The fastest wave

浪速
Naniwa

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[1] Hiroshi Nakanishi, 2016. Ch.6 Quantum adsorption states of small mass atoms on solid surfaces. In: H. Kasai, M. C. S. Escaño, ed. Physics of Surface, Interface and Cluster Catalysis. Bristol, UK, IOP Publishing.
[2] Hiroshi Nakanishi, Quantum States of the Hydrogen Isotope in Solid Materials and on Their Surfaces", J. Comput. Chem. Jpn., Vol. 15, No. 5, pp. 124–135 (2016).

Naniwa formulation from total Hamiltonian (ab initio)

Hamiltonian

$$H = \sum_{I=1}^{N_{\mathrm{nc.}}} \left(-\frac{\hbar^2}{2M_I} \right) \nabla_I^2 + \sum_{i=1}^{n_e} \left(-\frac{\hbar^2}{2m_e} \right) \nabla_i^2 + V(\mathbf{r}, \mathbf{R})$$

m_e, M_I : masses of electron and nucleus I

$n_e, N_{\mathrm{nc.}}$: numbers of electron and nucleus

Interactions

$$V(\boldsymbol{r}, \boldsymbol{R}) = \sum_{i=1}^{n_e} \sum_{I=1}^{N_{\mathrm{nc.}}} \frac{-Z_I e^2}{|r_i - R_I|} + \sum_{i=1}^{n_e} \sum_{j=1}^{i-1} \frac{e^2}{|r_j - r_i|} + \sum_{I=1}^{N_{\mathrm{nc.}}} \sum_{J=1}^{I-1} \frac{Z_J Z_I e^2}{|R_J - R_I|}$$

Z_I: atomic number of nucleus I

e : elementary charge

Particle position vectors

$$\boldsymbol{r} = \left(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \cdots, \boldsymbol{r}_i, \cdots \boldsymbol{r}_{n_e} \right)$$

$$\boldsymbol{R} = \left(\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{R}_3, \cdots, \boldsymbol{R}_I, \cdots, \boldsymbol{R}_{N_{\mathrm{nc.}}} \right)$$

$3(n_e + N_{\mathrm{nc.}})$

Schrödinger equation

$$H\Psi(\boldsymbol{r},\boldsymbol{R}) = E\Psi(\boldsymbol{r},\boldsymbol{R})$$

Born-Oppenheimer approximation

$$\Psi_{n,\omega}(\boldsymbol{r},\boldsymbol{R}) = \psi_{n;\boldsymbol{R}}(\boldsymbol{r}) \cdot \phi_{\omega;n}(\boldsymbol{R})$$

$\psi_{n;\boldsymbol{R}}(\boldsymbol{r})$: the n-th electron wave function in the case of the fixed nucleus position $\boldsymbol{R}$.

$\phi_{\omega;n}(\boldsymbol{R})$: the ω-th nucleus motion wave function in the case of the electron state $\boldsymbol{n}$.

Equation for electron state:

$$\left[\sum_{i=1}^{n_e}\left(-\frac{\hbar^2}{2m_e}\right)\nabla_i^2+V(\boldsymbol{r},\boldsymbol{R})\right]\psi_{n;\boldsymbol{R}}(\boldsymbol{r})=U_n(\boldsymbol{R})\,\psi_{n;\boldsymbol{R}}(\boldsymbol{r}) \quad \cdots \quad (*)$$

Equation for nucleus motion:

$$\left[\sum_{I=1}^{N_{\mathrm{nc.}}}\left(-\frac{\hbar^2}{2M_I}\right)\nabla_I^2+U_n(\boldsymbol{R})\right]\phi_{\omega;n}(\boldsymbol{R})=E_{\omega,n}\phi_{\omega;n}(\boldsymbol{R}) \quad \cdots \quad (**)$$

$$\boldsymbol{r}=\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,\cdots,\boldsymbol{r}_i,\cdots\boldsymbol{r}_{n_e}\right)$$

$$\boldsymbol{R}=\left(\boldsymbol{R}_1,\boldsymbol{R}_2,\boldsymbol{R}_3,\cdots,\boldsymbol{R}_I,\cdots,\boldsymbol{R}_{N_{\mathrm{nc.}}}\right)$$

Equation for electron state:

$$\left[\sum_{i=1}^{n_e}\left(-\frac{\hbar^2}{2m_e}\right)\nabla_i^2 + V(\boldsymbol{r},\boldsymbol{R})\right]\psi_{n;\boldsymbol{R}}(\boldsymbol{r}) = U_n(\boldsymbol{R})\,\psi_{n;\boldsymbol{R}}(\boldsymbol{r}) \qquad \cdots \quad (*)$$

For fixed $\boldsymbol{R}$, we can obtain the eigen energies, $U_n(\boldsymbol{R})$, and eigenstates, $\psi_{n;\boldsymbol{R}}(\boldsymbol{r})$ with the aid of the conventional first principles (*electron states*) calculation.

The eigenenergies, $U_n(\boldsymbol{R})$, as a function of $\boldsymbol{R}$ can be consider as the adiabatic potential energy surface for nucleus motion.

Equation for nucleus motion:

$$\left[\sum_{I=1}^{N_{\mathrm{nc.}}}\left(-\frac{\hbar^2}{2M_I}\right)\nabla_I^2+U_n(\boldsymbol{R})\right]\phi_{\omega;n}(\boldsymbol{R})=E_{\omega,n}\phi_{\omega;n}(\boldsymbol{R}) \quad \cdots \quad (**)$$

The eigen energy, $E_{\omega,n}$, corresponds to the total energy, *E,* appeared in the Schrödinger equation for total system: $H\Psi(\boldsymbol{r},\boldsymbol{R})=E\Psi(\boldsymbol{r},\boldsymbol{R})$

quantum numbers

ω : index of quantum state for nucleus motion

n : index of quantum state for electron system

Equation for electron state:

$$\left[\sum_{i=1}^{n_e}\left(-\frac{\hbar^2}{2m_e}\right)\nabla_i^2+V(\boldsymbol{r},\boldsymbol{R})\right]\psi_{n;\boldsymbol{R}}(\boldsymbol{r})=\boxed{U_n(\boldsymbol{R})}\,\psi_{n;\boldsymbol{R}}(\boldsymbol{r}) \qquad \cdots \quad (*)$$

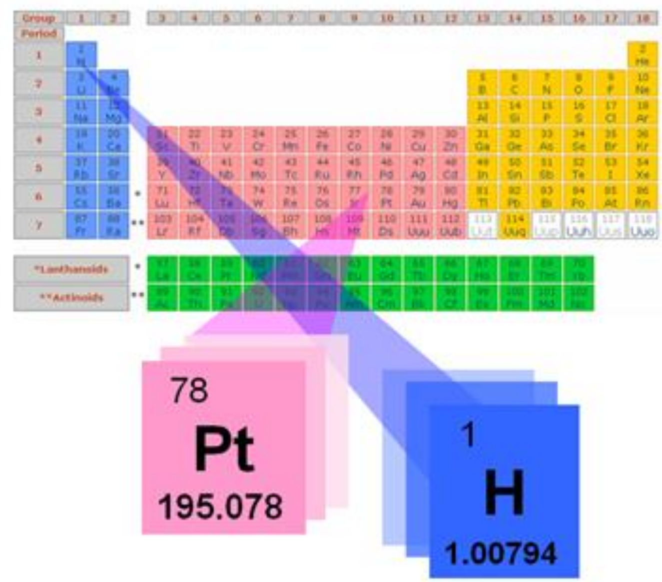
Equation for nucleus motion:

$$\left[\sum_{I=1}^{N_{\mathrm{nc.}}}\left(-\frac{\hbar^2}{2M_I}\right)\nabla_I^2+\boxed{U_n(\boldsymbol{R})}\right]\phi_{\omega;n}(\boldsymbol{R})=E_{\omega,n}\phi_{\omega;n}(\boldsymbol{R}) \qquad \cdots \quad (**)$$

$$\boldsymbol{r}=\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,\cdots,\boldsymbol{r}_i,\cdots\boldsymbol{r}_{n_e}\right)$$

$$\boldsymbol{R}=\left(\boldsymbol{R}_1,\boldsymbol{R}_2,\boldsymbol{R}_3,\cdots,\boldsymbol{R}_I,\cdots,\boldsymbol{R}_{N_{\mathrm{nc.}}}\right)$$

Our quantum simulation scheme: Naniwa



Interactions between nucleus is calculated by DFT based first principle calculations ･･･ (*)

Potential energy for nucleus motions: $U_n(\boldsymbol{R})$

Solve the Schrödinger equation for nucleus motion ･･･ (**)

Wave function for nucleus motion

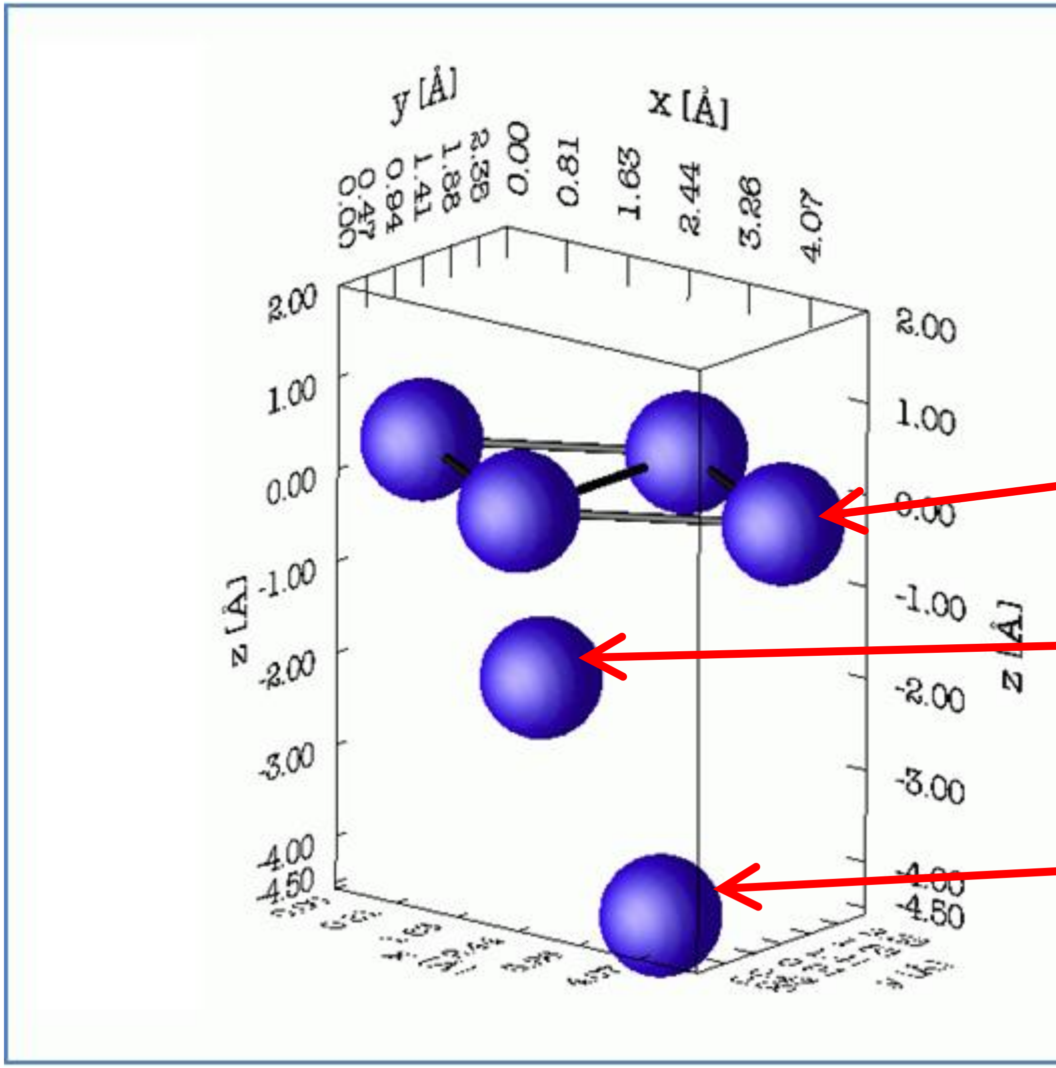
Derive the various physical quantities

-Parameters are only atomic number of elements

-No fitting and no artificial procedure

Example of $U_n(\boldsymbol{R})$: Potential energy for hydrogen nucleus motion

$U_0(\boldsymbol{R}_1), \quad \boldsymbol{R}_1 = (x_1, y_1, z_1)$ **Single hydrogen atom near Pd(111) surface**

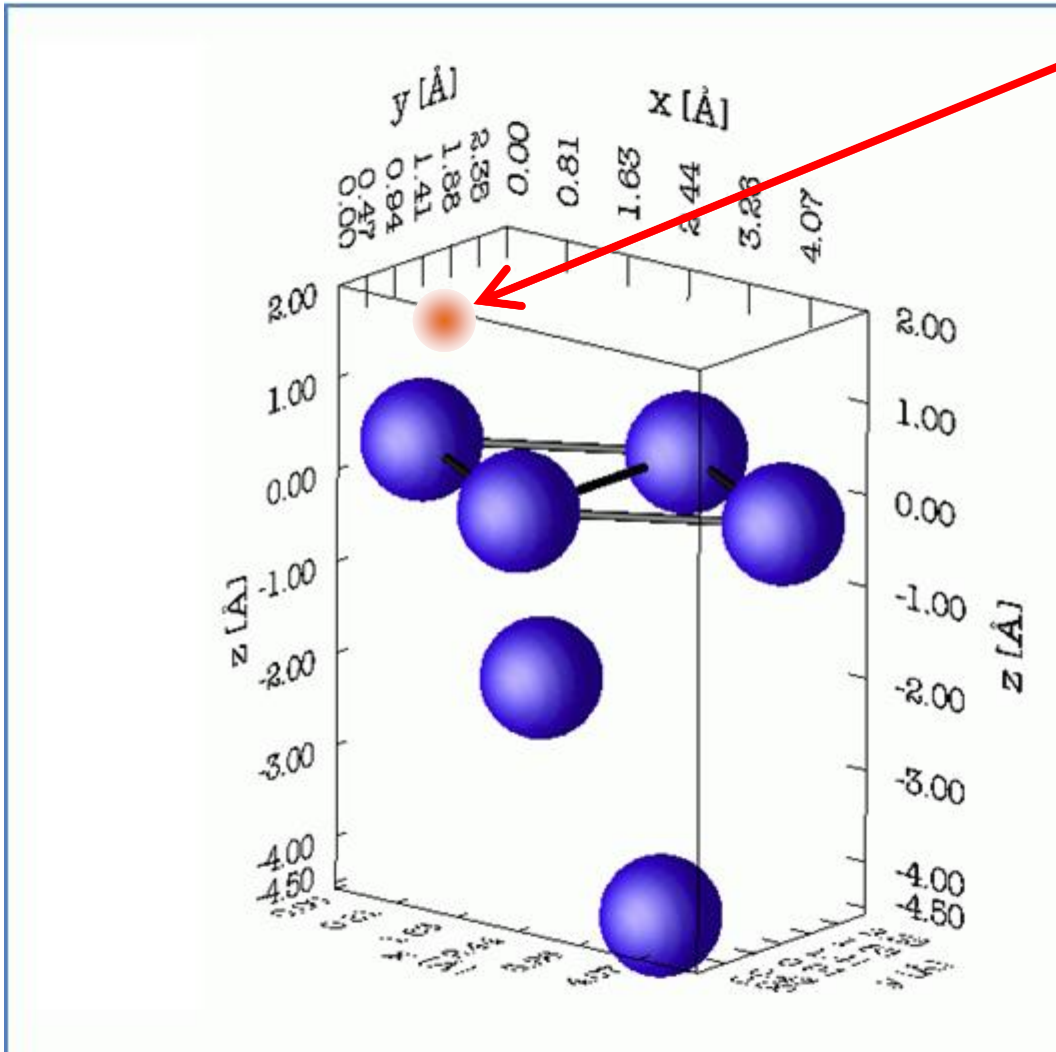


contour surface plots

adiabatic potential energy surface for nucleus motion.

Example of $U_n(\boldsymbol{R})$: Potential energy for hydrogen nucleus motion

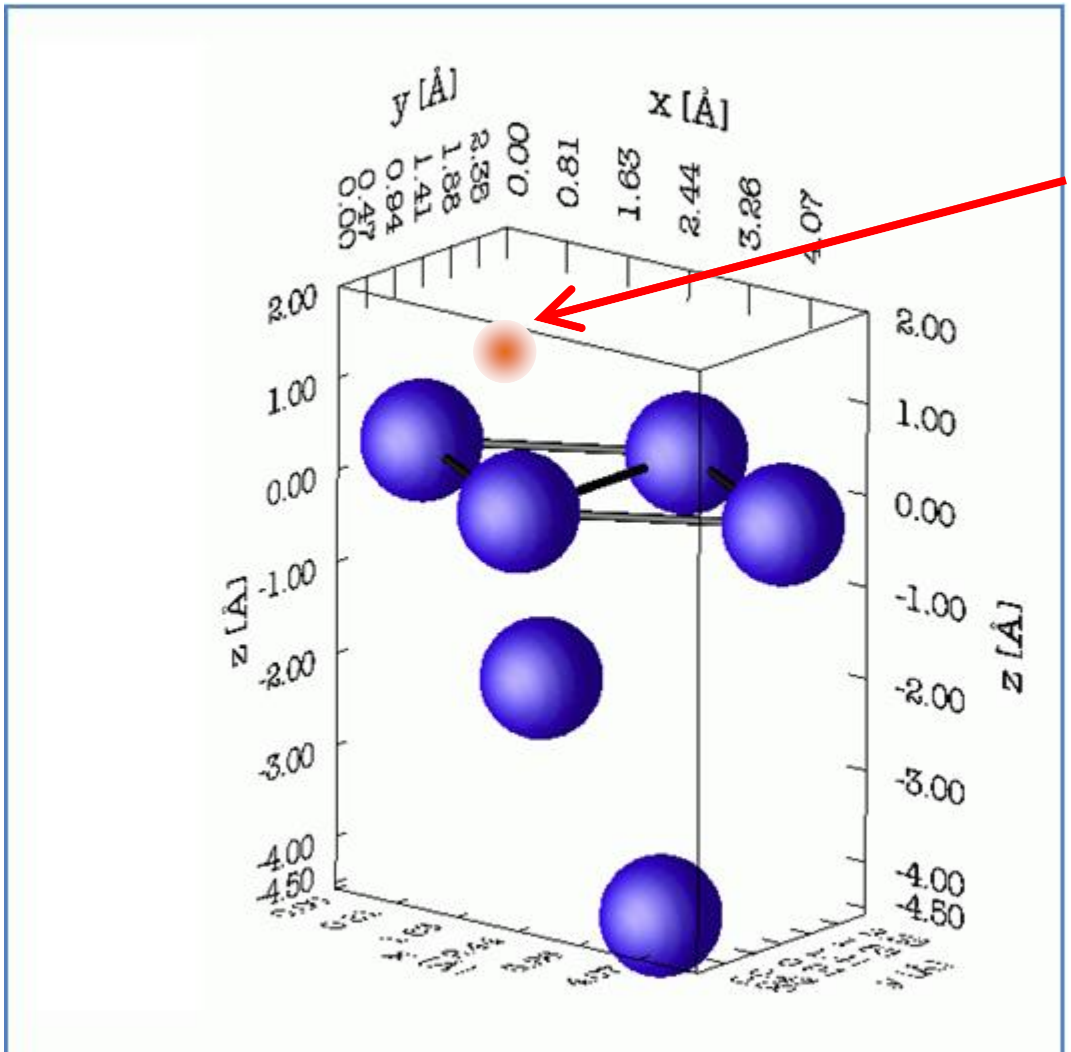
Single hydrogen atom near Pd(111) surface



$\boldsymbol{R}_1 = (x_1, y_1, z_1)$ ⇒ $U_0(\boldsymbol{R}_1)$,

Example of $U_n(\boldsymbol{R})$: Potential energy for hydrogen nucleus motion

Single hydrogen atom near Pd(111) surface



$$\boldsymbol{R}_1 = (x_1, y_1, z_1) \Rightarrow U_0(\boldsymbol{R}_1),$$

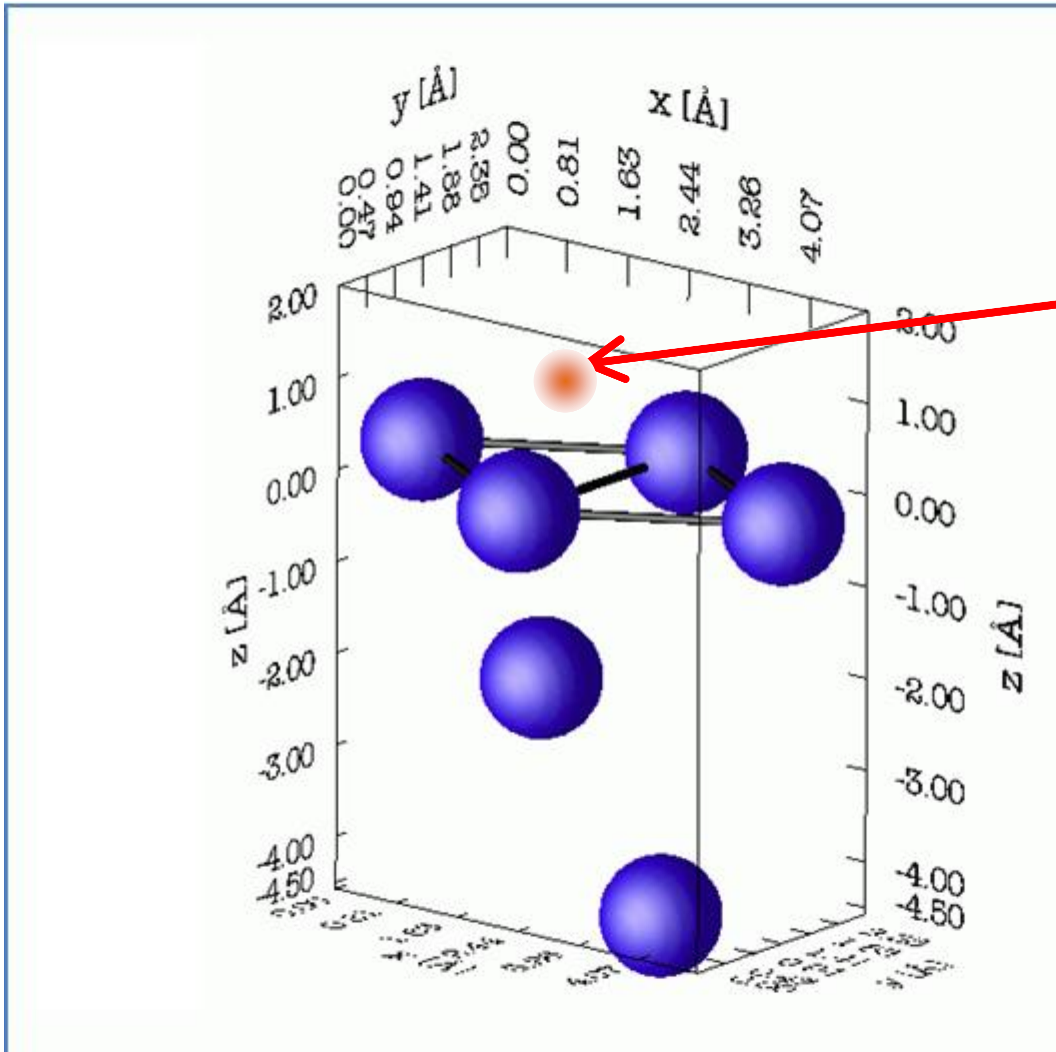
$$\boldsymbol{R}_2 = (x_2, y_2, z_2) \Rightarrow U_0(\boldsymbol{R}_2),$$

$$\boldsymbol{R}_3 = (x_3, y_3, z_3) \Rightarrow U_0(\boldsymbol{R}_3),$$

$$\boldsymbol{R}_4 = (x_4, y_4, z_4) \Rightarrow U_0(\boldsymbol{R}_4),$$

Example of $U_n(\boldsymbol{R})$: Potential energy for hydrogen nucleus motion

Single hydrogen atom near Pd(111) surface



$\boldsymbol{R}_1 = (x_1, y_1, z_1)$ ⇒ $U_0(\boldsymbol{R}_1)$,

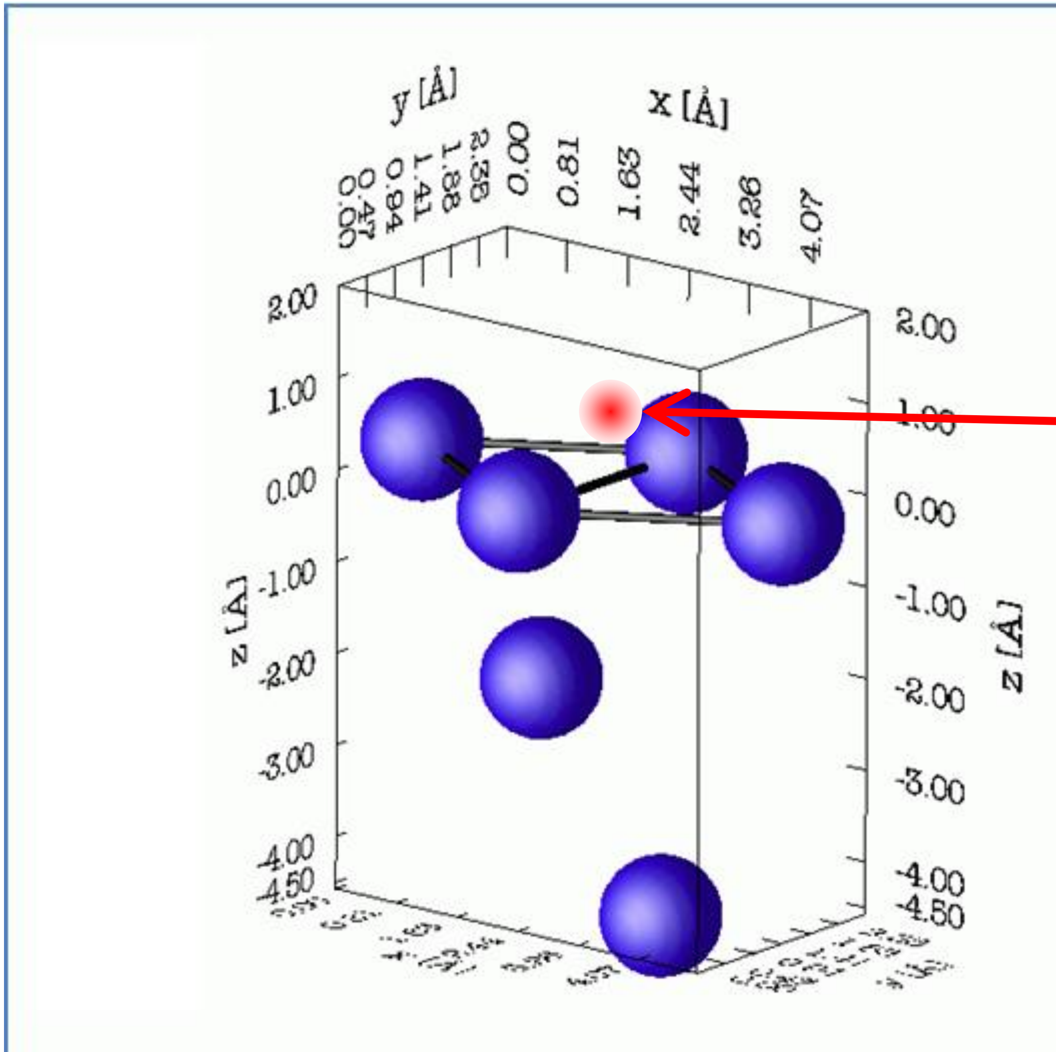
$\boldsymbol{R}_2 = (x_2, y_2, z_2)$ ⇒ $U_0(\boldsymbol{R}_2)$,

$\boldsymbol{R}_3 = (x_3, y_3, z_3)$ ⇒ $U_0(\boldsymbol{R}_3)$,

$\boldsymbol{R}_4 = (x_4, y_4, z_4)$ ⇒ $U_0(\boldsymbol{R}_4)$,

Example of $U_n(\boldsymbol{R})$: Potential energy for hydrogen nucleus motion

Single hydrogen atom near Pd(111) surface



$$\boldsymbol{R}_1 = (x_1, y_1, z_1) \Rightarrow U_0(\boldsymbol{R}_1),$$

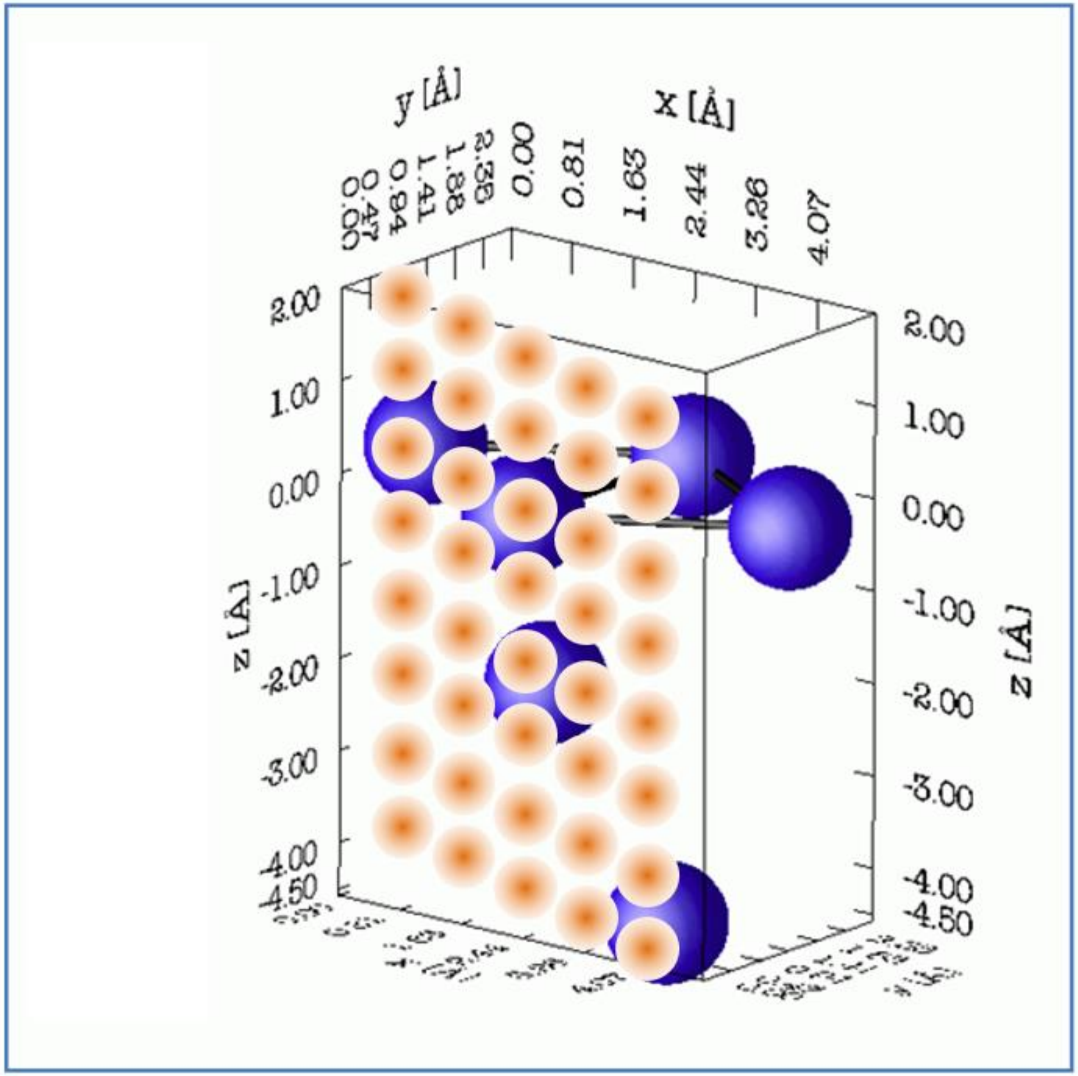
$$\boldsymbol{R}_2 = (x_2, y_2, z_2) \Rightarrow U_0(\boldsymbol{R}_2),$$

$$\boldsymbol{R}_3 = (x_3, y_3, z_3) \Rightarrow U_0(\boldsymbol{R}_3),$$

$$\boldsymbol{R}_4 = (x_4, y_4, z_4) \Rightarrow U_0(\boldsymbol{R}_4),$$

Example of $U_n(\boldsymbol{R})$: Potential energy for hydrogen nucleus motion

Single hydrogen atom near Pd(111) surface



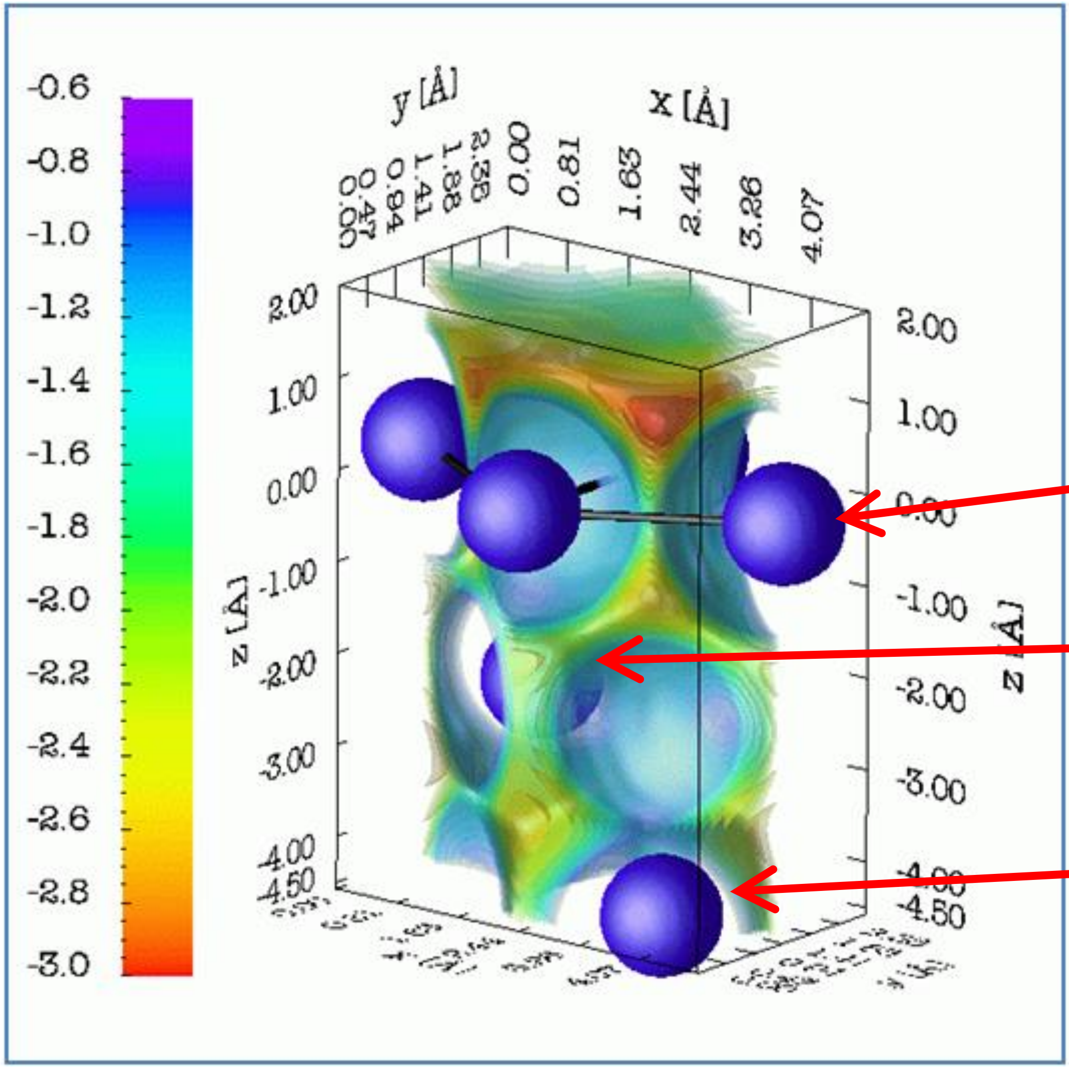
3-dimensional potential energy for hydrogen nucleus motion

$U_0(\boldsymbol{R})$,

Function of $\boldsymbol{R}$

Example of $U_n(\boldsymbol{R})$: Potential energy for hydrogen nucleus motion

$U_0(\boldsymbol{R}_1), \quad \boldsymbol{R}_1 = (x_1, y_1, z_1)$ **Single hydrogen atom near Pd(111) surface**

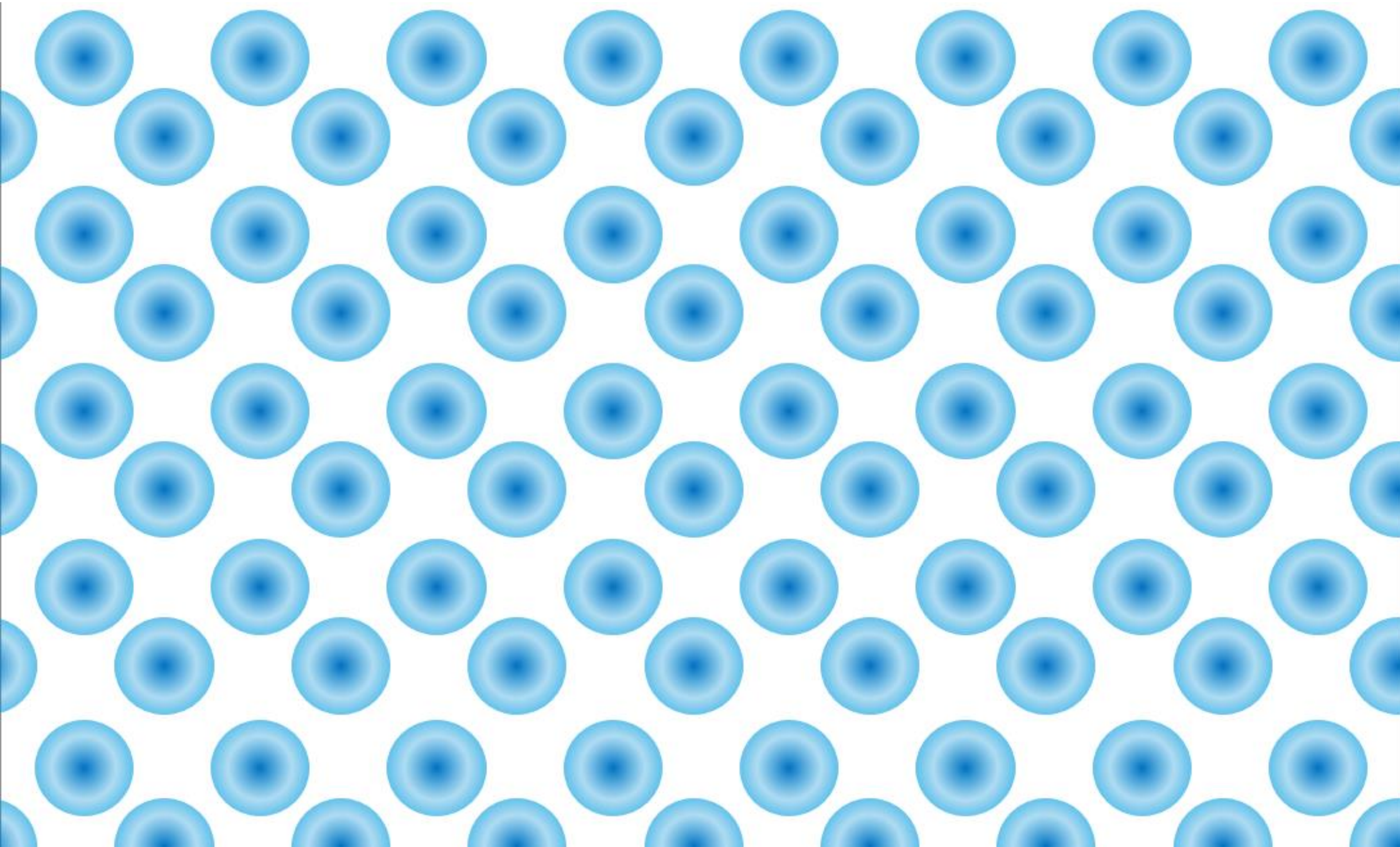


contour surface plots

adiabatic potential energy surface for nucleus motion.

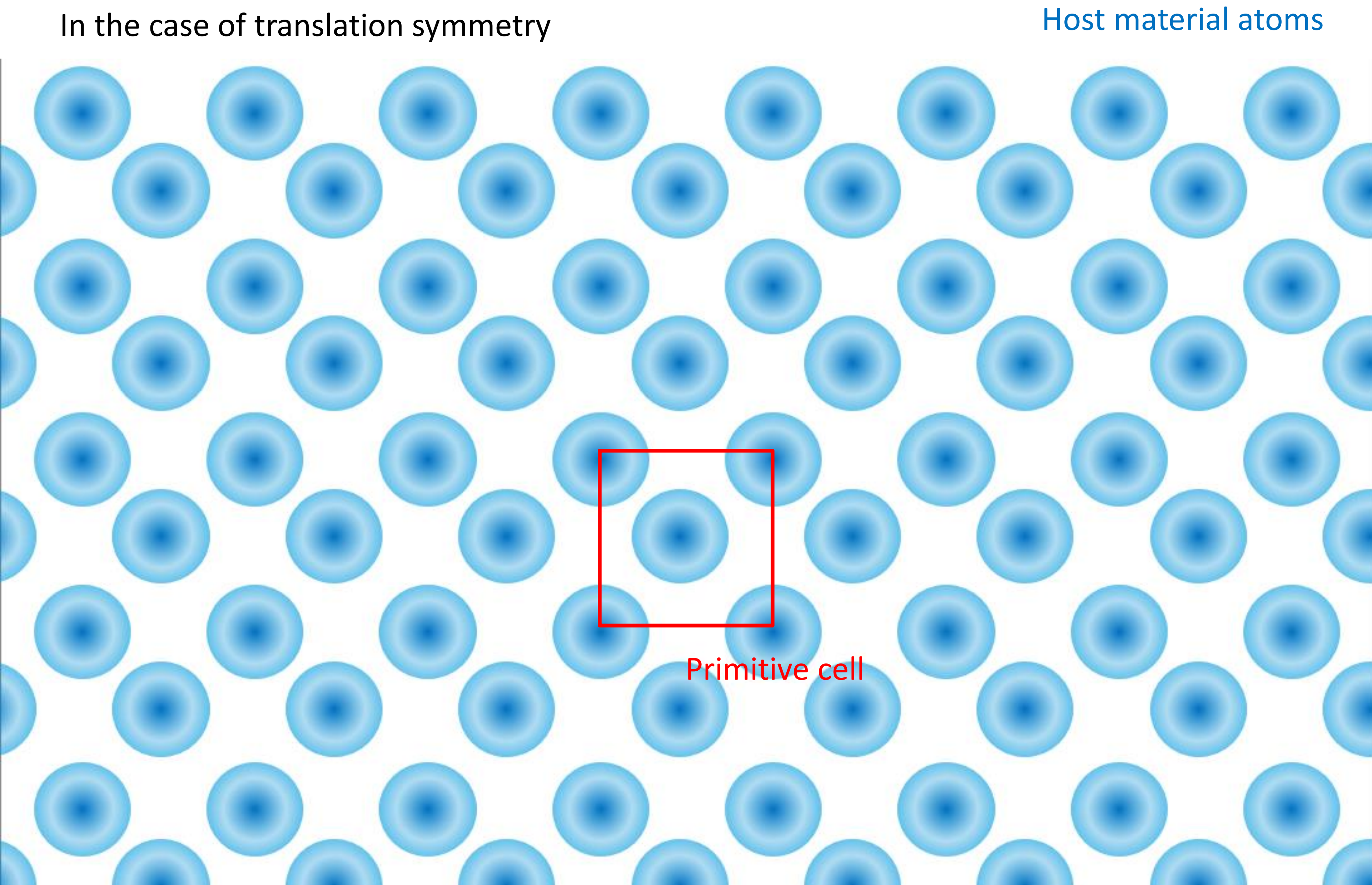
Important reminder for making potential energy surface

In the case of translation symmetry



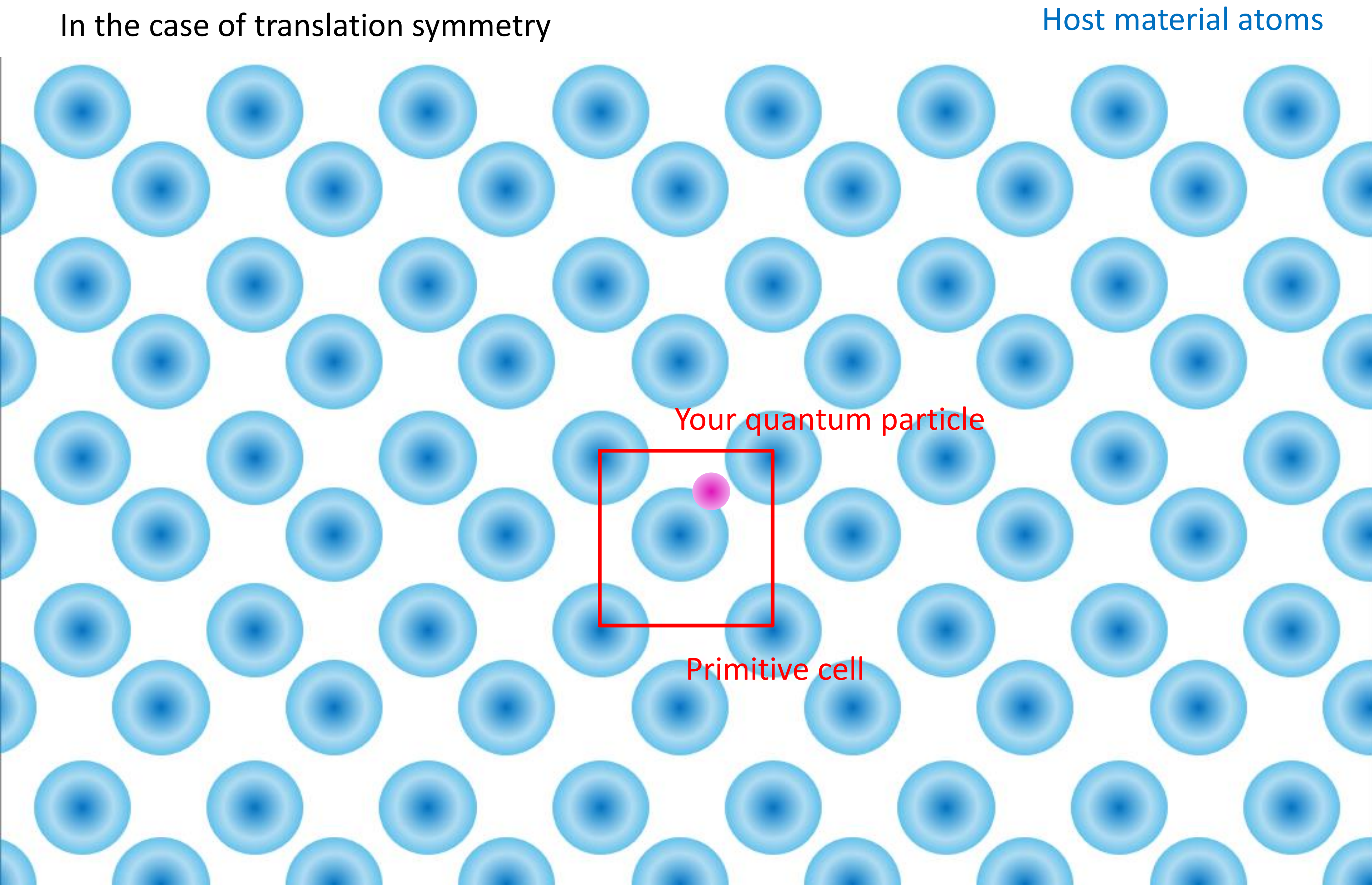
Important reminder for making potential energy surface

In the case of translation symmetry



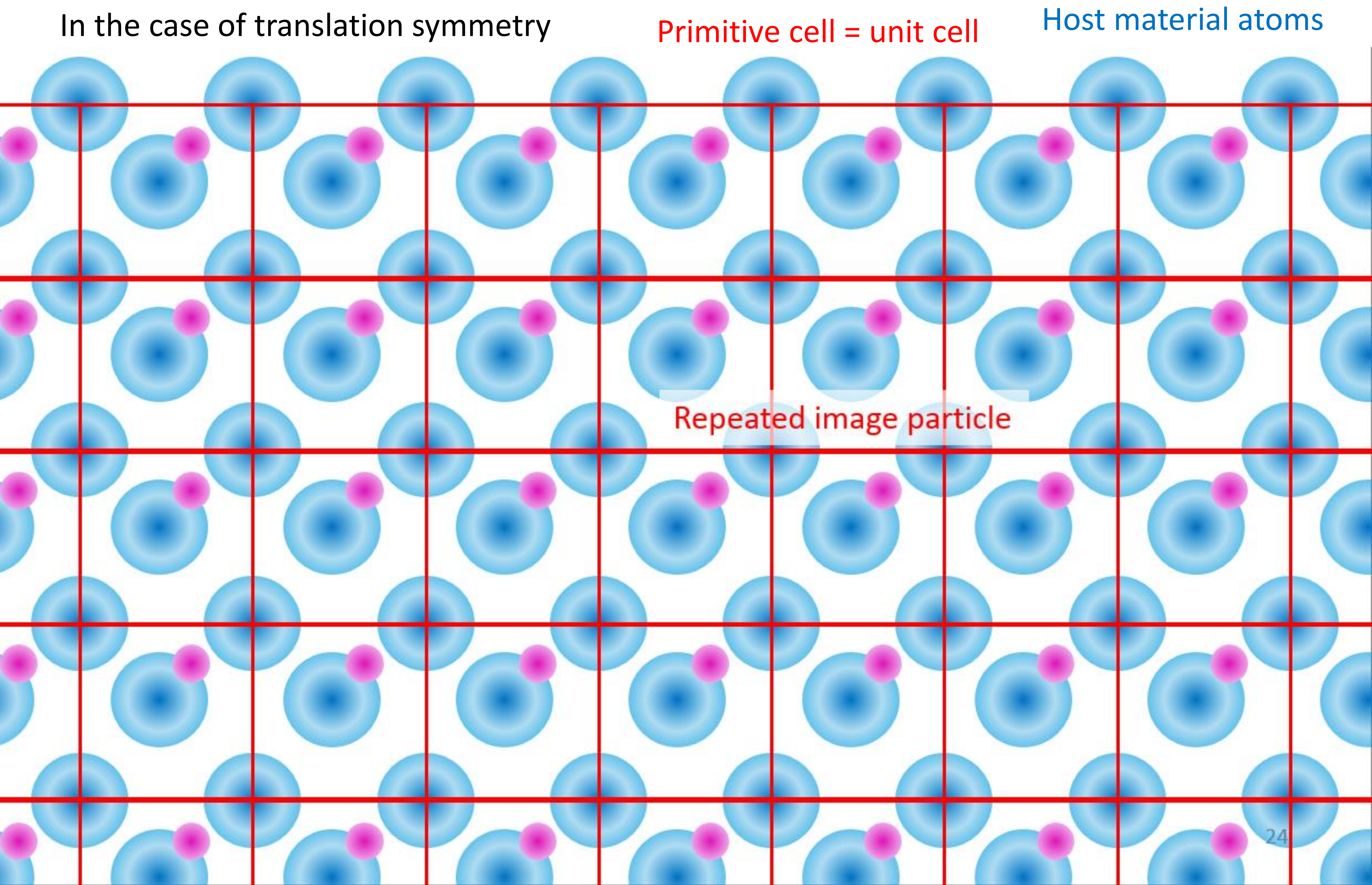
Important reminder for making potential energy surface

In the case of translation symmetry

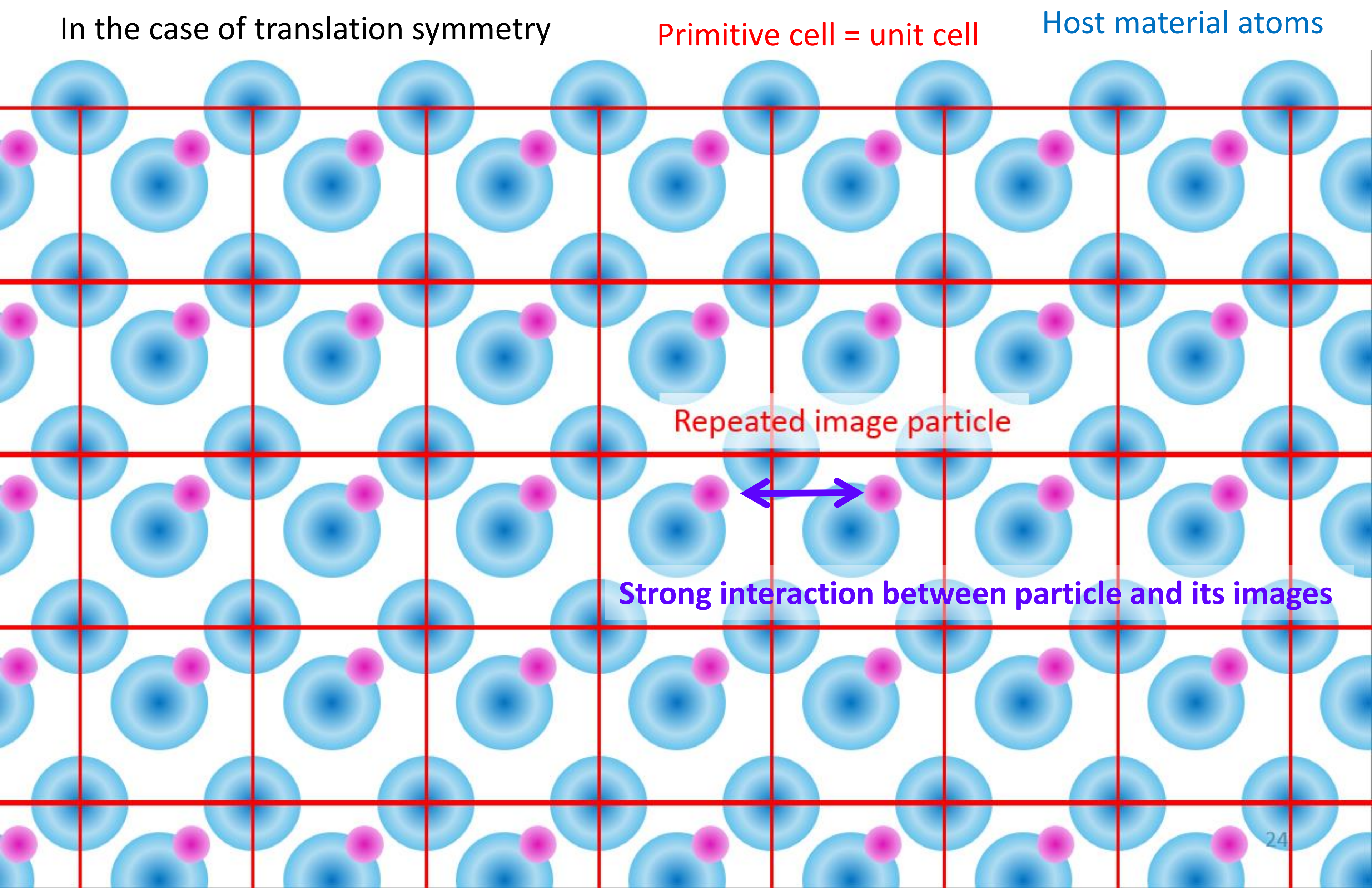


Important reminder for making potential energy surface

In the case of translation symmetry

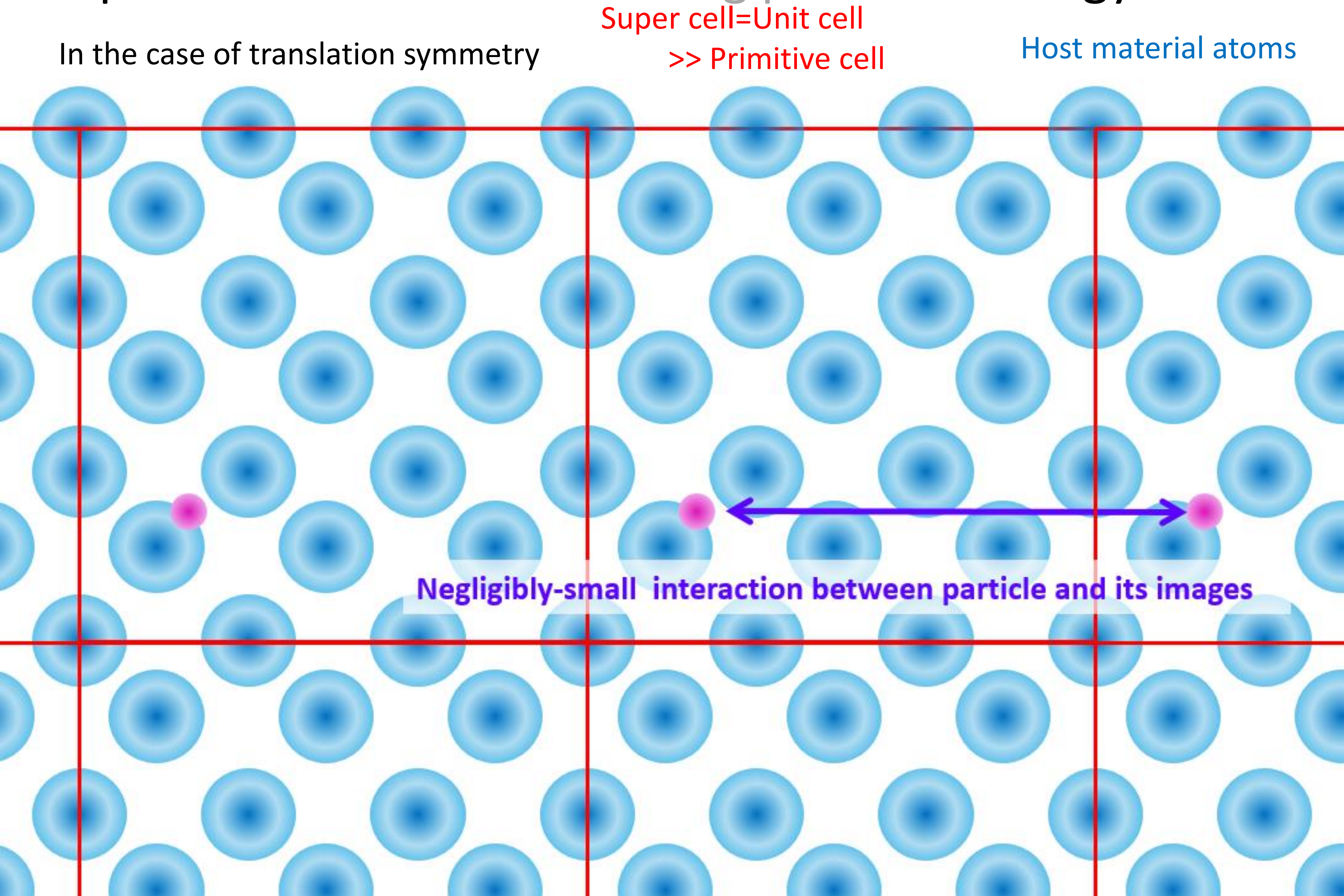


Important reminder for making potential energy surface

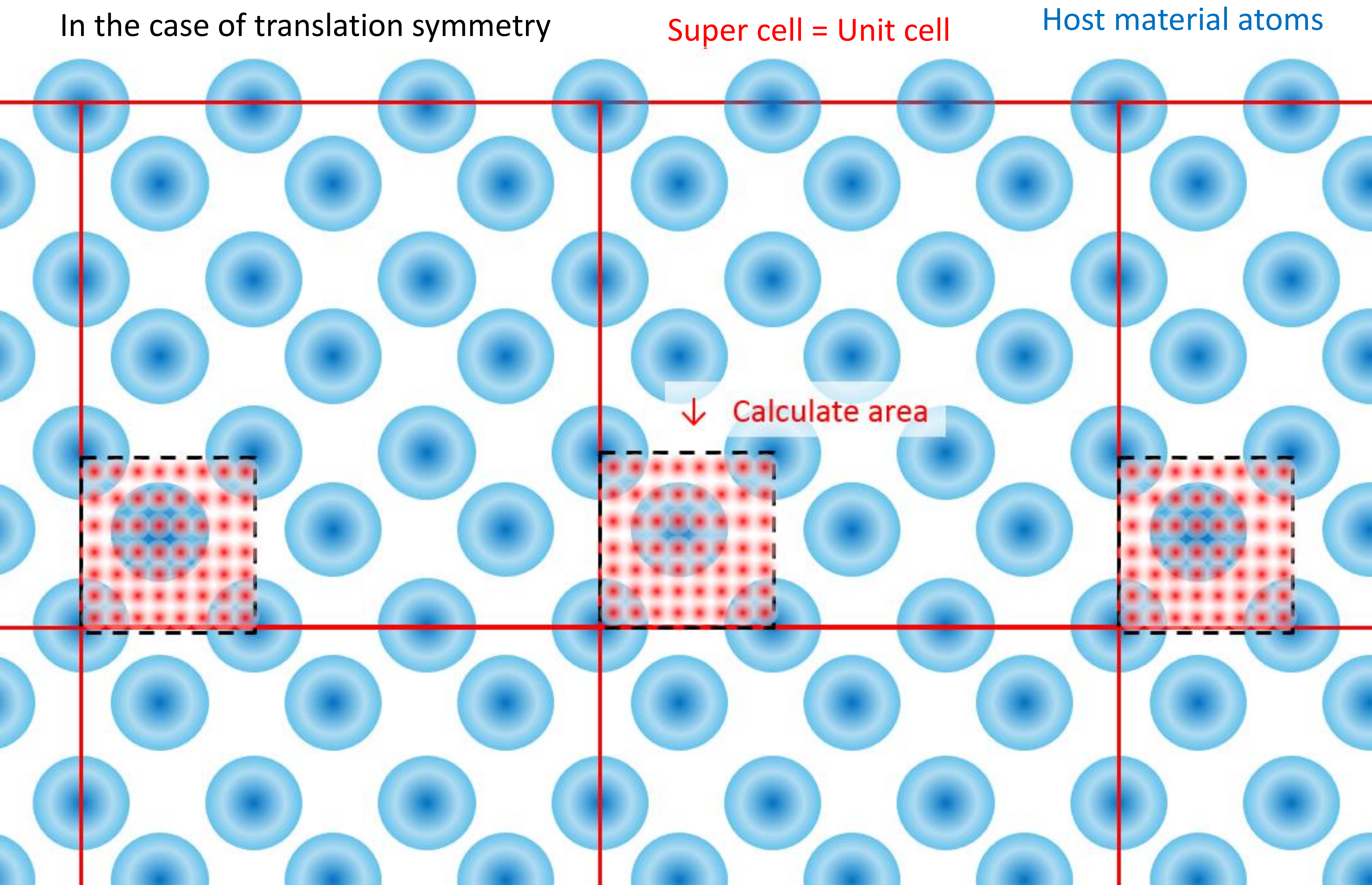


Important reminder for making potential energy surface

In the case of translation symmetry

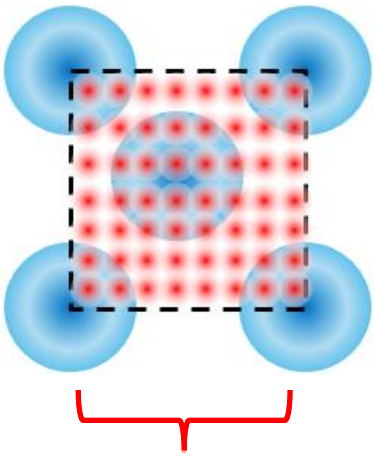


Important reminder for making potential energy surface



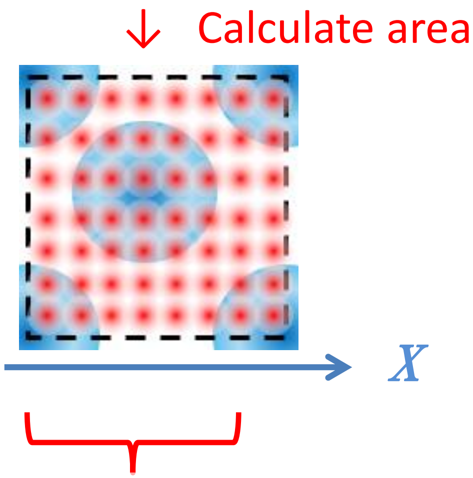
Important reminder for making potential energy surface

↓ Calculate area



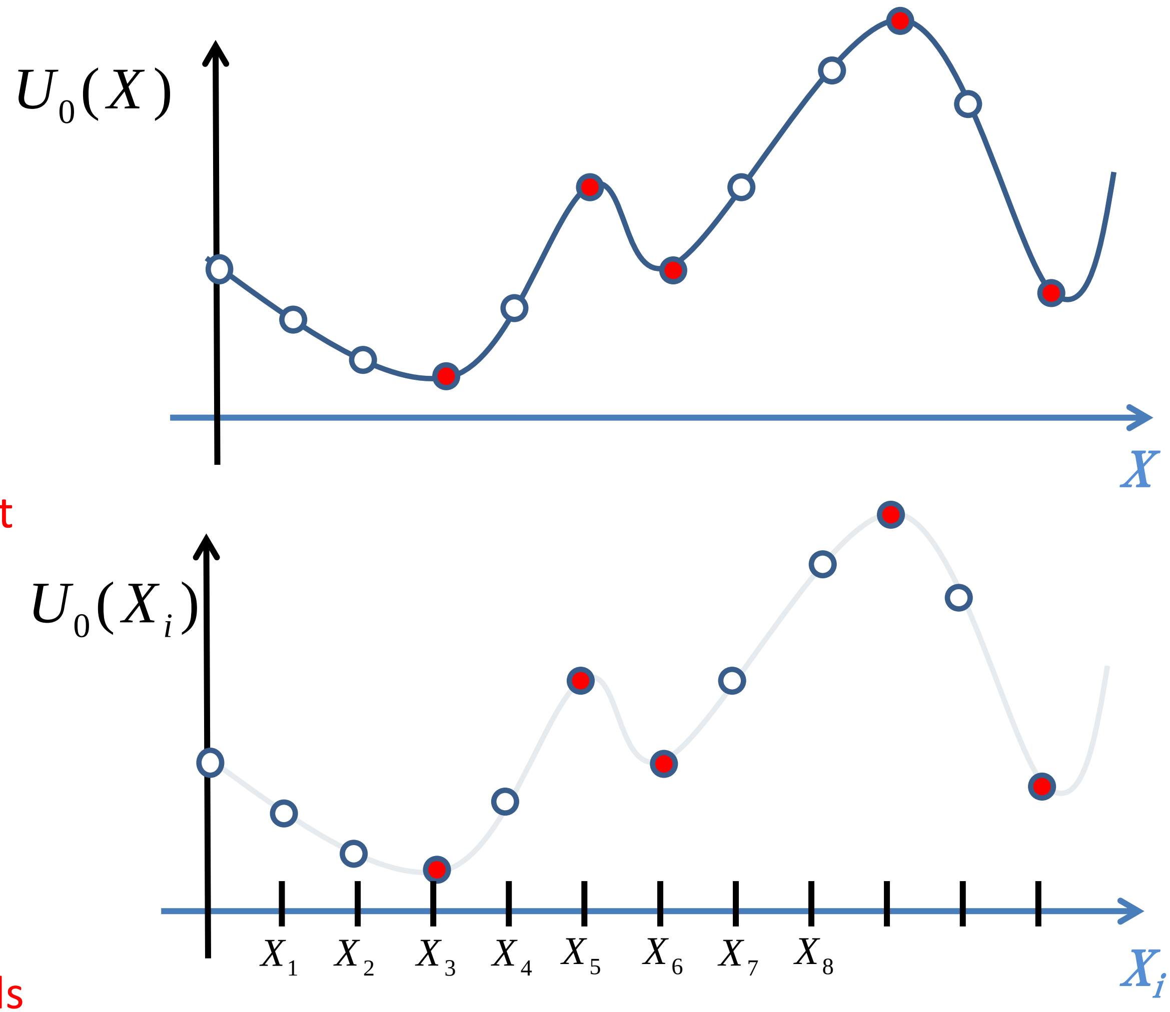
Number of calculating point → enough large

Important reminder for making potential energy surface



Number of calculating point

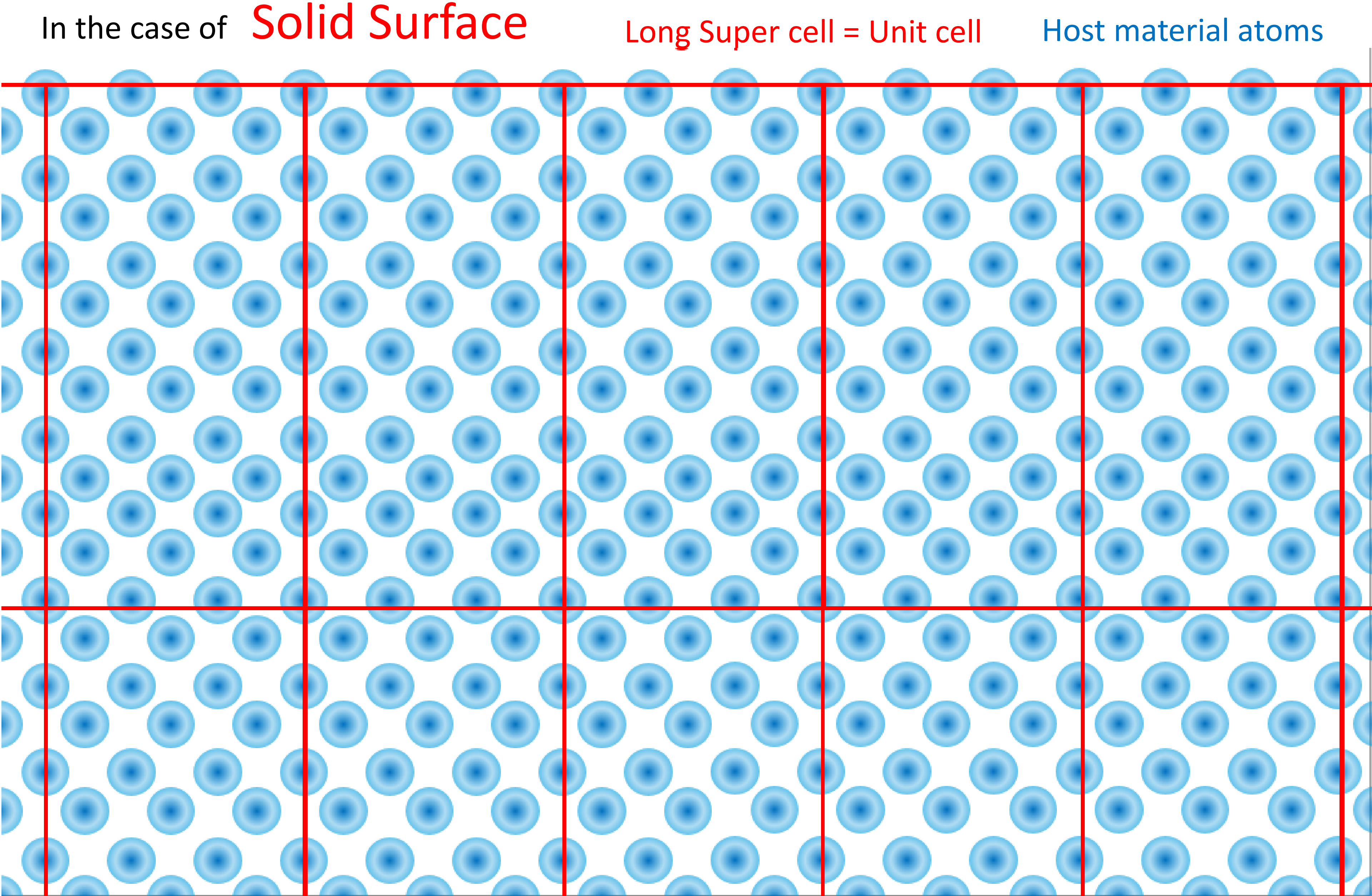
enough large number
to satisfy the following needs



- All extremums (maximals and minimals) have to be reproduced.
- Potential energy curves have to be smoothly connected

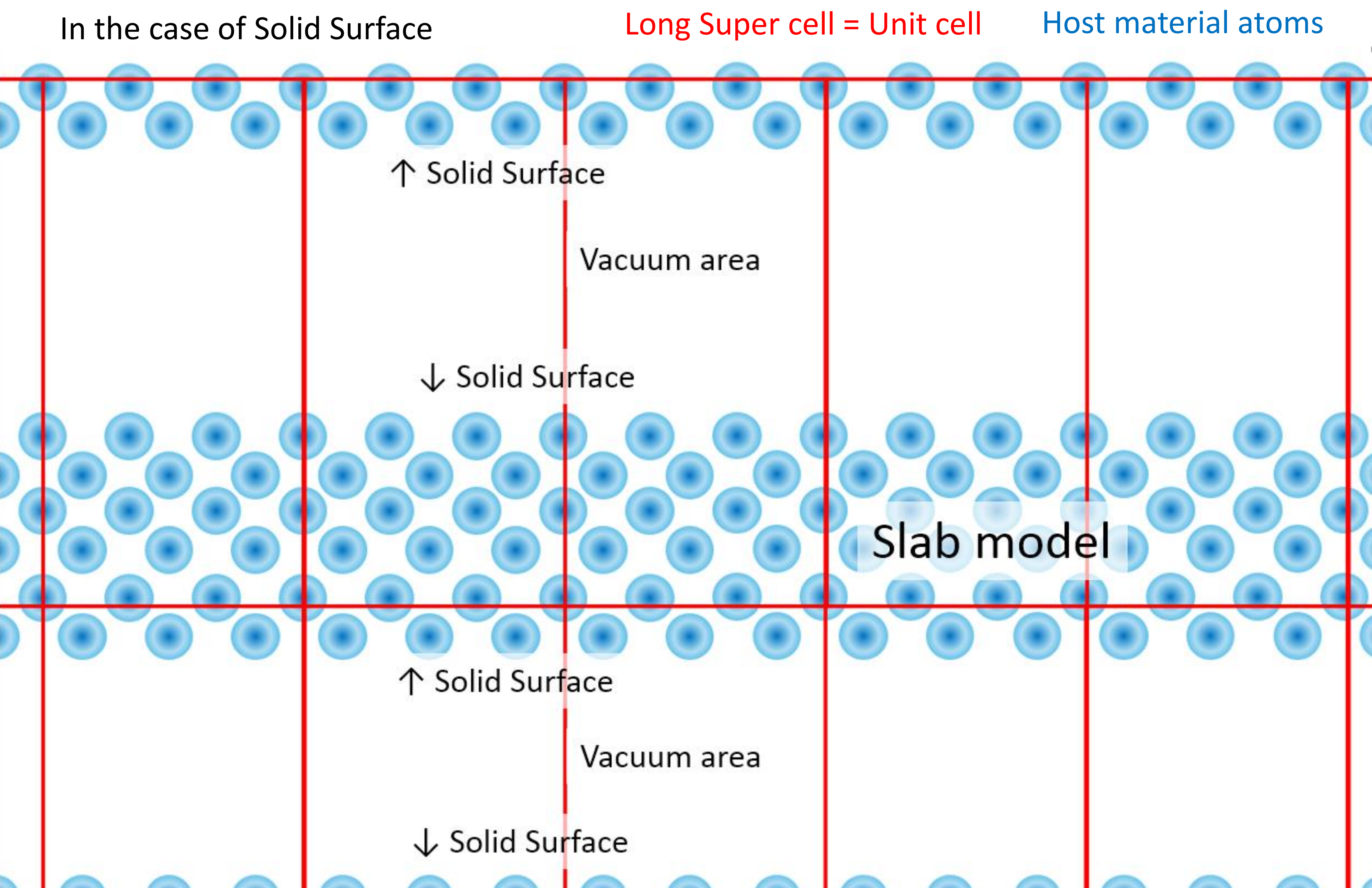
Important reminder for making potential energy surface

In the case of Solid Surface



Important reminder for making potential energy surface

In the case of Solid Surface

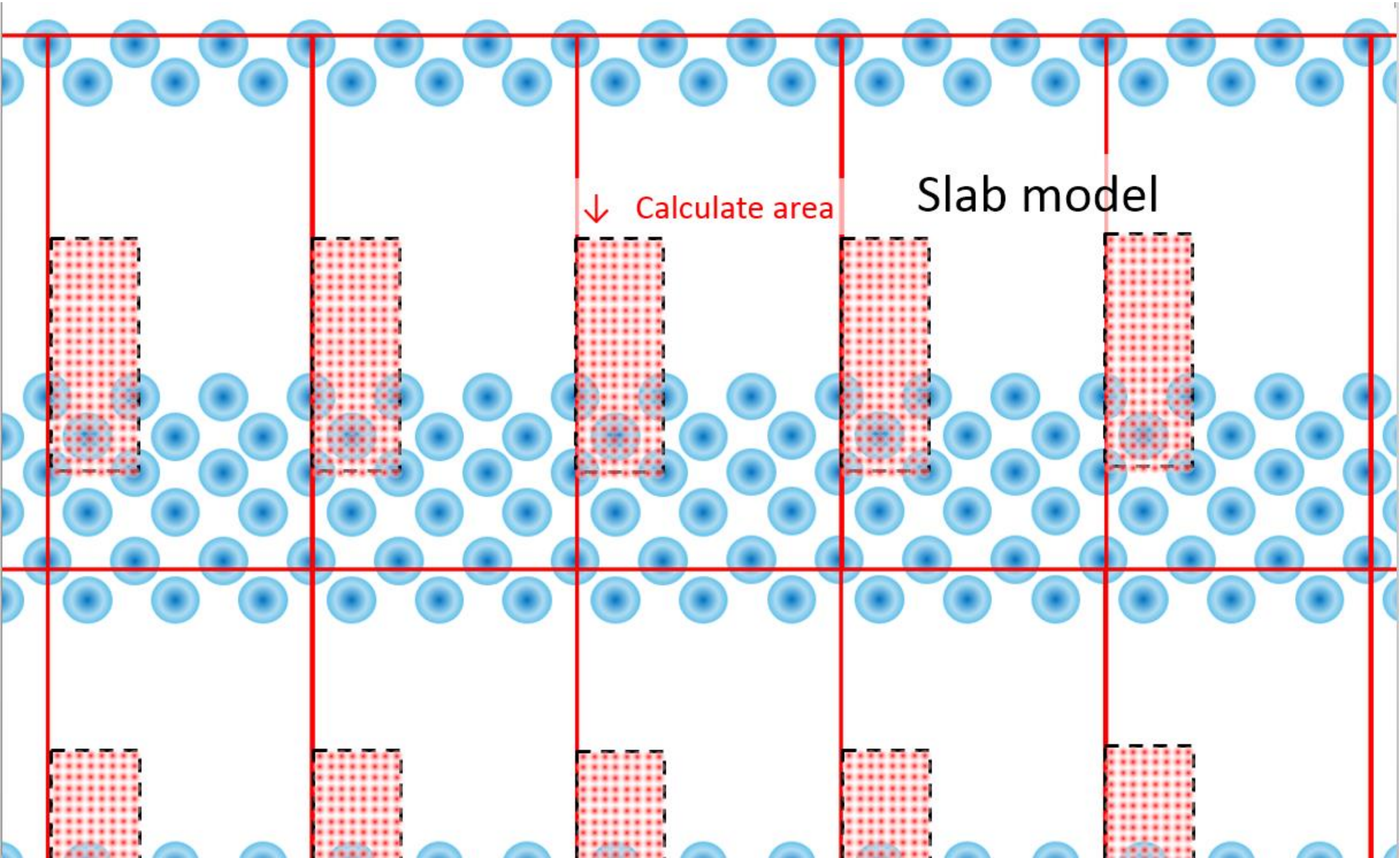


Important reminder for making potential energy surface

In the case of Solid Surface

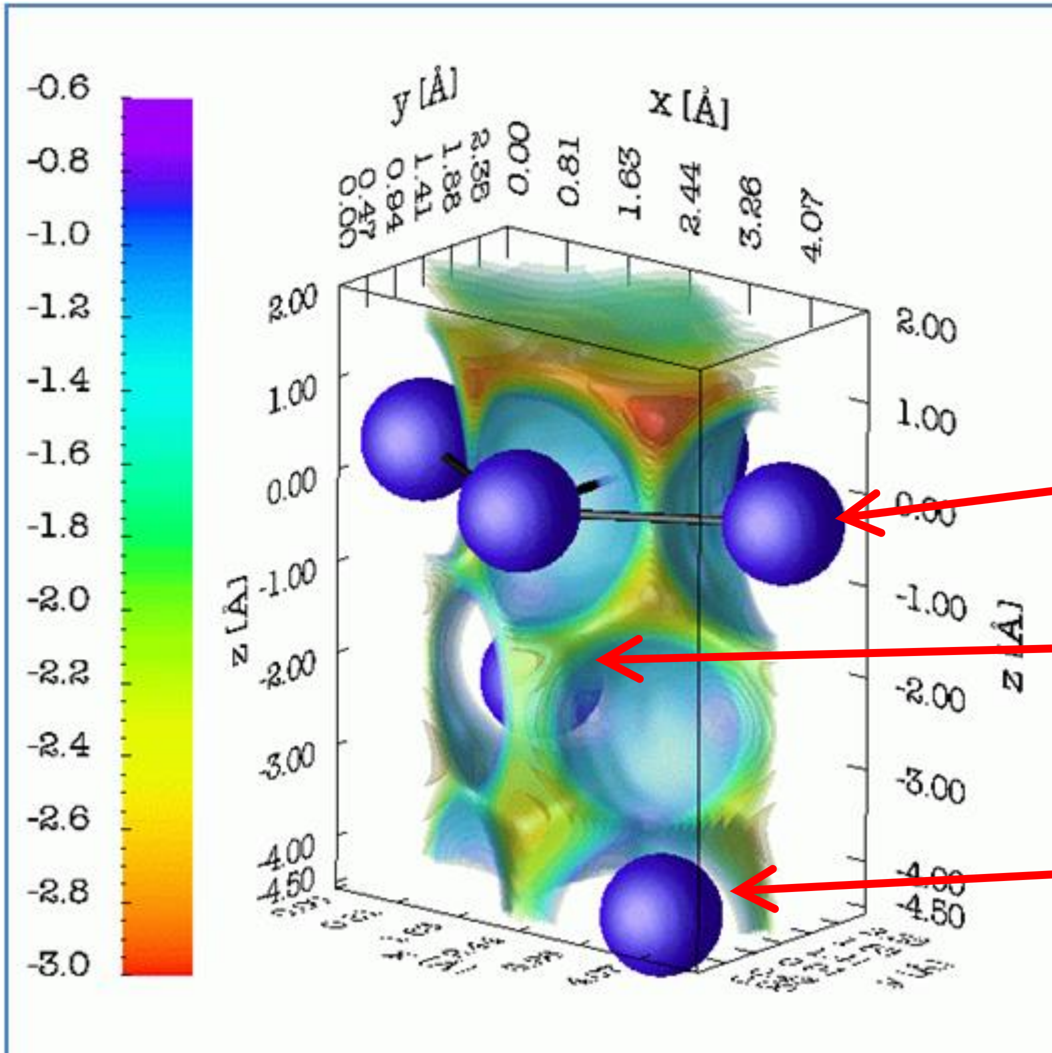
Long Super cell = Unit cell

Host material atoms



Example of $U_n(\boldsymbol{R})$: Potential energy for hydrogen nucleus motion

$U_0(\boldsymbol{R}_1), \quad \boldsymbol{R}_1 = (x_1, y_1, z_1)$ **Single hydrogen atom near Pd(111) surface**



contour surface plots

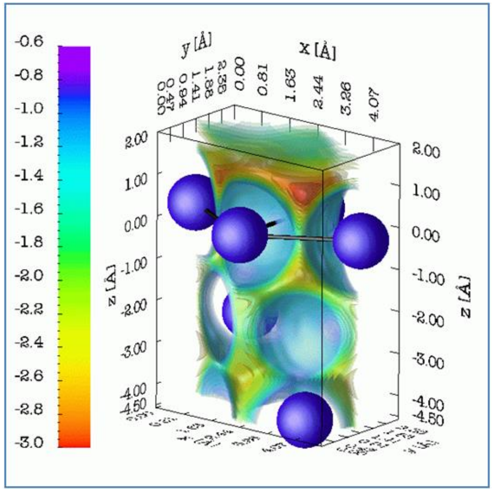
adiabatic potential energy surface for nucleus motion.

Next we solve the equation (**)
for a hydrogen atom motion
under given potential, $U_0(x,y,z)$.

$$\left[-\frac{\hbar^2}{2M_{\mathrm{Hydrogen}}}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+U_0(x,y,z)\right]\phi_{\omega;0}(x,y,z)=E_{\omega,0}\phi_{\omega;0}(x,y,z) \quad \cdots \quad (**)$$

(x,y,z) : Hydrogen atom position

$U_0(x,y,z)$



Difference in interaction potential with host

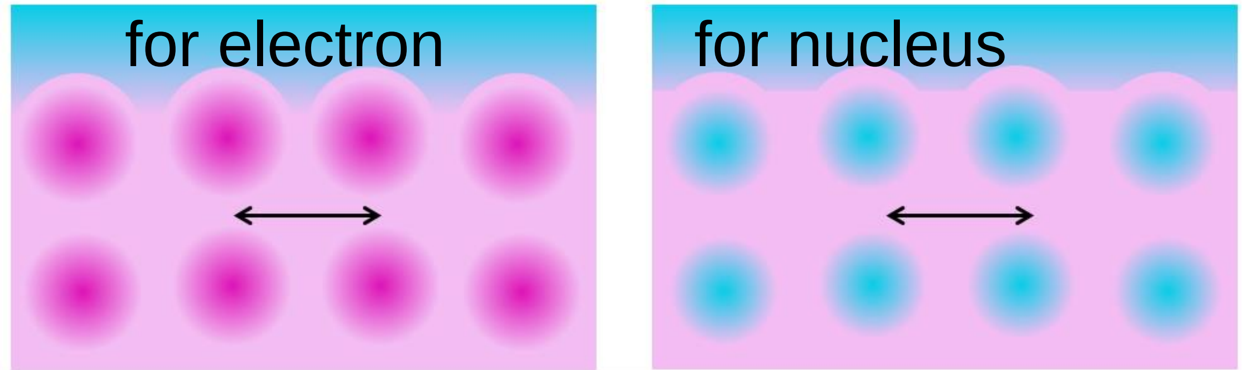
for electron state:

- Attractive potential from host nucleus
- Near surface, attractive potential into bulk side

for nucleus state:

- Repulsive potential from host nucleus
- Near surface, attractive potential into bulk side

Scale length is same in potential for electron and for nucleus



Difference in kinetic energy

for electron state:

$$\left[\left(-\frac{\hbar^2}{2m_e}\right)\left(\frac{\partial^2}{\partial^2 x_i}+\frac{\partial^2}{\partial^2 y_i}+\frac{\partial^2}{\partial^2 z_i}\right)+V(\boldsymbol{r},\boldsymbol{R})\right]$$

muon

hydrogen

Mass ratio: $\boxed{\gamma}=\dfrac{M_I}{m_e}=200,2000\sim5000$

for nucleus state:

$$\left[\left(-\frac{\hbar^2}{2M_I}\right)\left(\frac{\partial^2}{\partial^2 X_I}+\frac{\partial^2}{\partial^2 Y_I}+\frac{\partial^2}{\partial^2 Z_I}\right)+U(\boldsymbol{R})\right]=\left[\left(-\frac{\hbar^2}{2(\boxed{\gamma}\, m_e)}\right)\left(\frac{\partial^2}{\partial^2 X_I}+\frac{\partial^2}{\partial^2 Y_I}+\frac{\partial^2}{\partial^2 Z_I}\right)+U(\boldsymbol{R})\right]$$

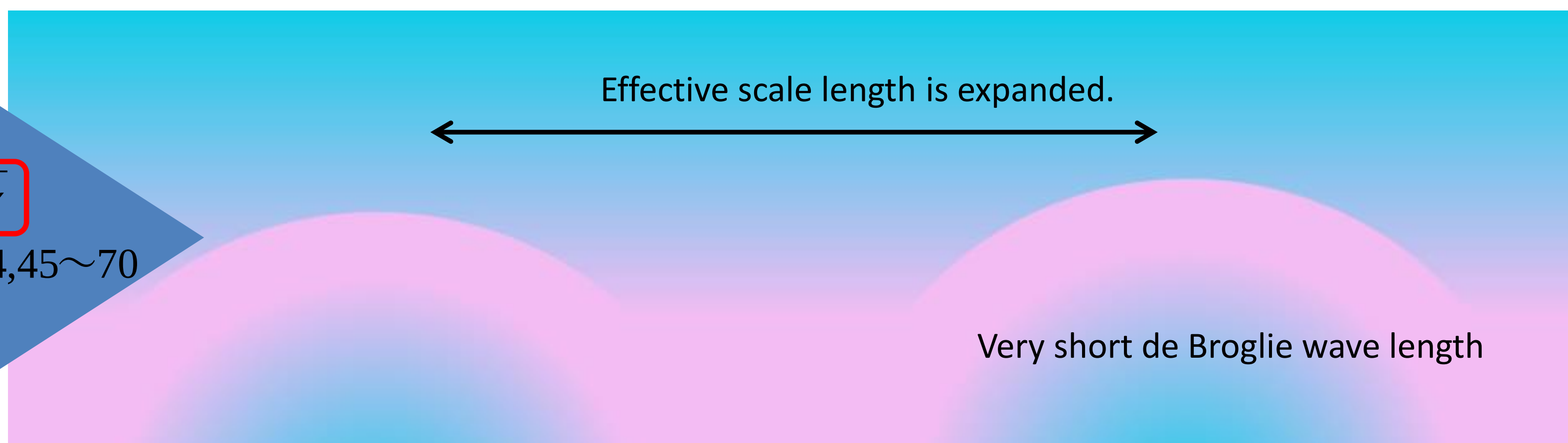
$$=\left[\left(-\frac{\hbar^2}{2m_e}\right)\left(\frac{\partial^2}{\partial^2 \xi_I}+\frac{\partial^2}{\partial^2 \eta_I}+\frac{\partial^2}{\partial^2 \zeta_I}\right)+U\left(\frac{\rho}{\boxed{\sqrt{\gamma}}}\right)\right]$$

variable transformation for particle position

$$\sqrt{\gamma}X_I=\xi_I,\ \sqrt{\gamma}Y_I=\eta_I,\ \sqrt{\gamma}Z_I=\xi_I,\ \sqrt{\gamma}R=\rho$$

$\times\boxed{\sqrt{\gamma}}$

$14,45\sim70$



Difference in kinetic energy

for electron state:

$$\left[\left(-\frac{\hbar^2}{2m_e}\right)\left(\frac{\partial^2}{\partial^2 x_i}+\frac{\partial^2}{\partial^2 y_i}+\frac{\partial^2}{\partial^2 z_i}\right)+V(\mathbf{r},\mathbf{R}\right.$$

Mass ratio: $\boxed{\gamma}=\frac{M_I}{m_e}=200\sim5000$

for nucleus state:

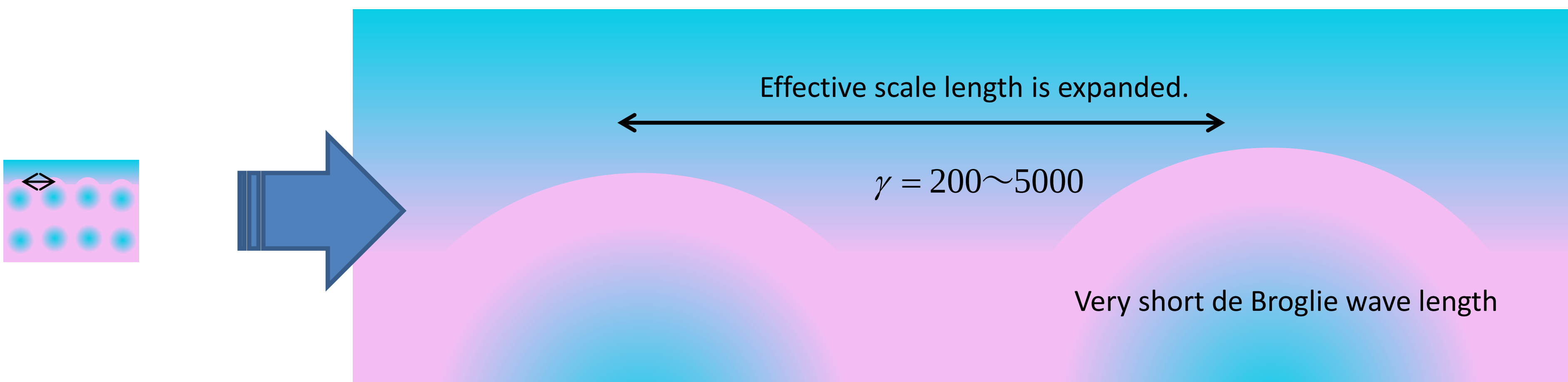
$$\left[\left(-\frac{\hbar^2}{2M_I}\right)\left(\frac{\partial^2}{\partial^2 X_I}+\frac{\partial^2}{\partial^2 Y_I}+\frac{\partial^2}{\partial^2 Z_I}\right)+U(\mathbf{R})\right]=\left[\left(-\frac{\hbar^2}{2(\boxed{\gamma}\, m_e)}\right)\left(\frac{\partial^2}{\partial^2 X_I}+\frac{\partial^2}{\partial^2 Y_I}+\frac{\partial^2}{\partial^2 Z_I}\right)+U(\mathbf{R})\right]$$

Plane wave is unsuitable as basis function describing the wave function of nucleus

Variable transformation for particle position

$\gamma x_I=\xi_I,\ \gamma y_I=\eta_I,\ \gamma\zeta_I=\xi_I,\ \gamma R=\rho$

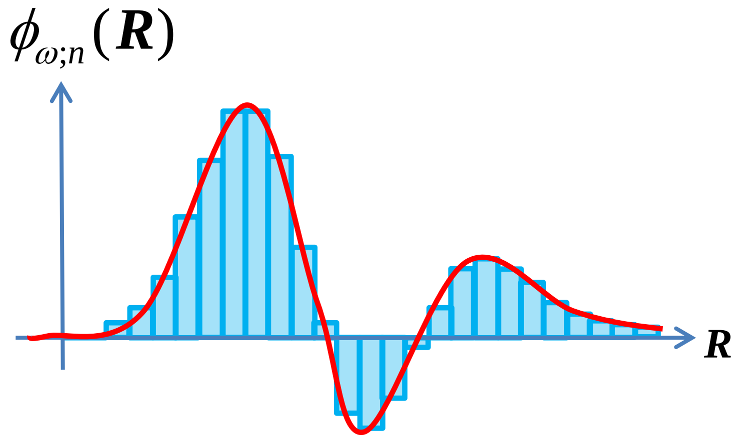
$$=\left[\left(-\frac{\hbar^2}{2m_e}\right)\left(\frac{\partial^2}{\partial^2 \xi_I}+\frac{\partial^2}{\partial^2 \eta_I}+\frac{\partial^2}{\partial^2 \zeta_I}\right)+U\left(\frac{\rho}{\boxed{\gamma}}\right)\right]$$



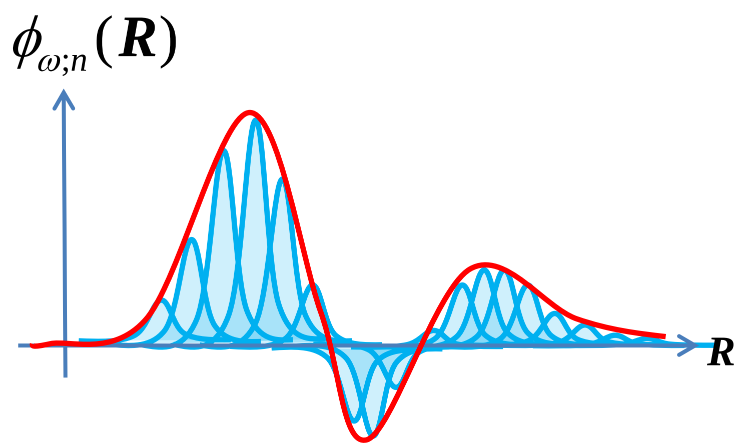
For describing the nucleus state.

Dividing up space into small areas,
localized function at each area can be suitable as basis function.

Rectangular function



Gauss function



linear combination of basis functions: $\phi_\omega(x,y,z)=\sum_{\ell}^{N_\mathrm{G}} C_{\omega,\ell} G_\ell(x,y,z)$

Variation method

$$\sum_{\ell'}\left[H_{\ell\ell'}-E_\omega S_{\ell\ell'}\right]C_{\omega,\ell}=0$$

$$H_{\ell\ell'}=K_{\ell\ell'}+U_{\ell\ell'}$$

$$K_{\ell\ell'}=\iint\int_{-\infty}^{+\infty} G_\ell(x,y,z)\left[-\frac{\hbar^2}{2M_{\mathrm{Hydrogen}}}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\right]G_{\ell'}(x,y,z)dxdydz$$

$$U_{\ell\ell'}=\iint\int_{-\infty}^{+\infty} G_\ell(x,y,z)U_0\left(x,y,z\right)G_{\ell'}(x,y,z)dxdydz$$

$$S_{\ell\ell'}=\iint\int_{-\infty}^{+\infty} G_\ell(x,y,z)\,G_{\ell'}(x,y,z)dxdydz$$

Secular equation $N_\mathrm{G}\times N_\mathrm{G}$

N_G: number of basis functions

$$\begin{vmatrix} H_{11}-E\,S_{11} & H_{12}-E\,S_{12} & \cdots & H_{1N_\mathrm{G}}-E\,S_{1N_\mathrm{G}} \\ H_{21}-E\,S_{21} & H_{22}-E\,S_{22} & \cdots & H_{2N_\mathrm{G}}-E\,S_{2N_\mathrm{G}} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N_\mathrm{G}1}-E\,S_{N_\mathrm{G}1} & H_{N_\mathrm{G}2}-E\,S_{N_\mathrm{G}2} & \cdots & H_{N_\mathrm{G}N_\mathrm{G}}-E\,S_{N_\mathrm{G}N_\mathrm{G}} \end{vmatrix}=0$$

For describing the nucleus state.

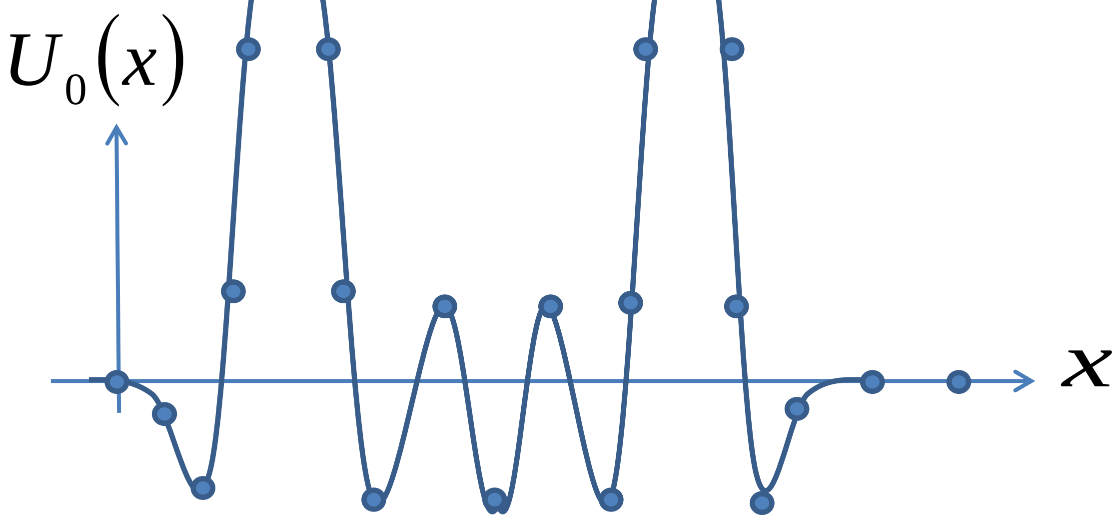
	$K_{\ell\ell'}$	$U_{\ell\ell'}$	$S_{\ell\ell'}$
Rectangular function	Approximate calculation	Diagonal	Diagonal
Gauss function	Analytically-integrated	Numerically-integrated	Analytically-integrated
Plane wave	analytically-integrated	FFT	Diagonal

For describing the nucleus state.

	$K_{\ell\ell'}$	$U_{\ell\ell'}$	$S_{\ell\ell'}$
Rectangular function	Approximate calculation	Diagonal	Diagonal
Gauss function	Analytically-integrated	Numerically-integrated	Analytically-integrated
Plane wave	analytically-integrated	FFT	Diagonal

$U_{\ell\ell'}$

Numerically-integrated



$U_n = U_0(x_n)$ Value at Sampling point R_n $n = 0,1,2,3,\cdots, N-1$

Discrete Fourier transform

$$U_n \to \tilde{U}_k$$

Inverse Fourier transform

$$U(x) = \frac{1}{N}\sum_{k=0}^{N-1} \tilde{U}_k \exp\left(\frac{2\pi i}{L}k \cdot x\right)$$

Not reproduce the blue solid line for continuous *x*: $U_0(x)$

k	0	1	2	$\cdots$	$\frac{N-1}{2}$	$\frac{N-1}{2}+1$	$\cdots$	N-2	N-1
$\tilde{U}$	$\tilde{U}_0$	$\tilde{U}_1$	$\tilde{U}_2$	$\cdots$	$\tilde{U}_{\frac{N-1}{2}}$	$\tilde{U}_{\frac{N-1}{2}+1}$	$\cdots$	$\tilde{U}_{N-2}$	$\tilde{U}_{N-1}$

Right circular shift by half data

k	$-\frac{N-1}{2}$		$\cdots$	-1	0	+1	$\cdots$		$\frac{N-1}{2}$
$\tilde{U}$	$\tilde{U}_{\frac{N-1}{2}+1}$		$\cdots$	$\tilde{U}_{N-1}$	$\tilde{U}_0$	$\tilde{U}_1$	$\cdots$		$\tilde{U}_{\frac{N-1}{2}}$

$$U(x) = \frac{1}{N} \sum_{k=-\frac{N-1}{2}}^{\frac{N-1}{2}} \tilde{U}_k \exp\left(\frac{2\pi i}{L} k \cdot x \right)$$

It can solve the missing part between sampling points.

$$U_{\ell\ell'} = \iint \int_{-\infty}^{+\infty} G_\ell(x,y,z) U_0(x,y,z) G_{\ell'}(x,y,z)\, dxdydz$$

is analytically integrated

$$G_\ell(x,y,z)=\left(\frac{8\beta_x\beta_y\beta_z}{\pi^3}\right)^{1/4}\exp\left\{-\beta_x(x-X_\ell)^2-\beta_y(y-Y_\ell)^2-\beta_z(z-Z_\ell)^2\right\}$$

3D-Gauss function whose center locates at glide point (X_l,Y_l,Z_l)

$$S_{\ell\ell'}=\exp\left\{-\frac{\beta_x}{2}(X_\ell-X_{\ell'})^2-\frac{\beta_y}{2}(Y_\ell-Y_{\ell'})^2-\frac{\beta_z}{2}(Z_\ell-Z_{\ell'})^2\right\}$$

$$K_{\ell\ell'}=\left(-\frac{\hbar^2}{2M}\right)\cdot S_{\ell\ell'}\cdot\left[\beta_x\left\{\beta_x(X_\ell-X_{\ell'})^2-1\right\}+\beta_y\left\{\beta_y(Y_\ell-Y_{\ell'})^2-1\right\}+\beta_z\left\{\beta_z(Z_\ell-Z_{\ell'})^2-1\right\}\right]$$

$$U_{\ell\ell'}=\frac{S_{\ell\ell'}}{N_1N_2N_3}\sum_{k_1=-(N_1-1)/2}^{(N_1-1)/2}\sum_{k_2=-(N_2-1)/2}^{(N_2-1)/2}\sum_{k_3=-(N_3-1)/2}^{(N_3-1)/2}\tilde{U}_{k_1,k_2,k_3}$$

$$\times\exp\left[-\frac{1}{8\beta_x}\left(\frac{2\pi(k_1)}{L_x}\right)^2-\frac{1}{8\beta_x}\left(\frac{2\pi(k_2)}{L_y}\right)^2-\frac{1}{8\beta_z}\left(\frac{2\pi(k_3)}{L_z}\right)^2\right.$$

$$\left.+i\left(\frac{\pi(k_1)}{L_x}\right)(X_\ell+X_{\ell'})+i\left(\frac{\pi(k_2)}{L_y}\right)(Y_\ell+Y_{\ell'})+i\left(\frac{\pi(k_3)}{L_z}\right)(Z_\ell+Z_{\ell'})\right]$$

All matrix elements are given by analytical from with use of shiftetd FFT.

For describing the nucleus state.

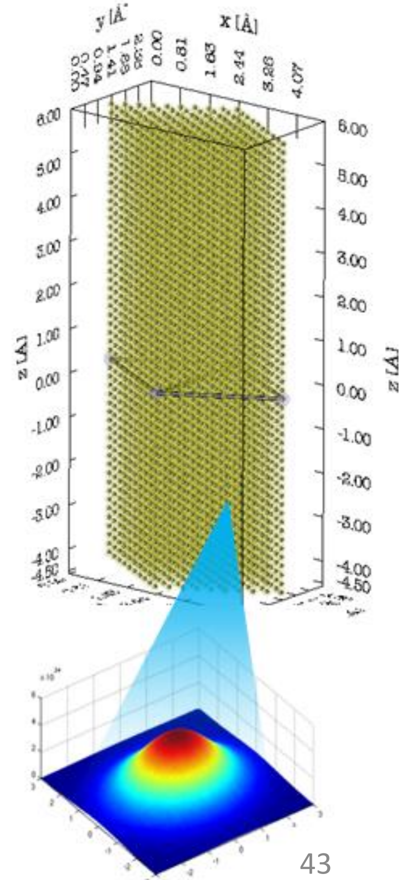
	$K_{\ell\ell'}$	$U_{\ell\ell'}$	$S_{\ell\ell'}$
Rectangular function	Approximate calculation	Diagonal	Diagonal
Gauss function	Analytically-integrated	Shifted FFT Naniwa	Analytically-integrated
Plane wave	analytically-integrated	FFT	Diagonal

Naniwa-Static: It is a nucleus version of the first principles quantum state calculations.

Equation for a single hydrogen atom motion:

$$\left[-\frac{\hbar^2}{2M_{\text{Hydrogen}}}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + U_0(x,y,z) \right] \phi_{\omega;0}(x,y,z) = E_{\omega,0}\phi_{\omega;0}(x,y,z) \quad \cdots (**)$$

(x, y, z) : Hydrogen atom position



The wave function for Hydrogen atom motion near the surface has position localized character. Then we described it by linear combination of the 3D-Gauss functions located at grid points, $(\xi_\ell, \eta_\ell, \varsigma_\ell)$.

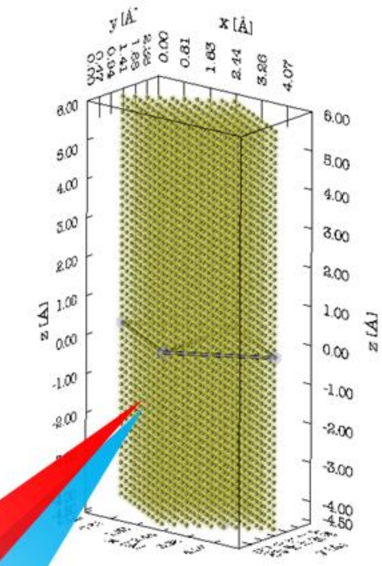
$$\phi_\omega(x,y,z) = \sum_{\ell}^{N_G} C_{\omega,\ell} G_\ell(x,y,z) \quad \cdots \quad (***)$$

$$G_\ell(x,y,z) = \left(\frac{\sigma_x \sigma_y \sigma_z}{\pi^3} \right)^{1/4} \exp\left\{ -\sigma_x (x-\xi_\ell)^2 - \sigma_y (y-\eta_\ell)^2 - \sigma_z (z-\varsigma_\ell)^2 \right\}$$

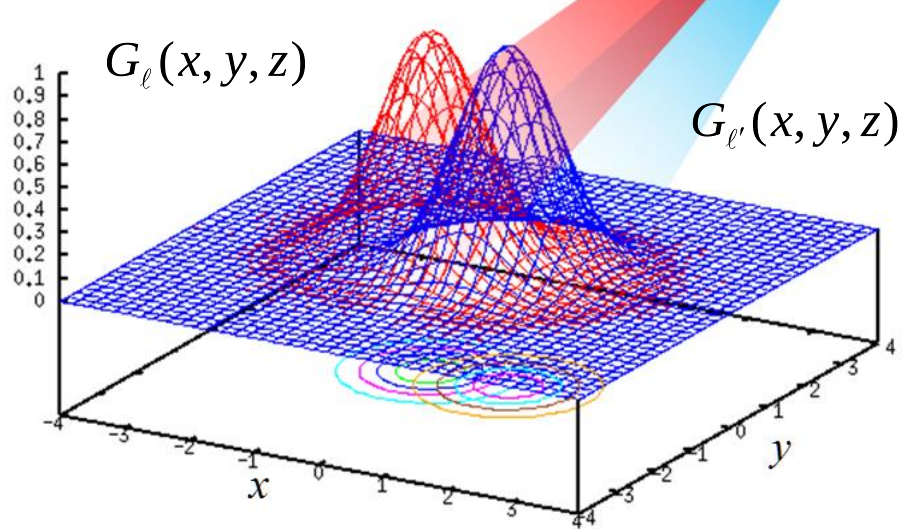
We solve eq.(**) by the variation method.

The ℓth 3D-Gauss function located at the ℓth grid point, $(\xi_\ell, \eta_\ell, \varsigma_\ell)$ is given by

$$G_\ell(x,y,z) = \left(\frac{\sigma_x \sigma_y \sigma_z}{\pi^3}\right)^{1/4} \exp\left\{-\sigma_x (x-\xi_\ell)^2 - \sigma_y (y-\eta_\ell)^2 - \sigma_z (z-\varsigma_\ell)^2\right\}$$



The nearest neighbor 3D-Gauss functions have to be overlapped.

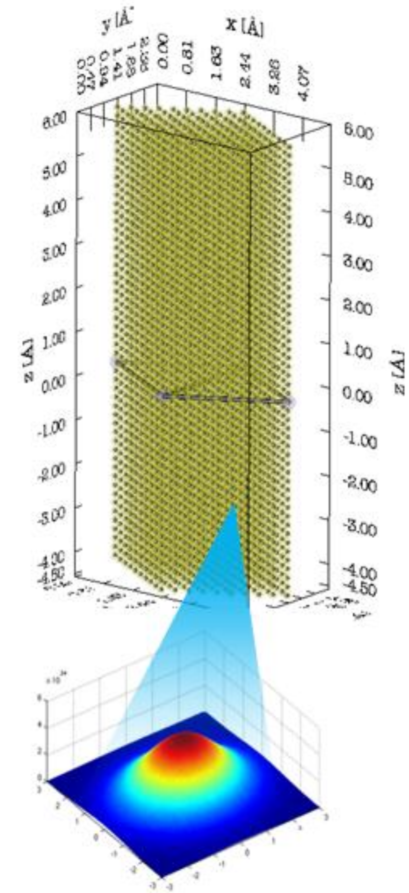


nearest neighbor $\langle \ell, \ell' \rangle$

Important reminder for making the grid set of 3D-Gauss functions

You have to check the convergence of numerical results by the some trial runs for various:

- ✓ Number of grid points N_{G}
- ✓ The decay factors $\sigma_x, \sigma_y, \sigma_z$



Variation method for eq.(**) by use of the trial function (***)

$$\sum_{\ell'}\left[H_{\ell\ell'} - E_{\omega} S_{\ell\ell'}\right] C_{\omega,\ell} = 0$$

$$H_{\ell\ell'} = K_{\ell\ell'} + U_{\ell\ell'}$$

$$K_{\ell\ell'} = \iint\int_{-\infty}^{+\infty} G_{\ell}(x,y,z)\left[-\frac{\hbar^2}{2M_{\mathrm{Hydrogen}}}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\right] G_{\ell'}(x,y,z)\,dxdydz$$

$$U_{\ell\ell'} = \iint\int_{-\infty}^{+\infty} G_{\ell}(x,y,z) U_0(x,y,z)\, G_{\ell'}(x,y,z)\,dxdydz$$

$$S_{\ell\ell'} = \iint\int_{-\infty}^{+\infty} G_{\ell}(x,y,z)\, G_{\ell'}(x,y,z)\,dxdydz$$

Secular equation $N_{\mathrm{G}} \times N_{\mathrm{G}}$

N_{G}: number of Gauss functions

$$\begin{vmatrix} H_{11} - E\ S_{11} & H_{12} - E\ S_{12} & \cdots & H_{1N_{\mathrm{G}}} - E\ S_{1N_{\mathrm{G}}} \\ H_{21} - E\ S_{21} & H_{22} - E\ S_{22} & \cdots & H_{2N_{\mathrm{G}}} - E\ S_{2N_{\mathrm{G}}} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N_{\mathrm{G}}1} - E\ S_{N_{\mathrm{G}}1} & H_{N_{\mathrm{G}}2} - E\ S_{N_{\mathrm{G}}2} & \cdots & H_{N_{\mathrm{G}}N_{\mathrm{G}}} - E\ S_{N_{\mathrm{G}}N_{\mathrm{G}}} \end{vmatrix} = 0$$

We can get the wave functions for hydrogen atom motion with their eigen enrgies.

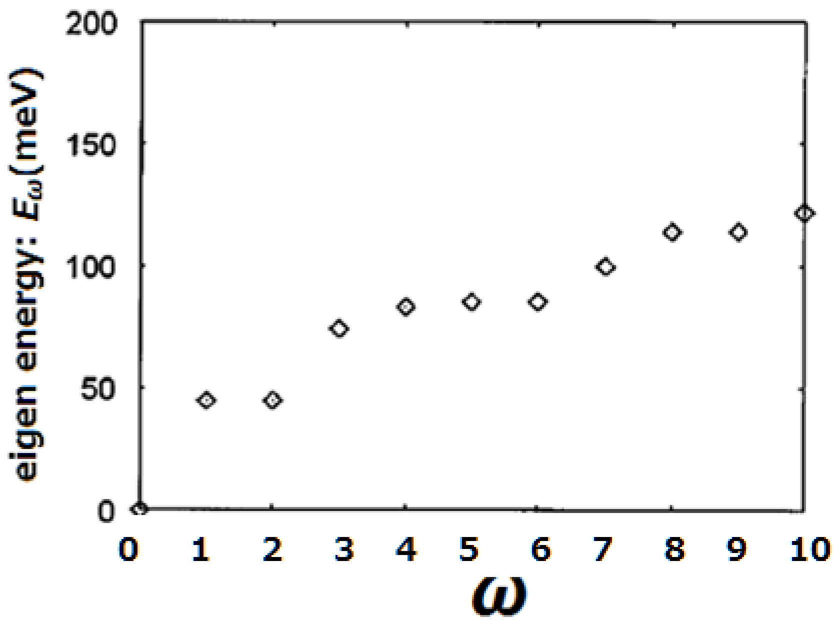
Example : H-Ir(111)2x2 (θ=1/4ML)

Eigen energy for quantum states of a hydrogen atom motion on the surface

$$\begin{vmatrix} H_{11}-E\,S_{11} & H_{12}-E\,S_{12} & \cdots & H_{1N_G}-E\,S_{1N_G} \\ H_{21}-E\,S_{21} & H_{22}-E\,S_{22} & \cdots & H_{2N_G}-E\,S_{2N_G} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N_G1}-E\,S_{N_G1} & H_{N_G2}-E\,S_{N_G2} & \cdots & H_{N_GN_G}-E\,S_{N_GN_G} \end{vmatrix} = 0$$

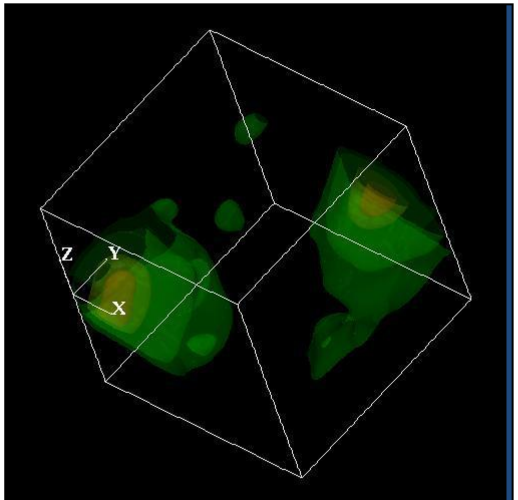
Secular equation

Eigen energy

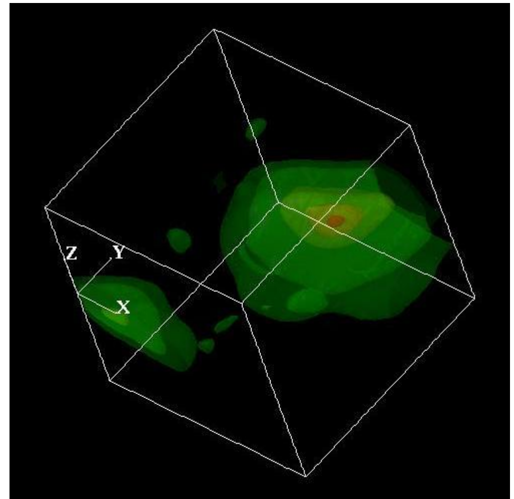


We can get the wave functions for hydrogen atom motion with their eigenenrgies.

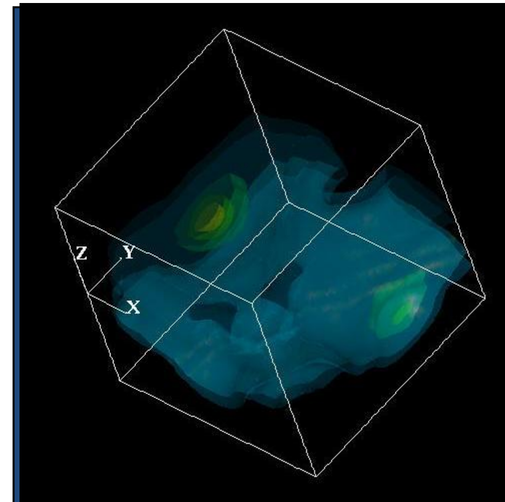
EX.
H-Ir(111)2x2
(θ=1/4ML)



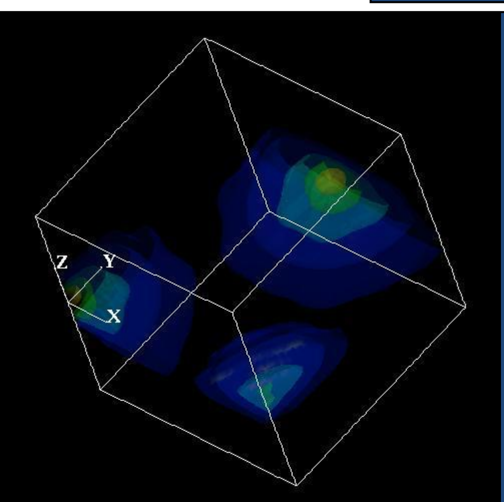
The 1^{st} excited state



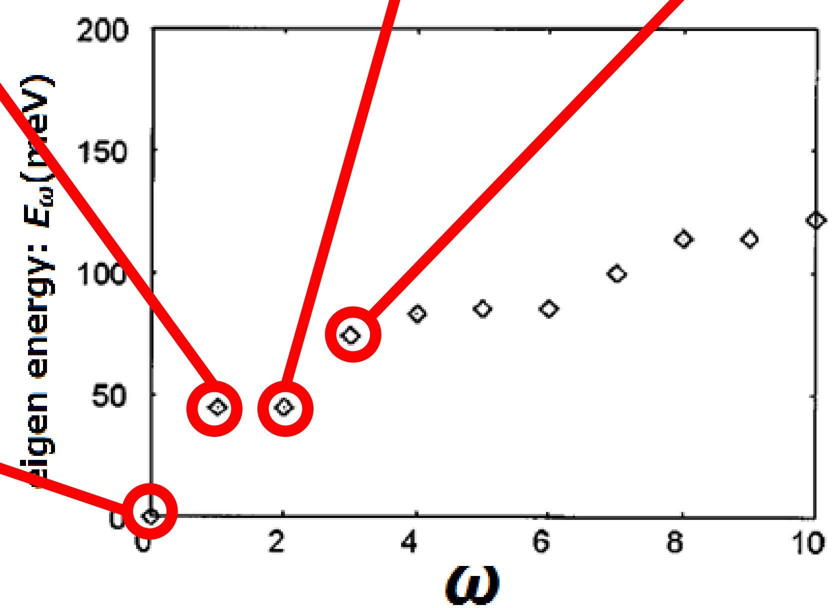
The 2^{nd} excited state



The 3^{rd} excited state



ground state



The expectation value of an observable, O, at ωth state is given by

$$\langle O \rangle_\omega = \iiint \phi_\omega^*(x, y, z) \hat{O} \phi_\omega(x, y, z)\, dxdydz$$
$$= \sum_{q=1}^{N_G} \sum_{q'=1}^{N_G} C_{\omega,q}^* C_{\omega,q'} \iiint G_q(x, y, z) \hat{O}\, G_{q'}(x, y, z)\, dxdydz$$

It is easy to calculate $<O>_\omega$ from obtained eigenvectors ($C_{\omega,1}, C_{\omega,2}, C_{\omega,3}, \cdots, C_{\omega,N_G}$).

Example of observable

Position: $\widehat{\vec{R}} = (x, y, z)$

Momentum: $\widehat{\vec{p}} = (\hat{p}_x, \hat{p}_y, \hat{p}_z)$

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}, \hat{p}_y = -i\hbar \frac{\partial}{\partial y}, \hat{p}_z = -i\hbar \frac{\partial}{\partial z}$$

Distribution of position:

$$\rho_{\text{position}}(x', y', z') = \delta(x' - x) \cdot \delta(y' - y) \cdot \delta(z' - z)$$

Distribution of momentum:

$$\rho_{\text{momentum}}(\vec{p}) = \delta(p_x - \hat{p}_x) \cdot \delta(p_y - \hat{p}_y) \cdot \delta(p_z - \hat{p}_z)$$

Electron density distribution : $\rho_{n,\omega}(\mathbf{r})$

$$\Psi_{n,\omega}(\boldsymbol{r},\boldsymbol{R}) = \psi_{n;\boldsymbol{R}}(\boldsymbol{r}) \cdot \phi_{\omega;n}(\boldsymbol{R}) \text{ ,} \qquad \mathbf{r} = \left(r_1, r_2, r_3, \cdots, r_i, \cdots r_{n_e}\right)$$

$$\rho_{n,\omega}(r) = \iint \left|\psi_{n;\mathbf{R}}(\mathbf{r})\right|^2 \cdot \left|\phi_{\omega;n}(\mathbf{R})\right|^2 \delta(r - r_1) d\mathbf{R} d\mathbf{r}$$

$$= \int \rho_{n;\mathbf{R}}(r) \cdot \left|\phi_{\omega;n}(\mathbf{R})\right|^2 d\mathbf{R}$$

From DFT based ab initio electron state calculation→$\rho_{n;\mathbf{R}}(r) = \sum_{\mathrm{occ.}\ell} \left|\varphi_{\ell;\mathbf{R}}(r)\right|^2$

***** Even in the adiabatic approximation, isotope effects appear in the electron states.

$\left|\phi_{\omega;n}(\mathbf{R})\right|^2 \Rightarrow$ broad, delocalized

as change of $T^+ \Rightarrow D^+ \Rightarrow H^+ \Rightarrow \mu^+$

The fastest wave

浪速

Naniwa

2. System Requirements [Recommended]

- Hardware
  - ✓ Computer Processor: 3.0GHz Intel Core i7 or better
  - ✓ Computer Memory: 8 GB or more

- Operating System: 64-bit Linux distribution

- Software

  (1) Naniwa package file : NaniwaSykXXXXXXXX.tar

  XXXXXXXX is version number. (ex. NaniwaSyk20170303.tar)

  (2) ab initio electronic state calculation package

  ex. State-Senri, Osaka2K, RSPACE, … GAUSIAN, VASP, …

For install

(1) Compiler: Intel® Fortran compiler

(2) Math library: Intel ® Math Kernel Library (MKL)

For use

(0) Unix shell: csh or tcsh

(1) Text editor: vi , mule … (as you like)

(2) Visualization tool: gnuplot, OpenDX, XCrySDen, VESTA, MATLAB,GNU Octave

For install

(1) Compiler: Intel® Fortran compiler

http://software.intel.com/en-us/articles/intel-composer-xe/

(2) Math library: Intel ® Math Kernel Library (MKL)

http://software.intel.com/en-us/articles/intel-mkl/

For use

(1) Text editor: vi , mule … (as you like)

(2) Visualization tool: gnuplot, OpenDX, VESTA, MATLAB, GNU Octave

"gnuplot"

: a command-line program that can make 2- and/or 3-dimensional plots of functions and data.

http://www.gnuplot.info/

"OpenDX"

: IBM Visualization Data Explorer program.

http://www.opendx.org/ (dead link: see appendix)

"XCrySDen"

:a crystalline and molecular structure visualization program.

http://www.xcrysden.org/

“VESTA”

:a Visualization program for Electronic and STructur al Analysis.

https://jp-minerals.org/vesta/

“MATLAB”

:a proprietary multi paradigm programming language and numeric computing environment developed by MathWorks.

http://mathworks.com

“GNU Octave”

:a programming language, which is mostly compatible with MATLAB.

https://www.gnu.org/software/octave/

3. How to install

(1) Copy the package file “NaniwaSykXXXXXXXX.tar” to your home directory.
XXXXXXXX is version number. (ex. NaniwaSyk20130110A.tar)

(2) Decompress the package file.

Type following command lines:

tar xvf NaniwaSykXXXXXXXX.tar [Enter]

You can get following directory on your home directory.

Installed directory structure

```
[your home directory]
      |-- naniwa -+
              |-- doc:        documents
              |-- SRC :       source codes
              |-- bin:        execution programs
              |-- work:       working directory
              |-- qs :        script for Grid Engine (Job scheduler)
              |-- etc -+
                   |-- OpenDX:       files for Visualization software OpenDX®
                   |--MATLAB: files for Visualization by MATLAB®
                   |--Octave: files for Visualization by GNU Octave
                   |-- potential:    files for making potential data
                   | -- example:     input data examples
                   |-- results:      simulation results
```

(3) Move to SRC directory

Type :

cd ./naniwa/SRC [Enter]

(4)Compile the source codes

Type :

make all [Enter]

The compilation must finish without errors, although warnings may be possible.

Error message

```
fastDFT3D_MKL.f(5): error #7002: Error in opening the compiled module file.
Check INCLUDE paths.   [MKL_DFTI]
      Use MKL_DFTI
----------^
fastDFT3D_MKL.f(10): error #6457: This derived type name has not been declared.
[DFTI_DESCRIPTOR]
      type(DFTI_DESCRIPTOR), POINTER :: hand
-----------^
compilation aborted for fastDFT3D_MKL.f (code 1)
make: *** [naniwa] Error 1
```

Please ask to your system administrator to compile mkl_dfti.f90.
Please do followings as root (super user).

```
cd    /opt/intel/mkl/include
ifort   –c   mkl_dfti.f90
```

** You can find some hints to solve your problem in "Makefile".*

(5) Move the execution file to binary directory

Type:

make all-install [Enter]

Check the execution files under bin directory

Type :

ls ../bin [Enter]

Naniwa runtime program

You can see following files:

BandStructure ChargeState eigen2spec naniwaSS_run poteng2xsf
BHGCAR2DX chgcar2xsf makeBHGCAR pec state2dx
cellexpander chkPOTENG makePOTENG poteng2dx state2xsf

(6) test run.

Move to work directory.

cd [Enter]

cd ./naniwa/work [Enter]

Copy the test data.

cp –r ../etc/example/test ./ [Enter]

cd test [Enter]

ls [Enter]

INSET POTENG run.csh

Execute the program

csh ./run.csh [Enter]

machine name
Job start date & time
Naniwa start date & time
finish naniwa
Naniwa terminate date & time

Cf. if you use the Sungrid Engine, type qsub ./run.csh *to submit your job.*

Check output files

ls *-al* [Enter]

```
total 104
drwxr-xr-x 3 hiro staff    72 Aug 20 12:53 .
drwxr-xr-x 3 hiro staff    17 Aug 20 12:52 ..
-rw-r--r-- 1 hiro staff   478 Aug 20 12:52 INSET
drwxr-xr-x 2 hiro staff  4096 Aug 20 12:55 kpoint0000
-rw-r--r-- 1 hiro staff  8305 Aug 20 12:55 LOG
-rw-r--r-- 1 hiro staff 90085 Aug 20 12:52 POTENG
-rw-r--r-- 1 hiro staff   290 Aug 20 12:52 run.csh
```

cat *LOG* [Enter]

If successful, you can get the following LOG file:

```
****************************************
*        Naniwa code                *
****************************************
  NaniwaSYk Version 2012.11.22
      created by NAKANISHI, Hiroshi
      OSAKA UNIVERSITY

----------------------------------------
 INSET title :
*


 Calculaton mode :          0
 *** Full calculation
----------------------------------------
 Atomic Mass =   1.00000000000000      (proton)
           =  1.672621637000000E-027 (kg)
----------------------------------------
Number of node index (No1,No2,No3)
        9          9          9
Gaussian decay factors (1/Angstrom Angstrom)
SigmaX=   5.00000000000000
SigmaY=   5.00000000000000
SigmaZ=   5.00000000000000
----------------------------------------
** No correction by symmetry.
```

```
12  0.1882954
        13  0.1882954
        14  0.1882954
        15  0.1882954
        16  0.1882954
        17  0.1931621
        18  0.1931621
        19  0.1931621
----------------------------------------
MSG:checking the probality of each eigenstates
All k-point calculation, which you requested,are done.



*******************************
*  Naniwa code is terminated *
*******************************
```

Program codes and files — Naniwa users manual Ch.4

- INPUT/ OUTPT files — § 4.2

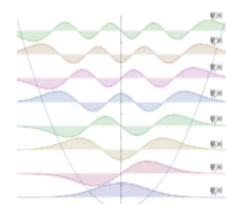
How to use — Ch. 5

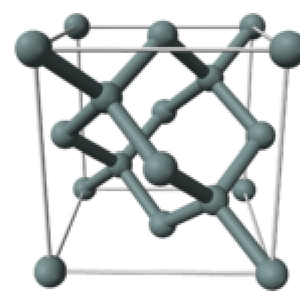
- Making 3D-potential energy surface for quantum particle in material. § 5.1
- Making the simulation setting § 5.2
- Executing the simulation program. § 5.3
- Check simulation results § 5.4
- How to see the Eigenenergies as a function of quantum number.
- How to see the Wave functions

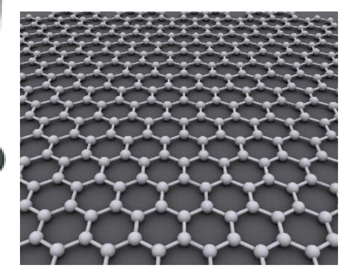
Naniwa practice menu

Quantum states of μ^+,H^+,D^+,T^+

1. near Pd (111) surface
2. on Pd（001）surface
3. in 3D harmonic potential
4. in Si crystal.
5. on graphene
6. in any potentials as you like





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Appendix

How to install "OpenDX" : IBM Visualization Data Explorer program.

http://www.opendx.org/ (dead link)

When your OS is Ubuntu, type following command in terminal to install OpenDX.

$sudo \quad apt \quad install \quad dx$ [Enter]

[sudo] password for XXXXX: *Your password* [Enter]

Reading package lists … Done
Building ….
…..
Do you want to continue?[Y/n] *y* [Enter]
…..
Processing triggers for libc-bin (2.273ubuntu1) …