Summer Cybertraining Workshop 2022

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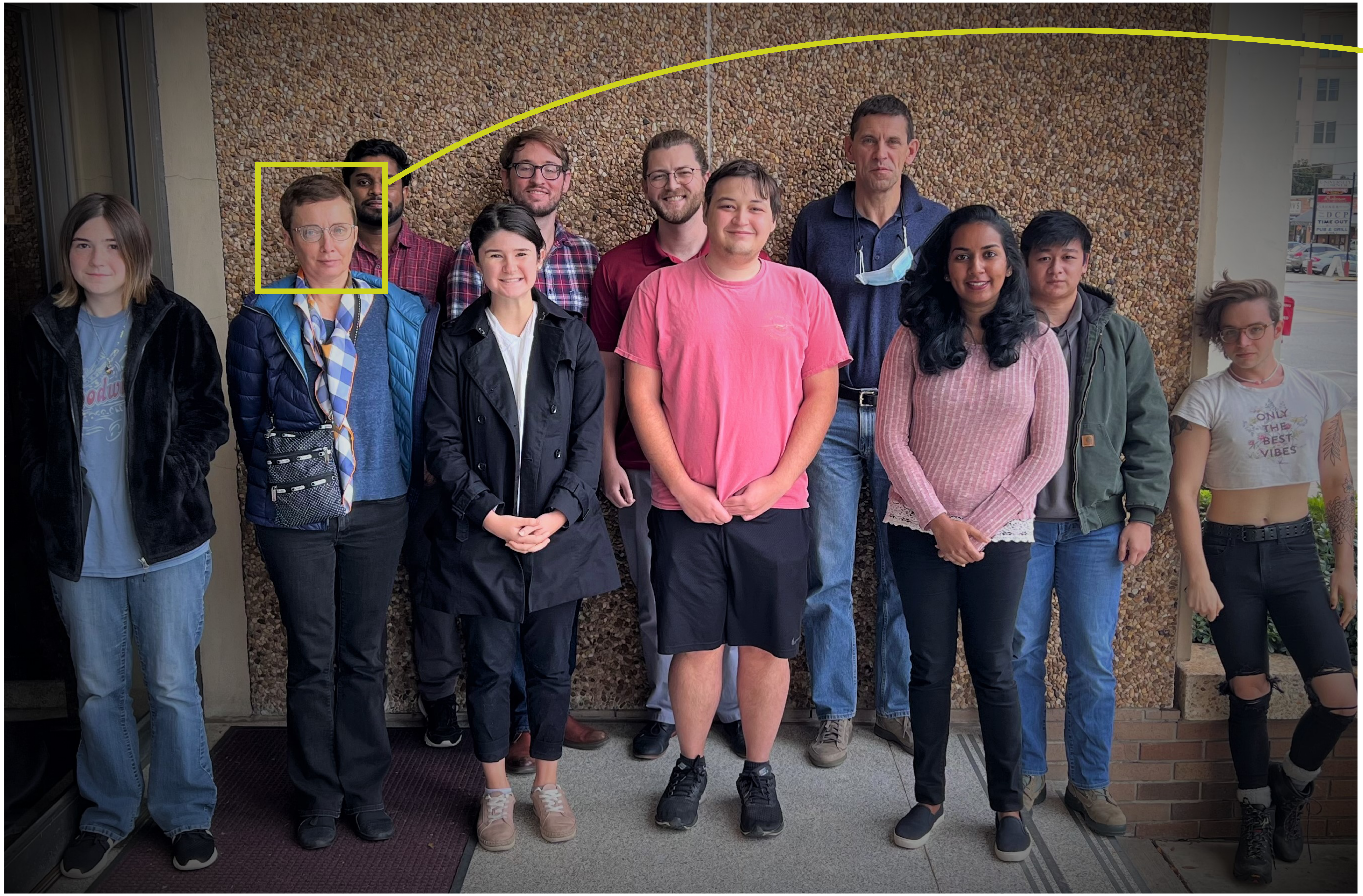
Presenter: Matthew Dutra

qtag



Prof. Sophya Garashchuk

Garashchuk/ Rassolov Research Groups **2021**

UofSC South Carolina

Libra

University at Buffalo

Prof. Alexey Akimov

Libra Winter School on Excited States and Nonadiabatic Dynamics in Materials 2022

Computational Chemistry Cyber Training

Solving the Time-Dependent Schrödinger Equation (TDSE)

Solving the Time-Dependent Schrödinger Equation (TDSE)

Fixed-Grid

Multi-Configurational Time-Dependent Hartree

Matching Pursuit/Split Operator Fourier Transform

Basis Expansion Leaping Multi-Configuration Gaussian

MCTDH: *Chem. Phys. Lett.*, **1990**, 165, 73-78
MP/SOFT: *J. Chem. Phys.*, **2004**, 121, 1676-1680
BEL-MCG: *J. Chem. Phys.*, **2018**, 149, 134113

Trajectory-Based

Ab Initio Multiple Spawning

Ab Initio Multi-Configurational Ehrenfest

Adaptive Trajectory-Guided Scheme

AIMS: *J. Phys. Chem. A.*, **2000**, 104, 22, 5161-5175
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J. Chem. Theory Comput. 2020, 16, 18–34
DOI: 10.1021/acs.jctc.9b00844

QTAG

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***Q**uantum **T**rajectory-guided **A**daptable **G**aussian*

Quantum Trajectories

Quantum Trajectories

PHYSICAL REVIEW VOLUME 85, NUMBER 2 JANUARY 15, 1952

A Suggested Interpretation of the Quantum Theory in Terms of "Hidden" Variables. I

DAVID BOHM*
Palmer Physical Laboratory, Princeton University, Princeton, New Jersey
(Received July 5, 1951)

The usual interpretation of the quantum theory is self-consistent, but it involves an assumption that cannot be tested experimentally, *viz.*, that the most complete possible specification of an individual system is in terms of a wave function that determines only probable results of actual measurement processes. The only way of investigating the truth of this assumption is by trying to find some other interpretation of the quantum theory in terms of at present "hidden" variables, which in principle determine the precise behavior of an individual system, but which are in practice averaged over in measurements of the types that can now be carried out. In this paper and in a subsequent paper, an interpretation of the quantum theory in terms of just such "hidden" variables is suggested. It is shown that as long as the mathematical theory retains its present general form, this suggested interpretation leads to precisely the same results for all physical processes as does the usual interpretation. Nevertheless, the suggested interpretation provides a broader conceptual framework than the usual interpretation, because it makes possible a precise and continuous description of all processes, even at the quantum level. This broader conceptual framework allows more general mathematical formulations of the theory than those allowed by the usual interpretation. Now, the usual mathematical formulation seems to lead to insoluble difficulties when it is extrapolated into the domain of distances of the order of 10^{-13} cm or less. It is therefore entirely possible that the interpretation suggested here may be needed for the resolution of these difficulties. In any case, the mere possibility of such an interpretation proves that it is not necessary for us to give up a precise, rational, and objective description of individual systems at a quantum level of accuracy.

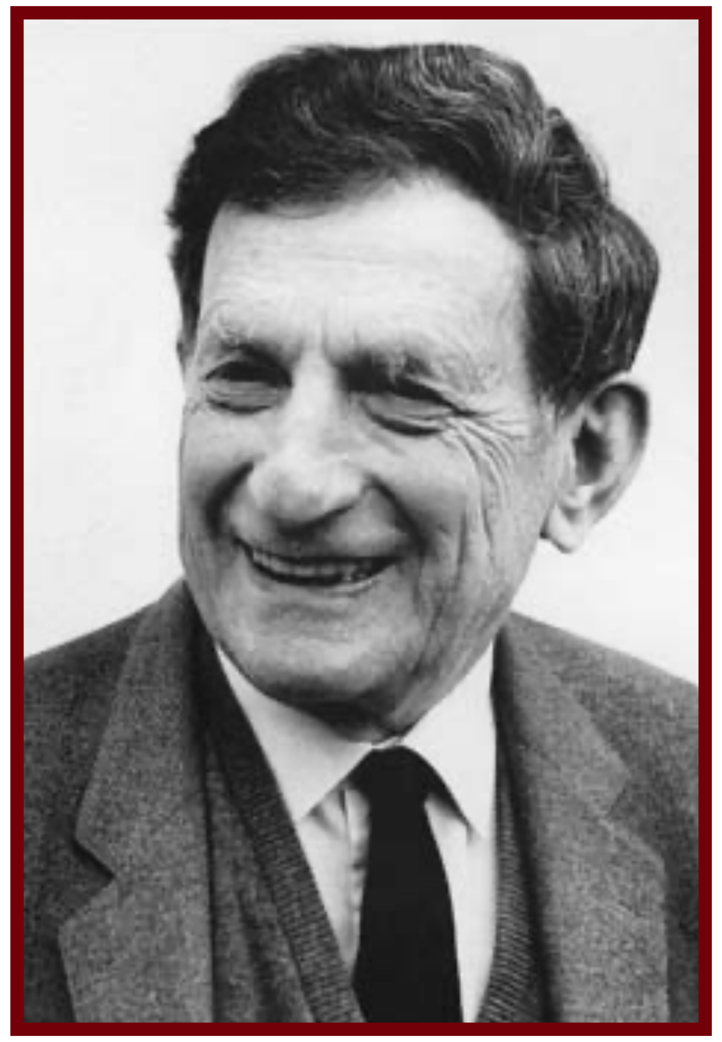
1. INTRODUCTION

THE usual interpretation of the quantum theory is based on an assumption having very far-reaching implications, *viz.*, that the physical state of an individual system is completely specified by a wave function that determines only the probabilities of actual results that can be obtained in a statistical ensemble of similar experiments. This assumption has been the object of severe criticisms, notably on the part of Einstein, who has always believed that, even at the quantum level, there must exist precisely definable elements or dynamical variables determining (as in classical physics) the actual behavior of each individual system, and not merely its probable behavior. Since these elements or variables are not now included in the quantum theory and have not yet been detected experimentally, Einstein has always regarded the present tions have as yet been suggested. The purpose of this paper (and of a subsequent paper hereafter denoted by II) is, however, to suggest just such an alternative interpretation. In contrast to the usual interpretation, this alternative interpretation permits us to conceive of each individual system as being in a precisely definable state, whose changes with time are determined by definite laws, analogous to (but not identical with) the classical equations of motion. Quantum-mechanical probabilities are regarded (like their counterparts in classical statistical mechanics) as only a practical necessity and not as a manifestation of an inherent lack of complete determination in the properties of matter at the quantum level. As long as the present general form of Schroedinger's equation is retained, the physical results obtained with our suggested alternative interpretation are precisely the same as those obtained

de Broglie - Bohm Mechanics

Bohm, D., A suggested interpretation of the quantum theory in terms of "hidden" variables. *Physical Review*, **1952**, 85 (2), 166-179

Louis de Broglie



David Bohm

https://en.wikipedia.org/wiki/Louis_de_Broglie
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de Broglie - Bohm Mechanics

$$\Psi(x,t) = A(x,t)e^{iS(x,t)/\hbar}$$

Polar wavefunction w/ real amplitude ***A(x,t)*** and phase ***S(x,t)***

$$i\hbar\frac{\partial\Psi}{\partial t} = -\left(\frac{\hbar^2}{2m}\right)\nabla^2\Psi + V(x)\Psi$$

Time-dependent Schrodinger Equation (TDSE)

$$\boxed{\frac{dx_t}{dt} = \frac{p_t}{m} \qquad p_t = Im\left(\frac{\nabla\psi}{\psi}\right)}$$

Trajectory position and momentum

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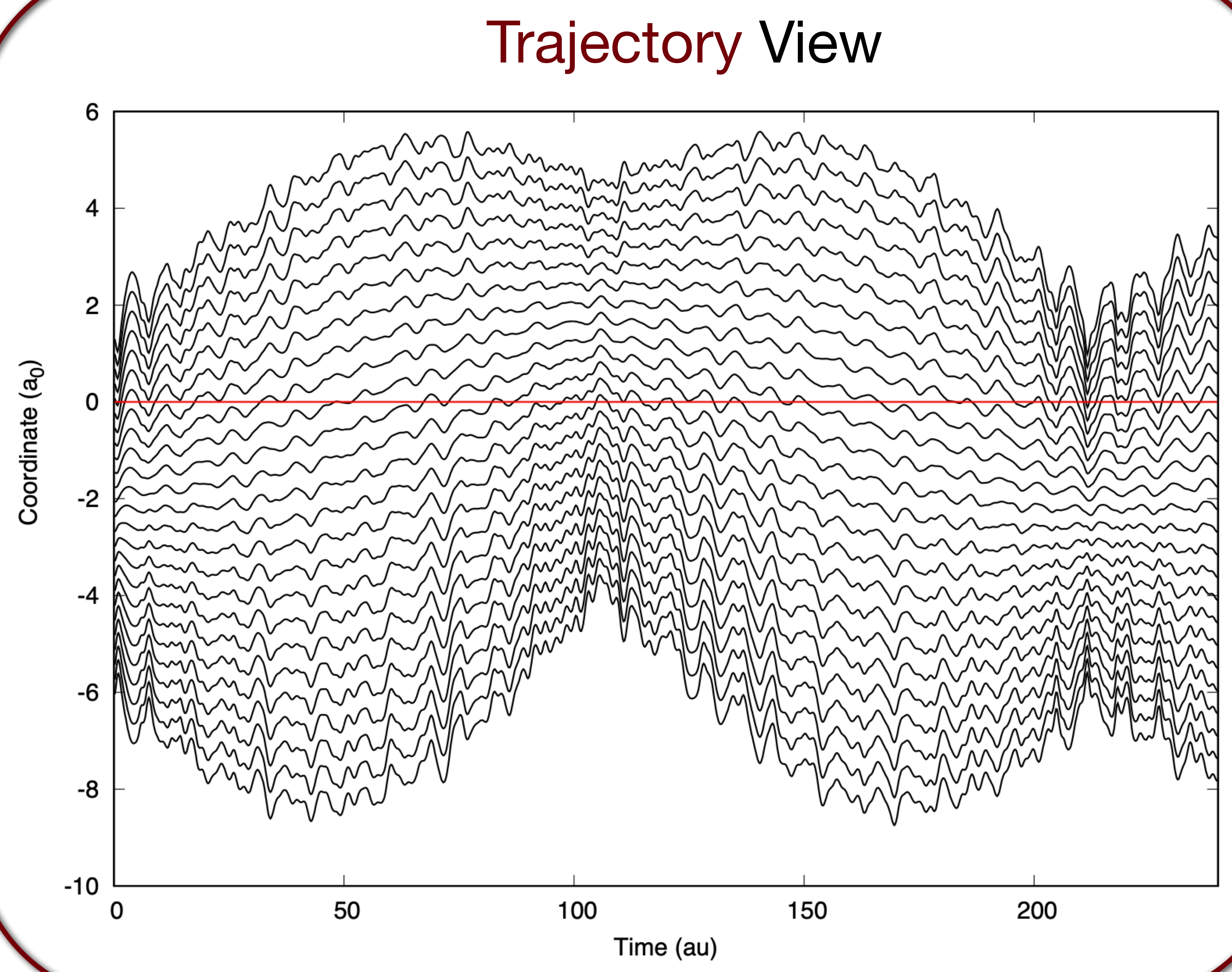
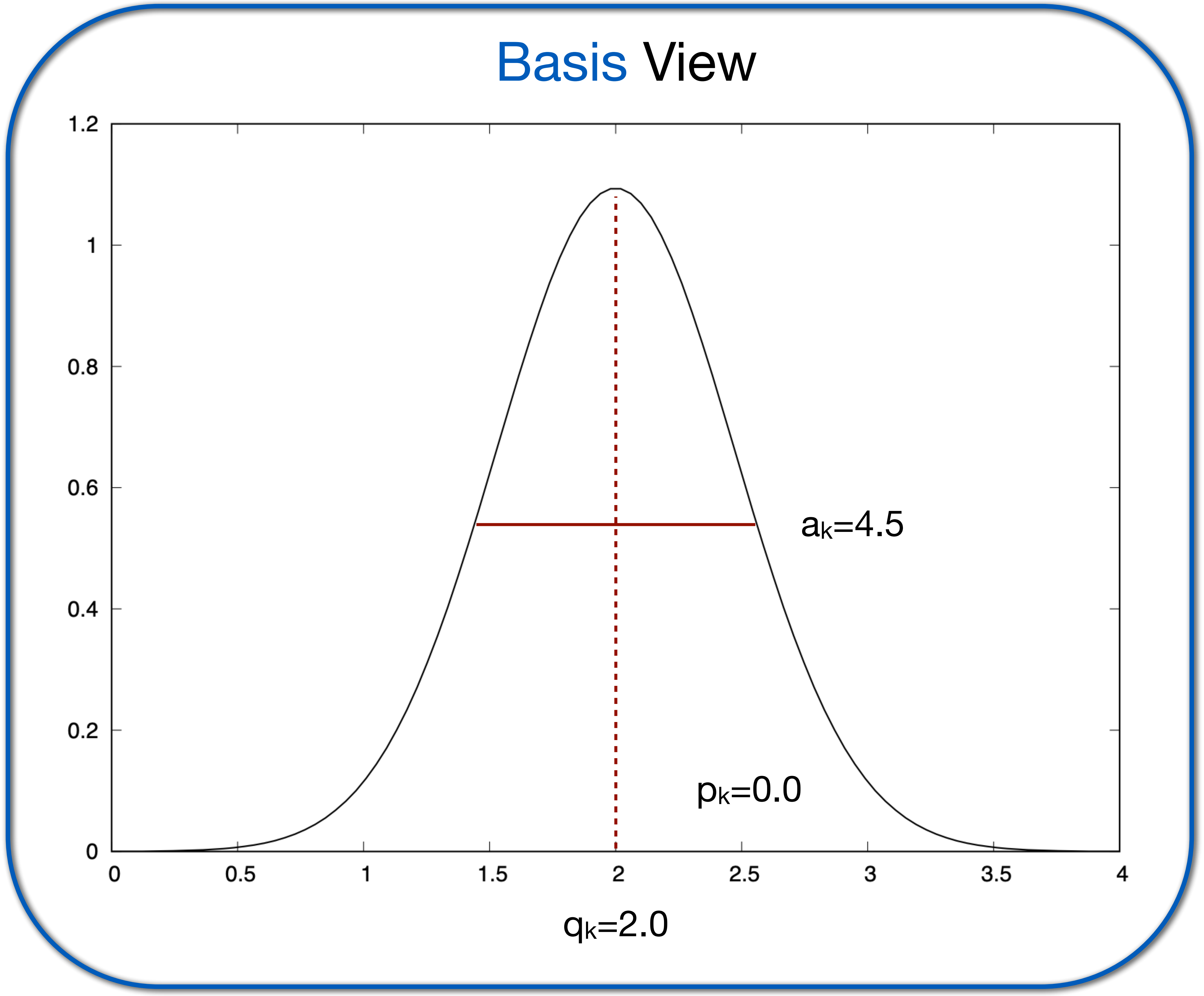


Adaptable ***G***aussians

Adaptable Gaussians

$$g_k = \prod_{\nu=1}^{N_d} \left(\frac{a_{\nu,k}}{\pi}\right)^{1/4} \exp\left(-\frac{a_{\nu,k}}{2}(x_\nu - q_{\nu,k})^2 + \imath p_{\nu,k}(x_\nu - q_{\nu,k})\right)$$

N_d-dimensional Gaussian basis function with position (***q***), phase (***p***), and width (***a***) parameters



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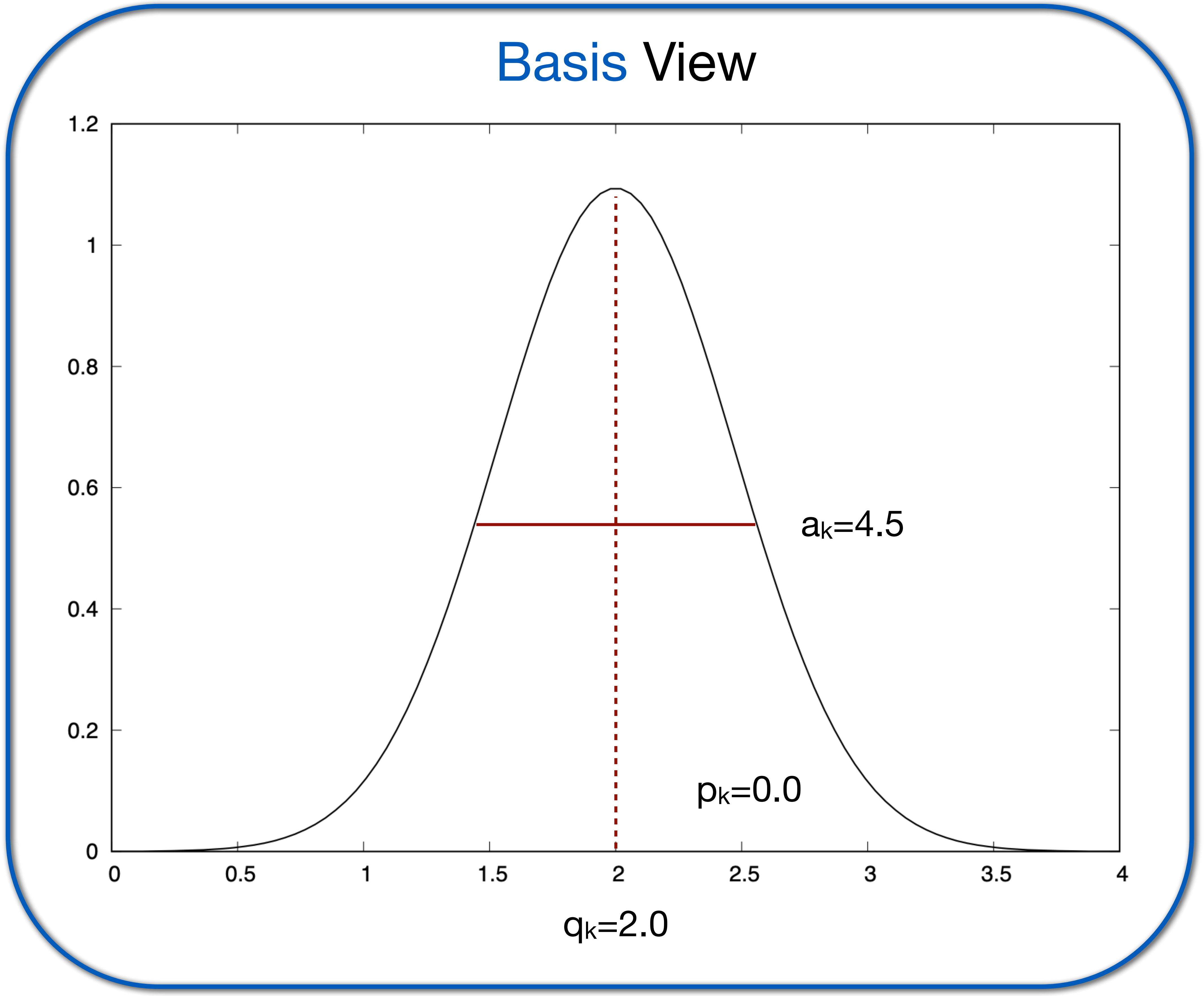
N_d-dimensional Gaussian basis function with position (***q***), phase (***p***), and width (***a***) parameters

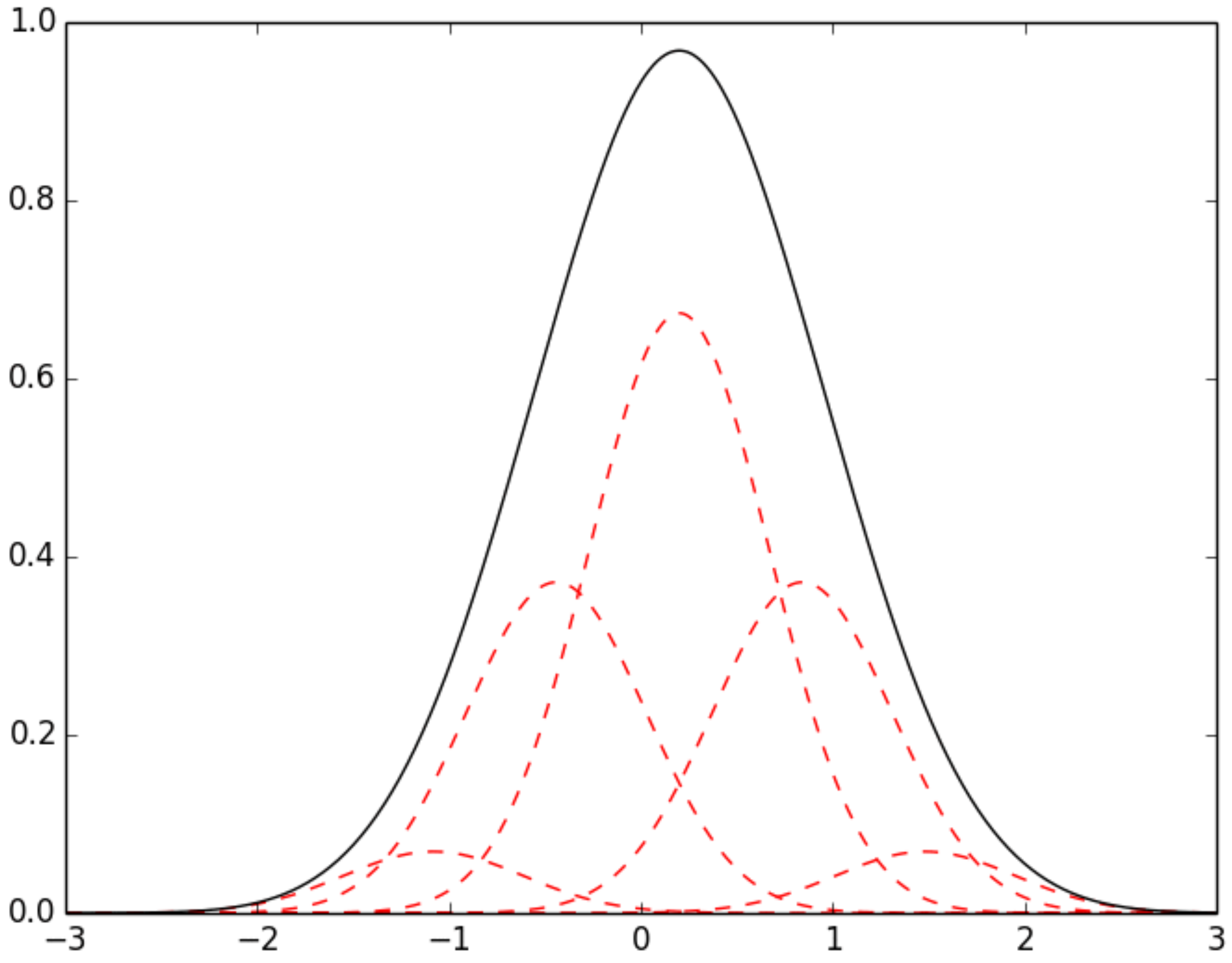
$$\psi(\mathbf{x}, t) = \sum_{k=1}^{N_b} c_k(t) g_k(\mathbf{x}, t)$$

Generic wavefunction constructed from Gaussian basis functions, each multiplied by a complex amplitude ***c(t)***



Quantum Trajectory-guided Adaptable Gaussians

Wavefunction View



Basis Functions

dyn_params {Python dictionary of dynamics parameters}
model_params {Python dictionary of potential parameters}

Basic User Interface

jupyter

compute_model( )
compute.run_qtag( )
plot.plotting_fxn( )

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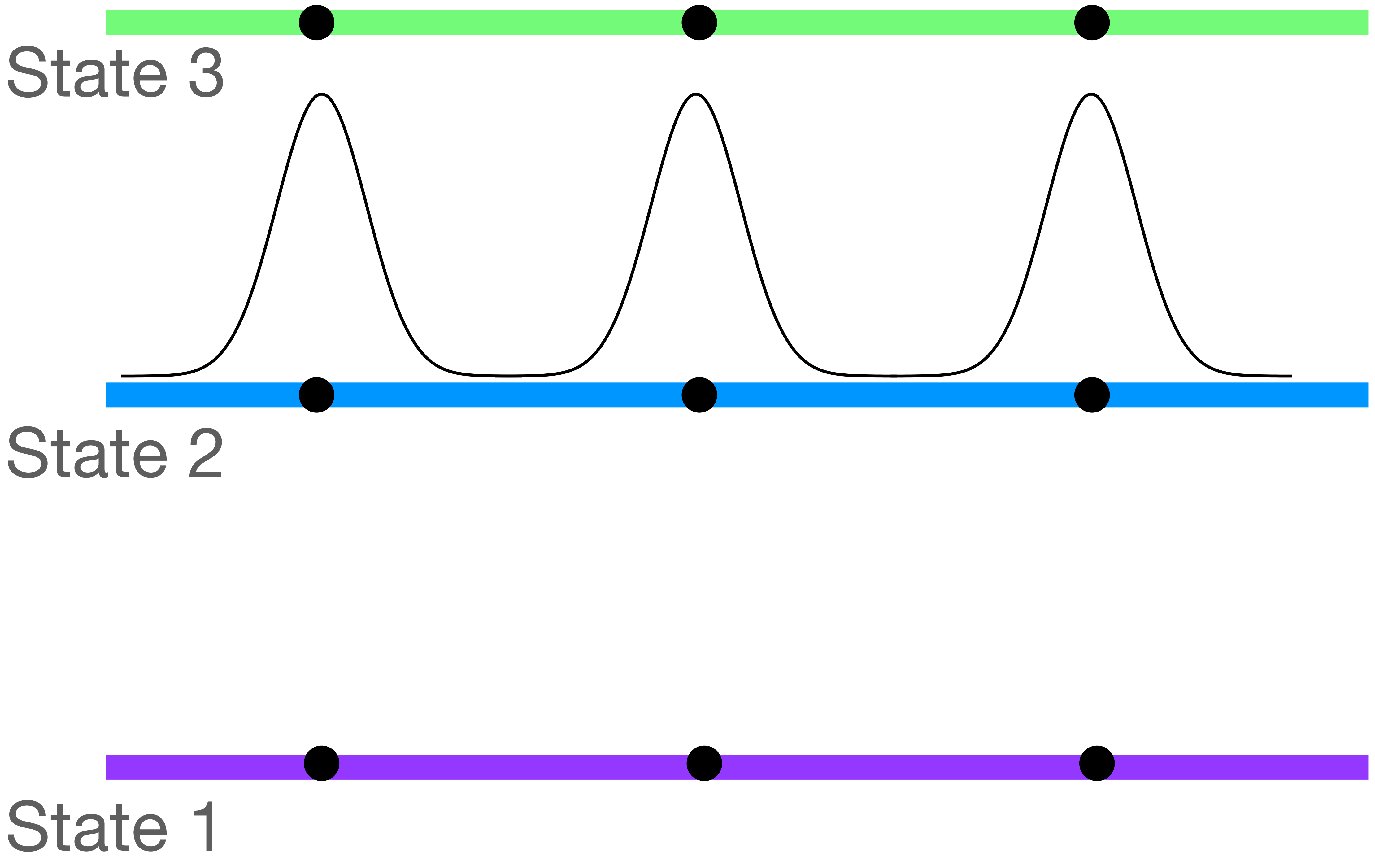

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Basic User Interface

Method Details

1. Computing Basis Coefficients

Compute Overlap Matrix Elements

↓

Compute Hamiltonian Matrix Elements

↓

Solve Eigenvalue Problem HZ=SZε

↓

Update Basis Coefficients from Eigenvalues/ vectors

↔

2. Updating Trajectory Parameters

Calculate Momentum from Wavefunction

↓

Update Basis Parameters {p,a,s}

↓

Update Positions

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$$S_{ij} = \langle g_i | g_j \rangle$$

$$H_{ij} = \langle g_i | K + V | g_j \rangle$$

(single-surface)

$$H_{ij} = \langle g_i | V_{cpl} | g_j \rangle$$

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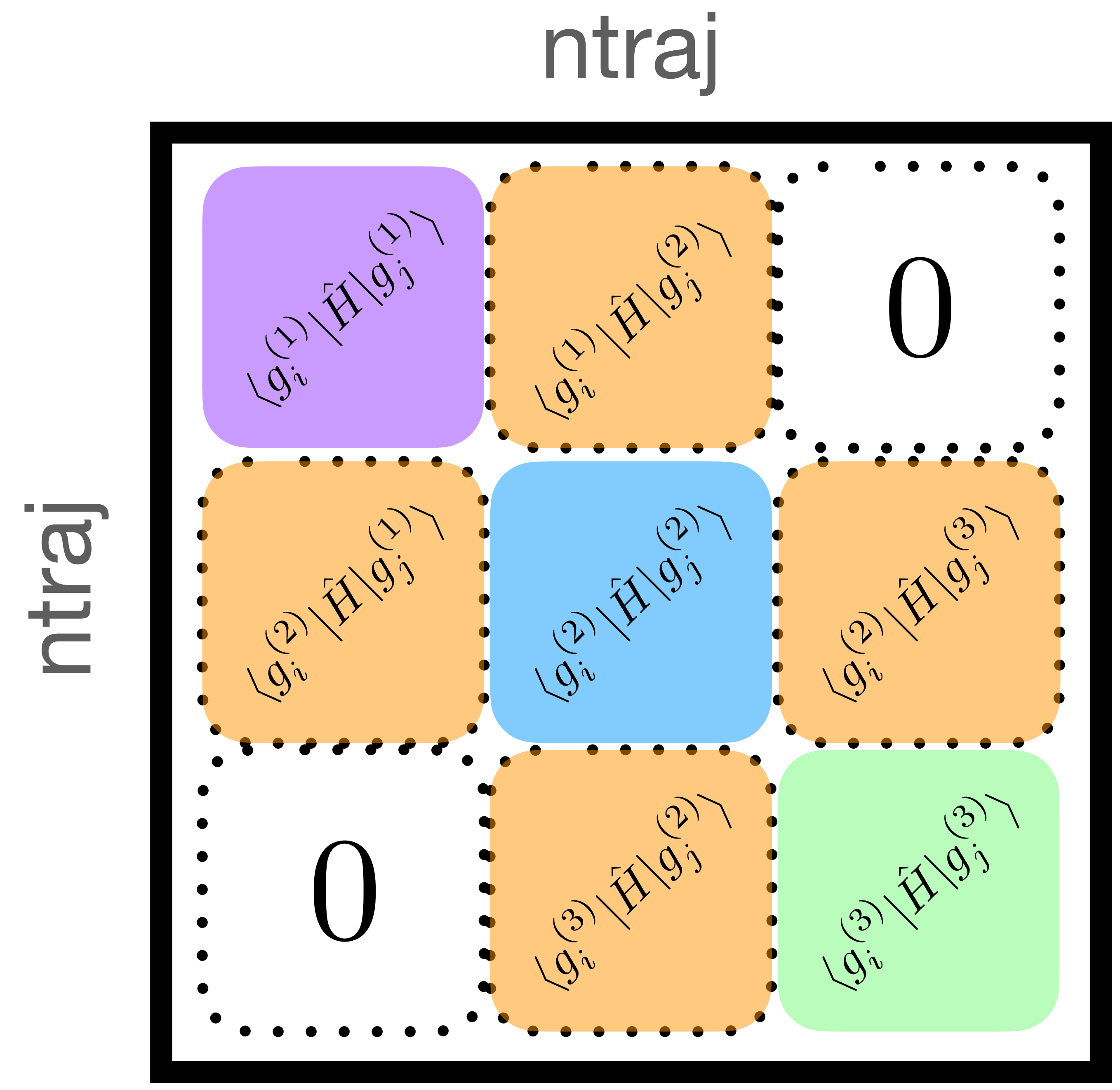

Hamiltonian Matrix

*LHA and BAT approximations to potential surface

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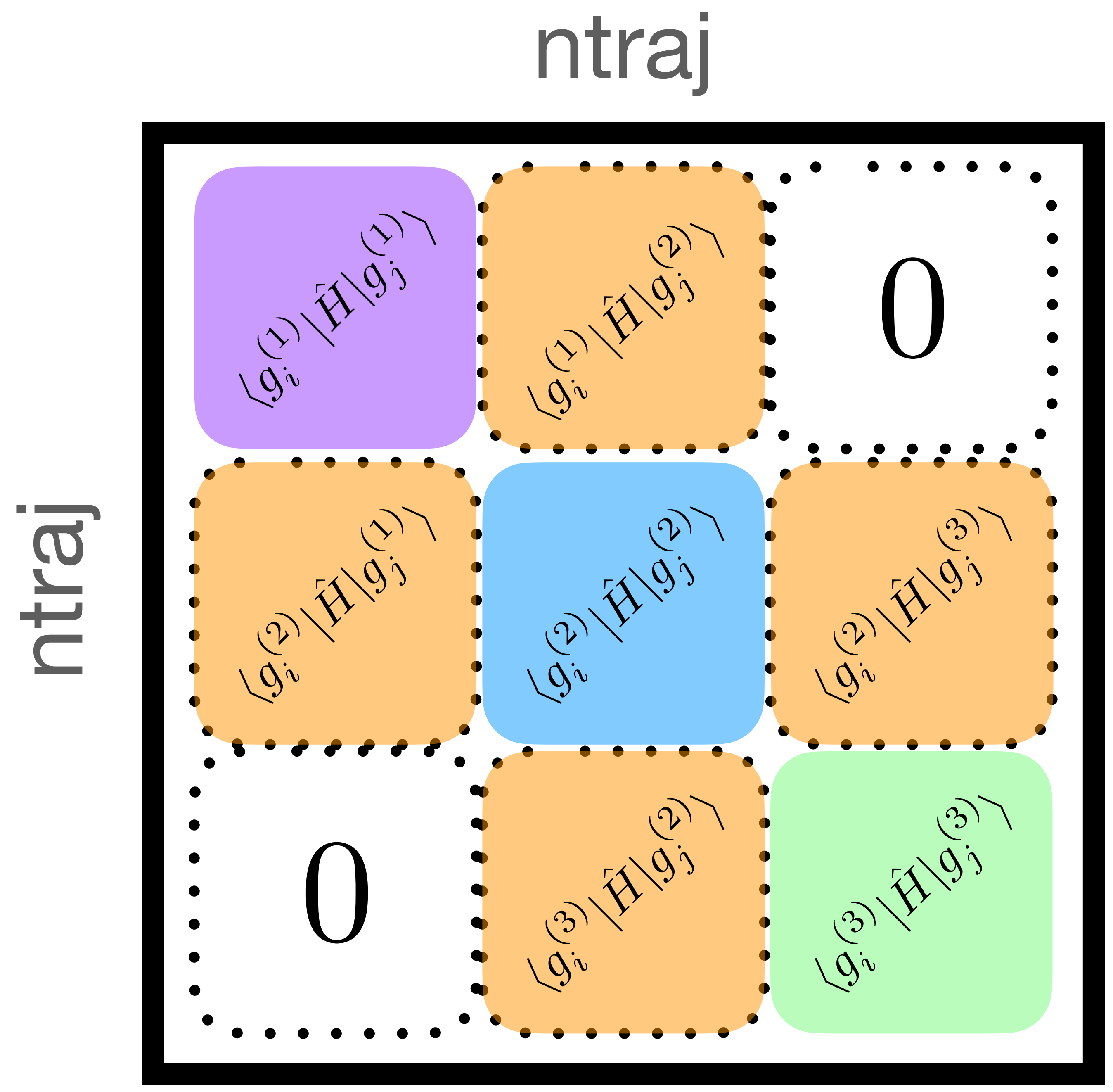
$$c^{(0)} = Z^{(0)} \exp(-i\epsilon^{(0)}\Delta t)(Z^{(0)})^{\dagger} b^{(0)}$$

(projection onto initial wavepacket)



Hamiltonian Matrix

*LHA and BAT approximations to potential surface

2. Updating Trajectory Parameters

Calculate Momentum from Wavefunction

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Update Basis Parameters {p,a,s}

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Update Positions

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Questions:

1. Quantum trajectories notorious for being unstable; how can we address this?
2. Trajectory momentum defined by wavefunction; how do we propagate unpopulated surface trajectories?

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Questions:

1. Quantum trajectories notorious for being unstable; how can we address this?
2. Trajectory momentum defined by wavefunction; how do we propagate unpopulated surface trajectories?

Solutions:

1. Many options, we choose fitting of trajectory momenta to stabilize.
2. Currently, ‘empty’ trajectories are synchronized to their populated counterparts

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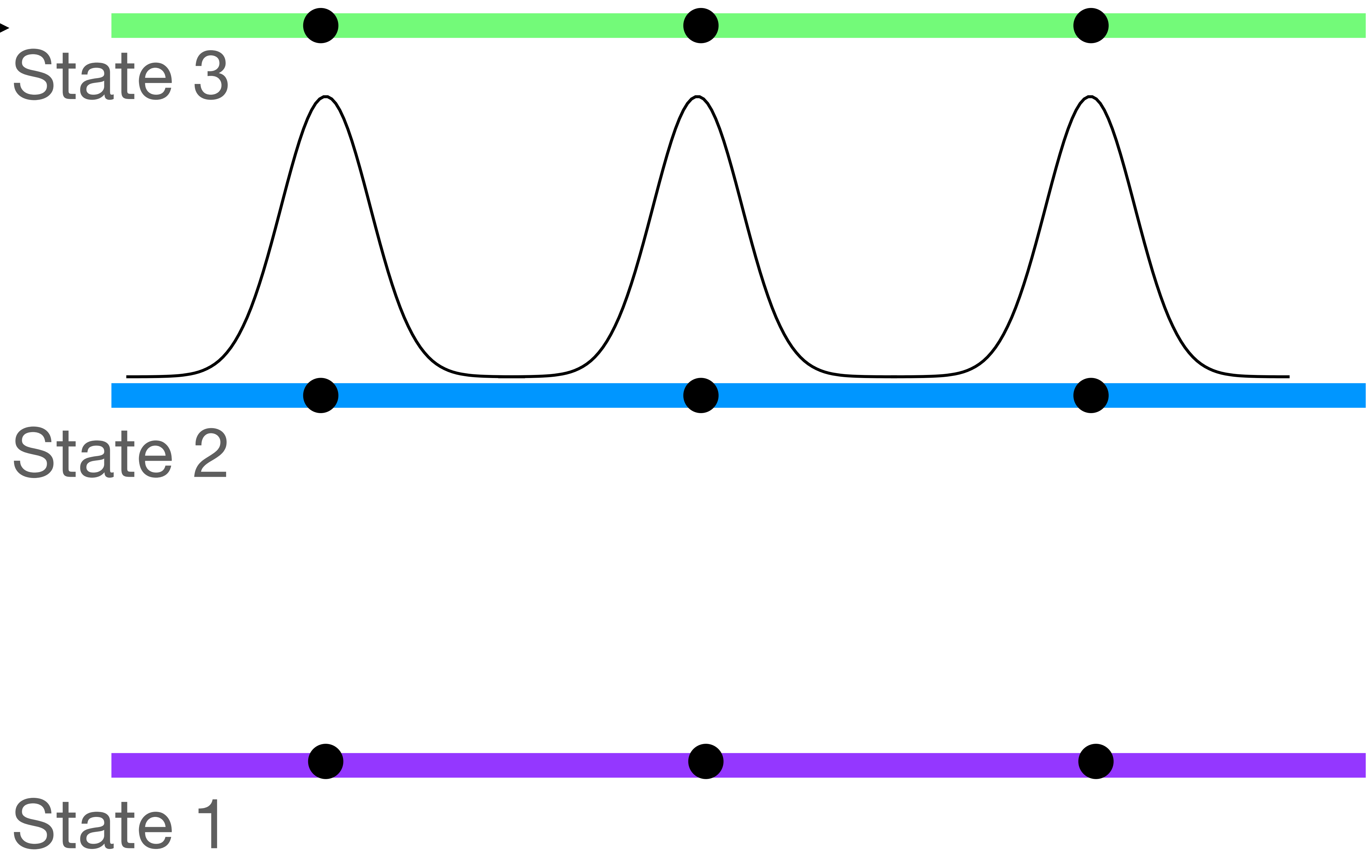

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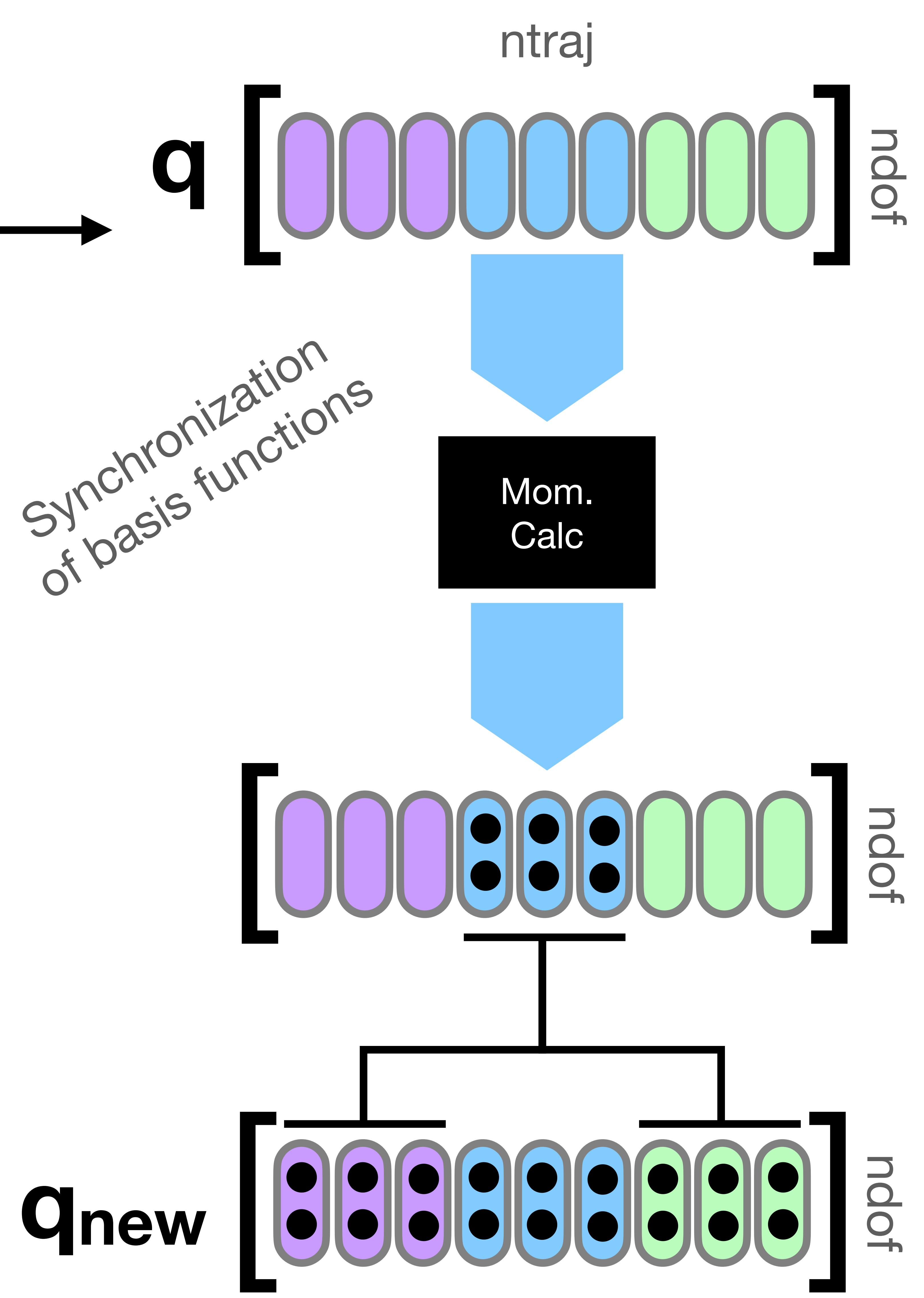

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$$
\begin{aligned}
p_{t+dt} &= Im(\nabla\psi/\psi) \\
a_{t+dt} &= a_t - dt(2a_t\nabla p)/m \\
s_{t+dt} &= 0 \\
q_{t+dt} &= q_t + dt \times p_t/m
\end{aligned}
$$

$$S_{ij} = \langle g_i^{(t+dt)} | g_j^{(t)} \rangle$$

In total...

$$\psi(x, N\tau) = (g^{(N-1)})^T \left(\prod_{n=2}^{N} K_\tau^{(n-1)} S^{(n-1,n-2)} \right) K_\tau^{(0)} b^{(0)}$$