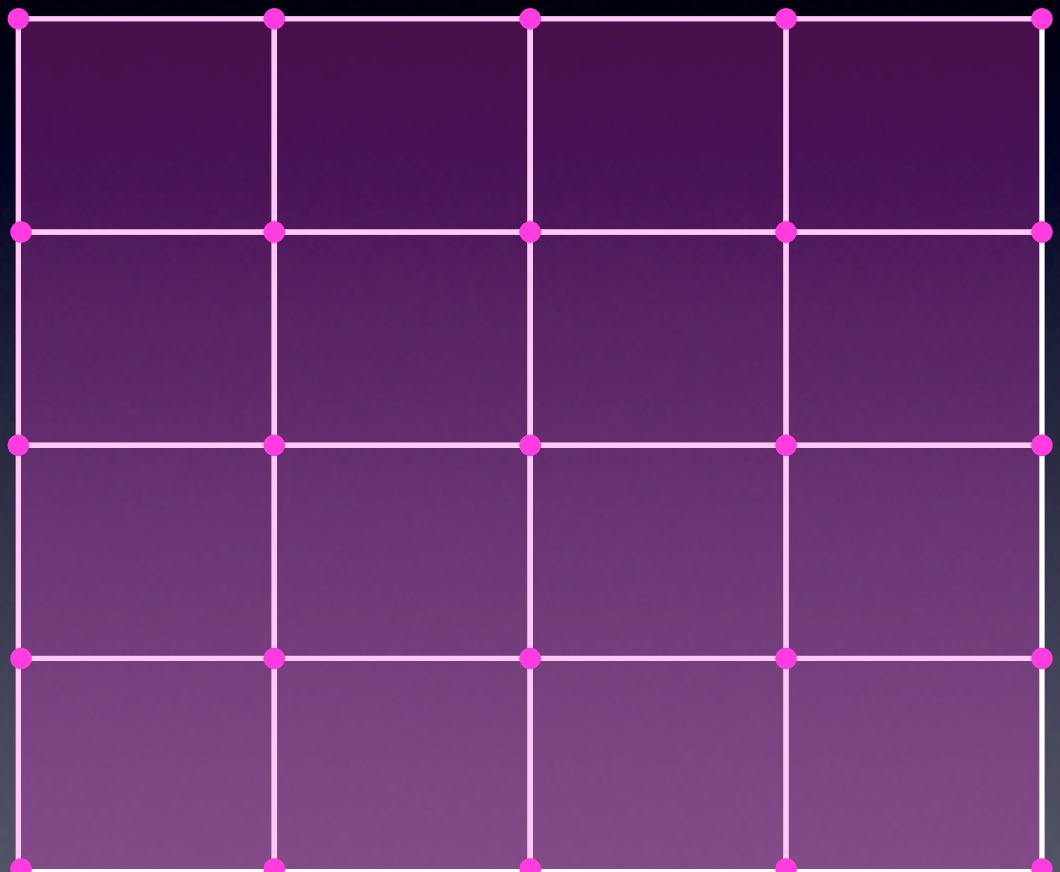

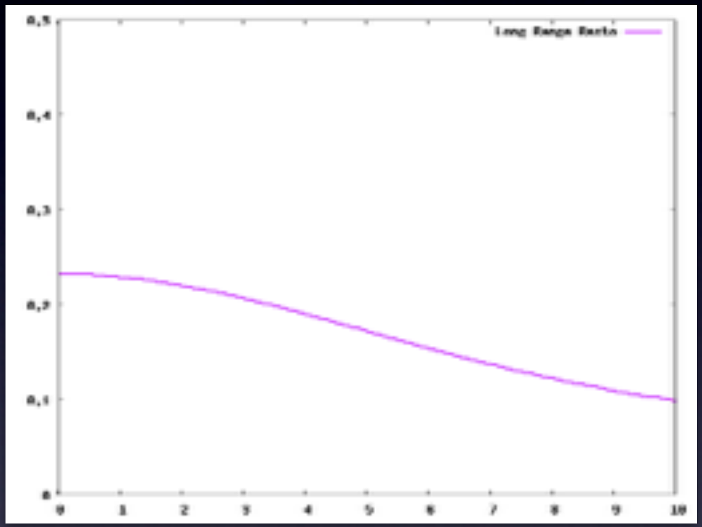
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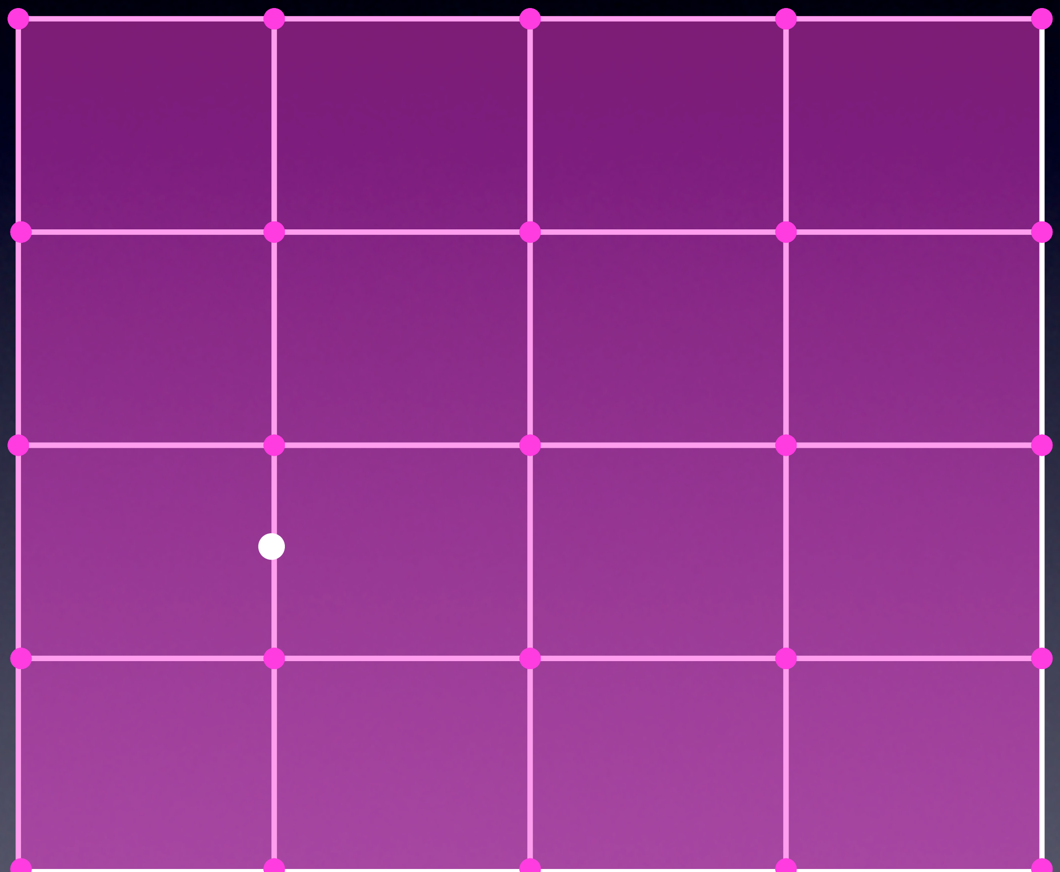

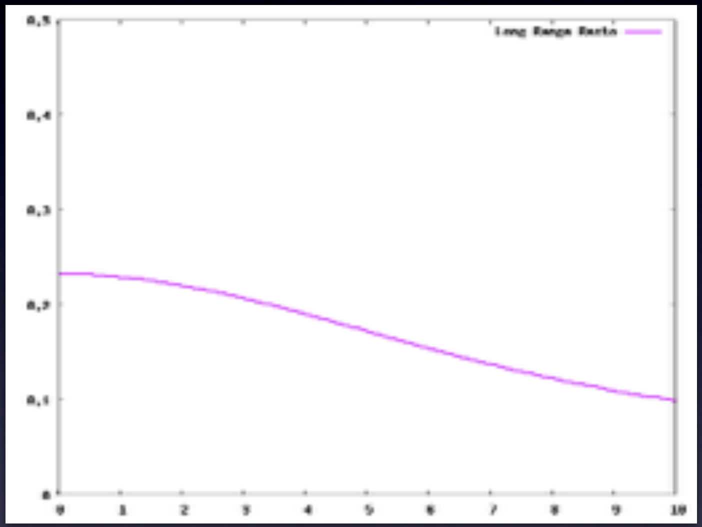
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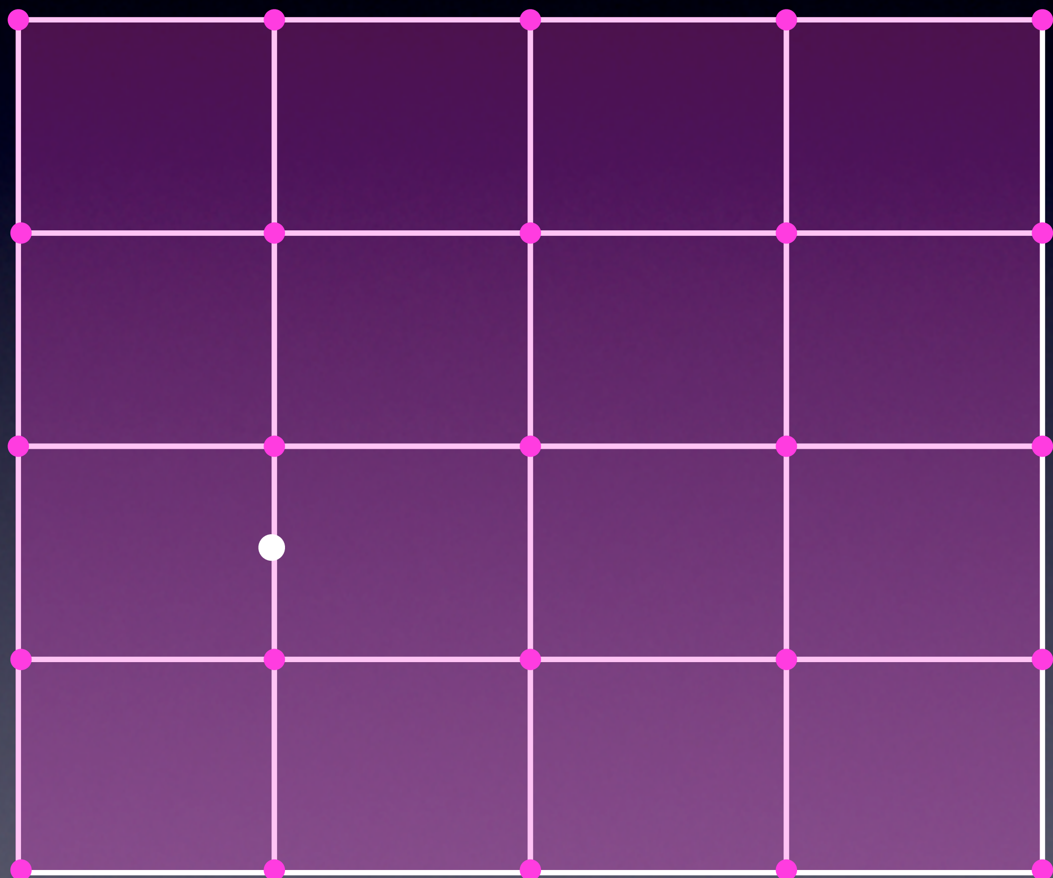
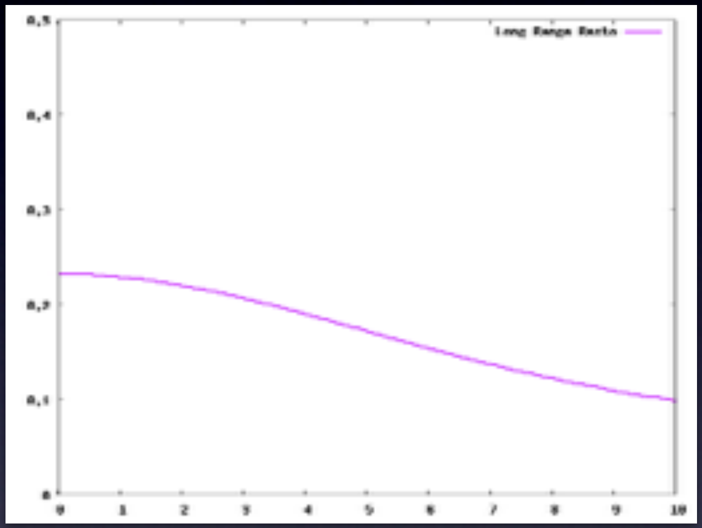
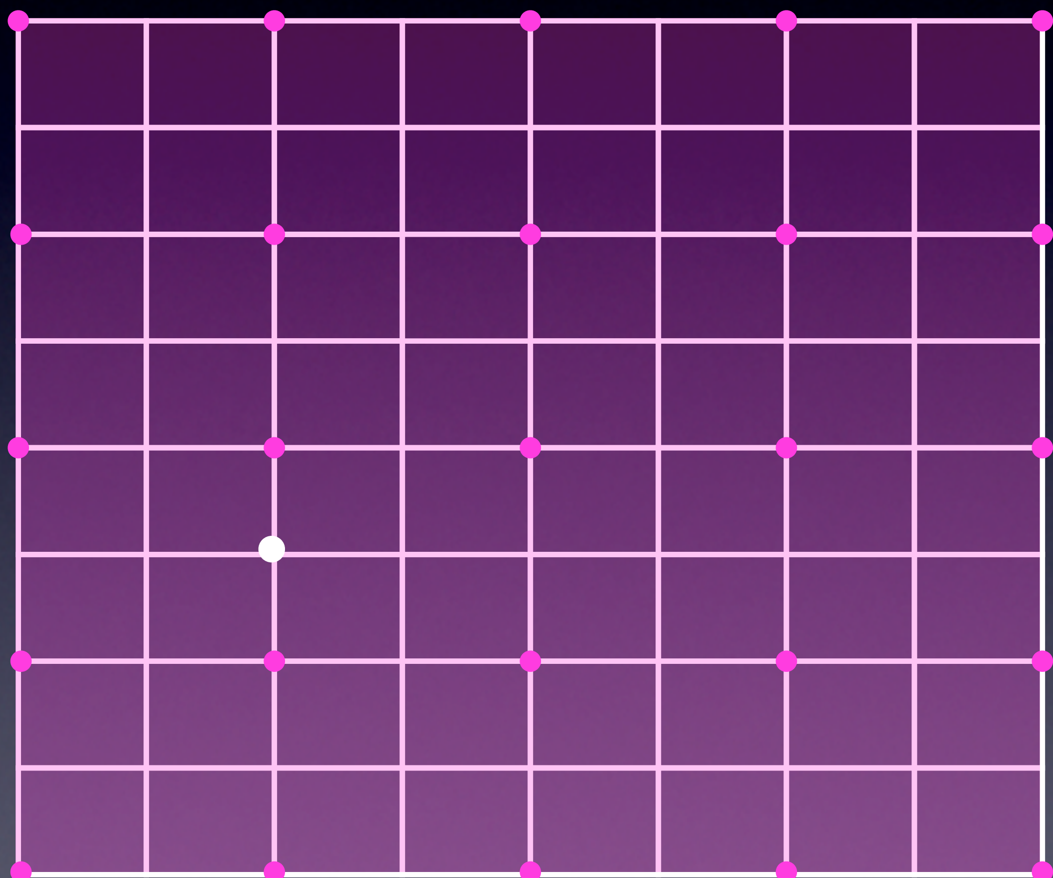
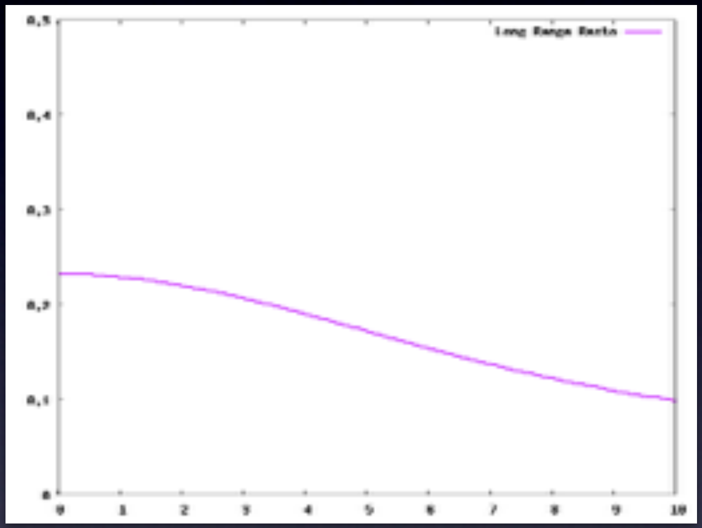




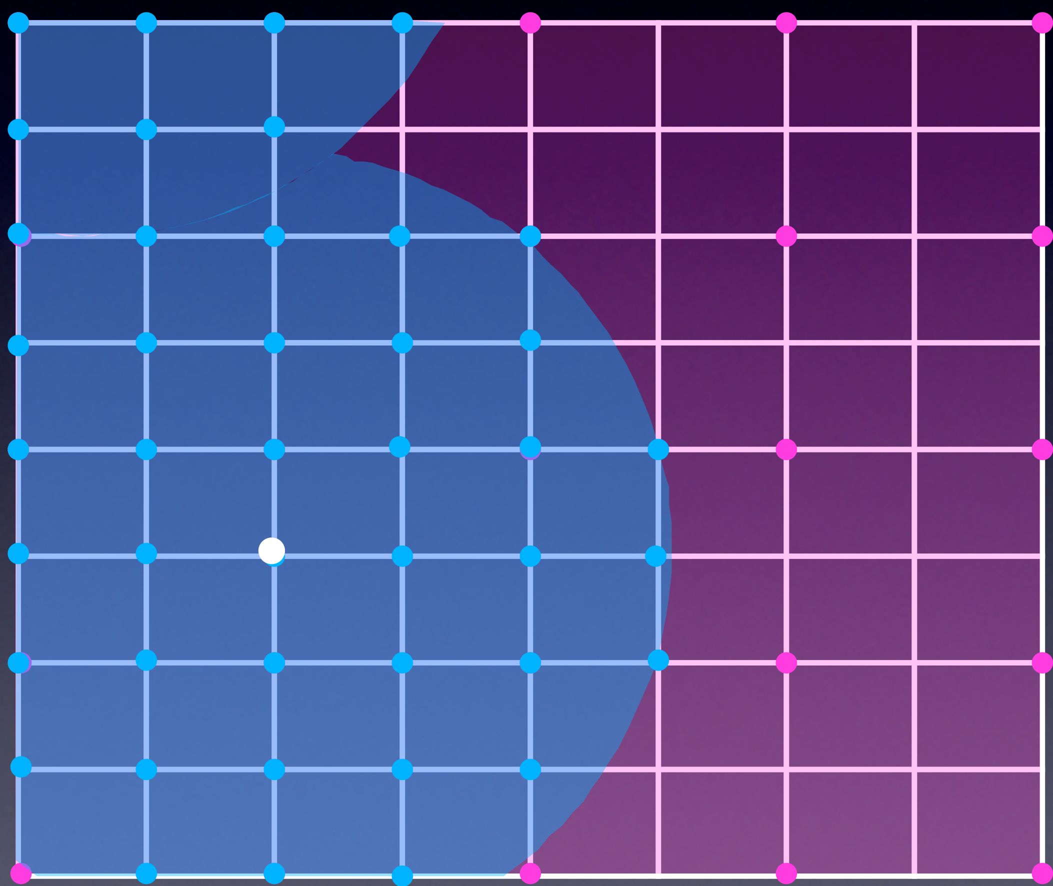
Scaling ~ Nc^3

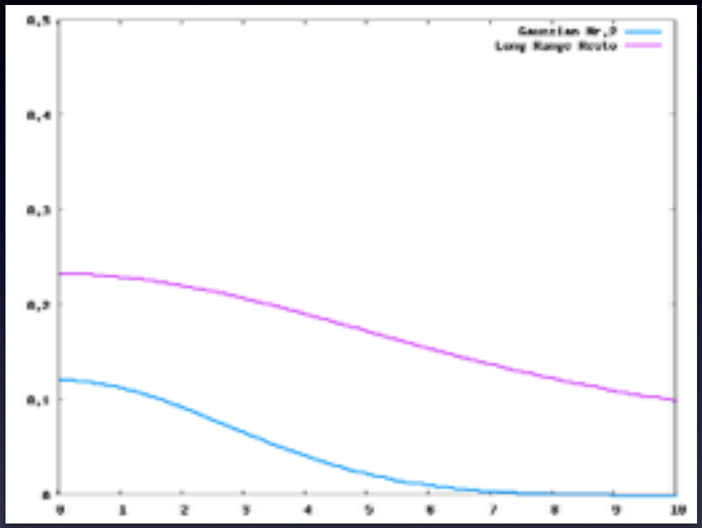




real space interpolation from coarsest to finest

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





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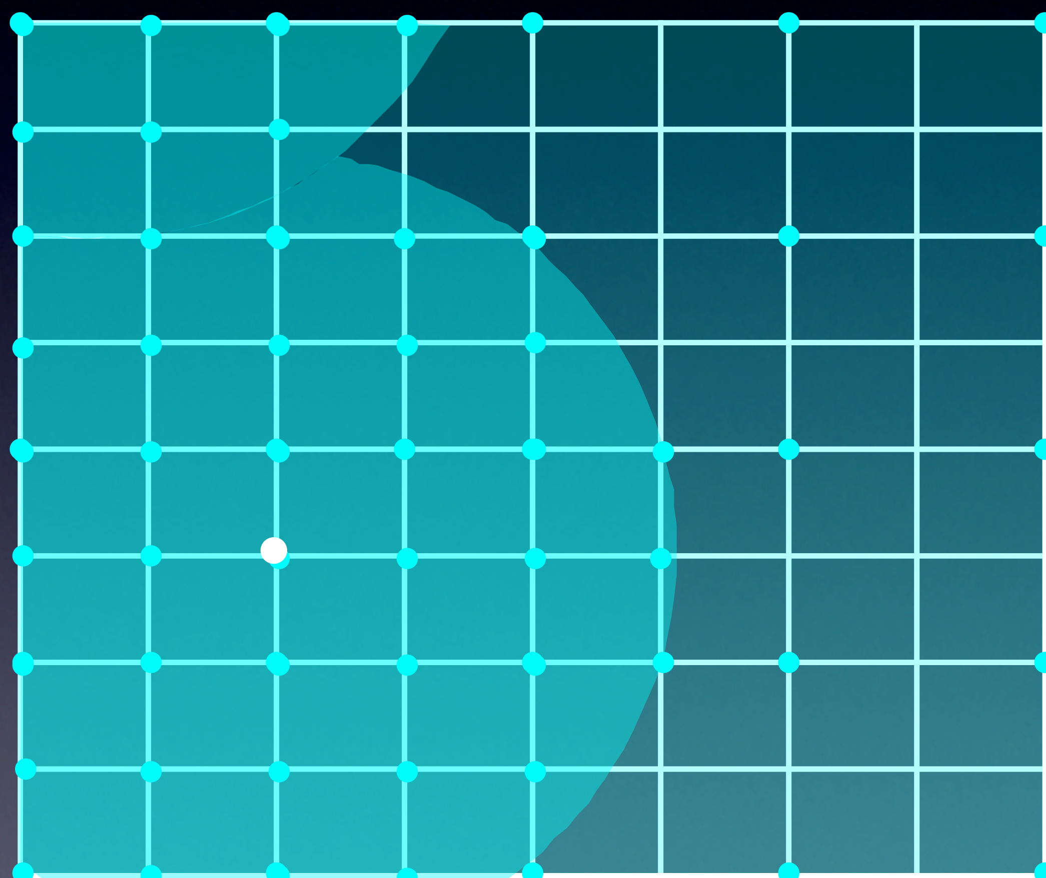
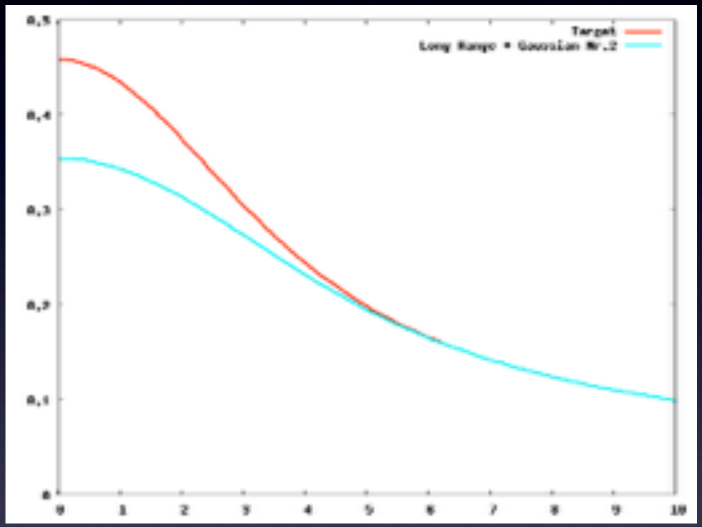
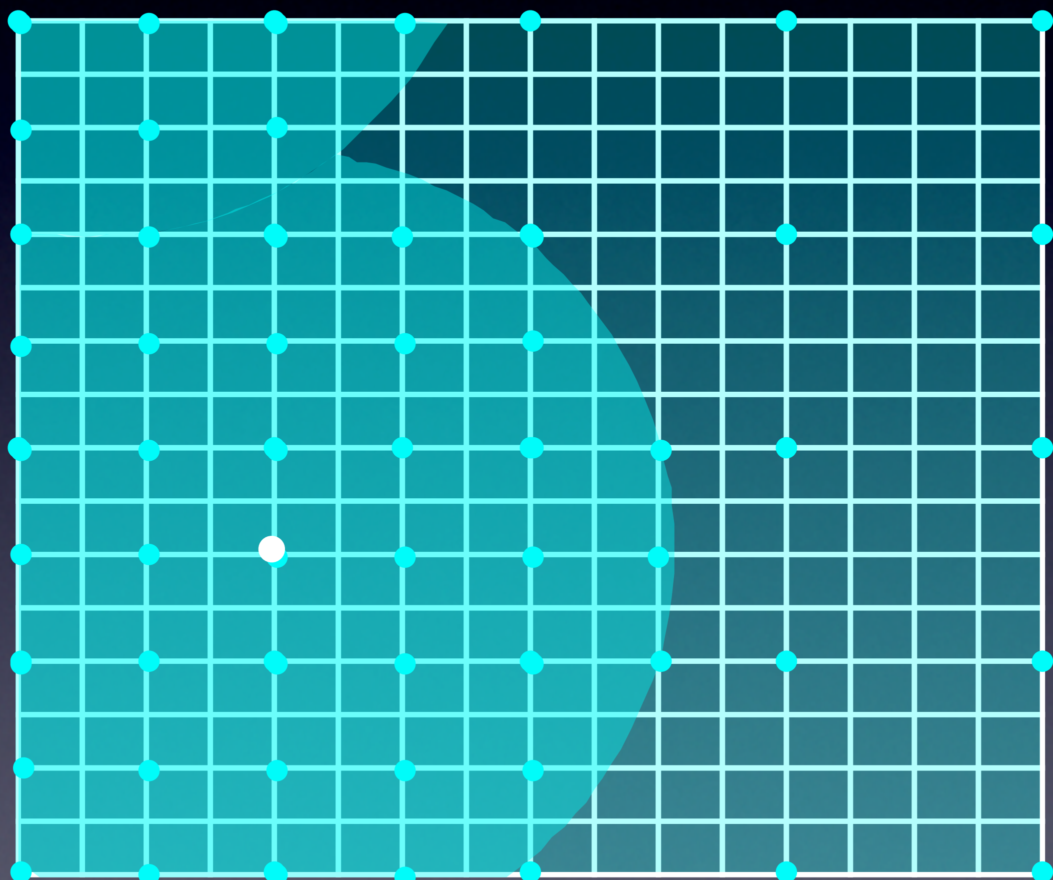
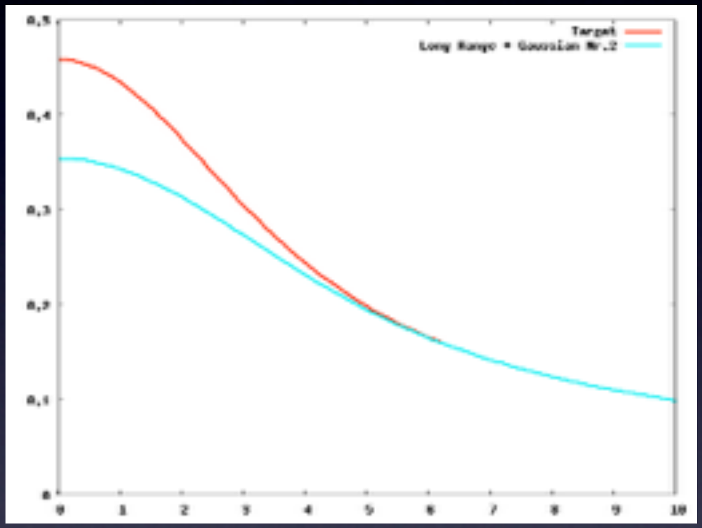


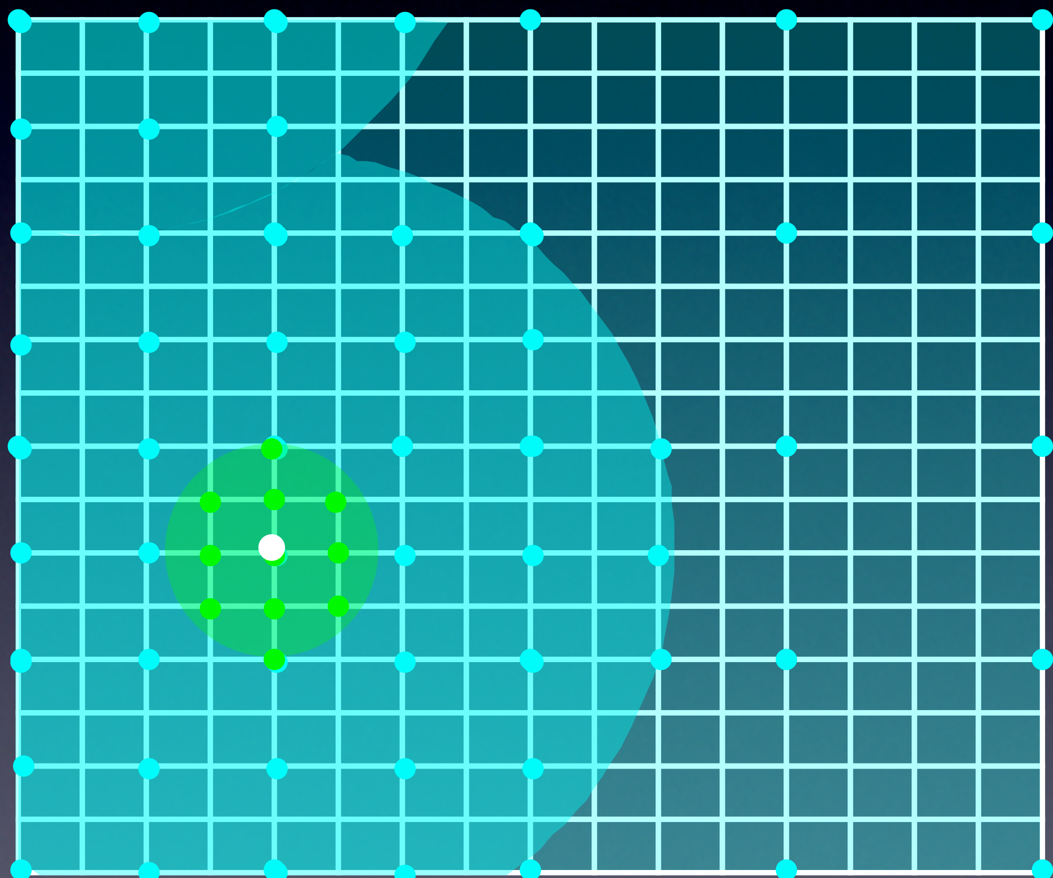


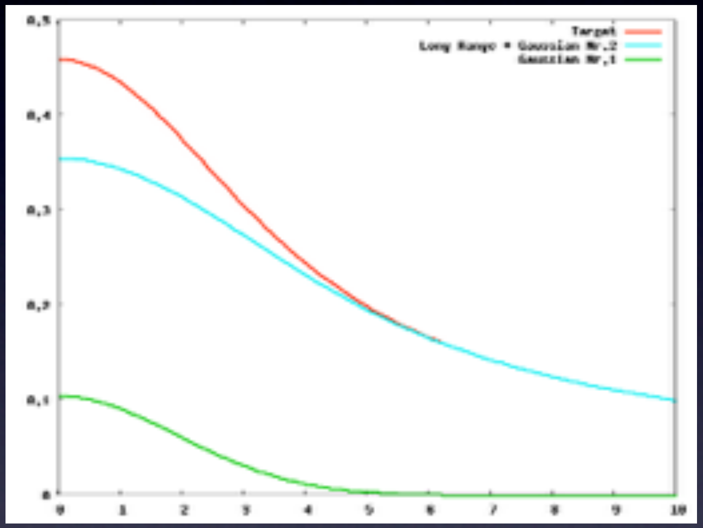
$$V^{\mathrm{QM/MM}}(\mathbf{r}, \mathbf{R}_{\mathrm{MM}}) = \sum_{i=\mathrm{coarse}}^{\mathrm{fine}} \prod_{k=i}^{\mathrm{fine}-1} I_{k-1}^{k} V_i^{\mathrm{QM/MM}}(\mathbf{r}, \mathbf{R}_{\mathrm{MM}})$$





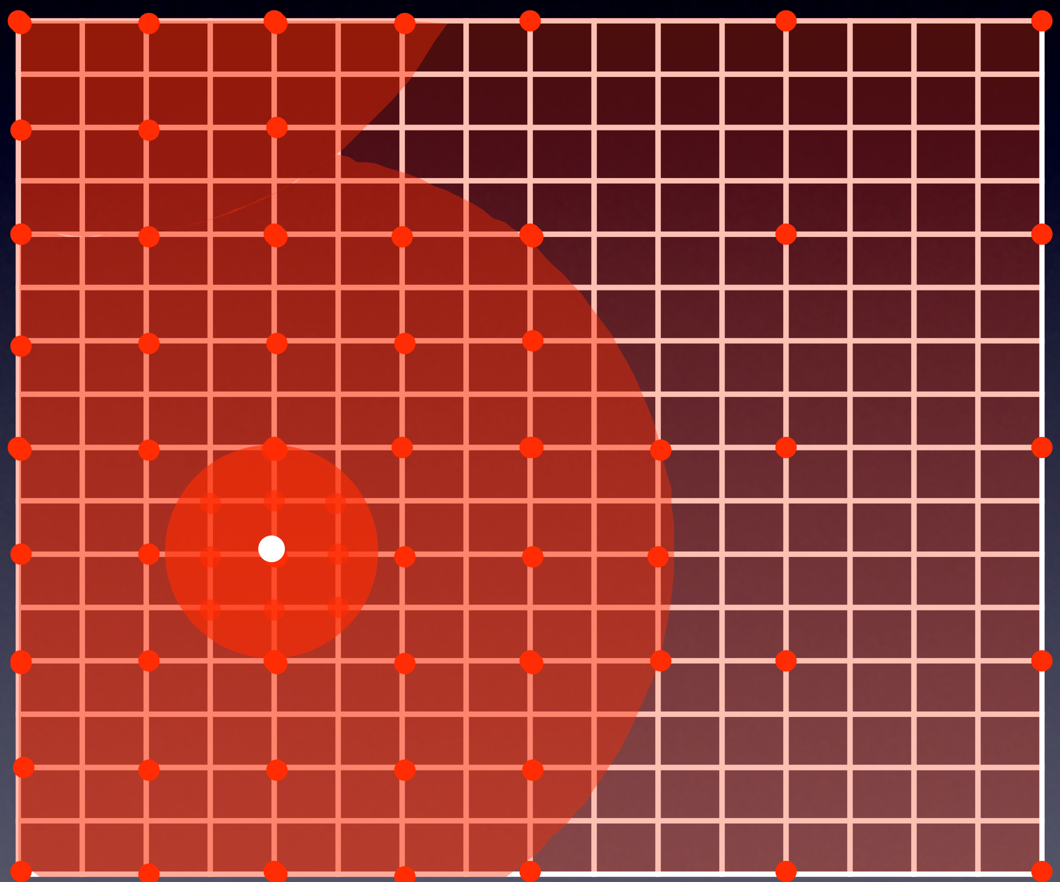
$$V^{\mathrm{QM/MM}}(\mathbf{r}, \mathbf{R}_{\mathrm{MM}}) = \sum_{i=\mathrm{coarse}}^{\mathrm{fine}} \prod_{k=i}^{\mathrm{fine}-1} I_{k-1}^{k} V_i^{\mathrm{QM/MM}}(\mathbf{r}, \mathbf{R}_{\mathrm{MM}})$$

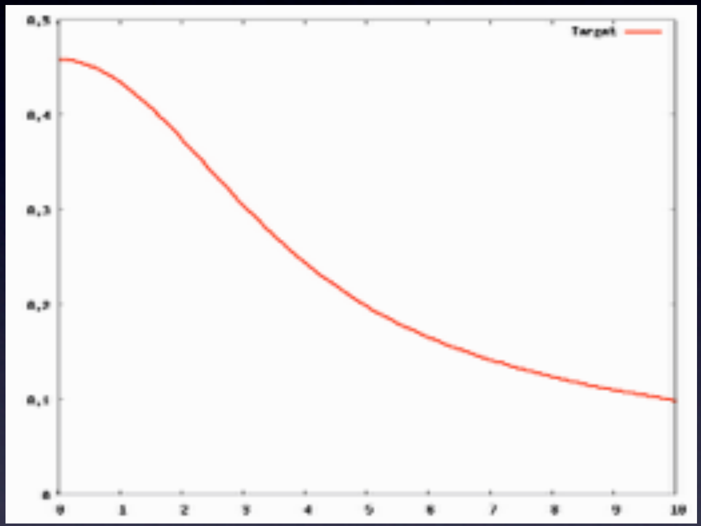




$$V^{\mathrm{QM/MM}}(\mathbf{r}, \mathbf{R}_{\mathrm{MM}}) = \sum_{i=\mathrm{coarse}}^{\mathrm{fine}} \prod_{k=i}^{\mathrm{fine}-1} I_{k-1}^{k} V_i^{\mathrm{QM/MM}}(\mathbf{r}, \mathbf{R}_{\mathrm{MM}})$$

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
```

```
&MM
 .....
&END MM

&DFT
 ....
&END DFT

&SUBSYS
  &CELL
    ABC 15.0 15.0 15.0
  &END CELL

  &TOPOLOGY
    COORD_FILE_NAME sys.pdb
    COORDINATE pdb
  &END TOPOLOGY
&END SUBSYS
```

Extension to PBC

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

Ewald Summation scheme:

$$
\begin{aligned}
V(\vec{r}) &= \sum_{MM} q_{MM} \frac{1}{|\vec{r} - \vec{r}_{MM}|} \\
&= \sum_{MM} q_{MM} \frac{Erf(\vec{r}\kappa) + Erfc(\vec{r}\kappa)}{|\vec{r} - \vec{r}_{MM}|} \\
&= V_{rec}(\vec{r}) + V_{real}(\vec{r})
\end{aligned}
$$

Extension to PBC

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

Ewald Summation scheme:

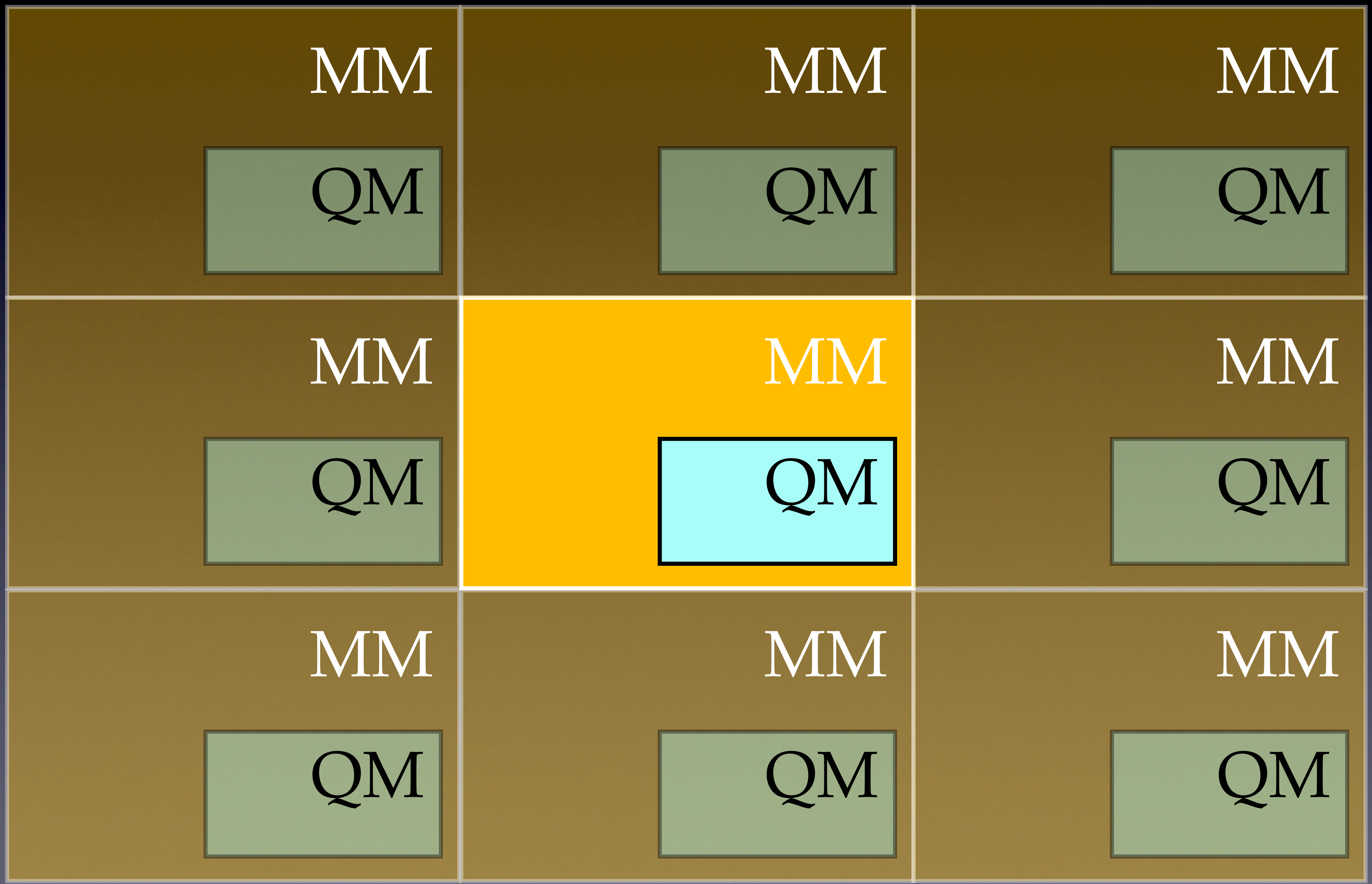
$$V_{rec}(\vec{r}) = \frac{4\pi}{\Omega} \sum_{\vec{k} \neq 0} \frac{e^{-\frac{|\vec{k}|^2}{4\kappa}}}{|\vec{k}|^2} \cdot \sum_{MM} q_{MM} e^{-\imath \vec{k} \cdot \vec{r}}$$

Reciprocal space

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

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

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

Total ES Energy

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

background charge

Total ES Energy

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

background charge

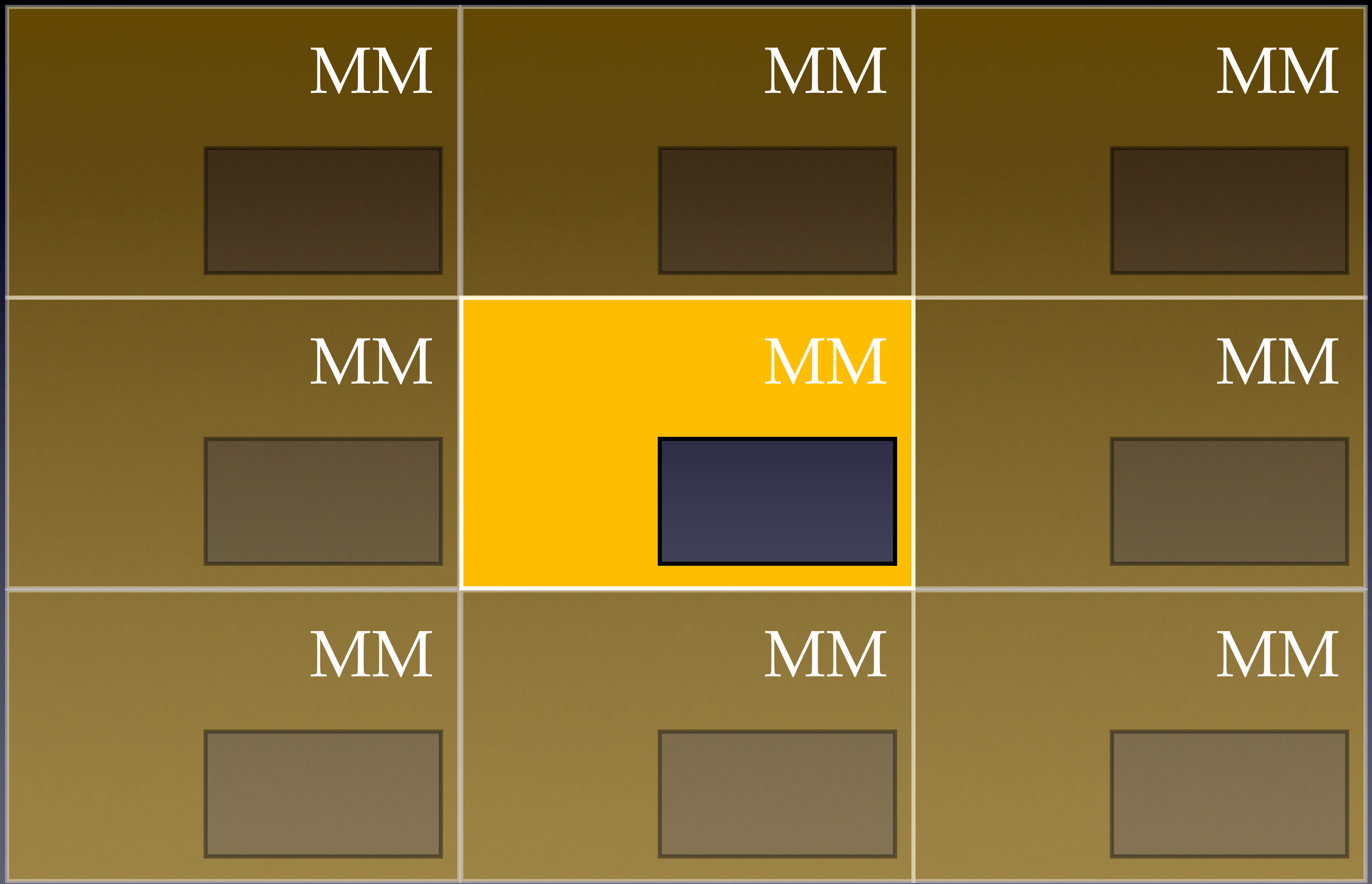
$$E^{\mathrm{TOT}} = \frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

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

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

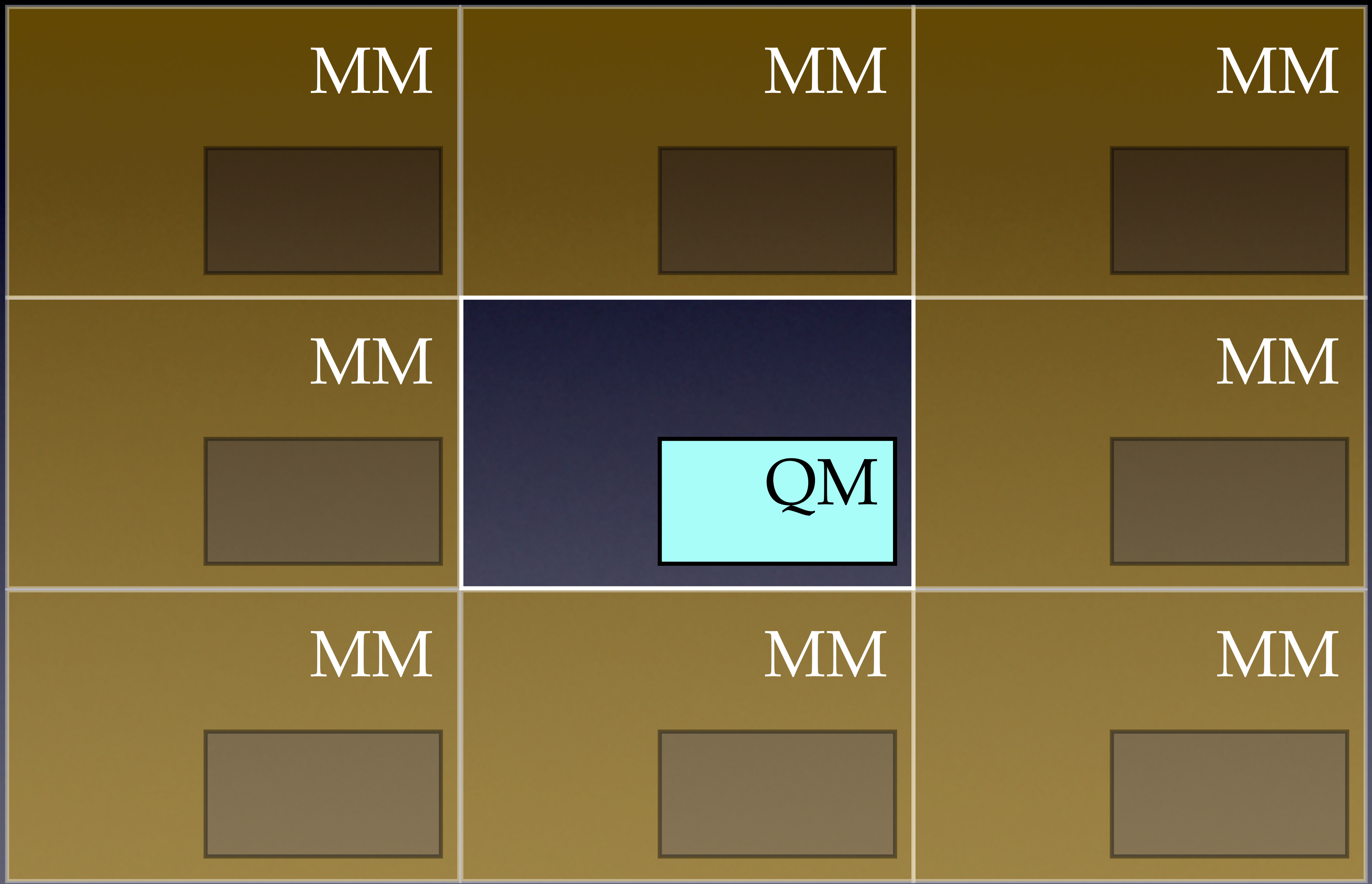
$$E^{\mathrm{QM/MM}} = \int\int d\mathbf{r}d\mathbf{r}'\frac{(n^{\mathrm{QM}}(\mathbf{r})+n^{B,\mathrm{QM}})(n^{\mathrm{MM}}(\mathbf{r}')+n^{B,\mathrm{MM}})}{|\mathbf{r}-\mathbf{r}'|}$$

MM/MM fully periodic



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

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

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

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

$$V(r)_{rec} = R_{low}(r)$$

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

GEEP with PBC

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

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

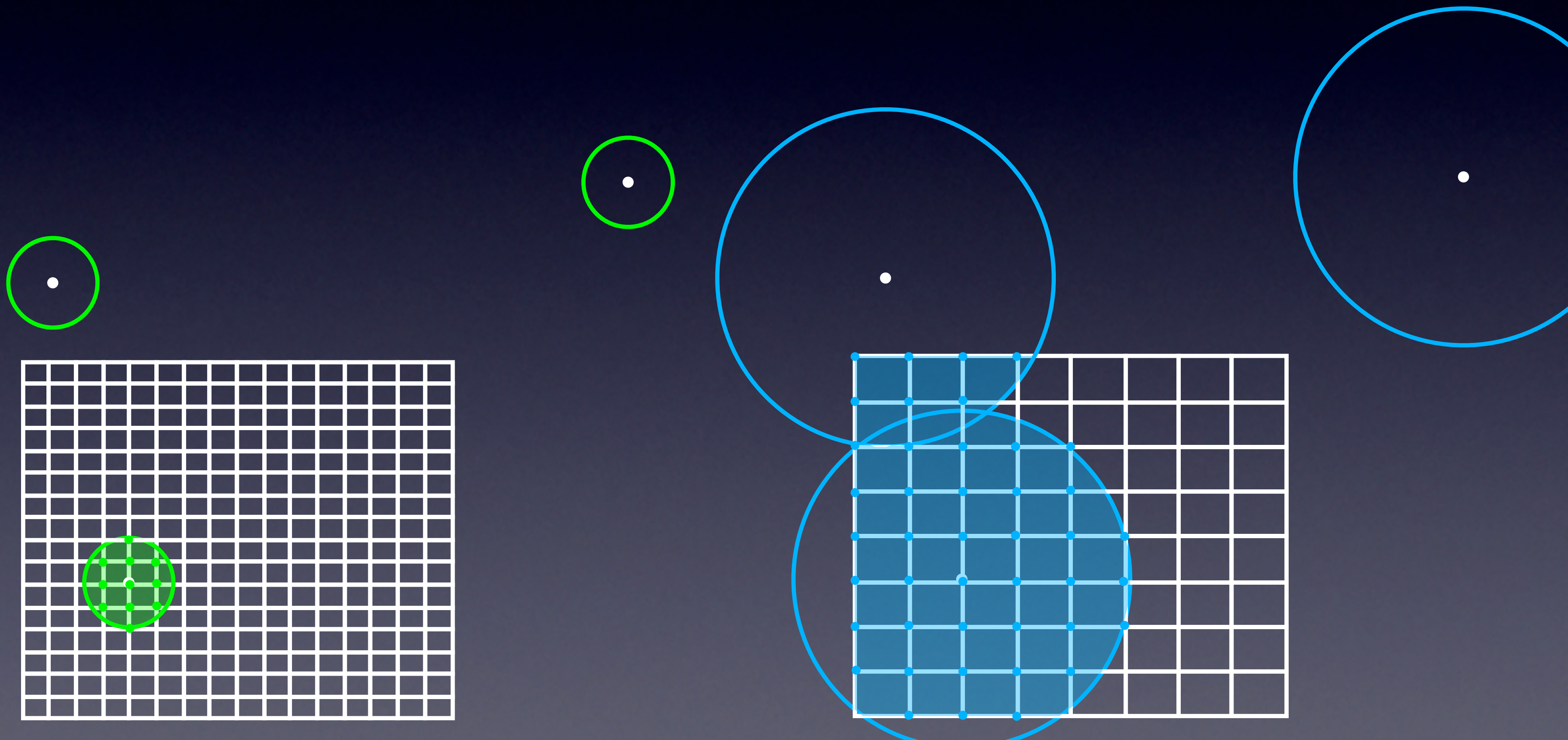
$$V(r)_{rec} = \frac{1}{\Omega} \sum_{k}^{k_{cut}} \tilde{R}_{low}(k) e^{\imath \vec{k}\cdot\vec{r}}$$

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

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

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

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

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

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

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  &END CELL

  ECOUPL GAUSS
  USE_GEEP_LIB 6

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

  &PERIODIC
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      EWALD_PRECISION 0.00000001
      RCUT 8.0
      NGRIDS  20 20 20
      ANALYTICAL_GTERM
    &END MULTIPOLE
  &END PERIODIC

&END QMMM
```

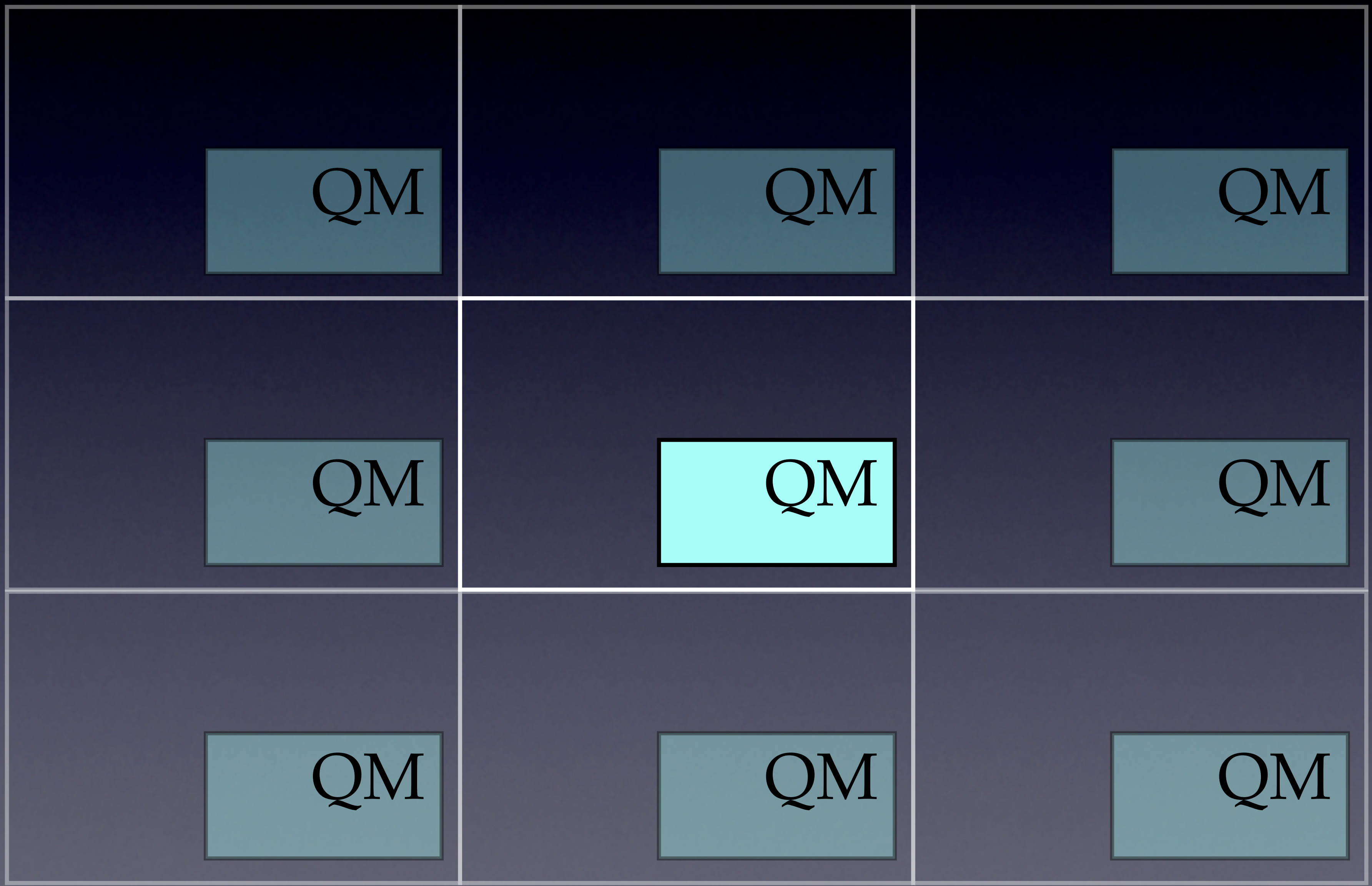
GEEP Summary

- GEEP 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)
- 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



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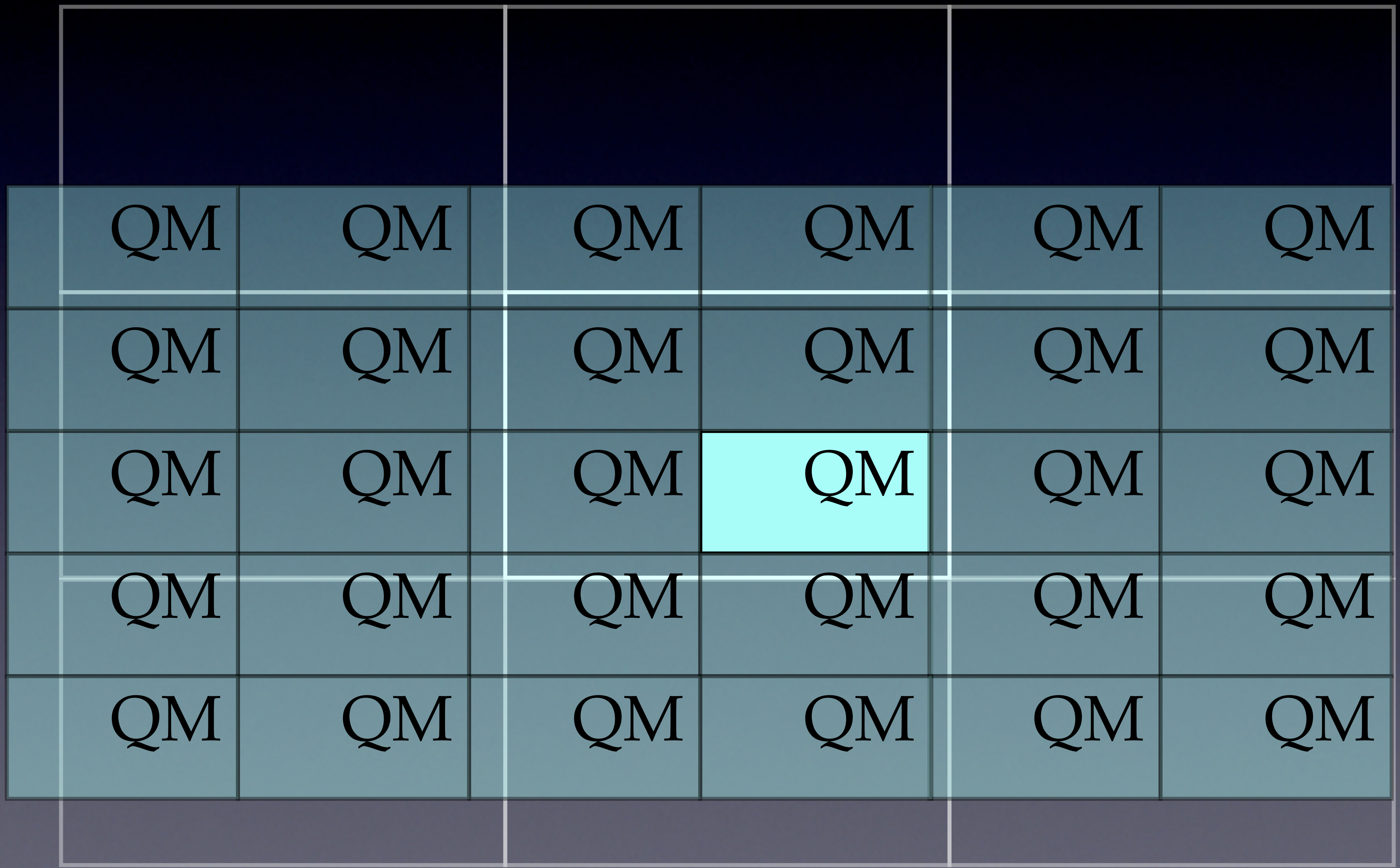
QM fully periodic



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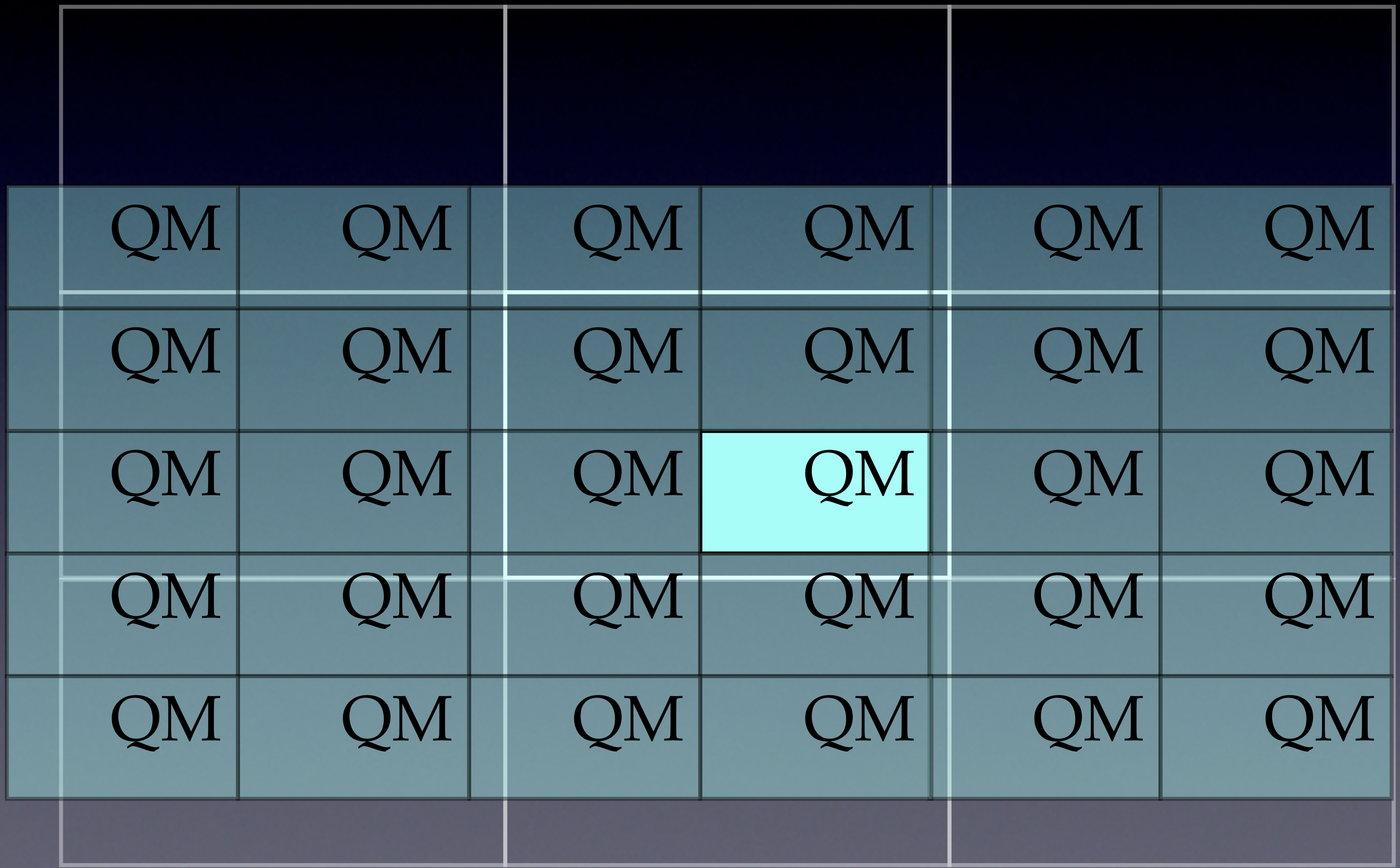
De-coupling and re-coupling



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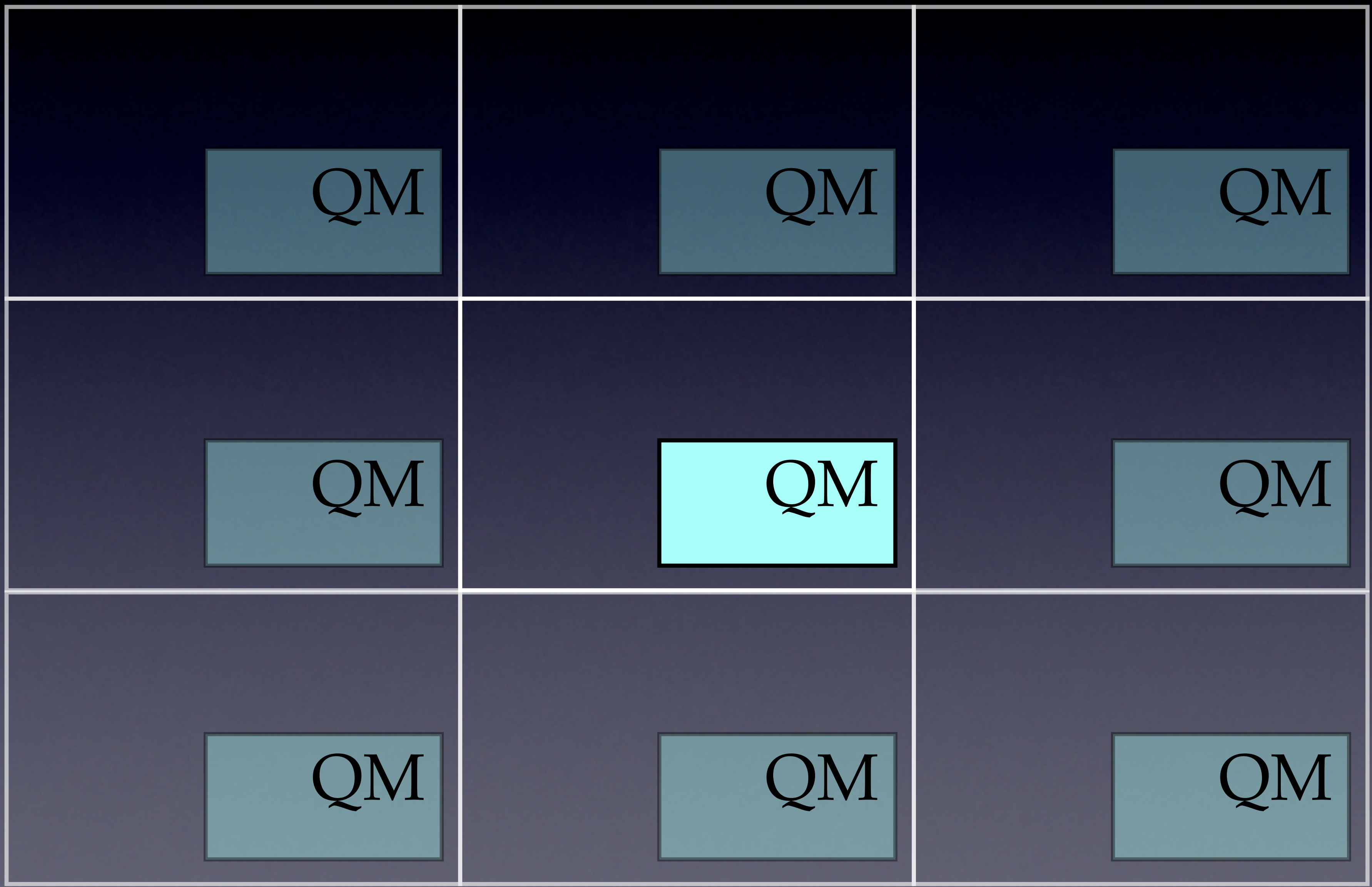


T. Laino, F. Mohamed, A. Laio and M. Parrinello, *J. Chem. Th. Comp.*, 2 (5), **2006**, pp.1370-1378

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

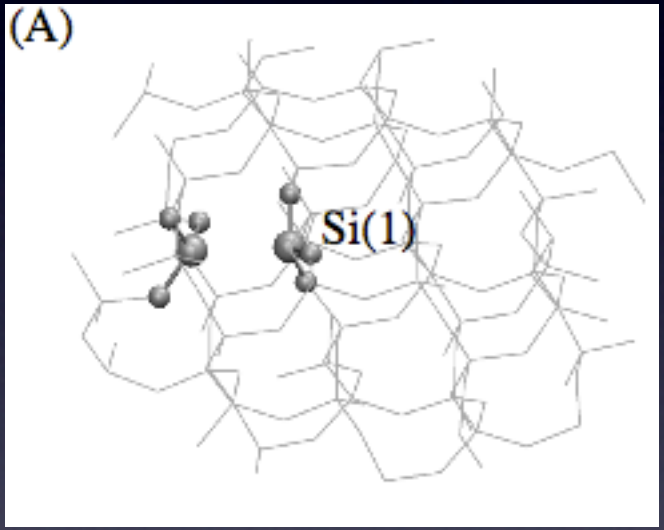
- Decoupling and Recoupling using these charges

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



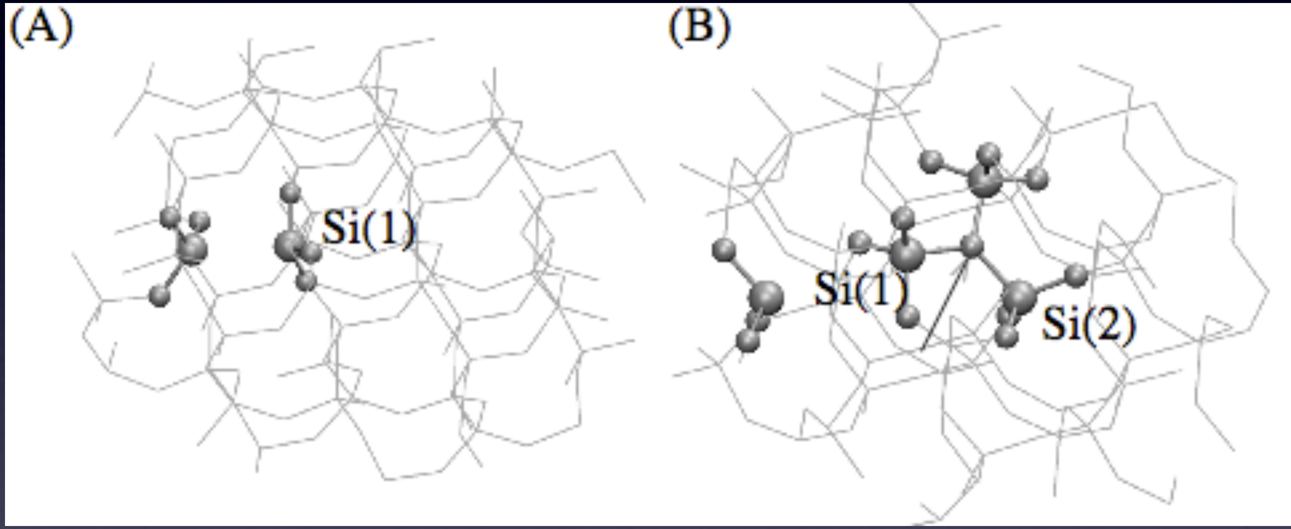
dimer
deloc. el.

E'_δ

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

Charged OV

Migration of charged oxygen vacancy defects in silica



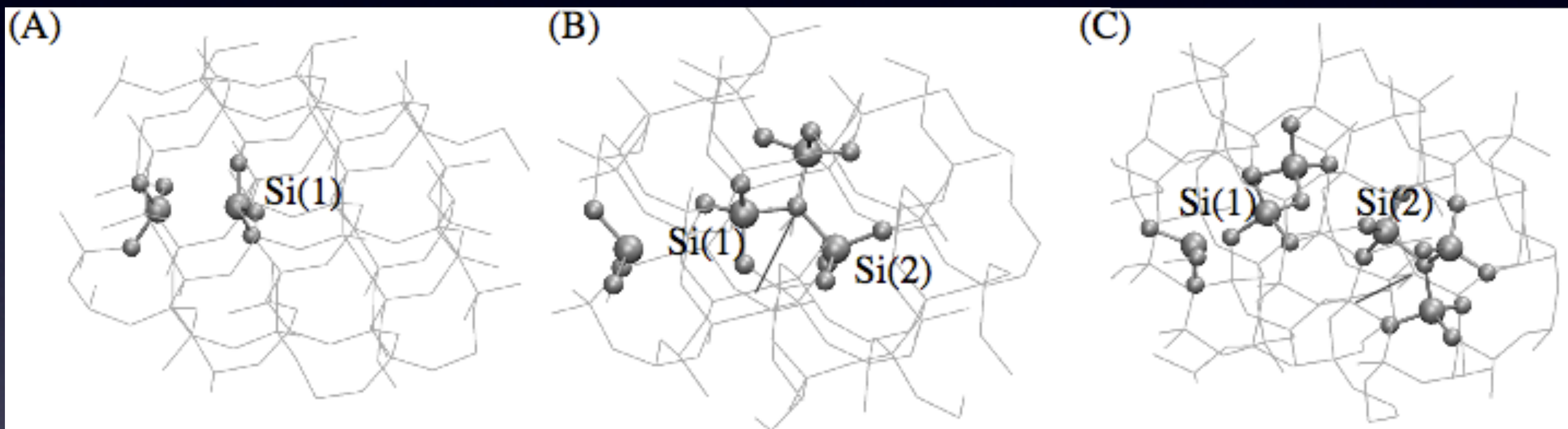
dimer
deloc. el.

E'_δ E'_1

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

Charged OV

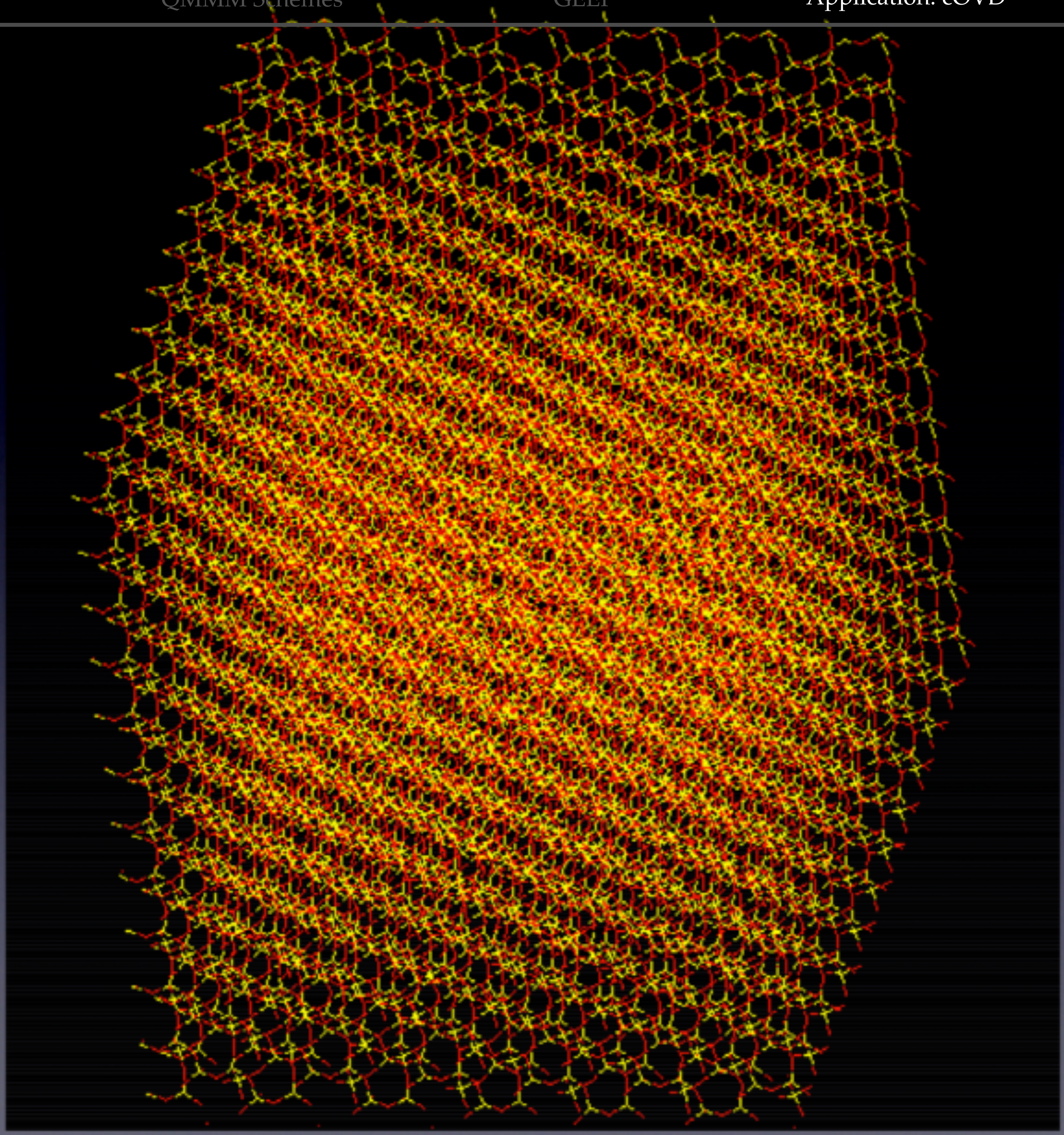
Migration of charged oxygen vacancy defects in silica

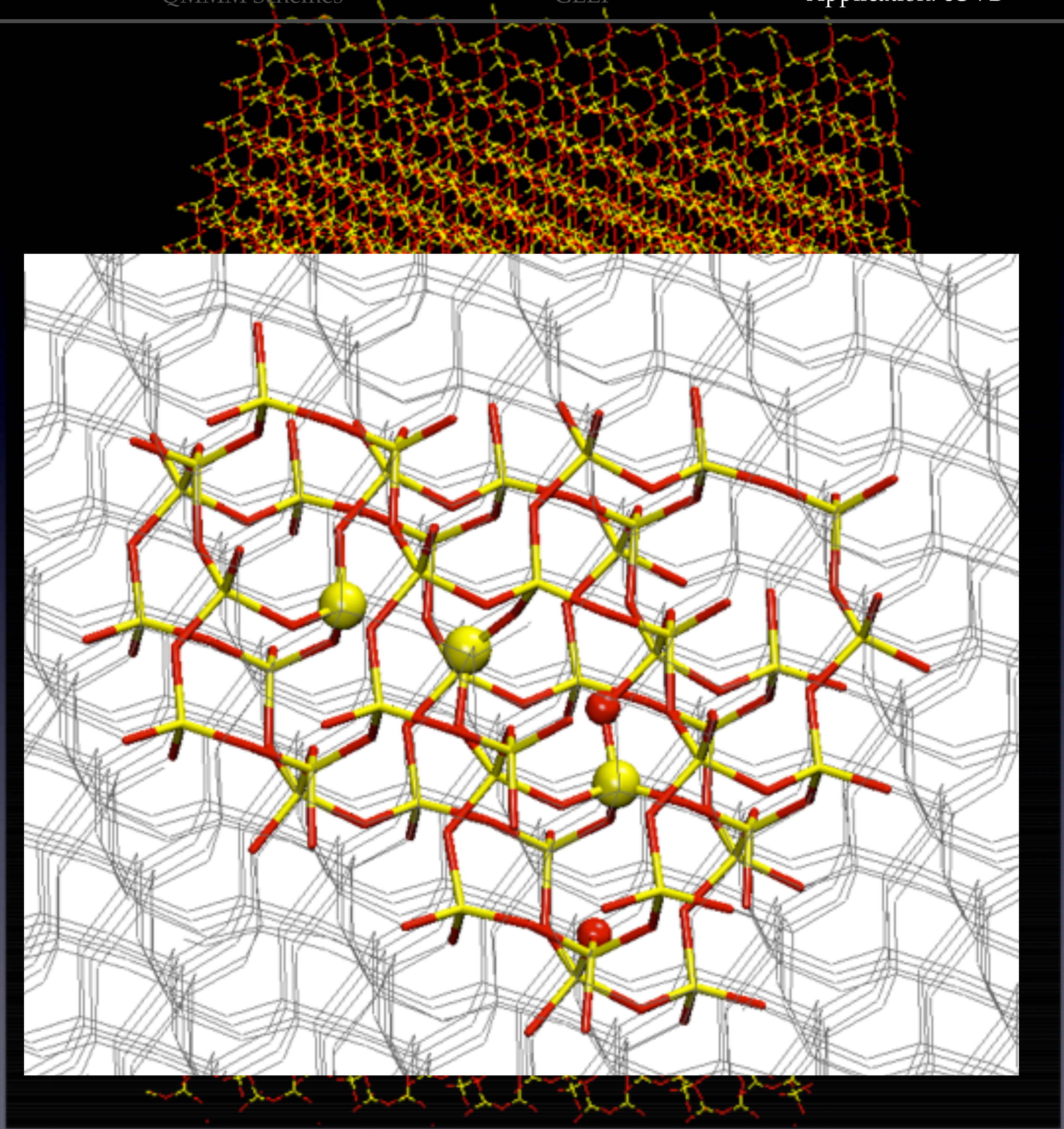


dimer
deloc. el.

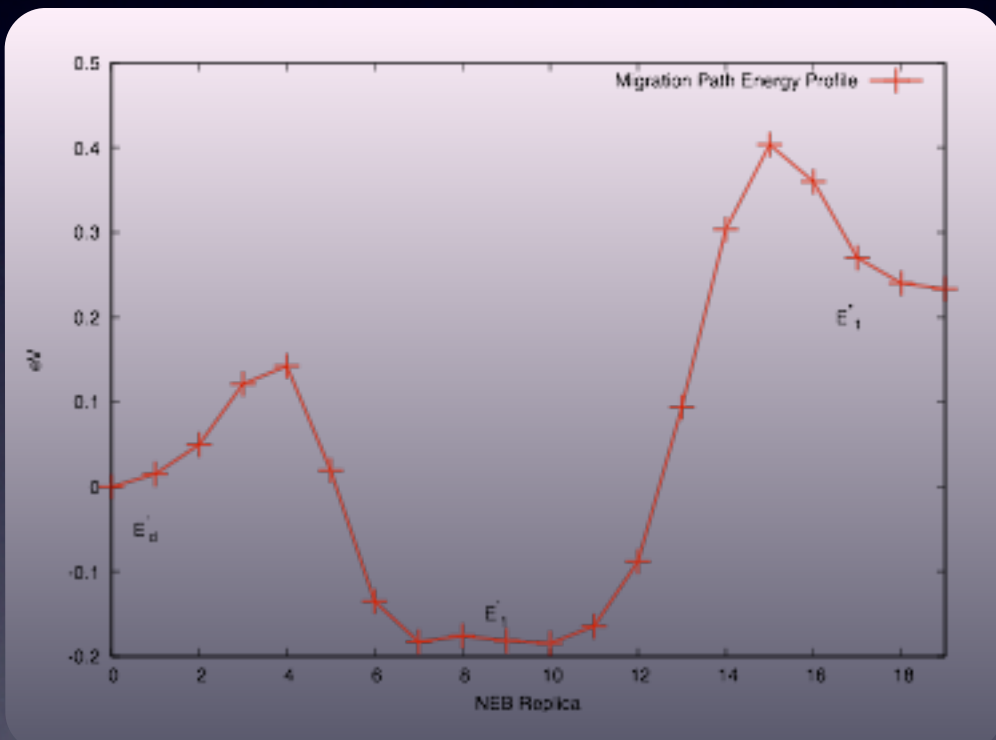
E'_{δ} E'_{1} E^{*}_{1}

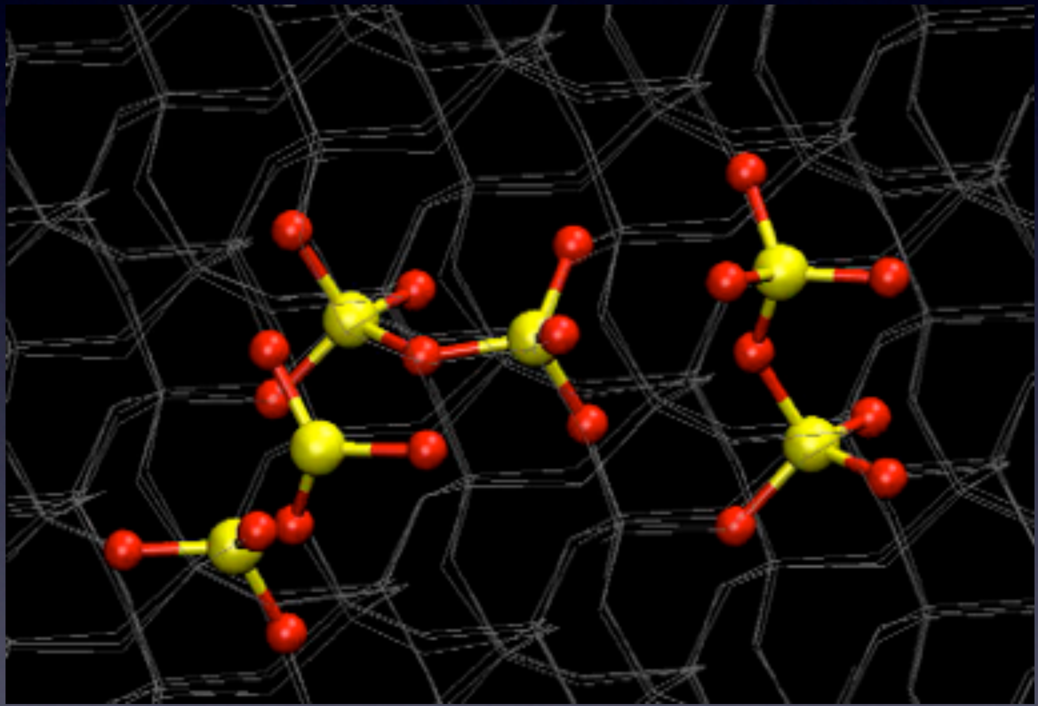
T. Laino, D. Donadio, I-Feng W. Kuo, *Phys. Rev. B*, 2007





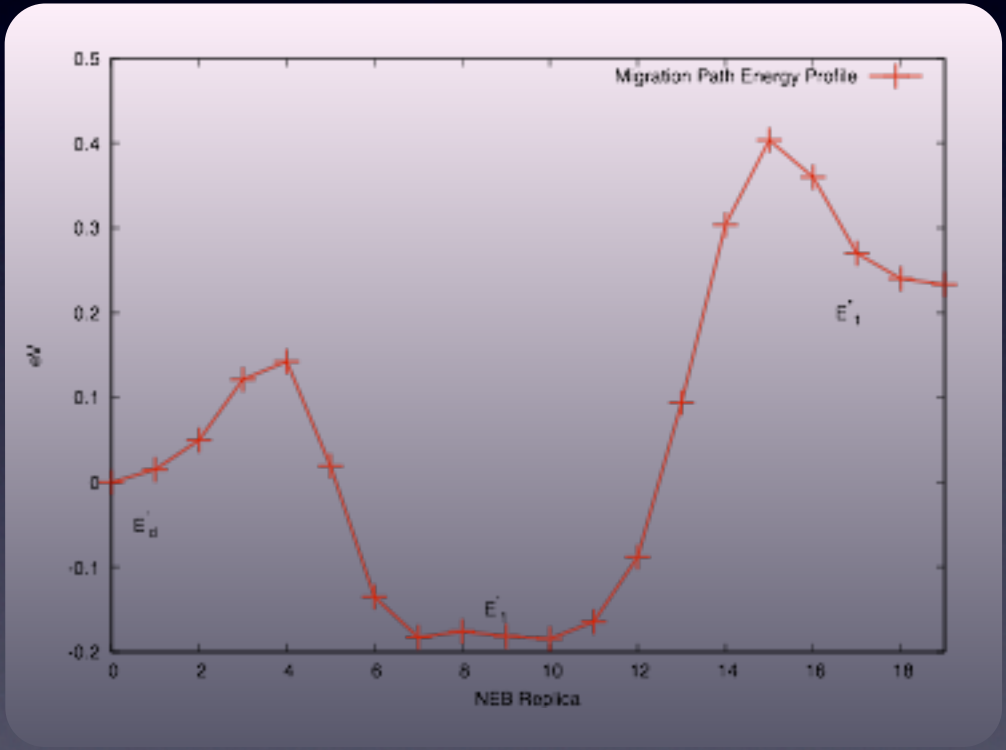
NEB: Minimum Energy Path

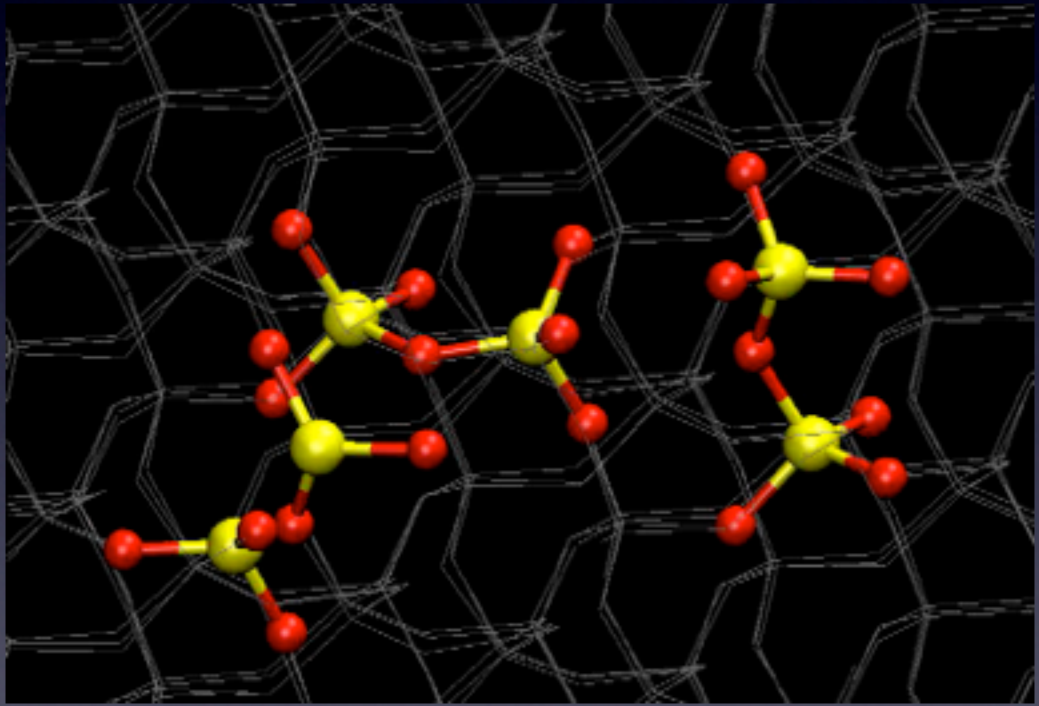




T. Laino, D. Donadio, I-Feng W. Kuo, *Phys. Rev. B*, 2007

NEB: Minimum Energy Path



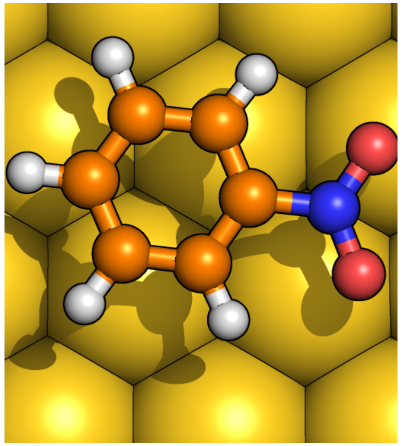


T. Laino, D. Donadio, I-Feng W. Kuo, *Phys. Rev. B*, 2007

Image Charge & QMMM

QM molecule + EAM metal

nitrobenzene/Au(111)

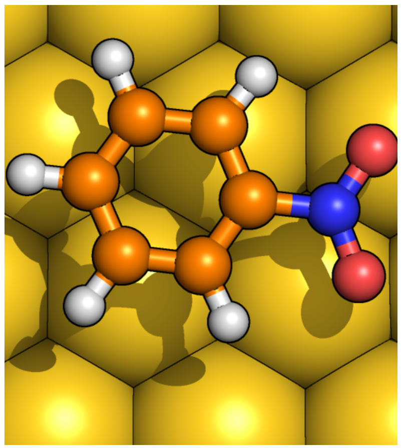


Siepmann Sprik., JCP (1995) **102**
Golze Iannuzzi Passerone Hutter, JCTC (2013)

Image Charge & QMMM

QM molecule + EAM metal

nitrobenzene/Au(111)



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

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

IC induce polarization, solved selfconsistently

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

Image Charge & QMMM

QM molecule + EAM metal

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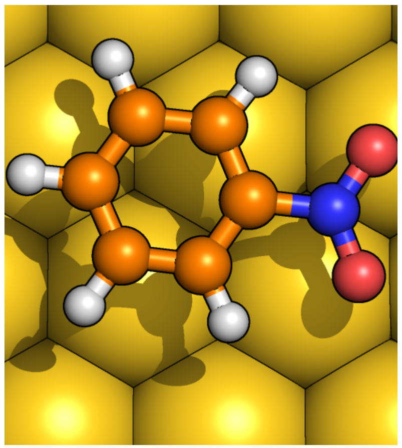

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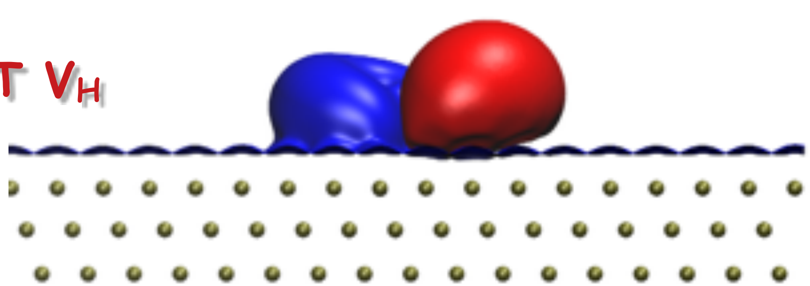
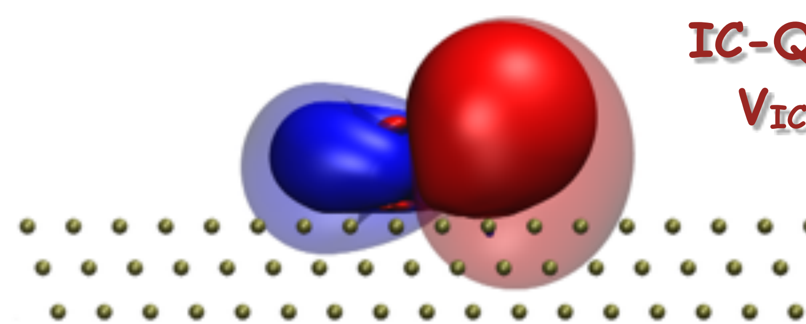
Siepmann Sprik., JCP (1995) **102**
Golze Iannuzzi Passerone Hutter, JCTC (2013)

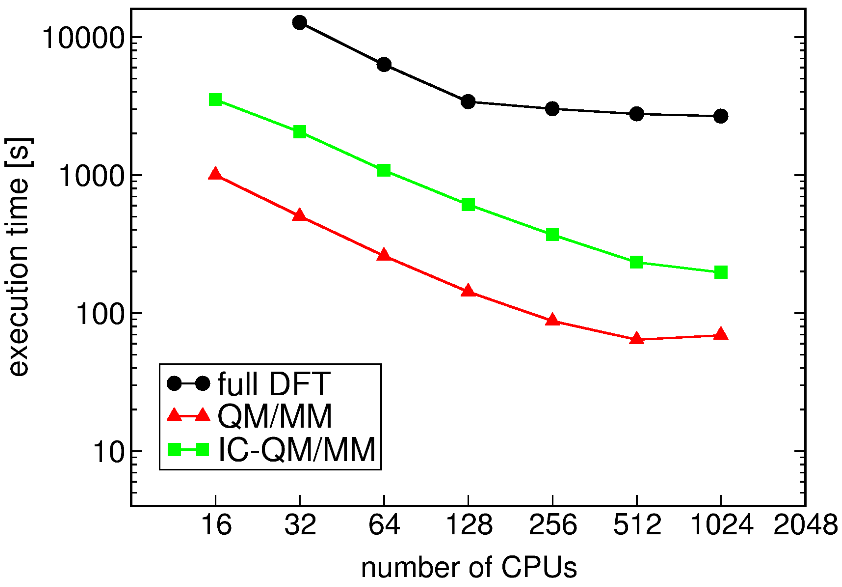
DFT V_H





IC-QMMM
$V_{IC}+V_H$

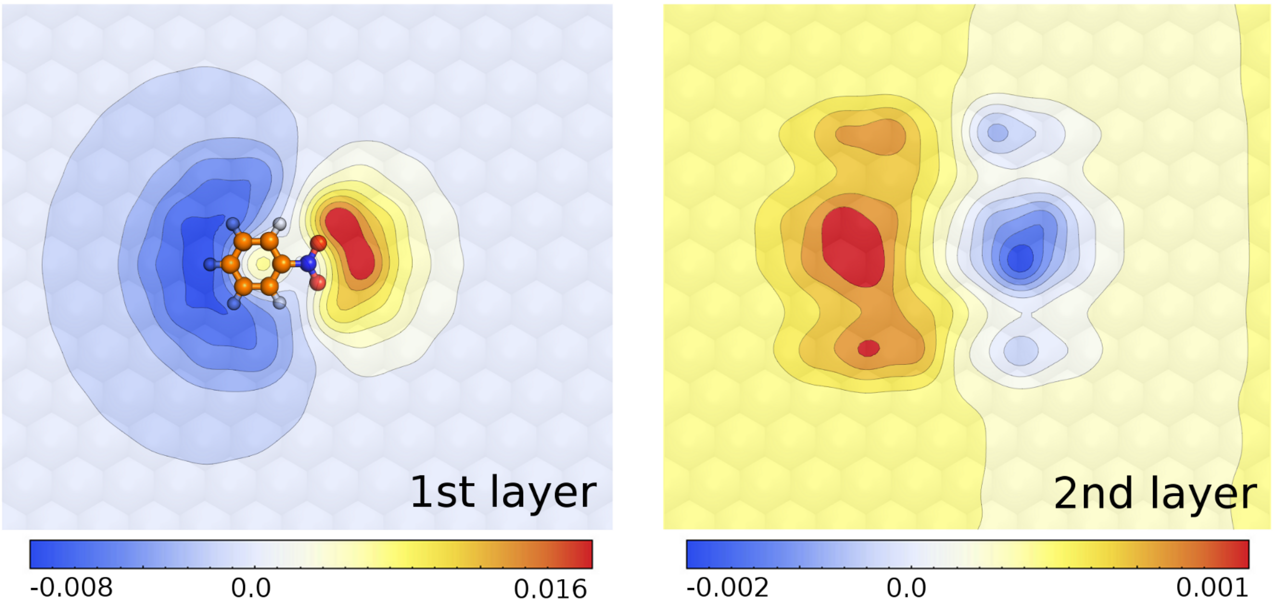
IC distribution



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

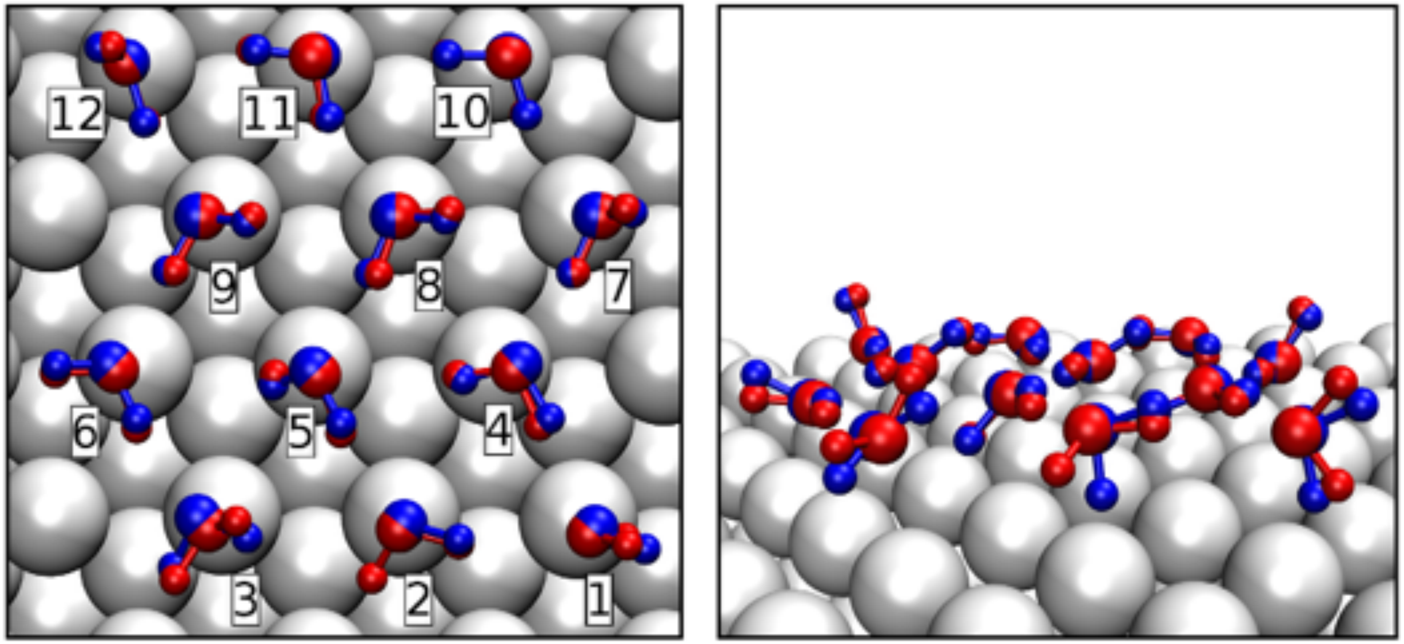
$$\int \left(V_H(\mathbf{r}) - V_0\right) g_I(\mathbf{r}) + \sum_J C_J \int\int \frac{g_J(\mathbf{r}')g_I(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

linear set of eq. (CG iterative scheme)



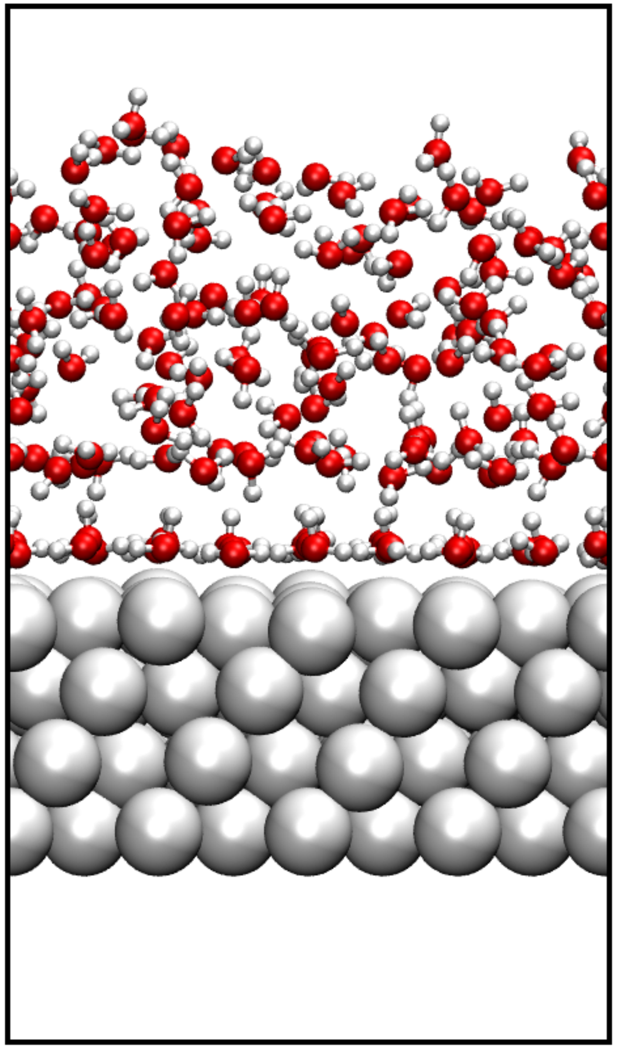
H_2O cluster on Pt(1 1 1)

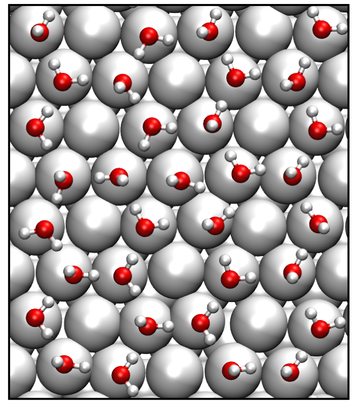
H_2O QM, Pt EAM, H_2O-Pt Siepmann-Sprik + IC



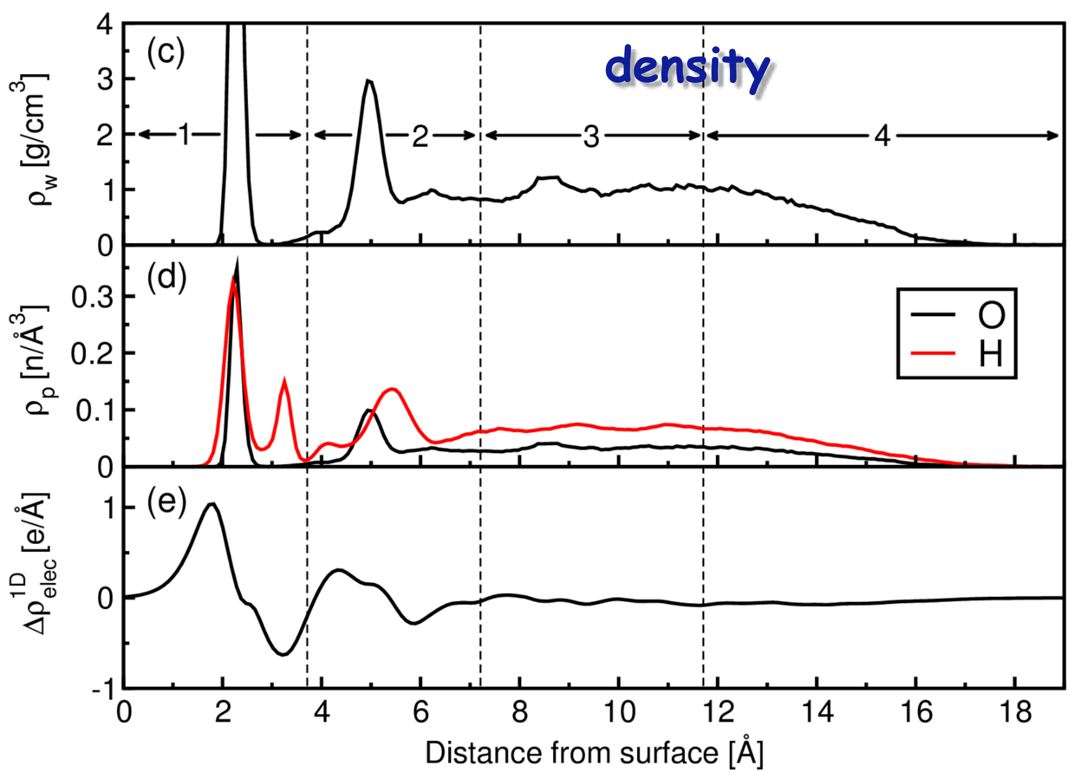
kJ/mol	1 H_2O		2H_2O			12H_2O		
	E_{int}	E_{ads}	E_{int}	E_{ads}	E_{H-bond}	E_{int}	E_{ads}	E_{H-bond}
QM/MM	−41.6	−37.3	−40.9	−49.2	−10.6	−36.4	−61.9	−26.0
IC-QM/MM	−44.2	−43.6	−43.7	−52.9	−10.5	−42.8	−66.6	−24.4
full DFT	−44.9	−43.5	−50.6	−56.8	−7.0	−44.2	−63.0	−19.7

Liquid Water at Pt(1 1 1)





honeycomb arrangement
70% on-top site occupied



H-bond distribution