About the Maximal Probability Domains (MPDs) in Quantum Chemistry

Third matinee for young researchers – Scientific calculus at interfaces

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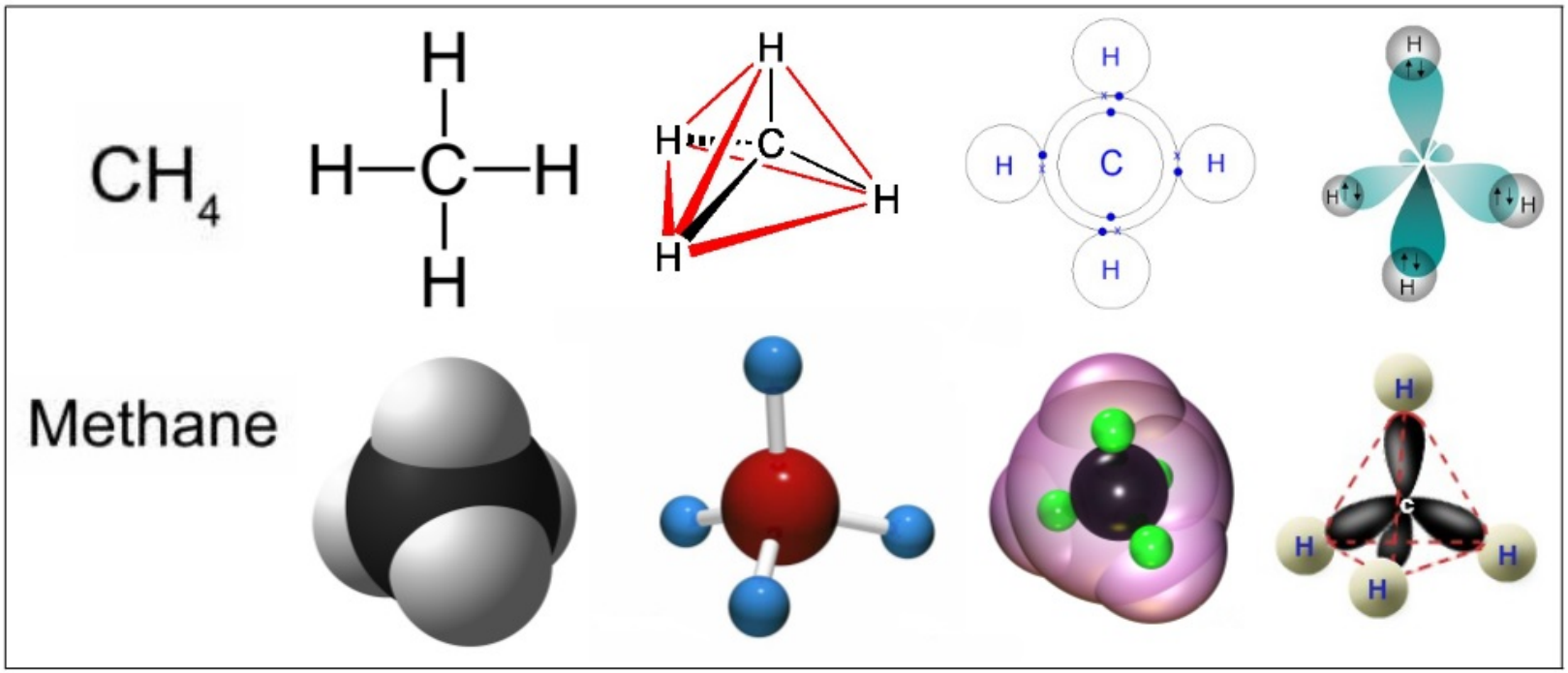
The way chemists understand how molecules interact

On the one hand, the traditional chemical intuition tends to localize electrons around the cores in the real three-dimensional space.



Examples: Lewis' electron pairs, Langmuir's octet rule, Pauling's classification of bounds (covalent, ionic), resonating structures, shells.

The wave function of a system in Quantum Mechanics

On the other hand, a quantum system of N electrons is characterized by its $3N$-dimensional wave function, allowing electrons to be delocalized over the whole space:

$$\Psi : \underbrace{\mathbb{R}^3 \times \ldots \times \mathbb{R}^3}_{N \text{ times}} \longrightarrow \mathbb{R}.$$

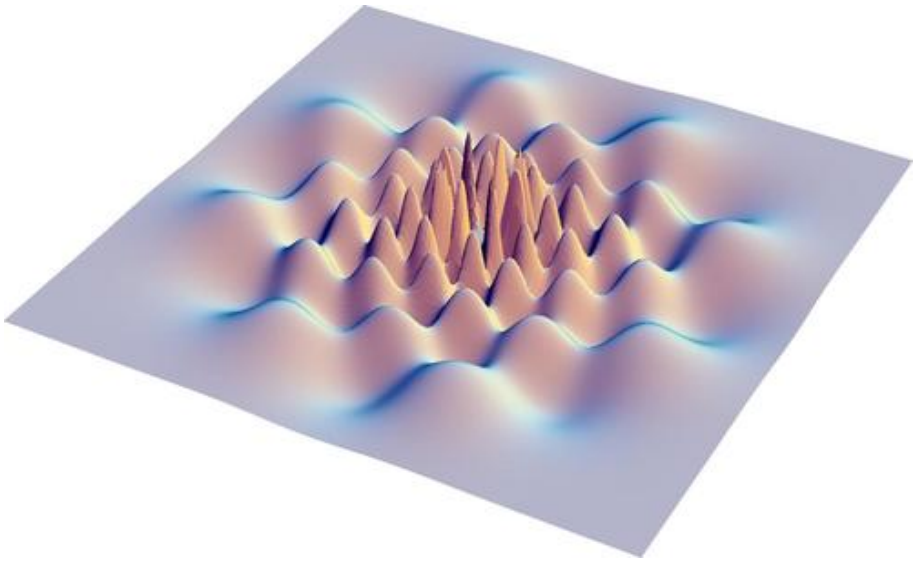


Figure : *it is the value of a wave function associated with the electron of an hydrogen atom in the plane perpendicular to the angular momentum vector.*

Motivations for computing maximal probability domains

Quantum Chemistry tries to reconnect the traditional chemical vision with the results of accurate quantum mechanical calculations.

Goal: find a clear and simple way to divide the space in significant regions of chemical and physical meaning.

Examples: minima of radial density (Parr), the model of loges (Daudel), atoms in molecules (Bader), basins of the electron localization function.

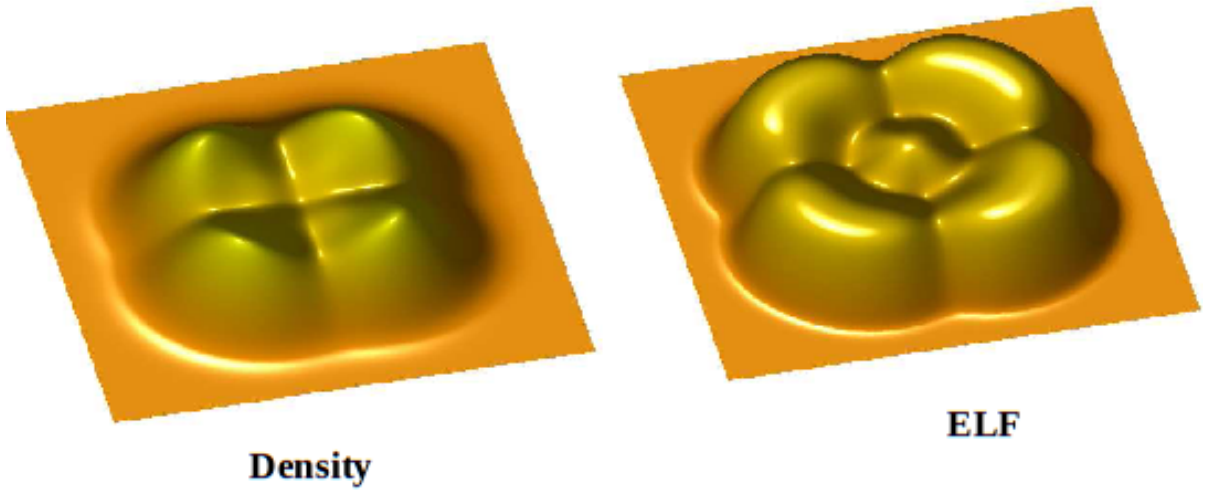
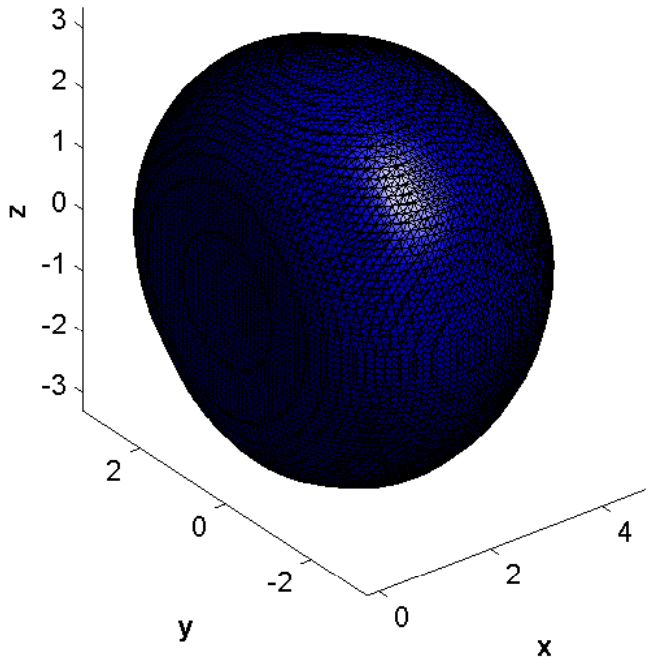


Figure : *the electron localization function (ELF) of a 12-electron quantum dot.*

Motivations for computing maximal probability domains

Idea: a solution is to remove the problematical high-dimensionality of the wave function by averaging correctly over the positions of electrons.



Maximal probability domains seems to be one rigorous entry point to recover standard chemical concepts from wave functions in the real space.

The probability to find a number of electrons in a domain

Let us consider:

- a quantum system of N electrons completely characterized by its wave function:
$$\Psi : \underbrace{\mathbb{R}^3 \times \ldots \times \mathbb{R}^3}_{N \text{ times}} \longrightarrow \mathbb{R};$$
- a fixed number $\nu \in \{0, \ldots, N\}$ of electrons;
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- a given three-dimensional domain $\Omega \subseteq \mathbb{R}^3$.

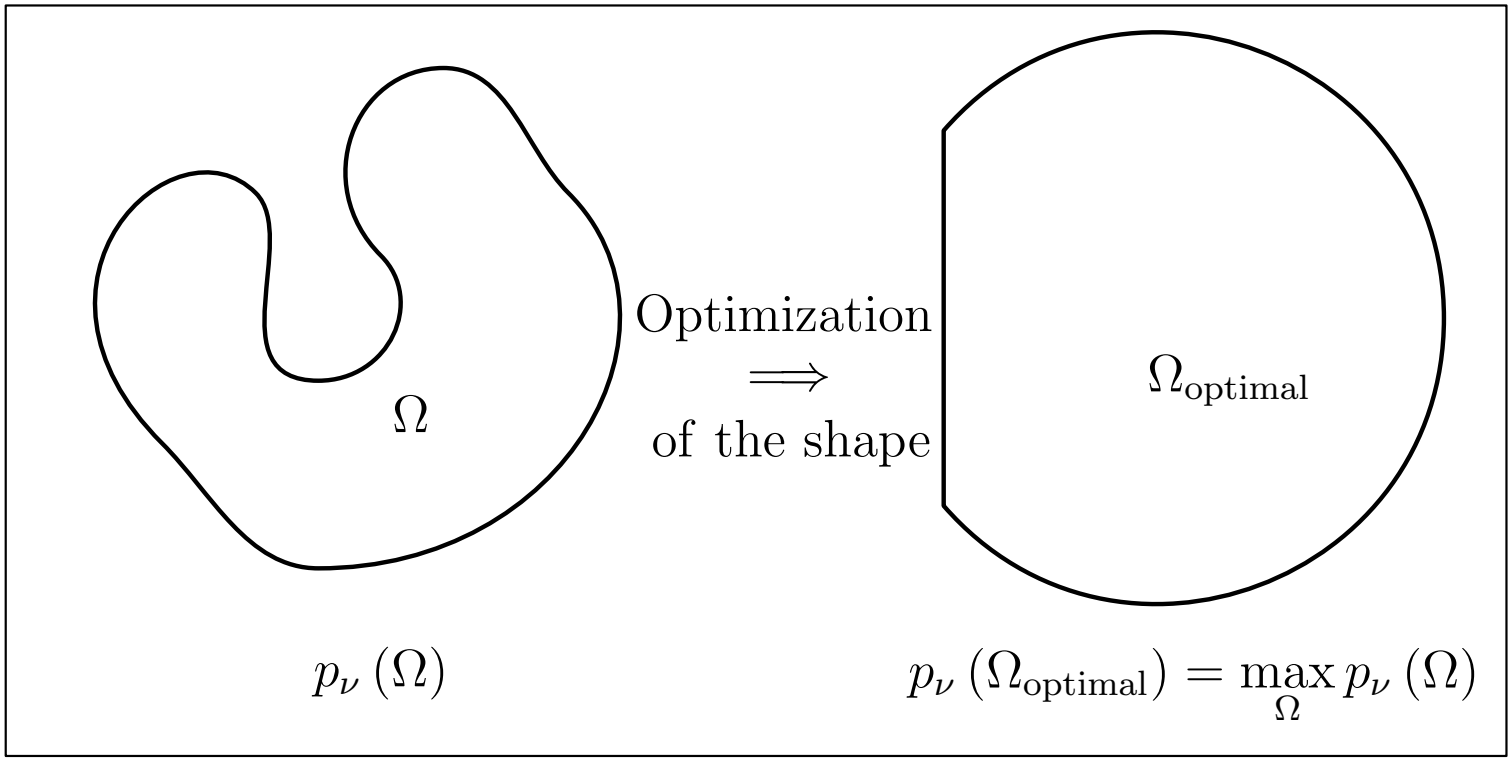
The probability $p_\nu(\Omega)$ to find ν electrons in the spatial domain Ω is

$$p_\nu(\Omega) = \binom{N}{\nu} \int_{\underbrace{\Omega \times \ldots \times \Omega}_{\nu \text{ times}} \times \underbrace{(\mathbb{R}^3 \backslash \Omega) \times \ldots \times (\mathbb{R}^3 \backslash \Omega)}_{N-\nu \text{ times}}} |\Psi|^2.$$

We can thus define a shape functional $p_\nu : \Omega \longmapsto p_\nu(\Omega)$.

MPDs are the solutions of a shape optimization problem

Goal: we are searching for the domains maximizing the probability p_ν because they give a simple partition of the real space, from which we can recover chemical informations on the system (symmetries, interactions).



Job: we are interested in the theoretical and numerical study of this shape optimization problem, and also on the implementation of an efficient algorithm to compute these maximal probability domains.

The theoretical and numerical analysis of the problem

An open theoretical question: the mathematical existence and regularity of a maximizer to the shape optimization problem:

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Direct method from Calculus of Variations:

- Introduce a class of **admissible** sets $\mathcal{A}_{\mathrm{adm}}$ among domains of $\mathbb{R}^3$.
- Consider a **minimizing** sequence $p_\nu(\Omega_i) \longrightarrow_{i \to +\infty} \sup_\Omega p_\nu(\Omega)$.
- Define a topology on $\mathcal{A}_{\mathrm{adm}}$ to get the **compactness** of a sequence $(\Omega_i \to \Omega^*)$ and the **continuity** of the functional $(p_\nu(\Omega_i) \to p_\nu(\Omega^*))$.
- Ensure the **regularity** and admissibility of the maximizer $\Omega^* \in \mathcal{A}_{\mathrm{adm}}$.

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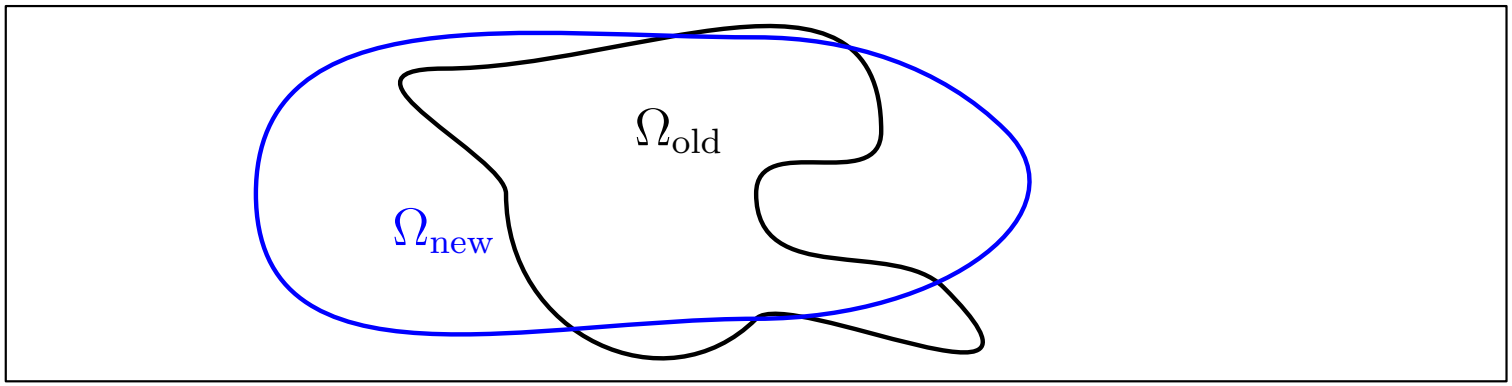
Concerning the numerical analysis:

- How to deform a domain into a new one in order to increase the probability (concepts of shape derivative and shape gradient)?
- How can we represent the domain in order to handle the possible changes of topology in the evolution of the interfaces (level-set methods)?
- How can we discretize the domain efficiently to reduce the numerical errors and the computation time (techniques of adaptive mesh)?

The concept of shape derivative through an example

Question: how can we deform a domain to increase the functional? What is a small perturbation of a domain?



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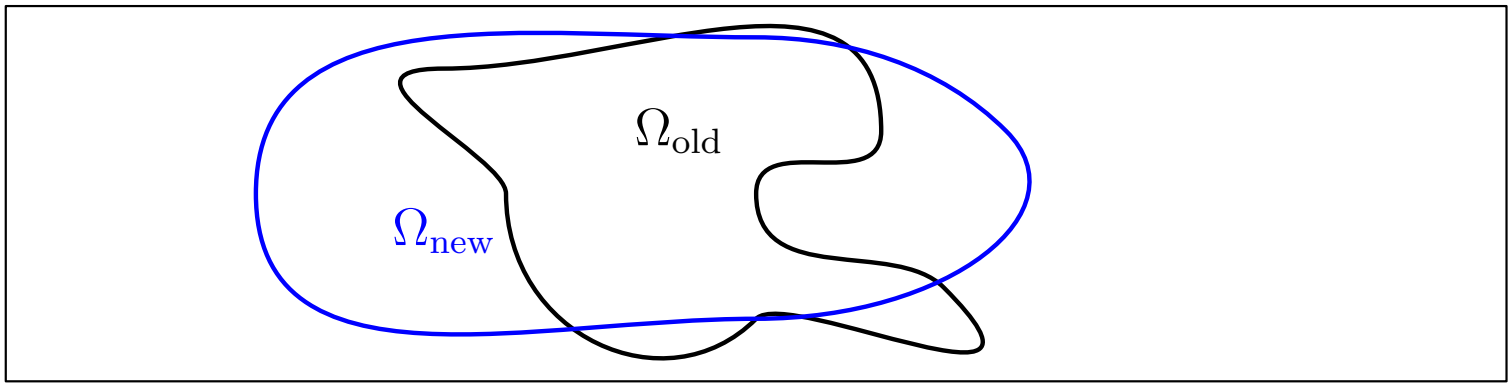
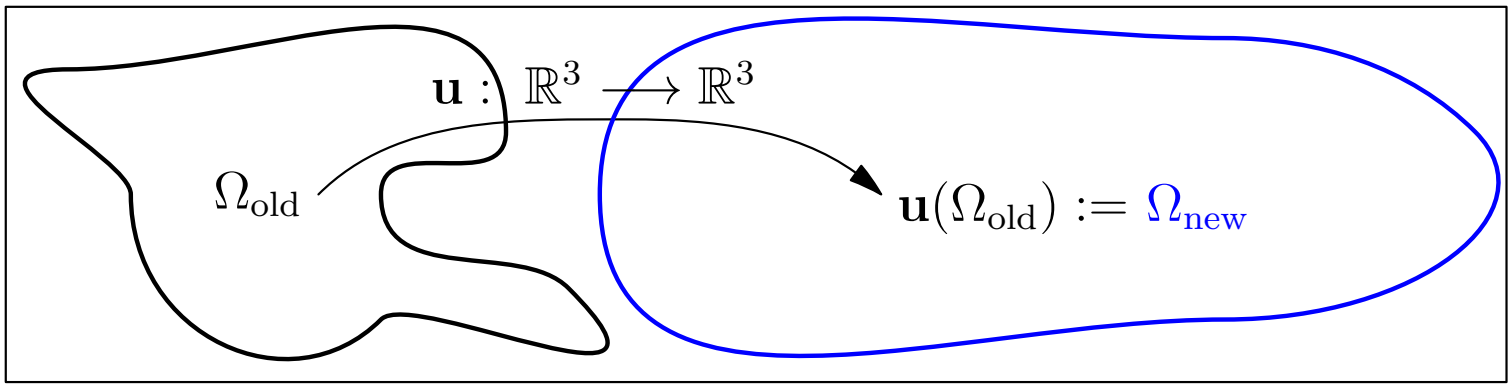


Idea: identify the deformation of domains by their images through maps.



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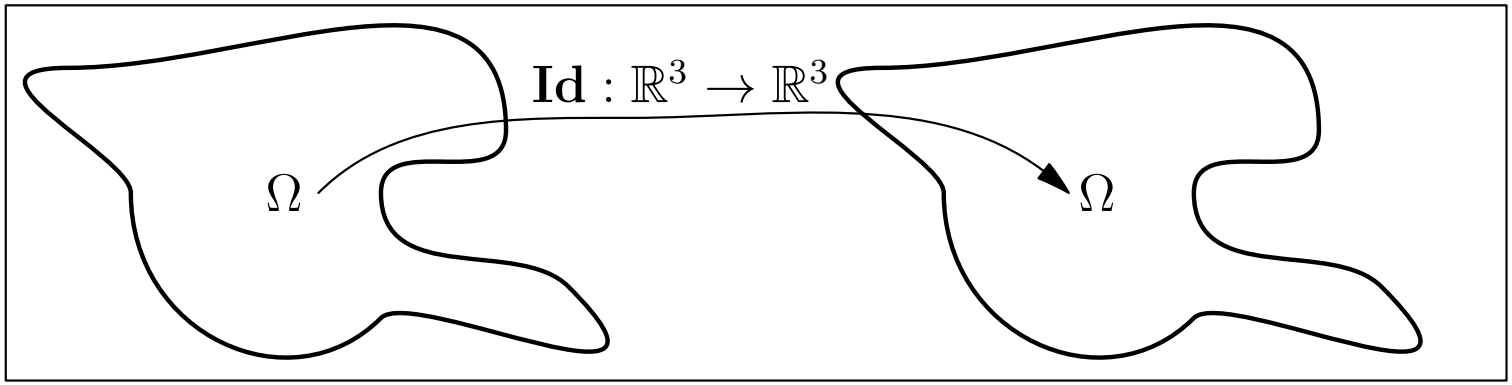
We can thus work on the maps $\mathbf{u} : \mathbb{R}^3 \to \mathbb{R}^3$ (functional analysis) instead of dealing with domains (no topology on the subsets of $\mathbb{R}^3$).

No deformation: it is the identity map $Id : \mathbf{x} \in \mathbb{R}^3 \longmapsto \mathbf{x} \in \mathbb{R}^3$.



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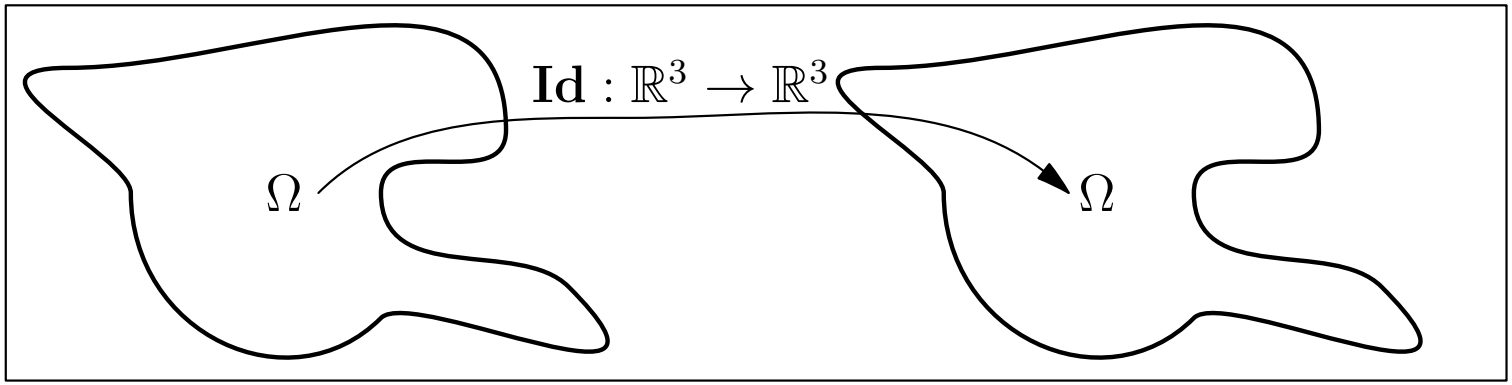
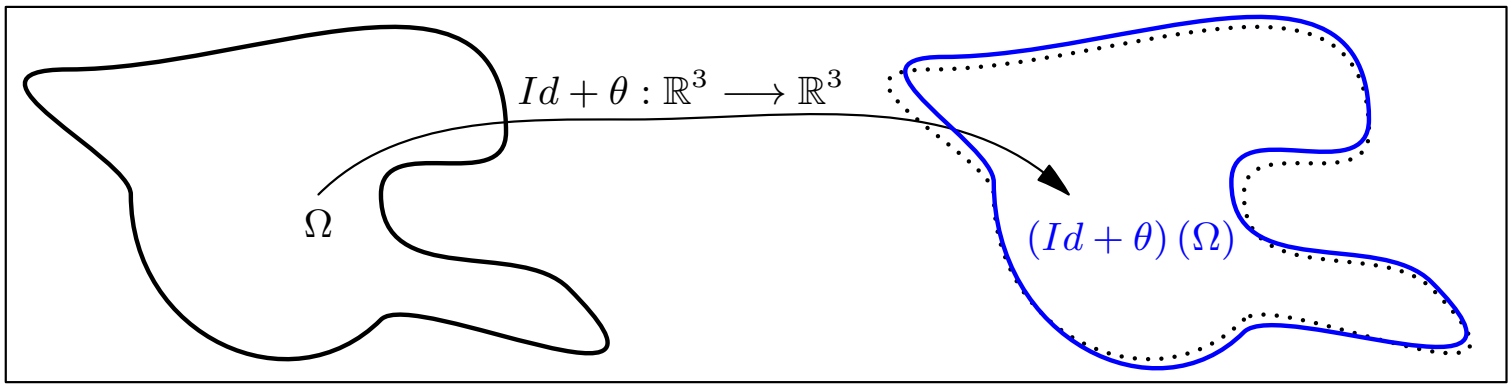


A small deformation: it is a perturbation $\theta : \mathbb{R}^3 \to \mathbb{R}^3$ of the identity.



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Shape derivative of F: a first-order Taylor expansion of $\widetilde{F}$ in $\theta = \mathbf{0}$.

$$\widetilde{F}(\theta) \quad = \quad \widetilde{F}(\mathbf{0}) \quad + \quad D_{\mathbf{0}}\widetilde{F}(\theta) \quad + \quad o(\theta) \Big|$$

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Cauchy-Schwarz inequality: optimal bound for the term we maximize

$$\int_{\partial\Omega} f\theta_{\mathbf{n}} \leqslant \sqrt{\int_{\partial\Omega} f^2} \sqrt{\int_{\partial\Omega} \theta_{\mathbf{n}}^2},$$

where the equality holds if and only if $\theta_{\mathbf{n}} = tf$ where $t > 0$.

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Shape gradient: best local choice of perturbation $\boxed{\theta(\mathbf{x}) = tf(\mathbf{x})\mathbf{n}_{\partial\Omega}(\mathbf{x})}$ a priori defined only for any $\mathbf{x} \in \partial\Omega$ and extended to the whole space

$$\int_{(Id+\theta)(\Omega)} f = \int_{\Omega} f + t\left(\int_{\partial\Omega} f^2\right) + o(t) \geqslant \int_{\Omega} f,$$

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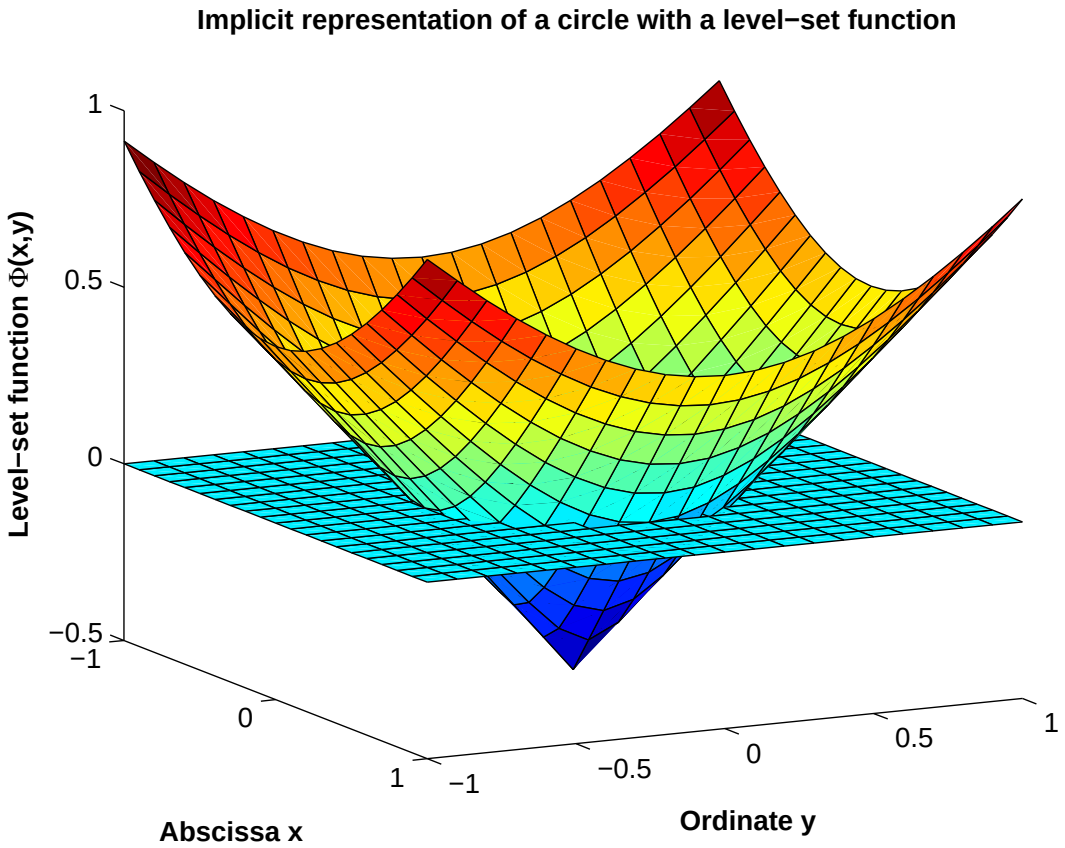
Physical interpretation: the shape gradient defined on the boundary gives the intensity at which we have to push the surface along the normal in order to (locally) increase the functional in an optimal way.

The evolution of interfaces with a level-set method

The level-set method consists in representing implicitly the interface $\partial\Omega$ as the zero of a continuous map $\Phi : \mathbb{R}^3 \to \mathbb{R}$:

$$\partial\Omega = \left\{\mathbf{x} \in \mathbb{R}^3, \quad \Phi(\mathbf{x}) = 0\right\} \quad \text{et} \quad \Omega = \left\{\mathbf{x} \in \mathbb{R}^3, \quad \Phi(\mathbf{x}) < 0\right\}.$$



The evolution of interfaces with a level-set method

Advantages: this representation does not depend on the dimension, handles very-well the changes of topology, gives access to the geometrical properties of the surface (normal, fundamental forms) and extends them naturally to the whole space:

$$\forall \mathbf{x} \in \partial\Omega, \quad \mathbf{n}_{\partial\Omega}^{\text{ext}}(\mathbf{x}) = \frac{\nabla\Phi(\mathbf{x})}{\|\nabla\Phi(\mathbf{x})\|} \quad \text{and} \quad H_{\partial\Omega}(\mathbf{x}) = \operatorname{div}\left(\frac{\nabla\Phi(\mathbf{x})}{\|\nabla\Phi(\mathbf{x})\|}\right).$$

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Assume that the shape $\Omega(t)$, implicitly represented by the level-set function $\varphi(t,\bullet)$, is evolving according to a vector field $\theta_n(\bullet)\frac{\nabla\varphi(t,\bullet)}{\|\nabla\varphi(t,\bullet)\|}$, namely the shape gradient from the previous analysis.

$$\dot{\mathbf{x}}(t) = \theta_n(\mathbf{x}(t))\frac{\nabla\varphi(t,\mathbf{x}(t))}{\|\nabla\varphi(t,\mathbf{x}(t))\|} \quad \text{and} \quad \varphi(t,\mathbf{x}(t)) = 0.$$

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Hence, we have to solve the following partial differential equation which is an Hamilton-Jacobi type of equation:

$$\boxed{\frac{\partial \varphi}{\partial t}(t, \mathbf{x}) + \theta_n(\mathbf{x}) \|\nabla \varphi(t, \mathbf{x})\| = 0 \quad t > 0, \ \mathbf{x} \in \mathbb{R}^3.}$$

An algorithm using the techniques of adaptive mesh

1. Generate an initial mesh adapted to the initial domain Ω_0 and its associated level-set function:

$$\varphi_0 : \mathbf{x} \in \mathbb{R}^3 \mapsto d(\mathbf{x}, \overline{\Omega_0}) - d(\mathbf{x}, \mathbb{R}^3 \backslash \Omega_0).$$

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3. Solve the Hamilton-Jacobi equation on a small interval $[0, \Delta t]$ and adapt the mesh to the new surface:

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4. Reduce the numerical errors by modifying the level-set function so that:

$$\|\nabla \varphi_1\| = 1.$$

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2. Adapt the mesh in order to compute the shape gradient of the probability at the point of the surface. Extend it to the whole mesh.

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$$\partial\Omega_1 = \{\mathbf{x} \in \mathbb{R}^3, \varphi(\Delta t, \mathbf{x}) = 0\} \quad \text{and} \quad \Omega_1 = \{\mathbf{x} \in \mathbb{R}^3, \varphi(\Delta t, \mathbf{x}) < 0\}.$$

4. Reduce the numerical errors by modifying the level-set function so that:

$$\|\nabla \varphi_1\| = 1.$$

5. Get back to the first step if the shape gradient is not zero on the boundary and/or if the probability stops increasing.

Conclusion: contributions, difficulties and challenges

Contributions:

- Derivation of the second-order shape derivative of the probability in the particular case of a single Slater determinant wave function;
- Evaluation of the first-order shape derivative of the probability in the general case of multi-determinant wave functions;
- 2D and 3D programs in Matlab to study very simple molecules.
  Improvement of the 3D Program in C with adaptive mesh techniques.

Conclusion: contributions, difficulties and challenges

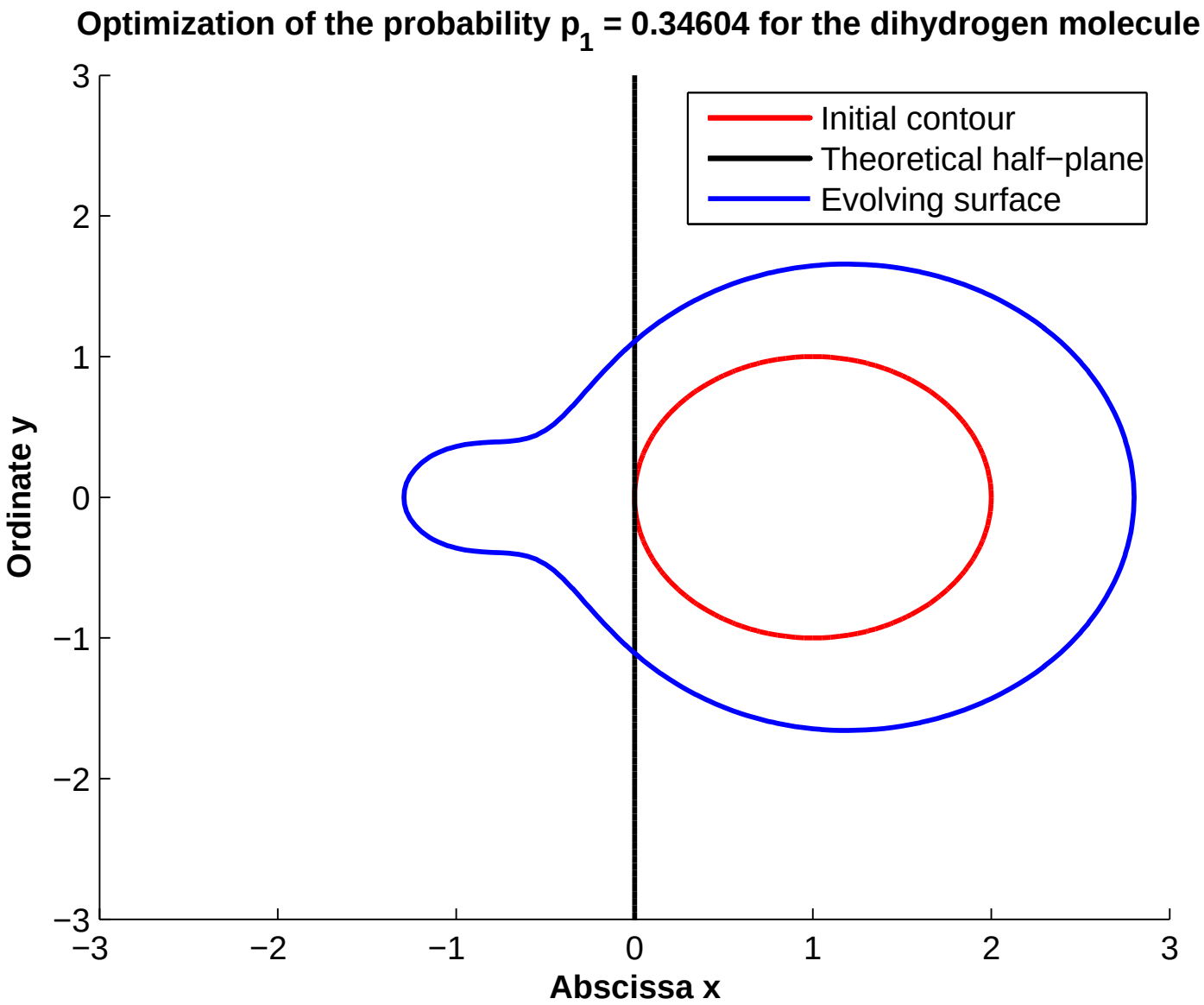
Contributions:

- Derivation of the second-order shape derivative of the probability in the particular case of a single Slater determinant wave function;
- Evaluation of the first-order shape derivative of the probability in the general case of multi-determinant wave functions;
- 2D and 3D programs in Matlab to study very simple molecules. Improvement of the 3D Program in C with adaptive mesh techniques.

Difficulties/Challenges:

- Problem of numerical convergence of the domain/Set up a Newton shape optimization method;
- Quantify the numerical errors of the algorithm/Accurate choice of the numerical box;
- Parallelize the calculations/Generalize the algorithm to the general case;
- Sensitivity to the initialization/Study the chemical informations of MDPs.

Thank you for your attention. Do you have any questions?



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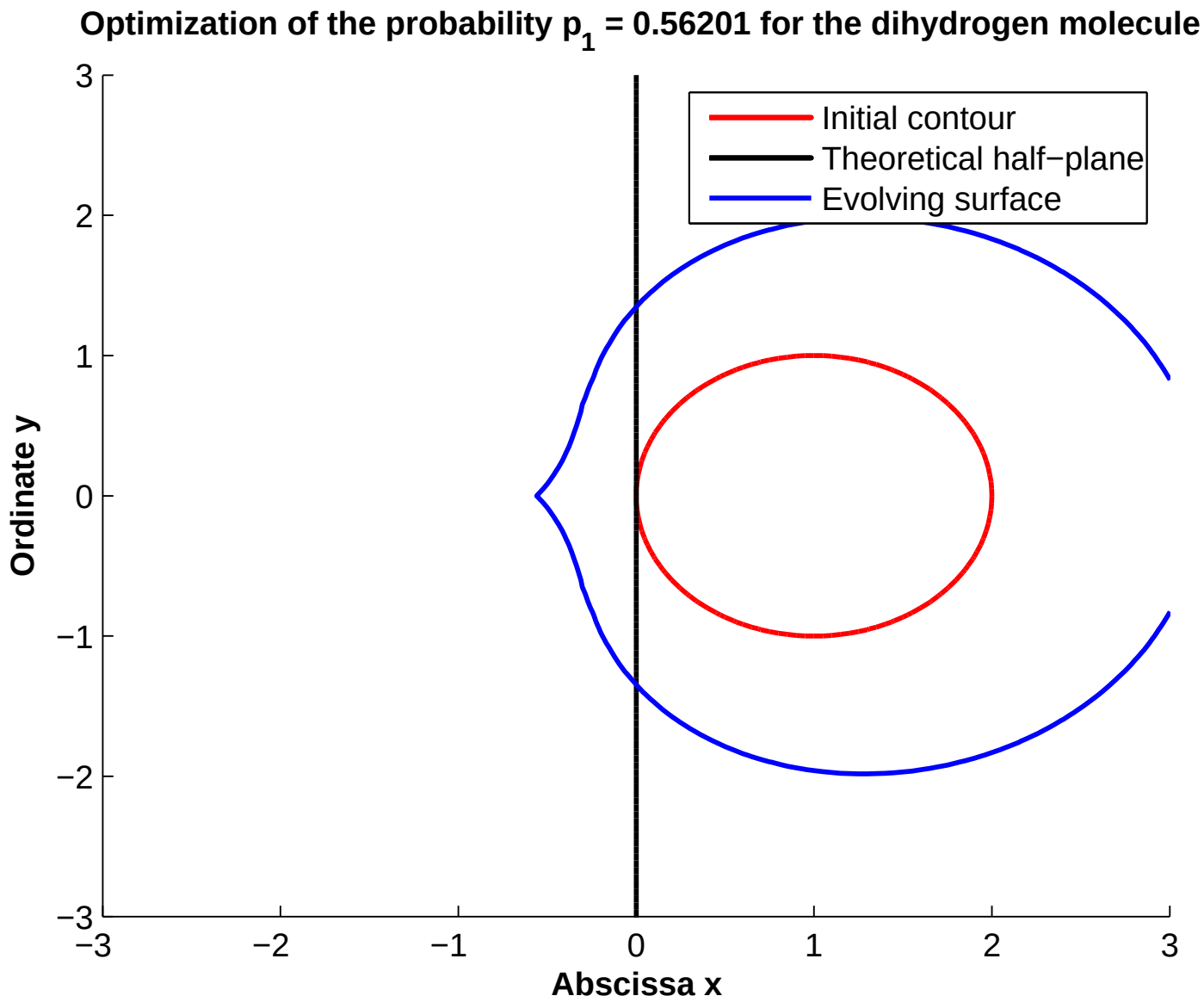

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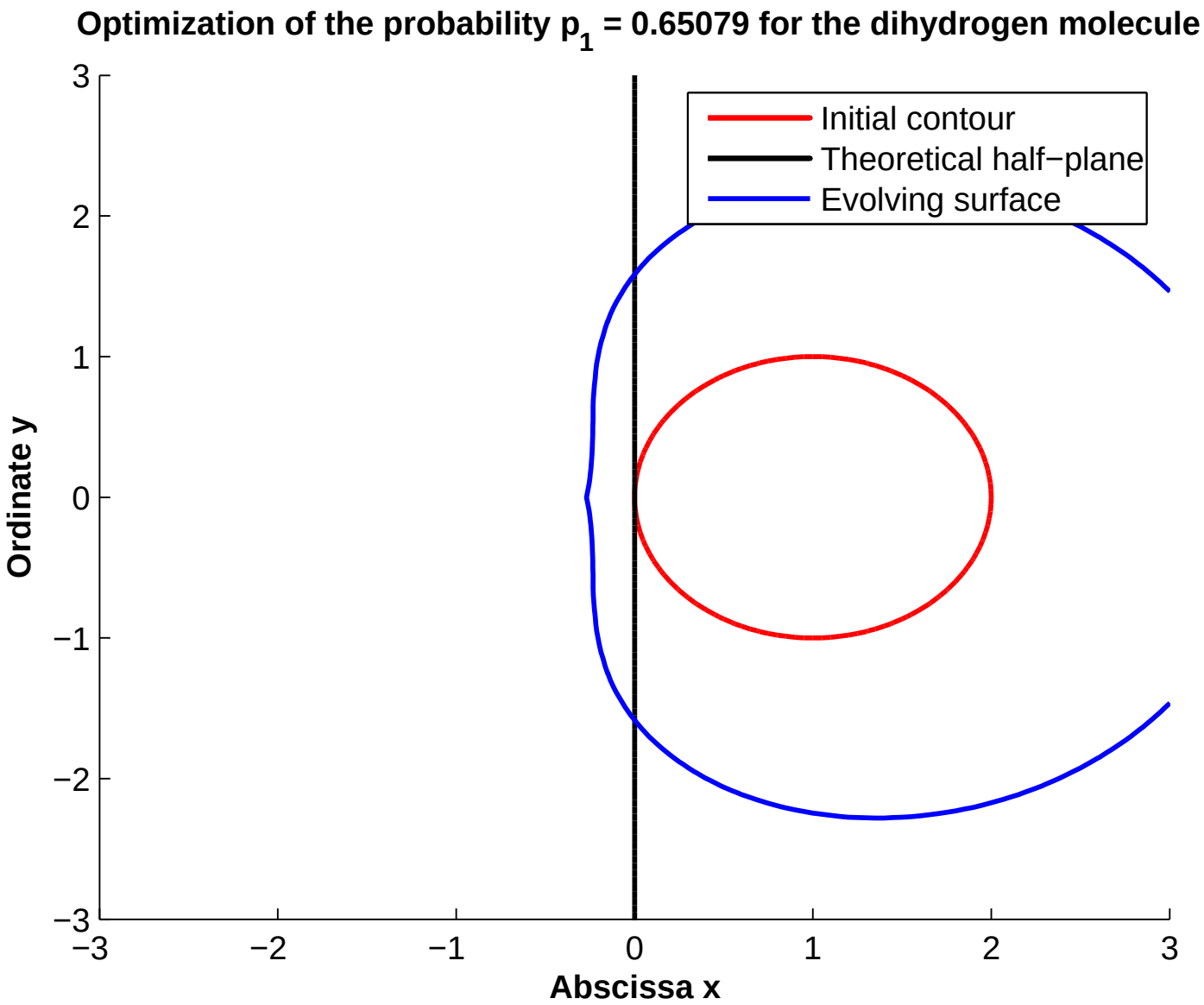

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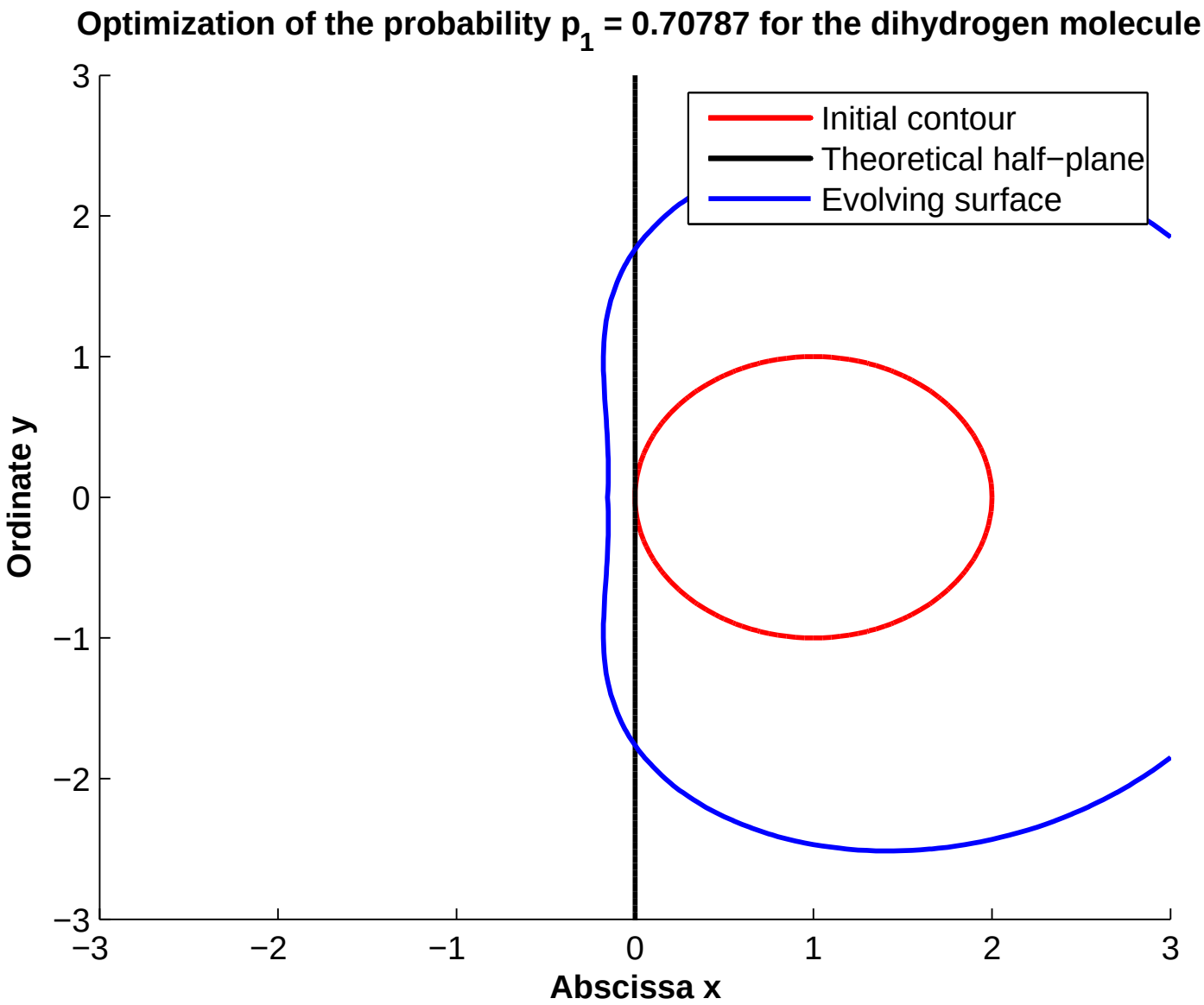

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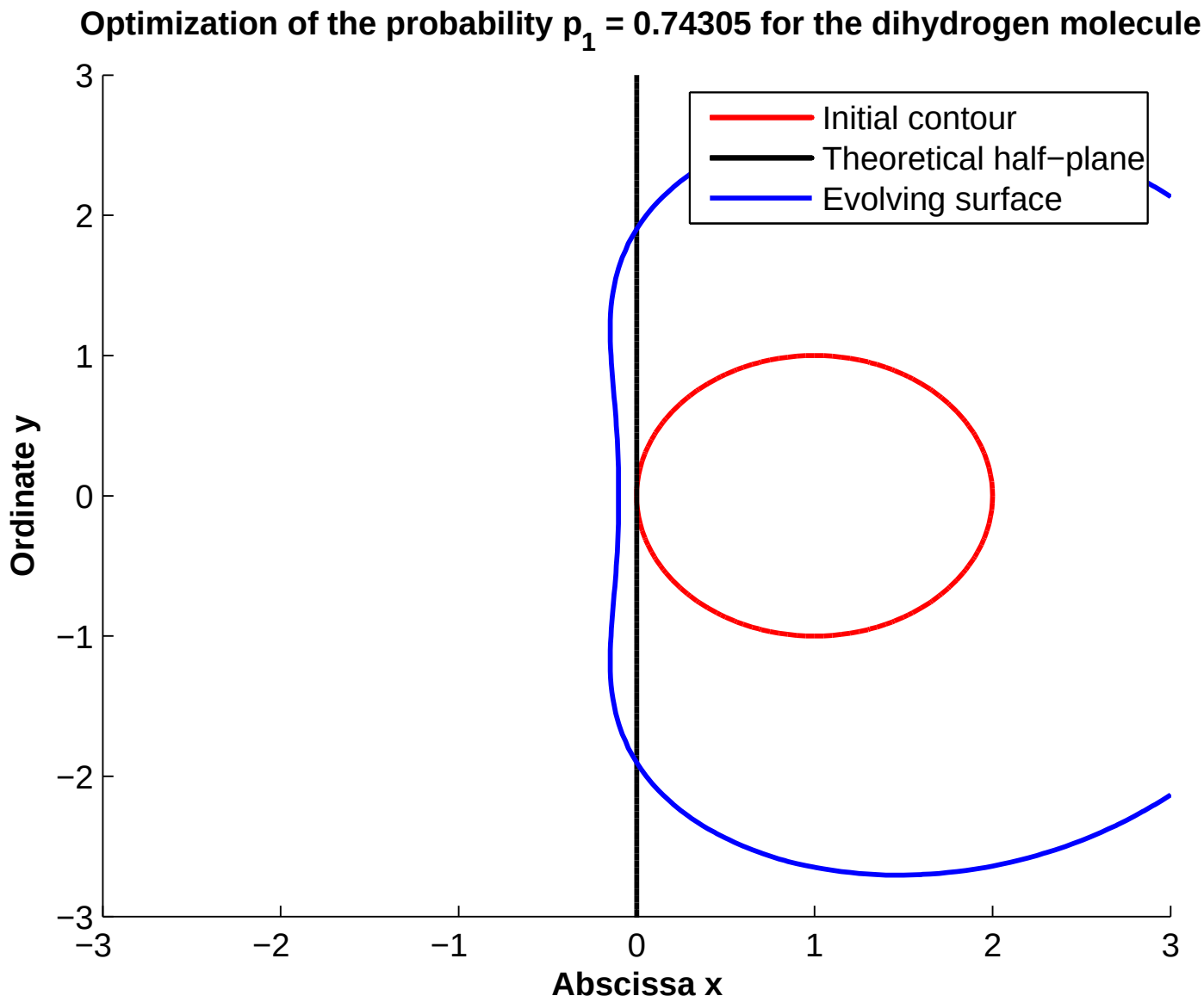

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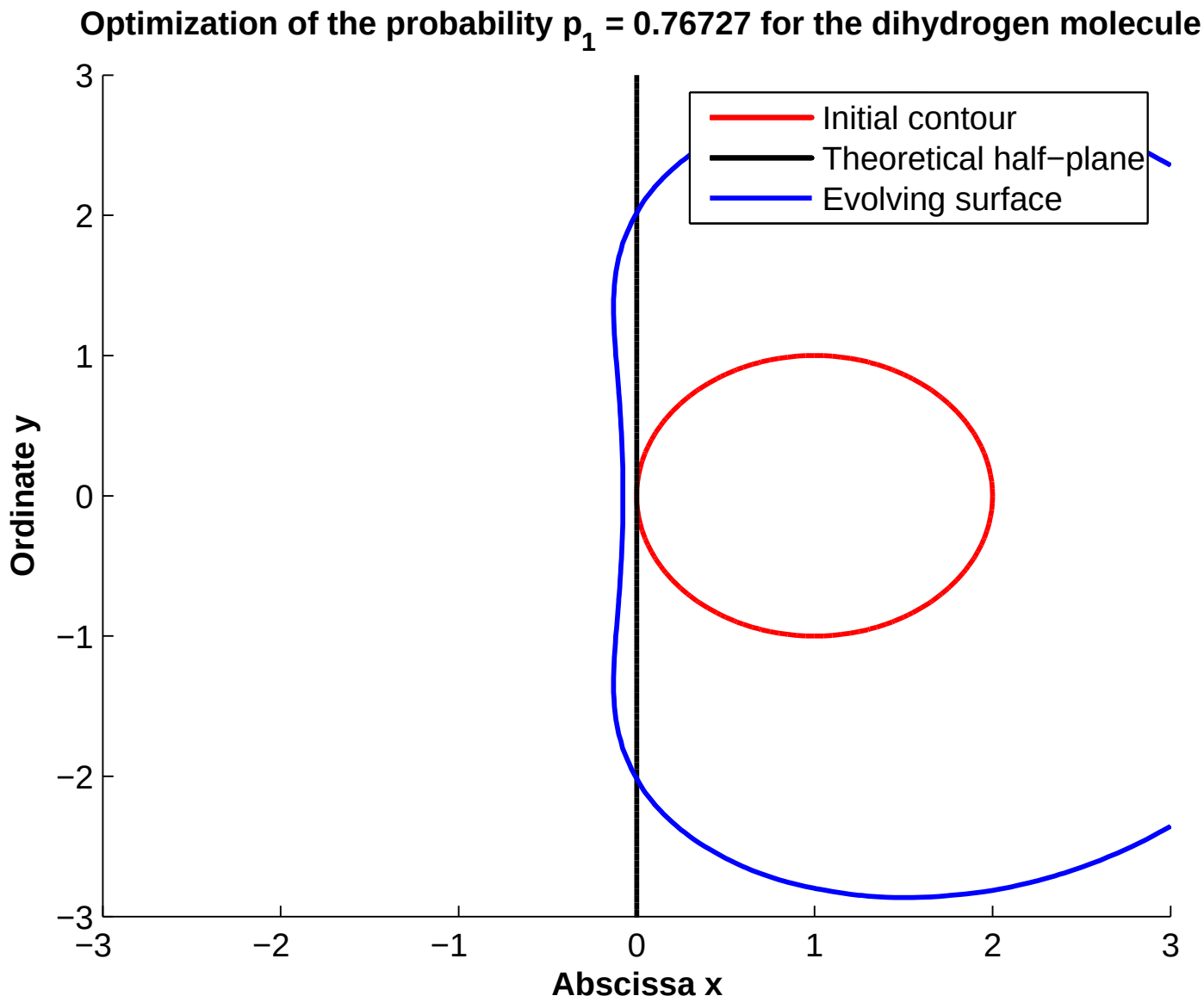

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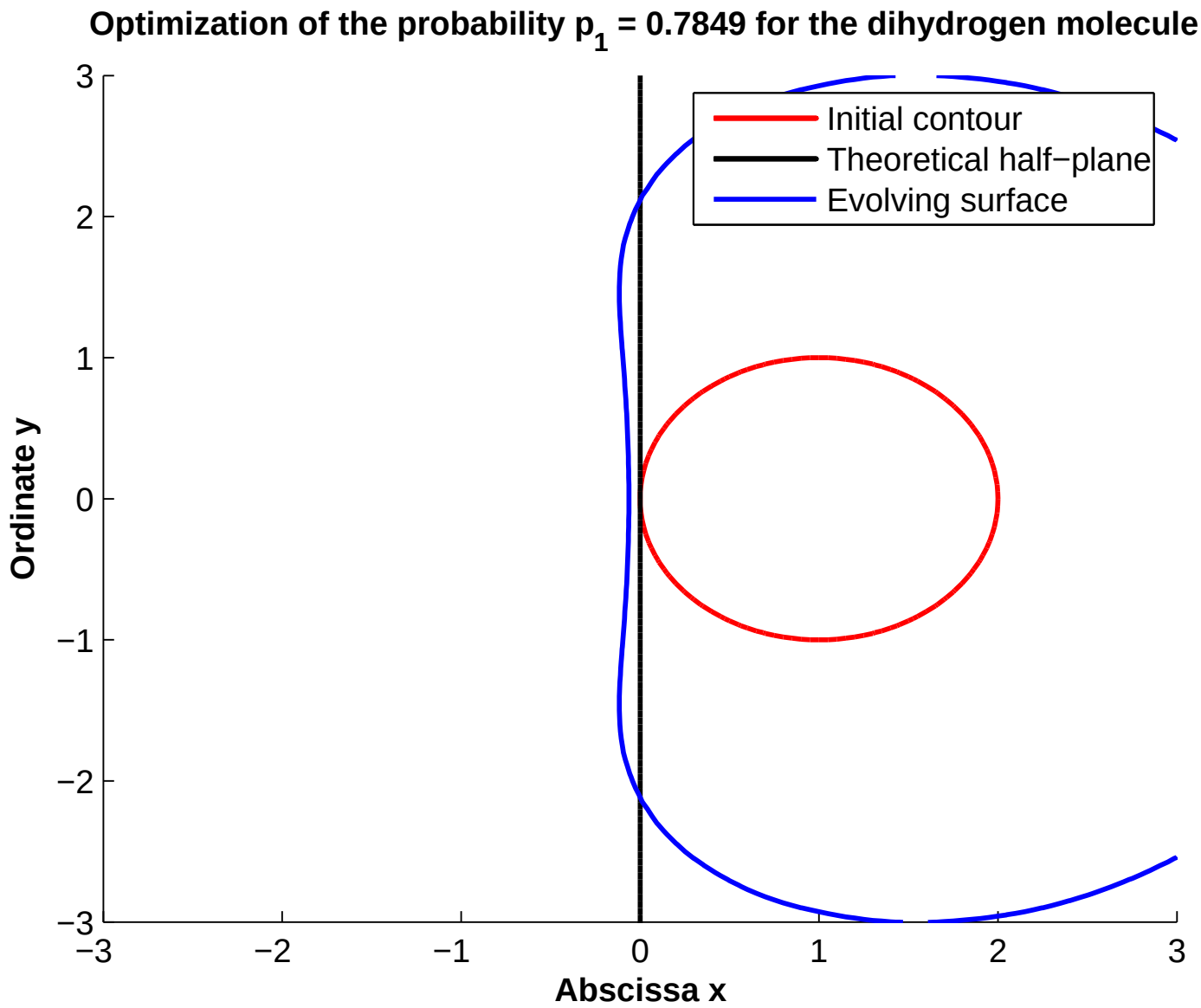

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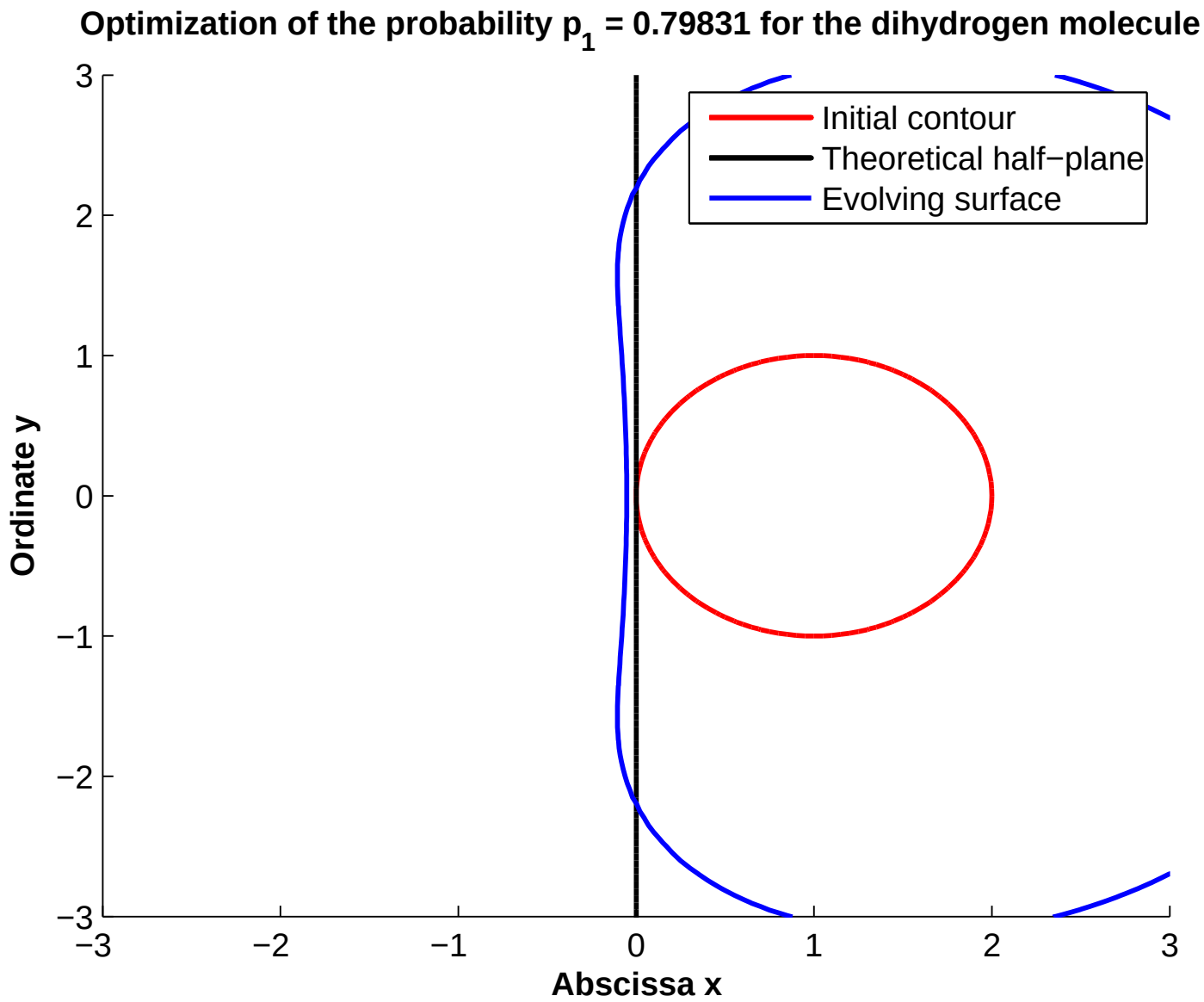

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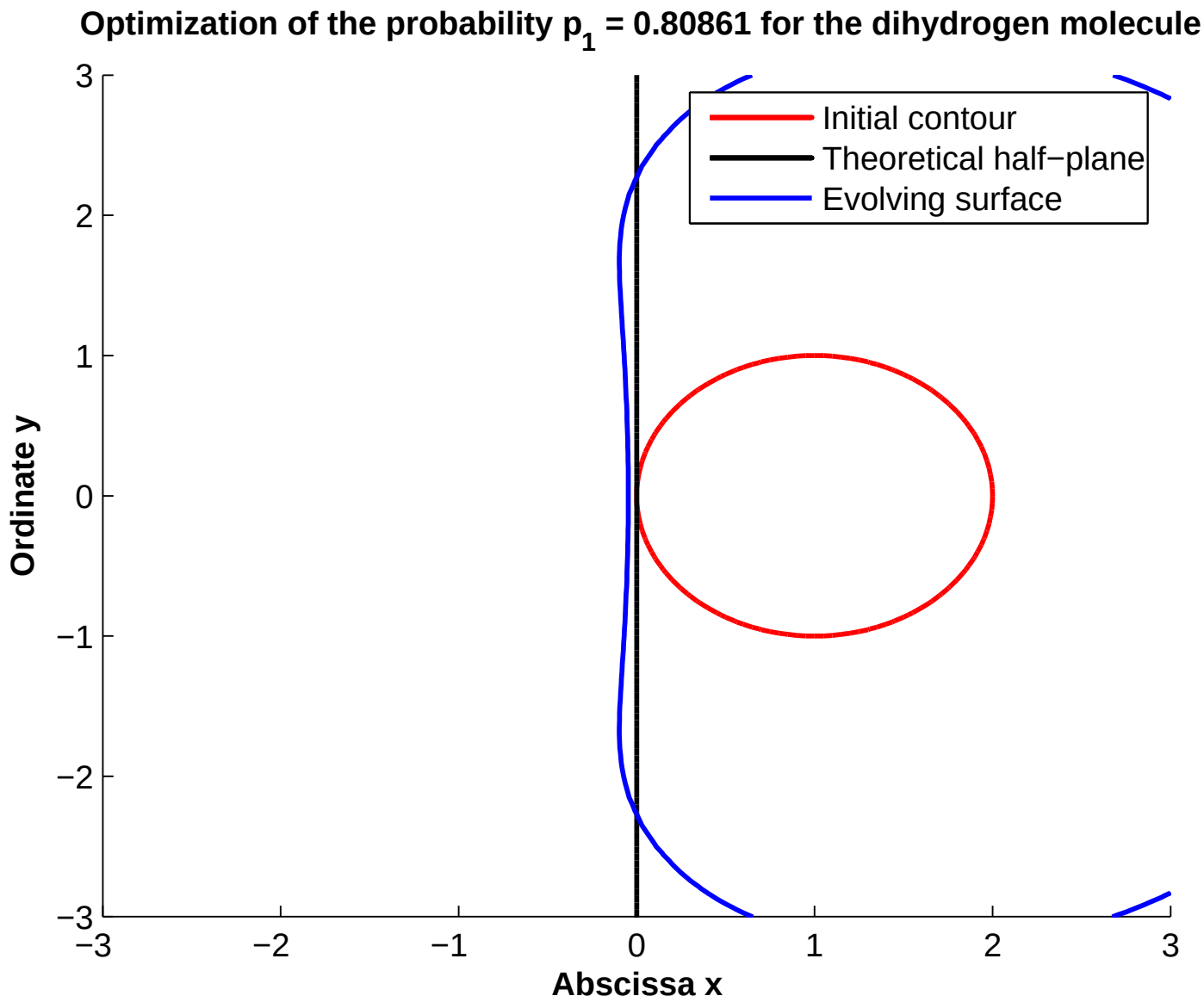

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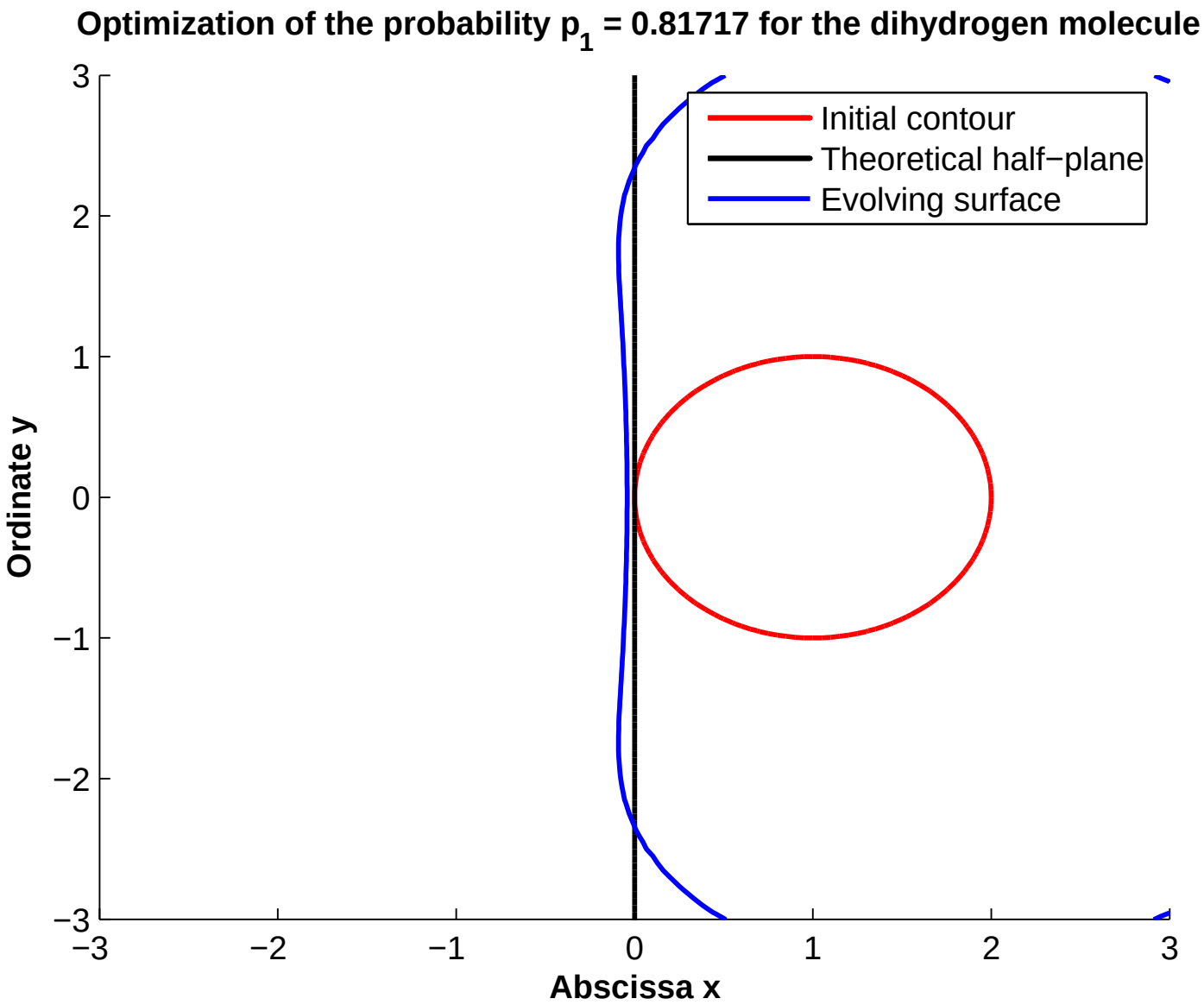

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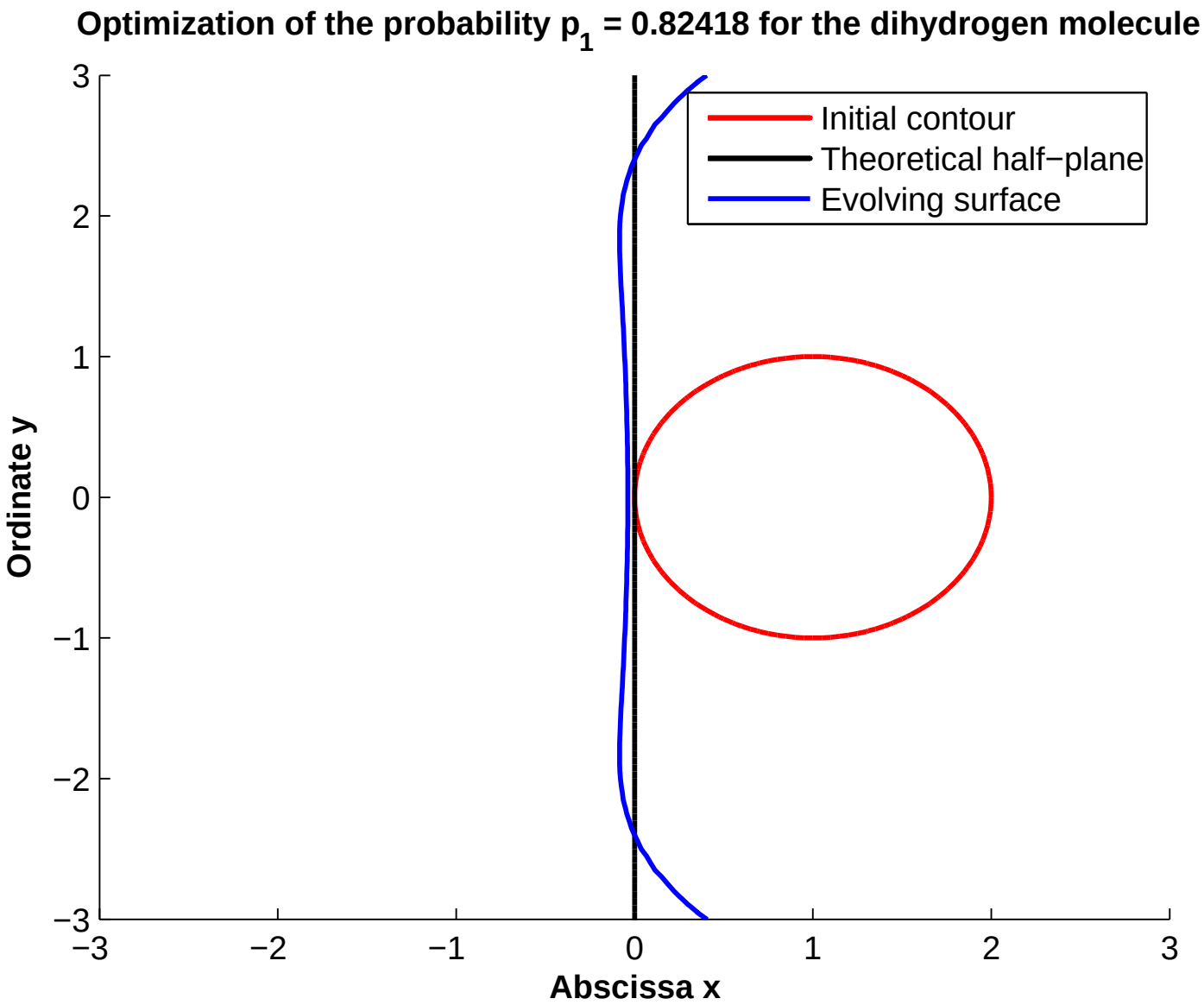

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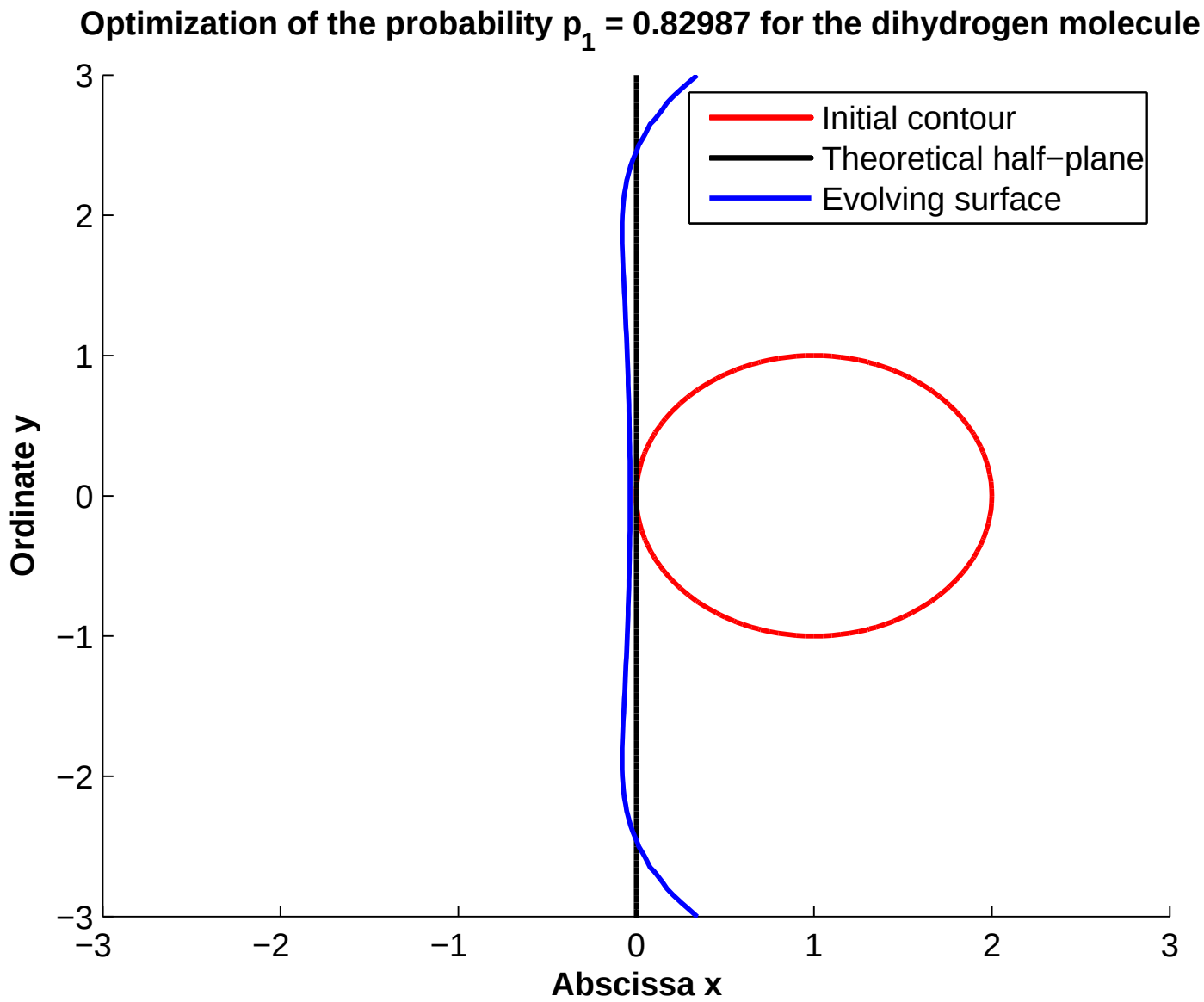

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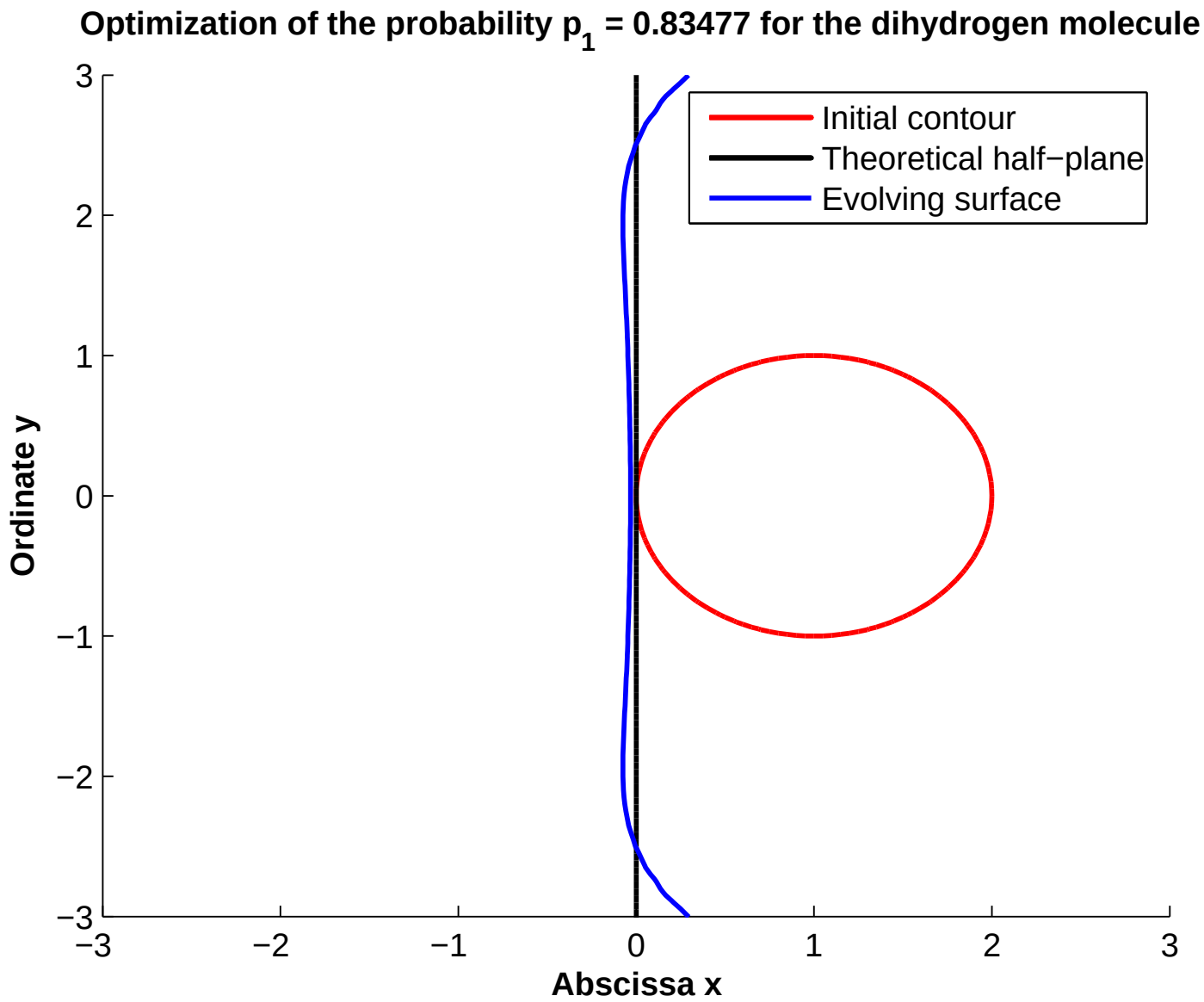

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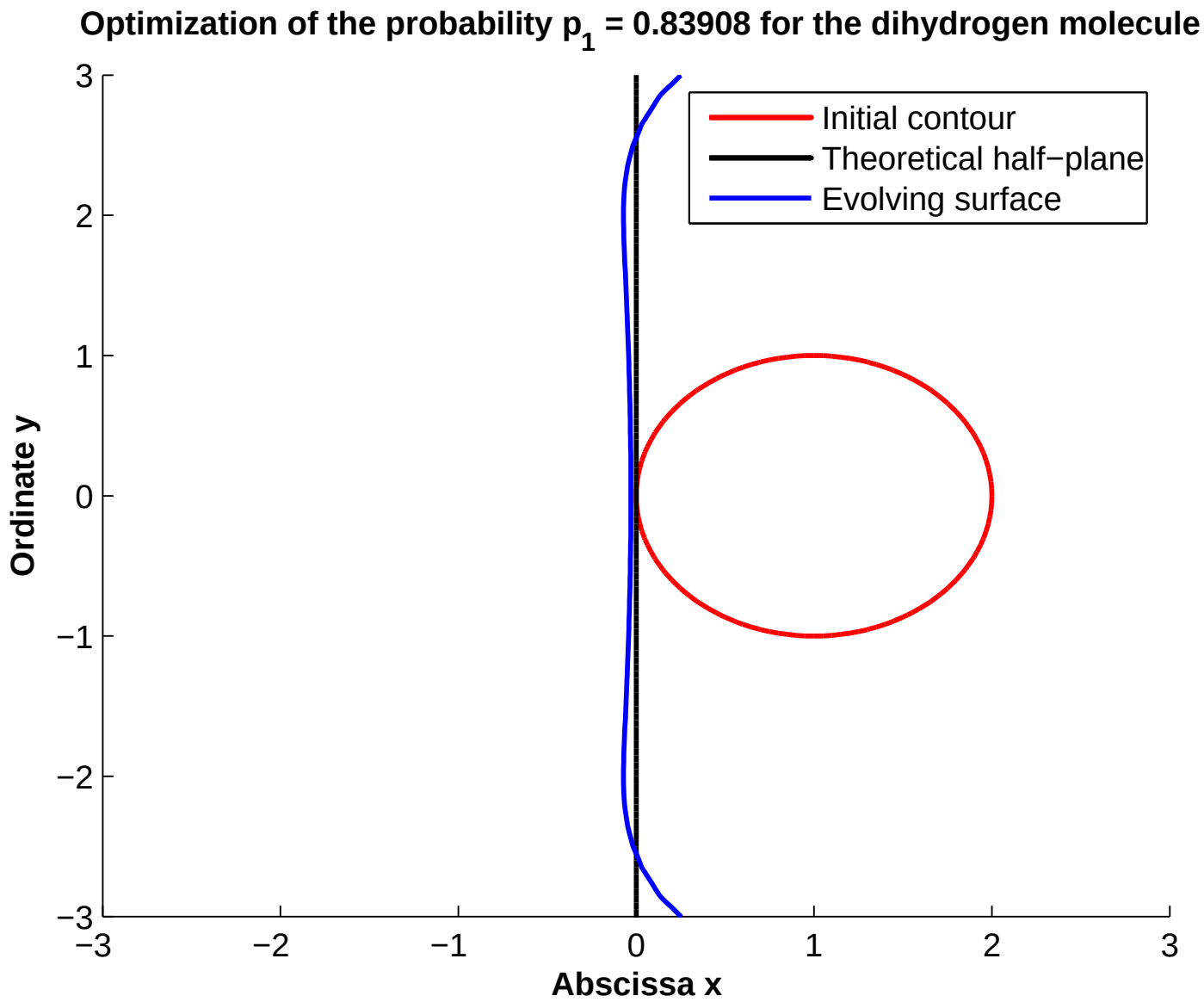

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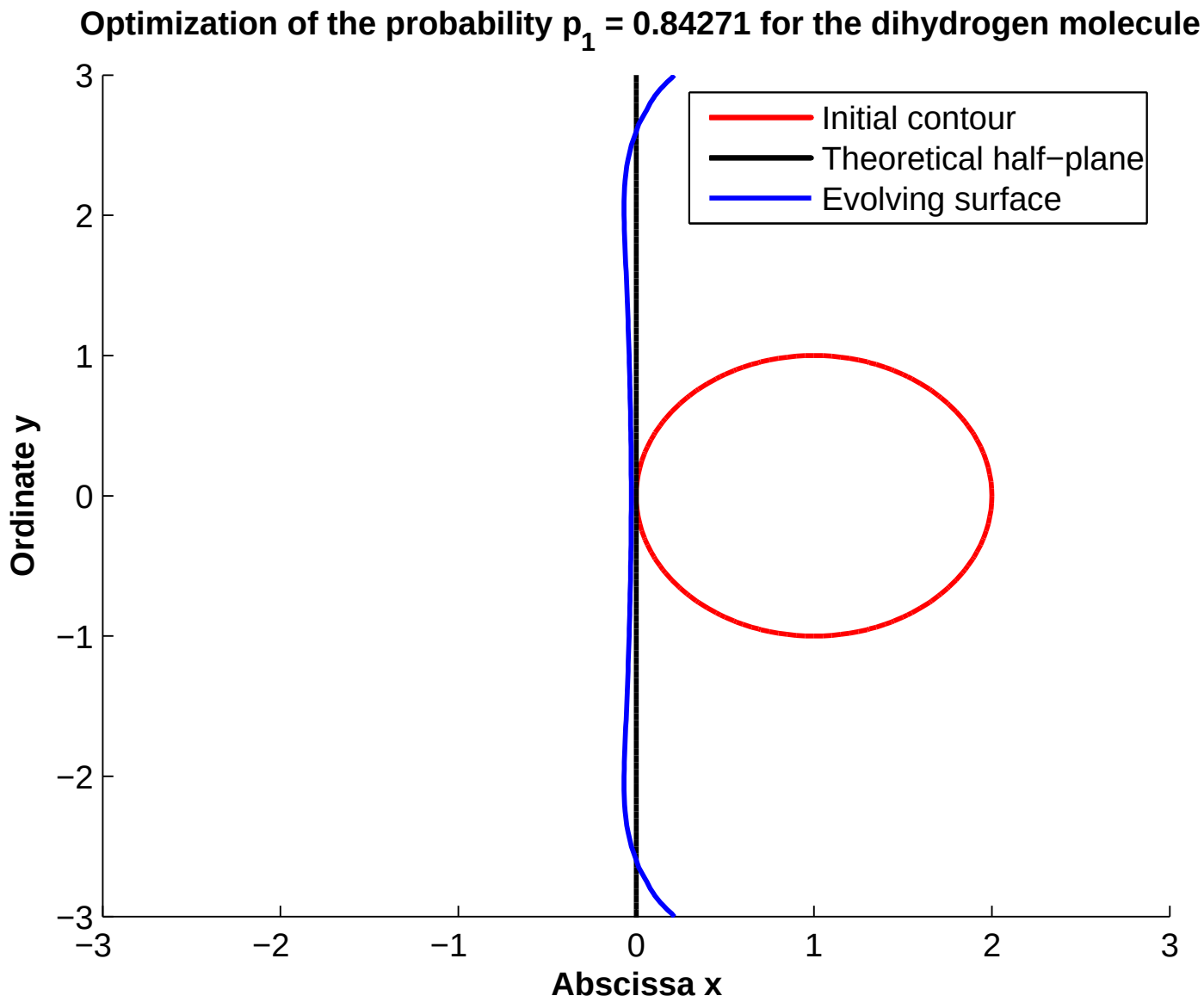

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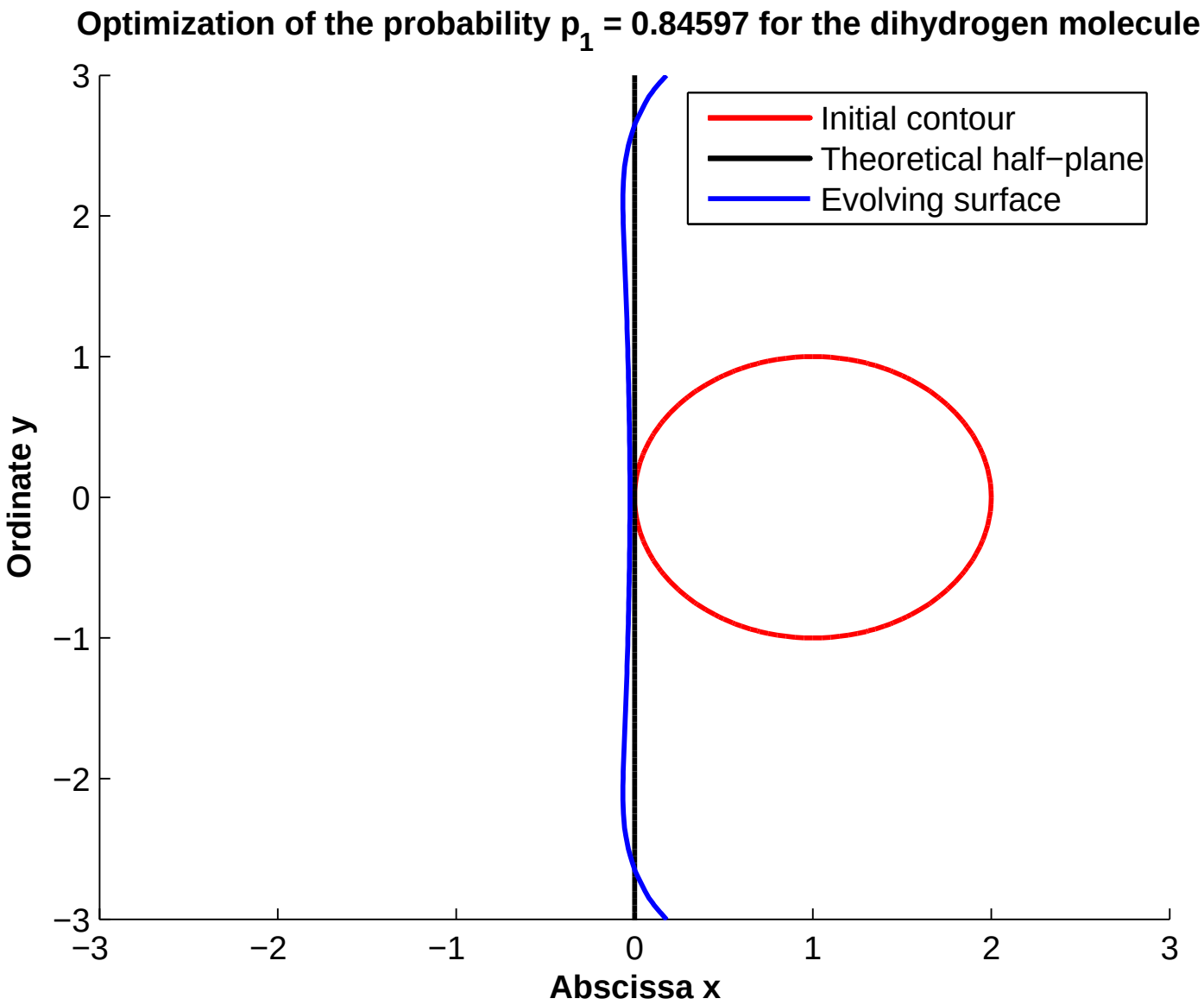

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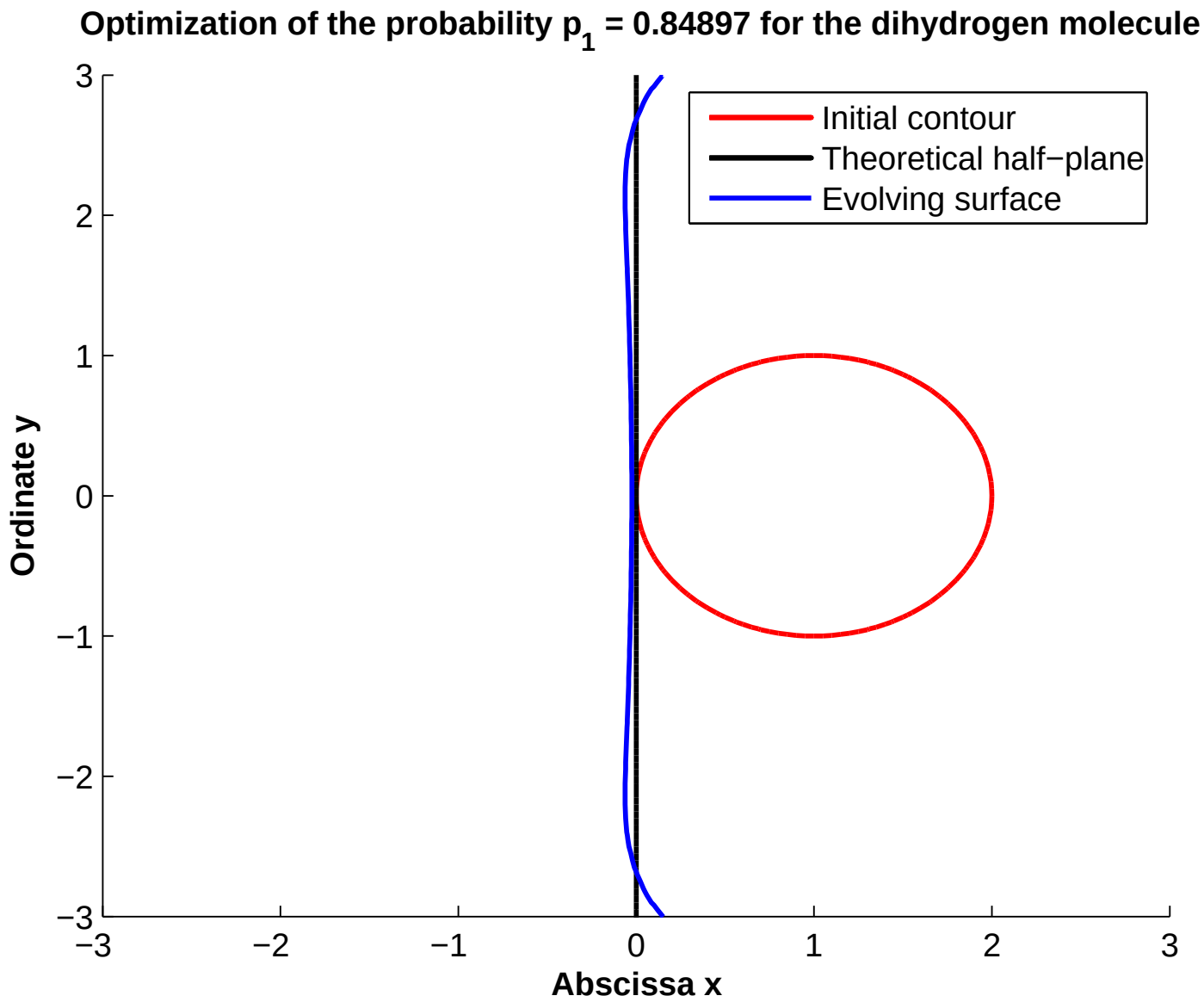

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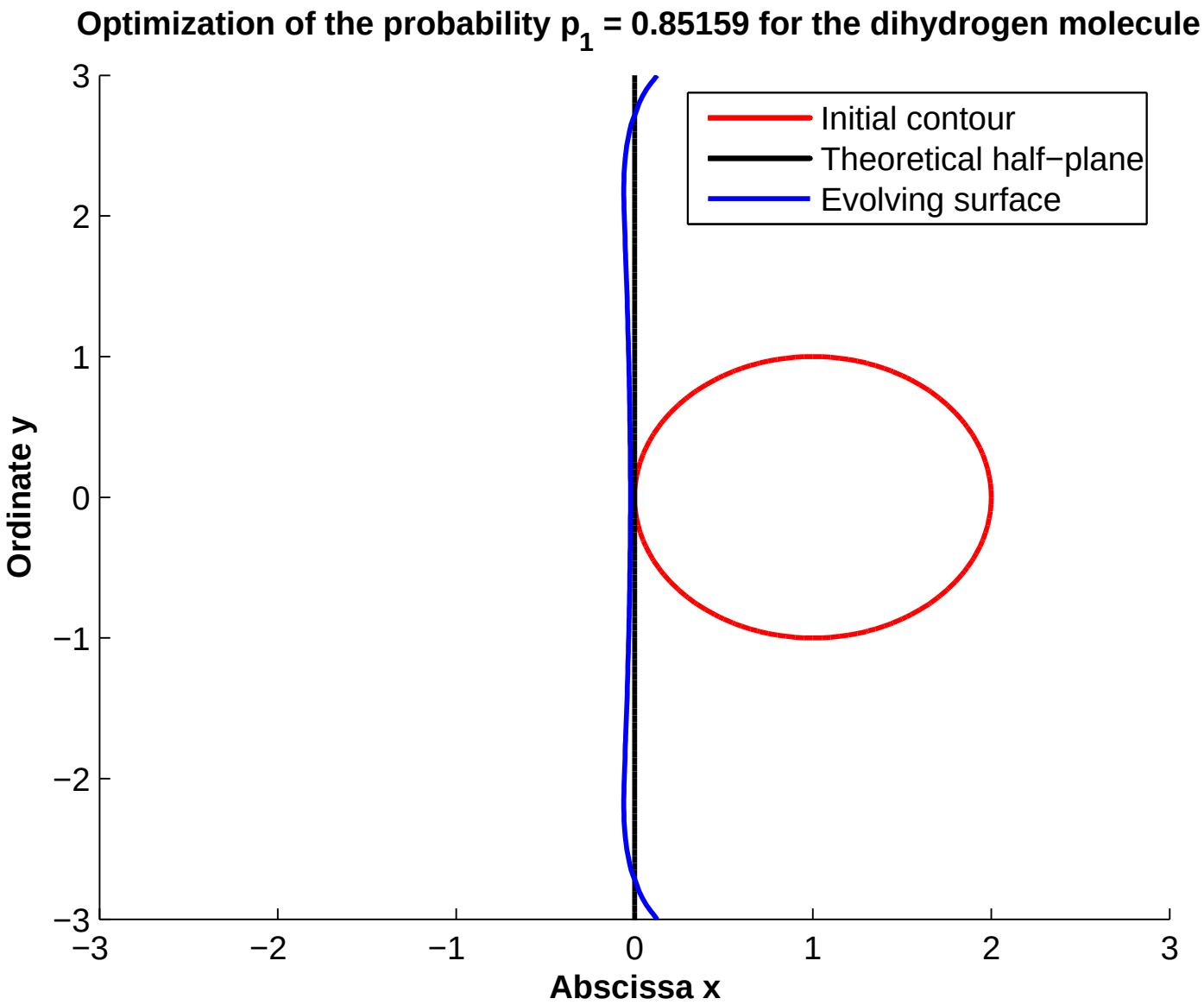

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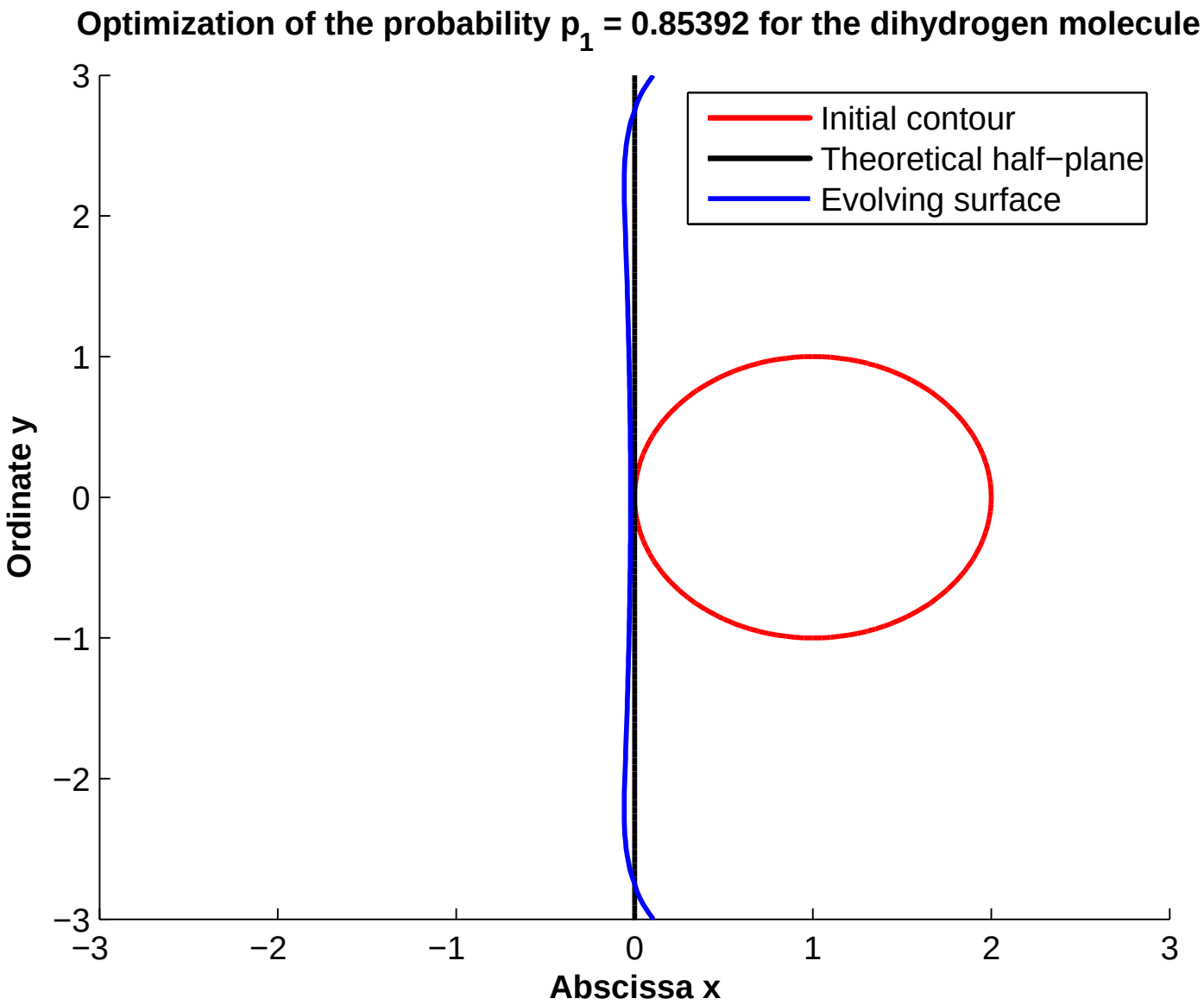

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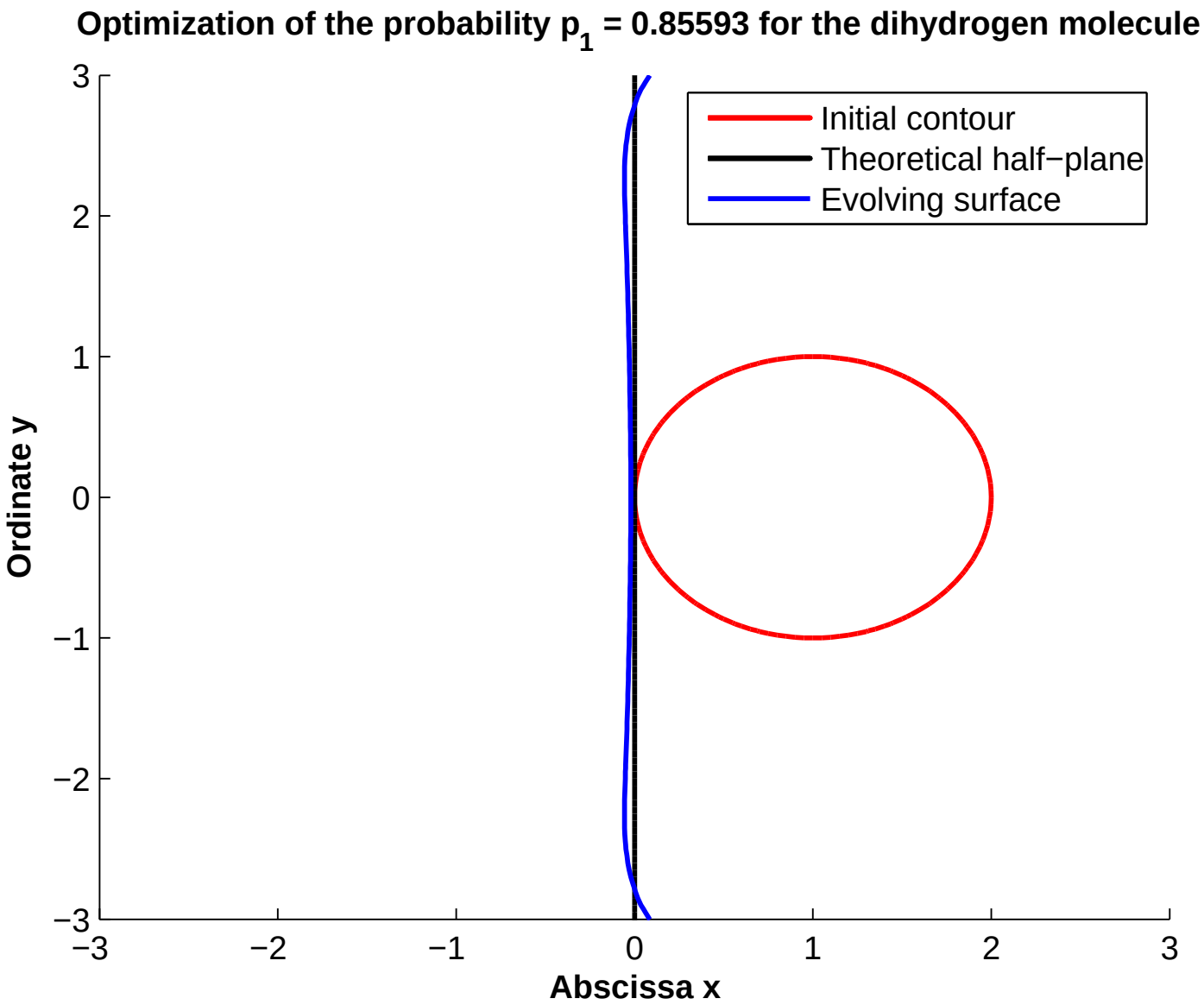

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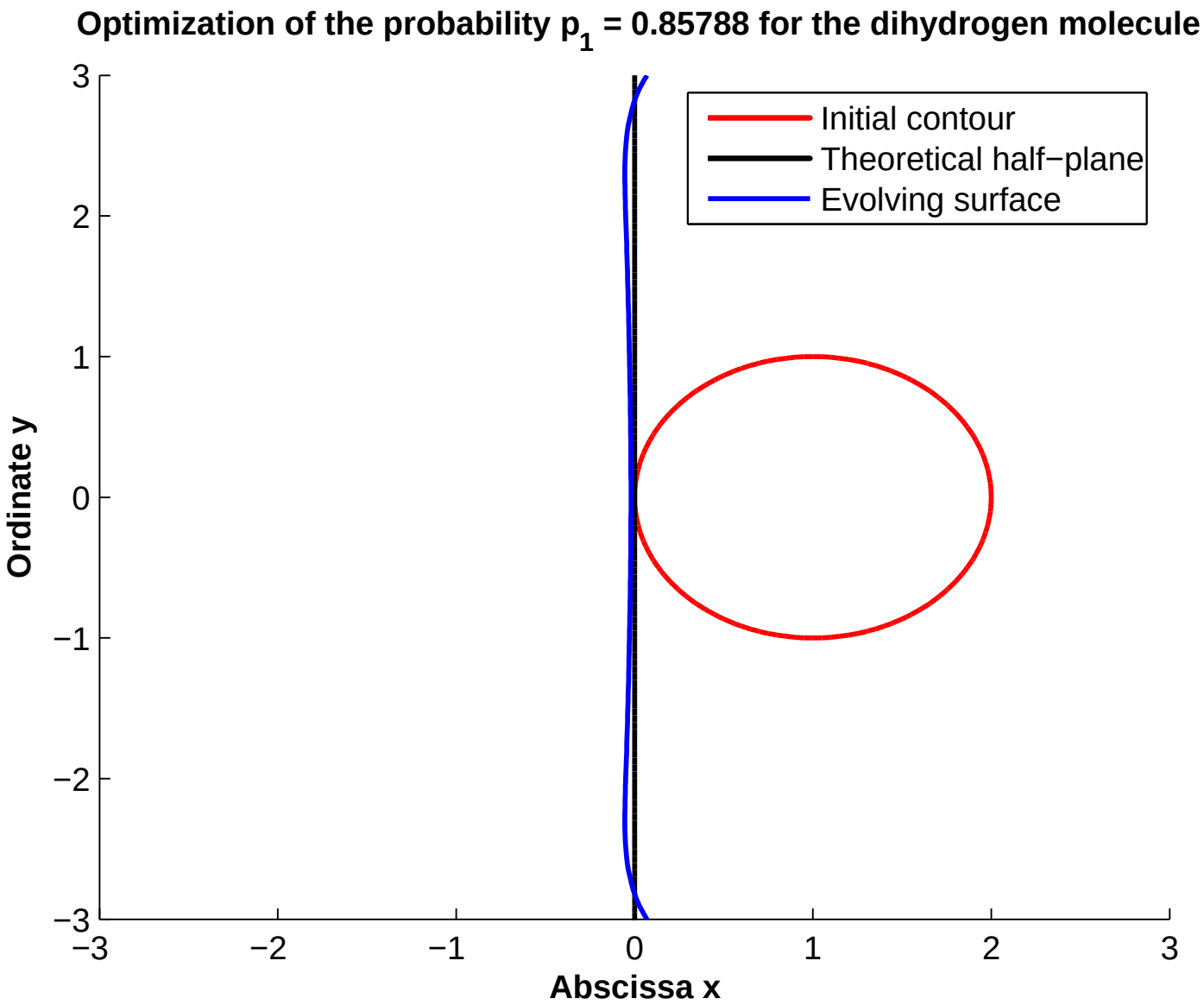

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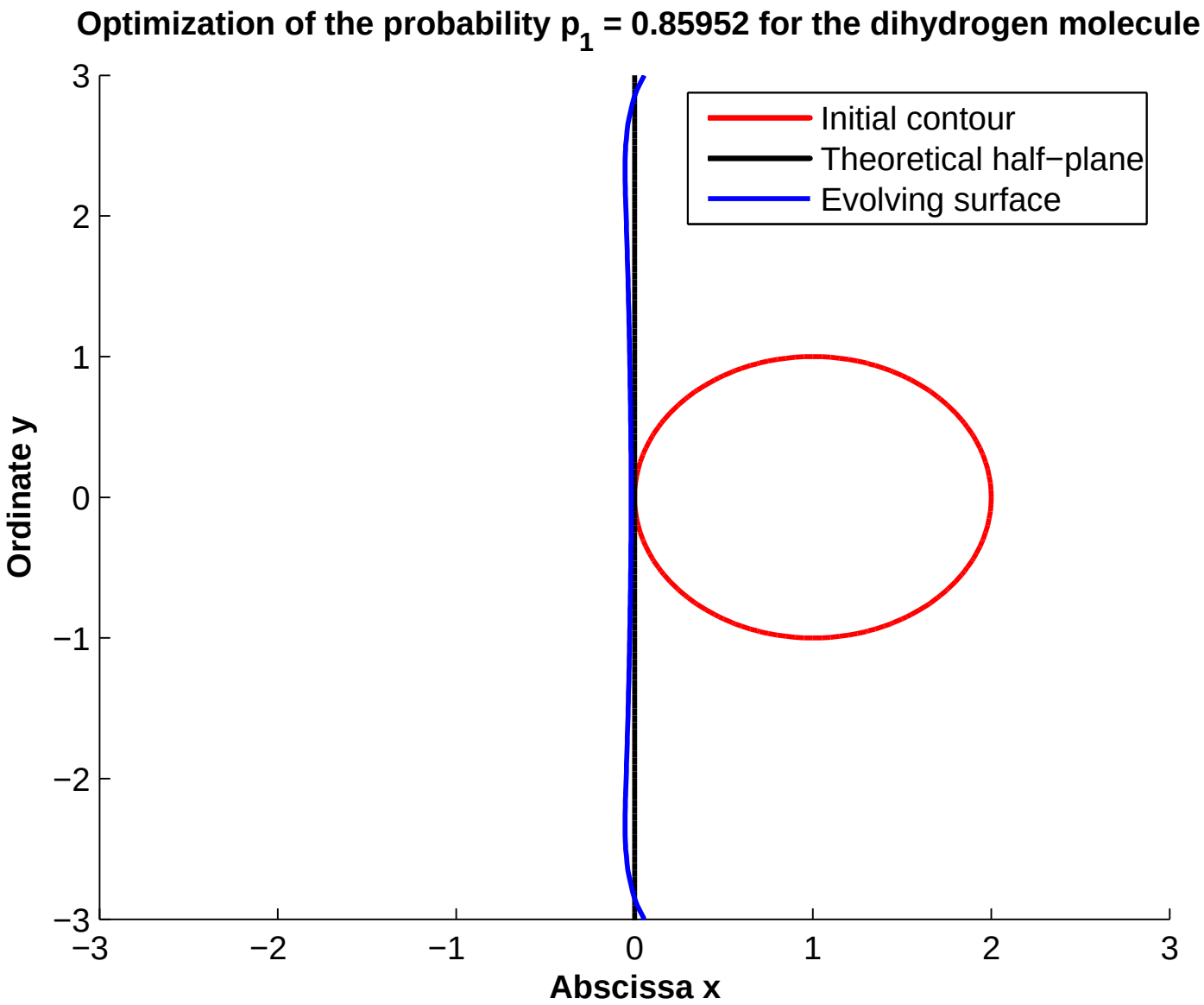

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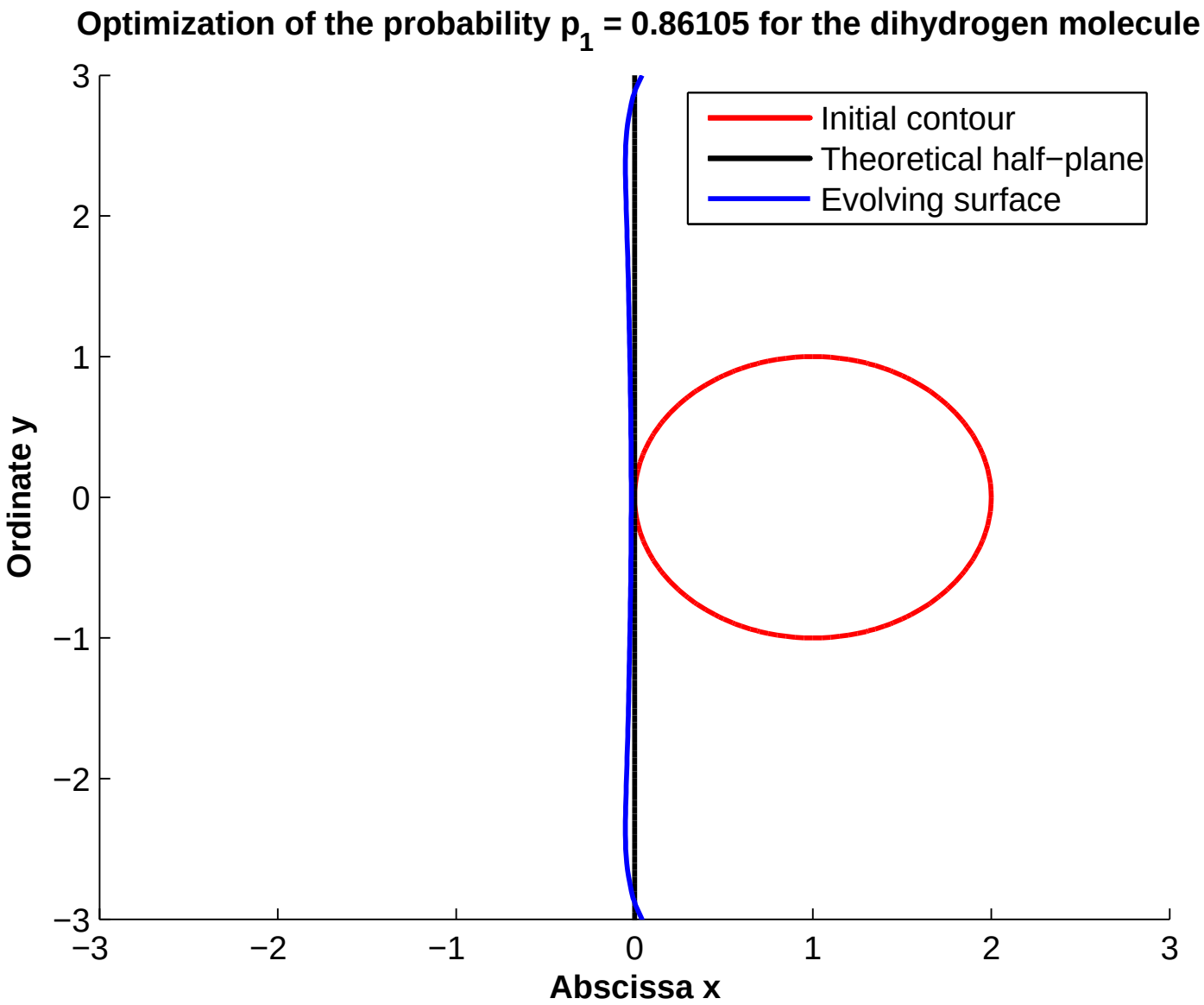

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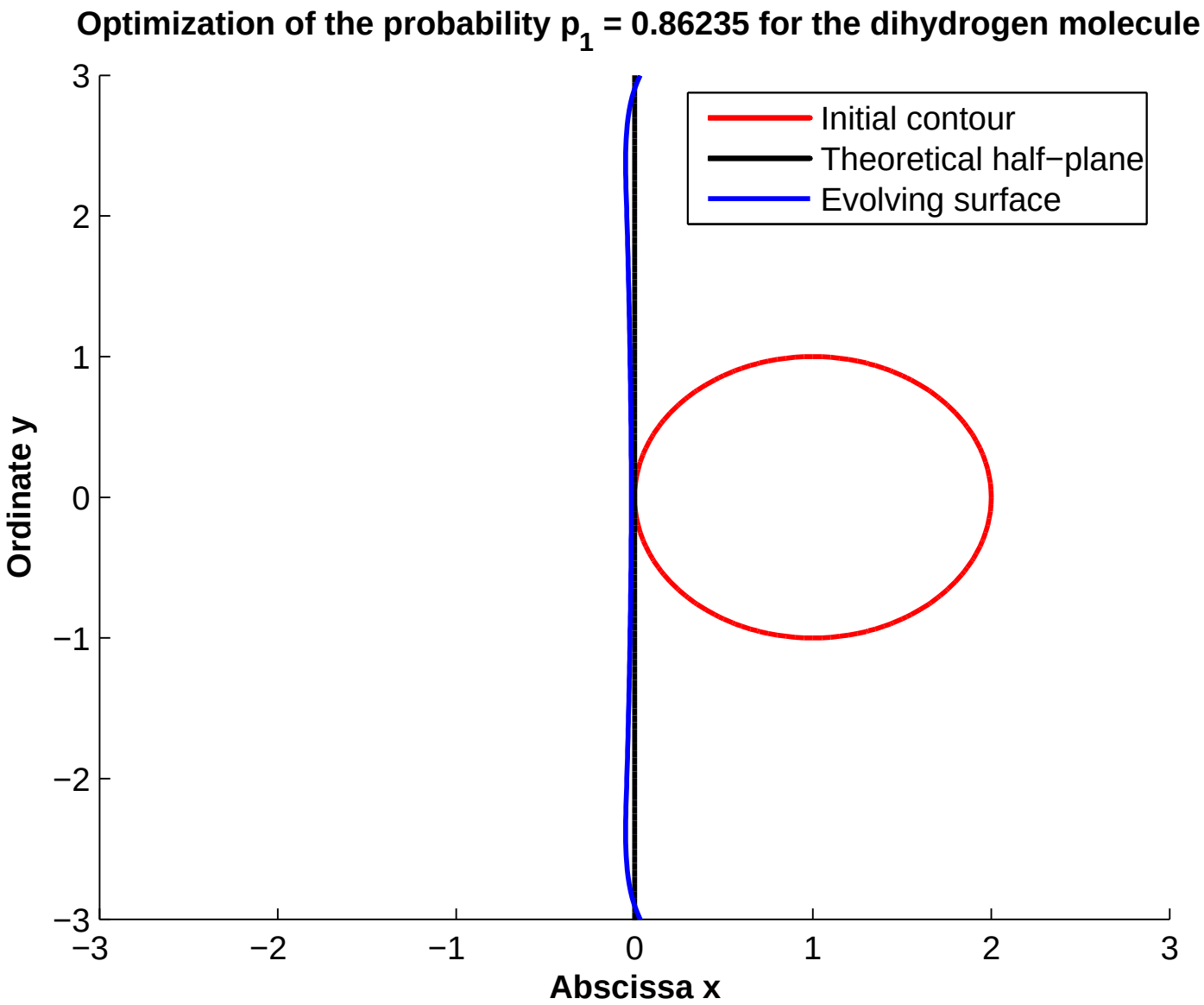

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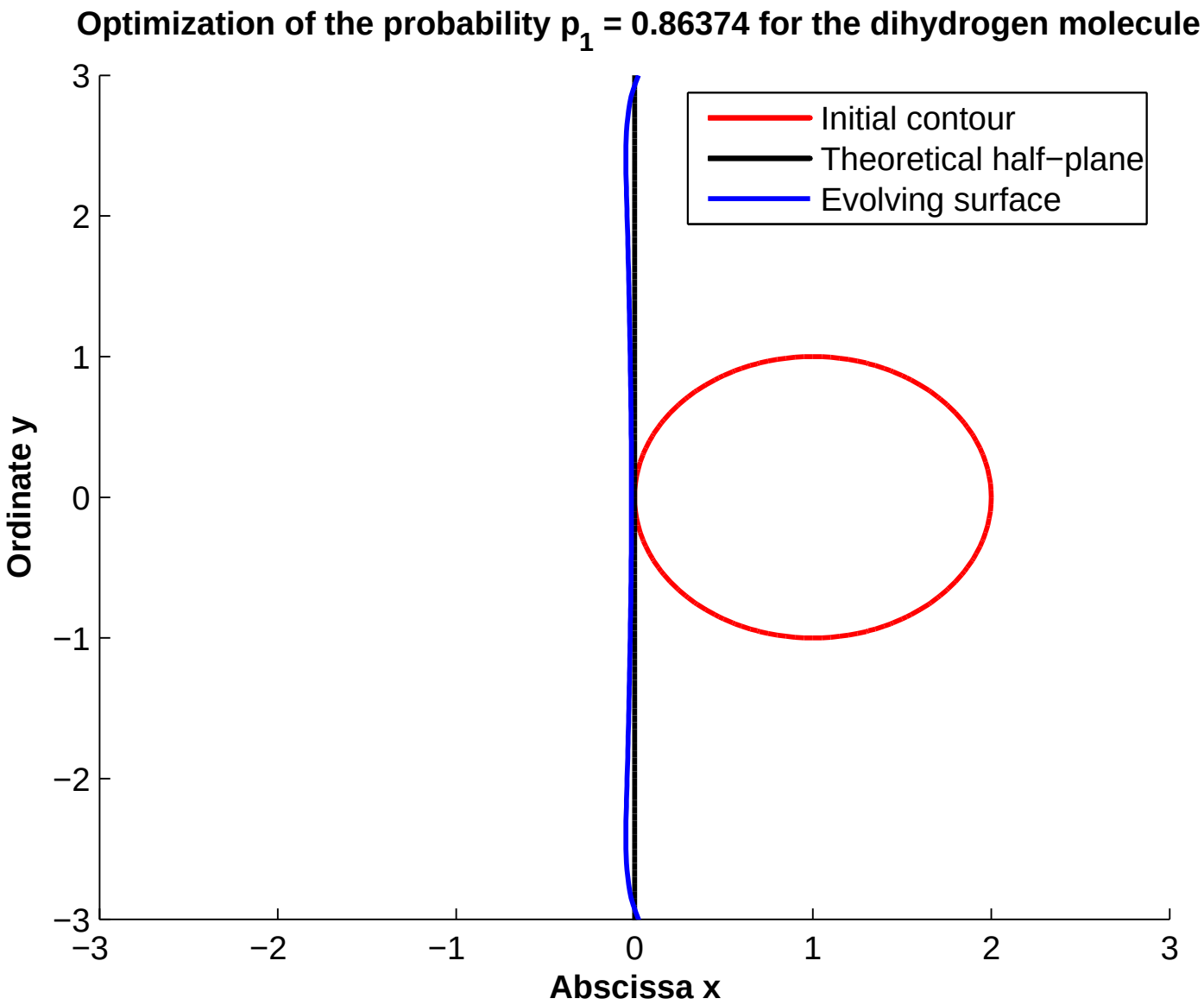

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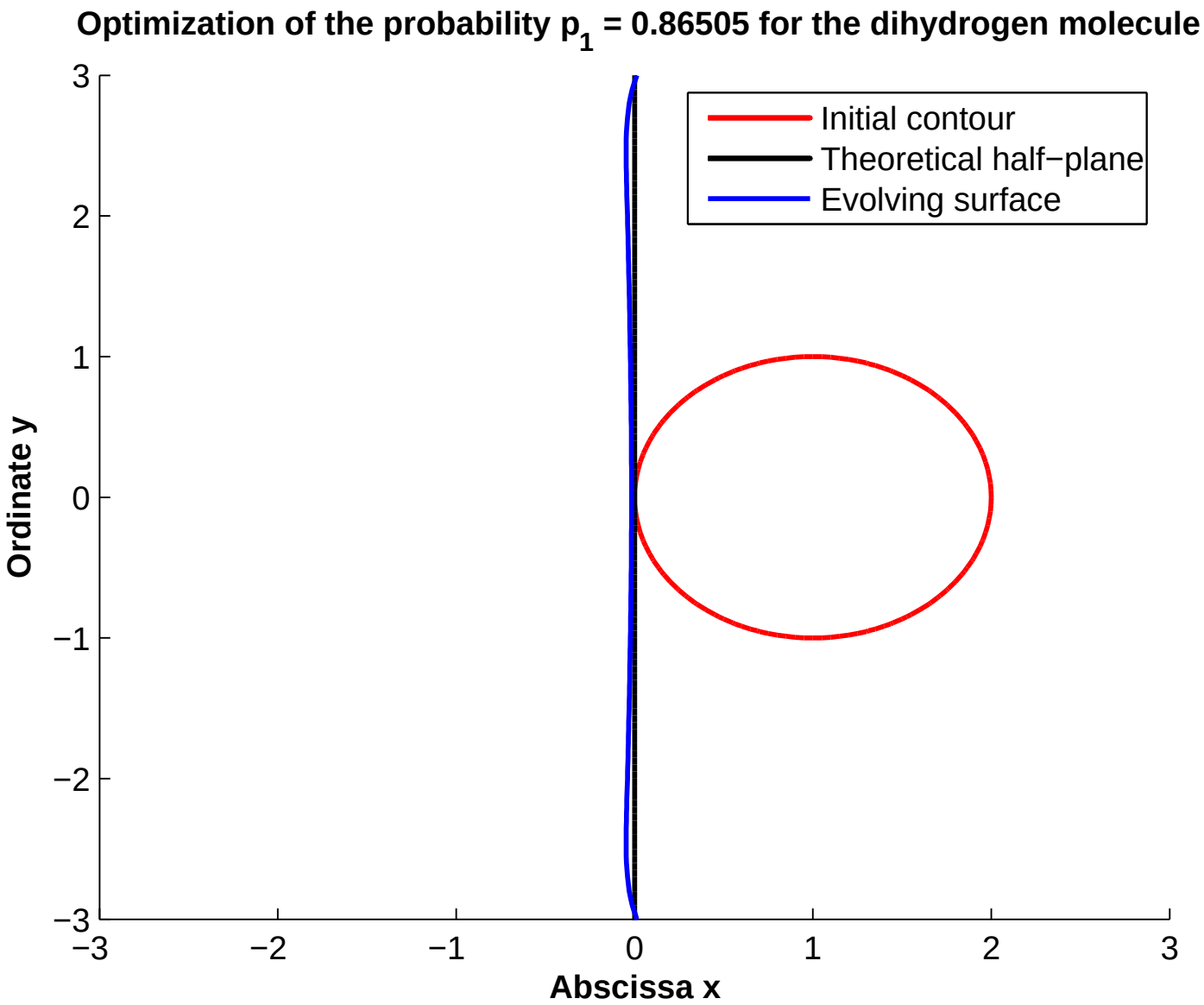

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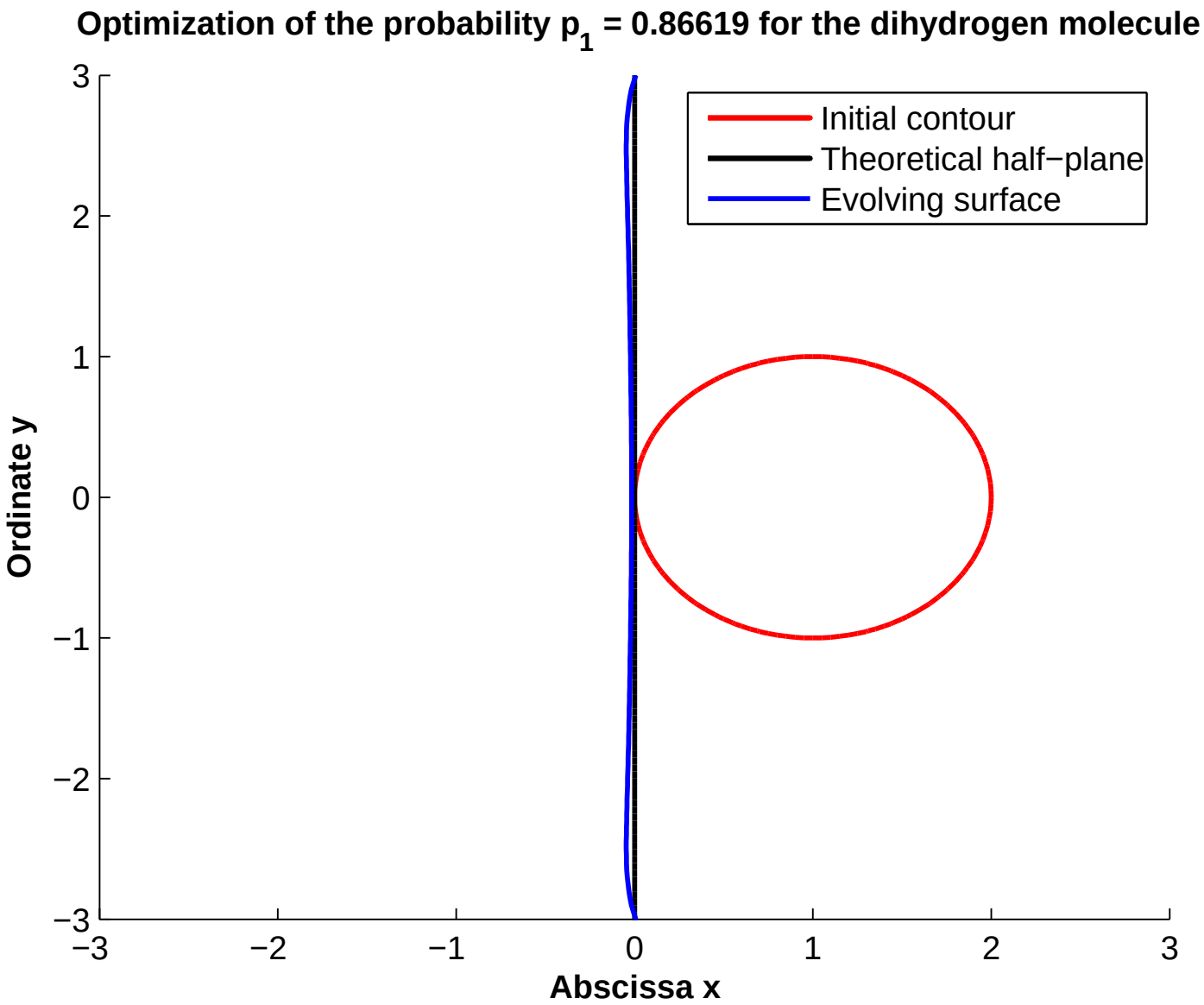

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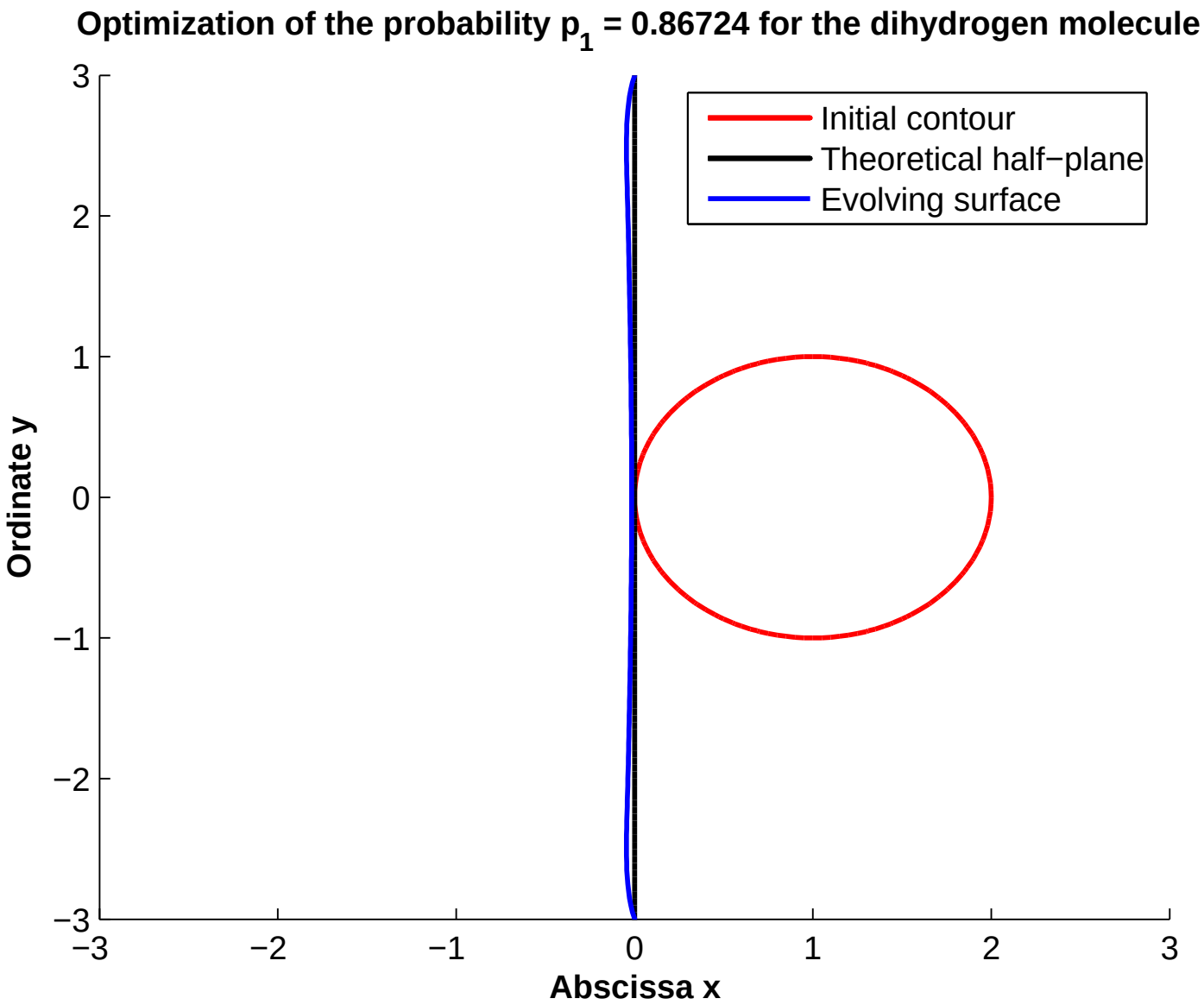

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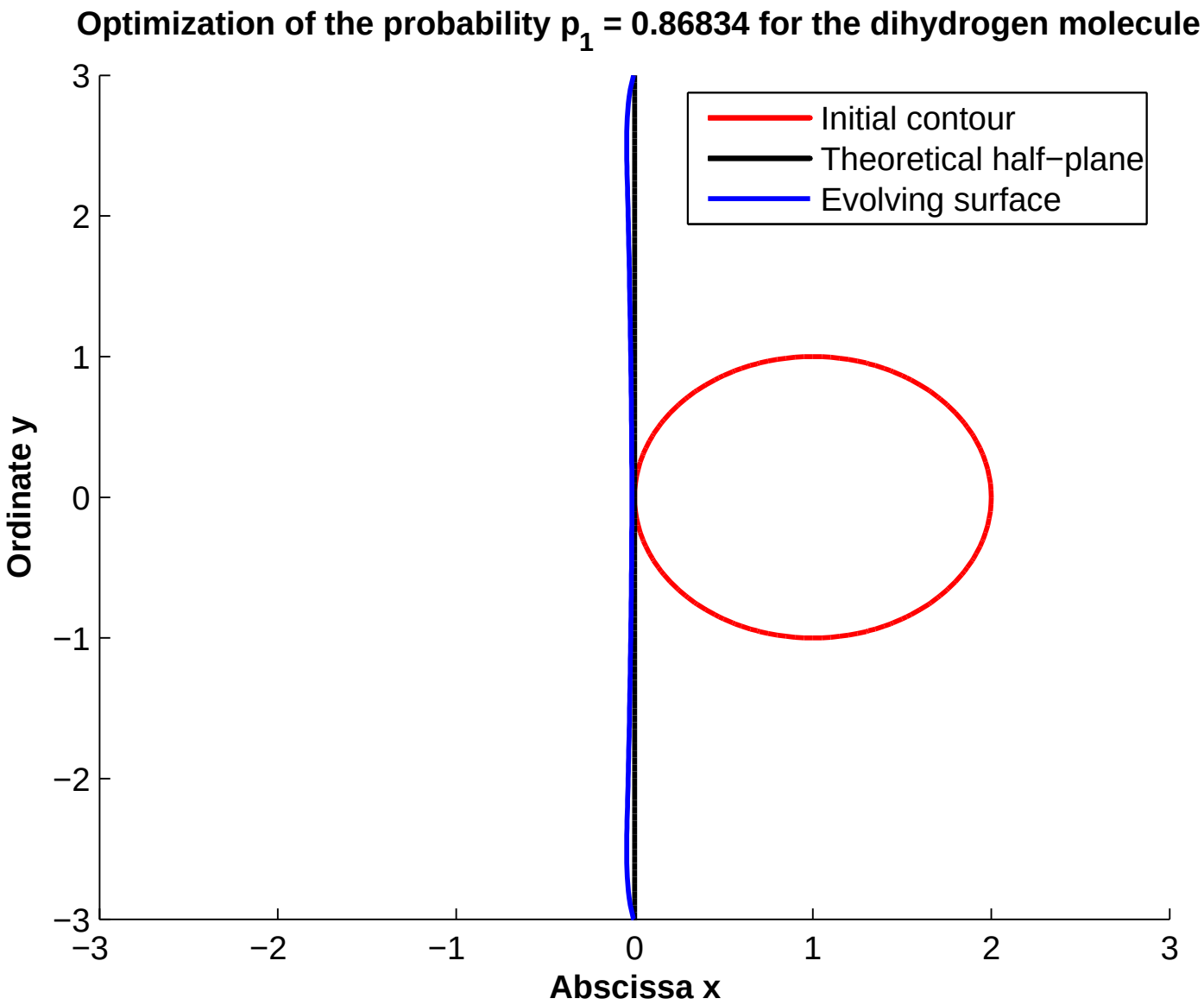

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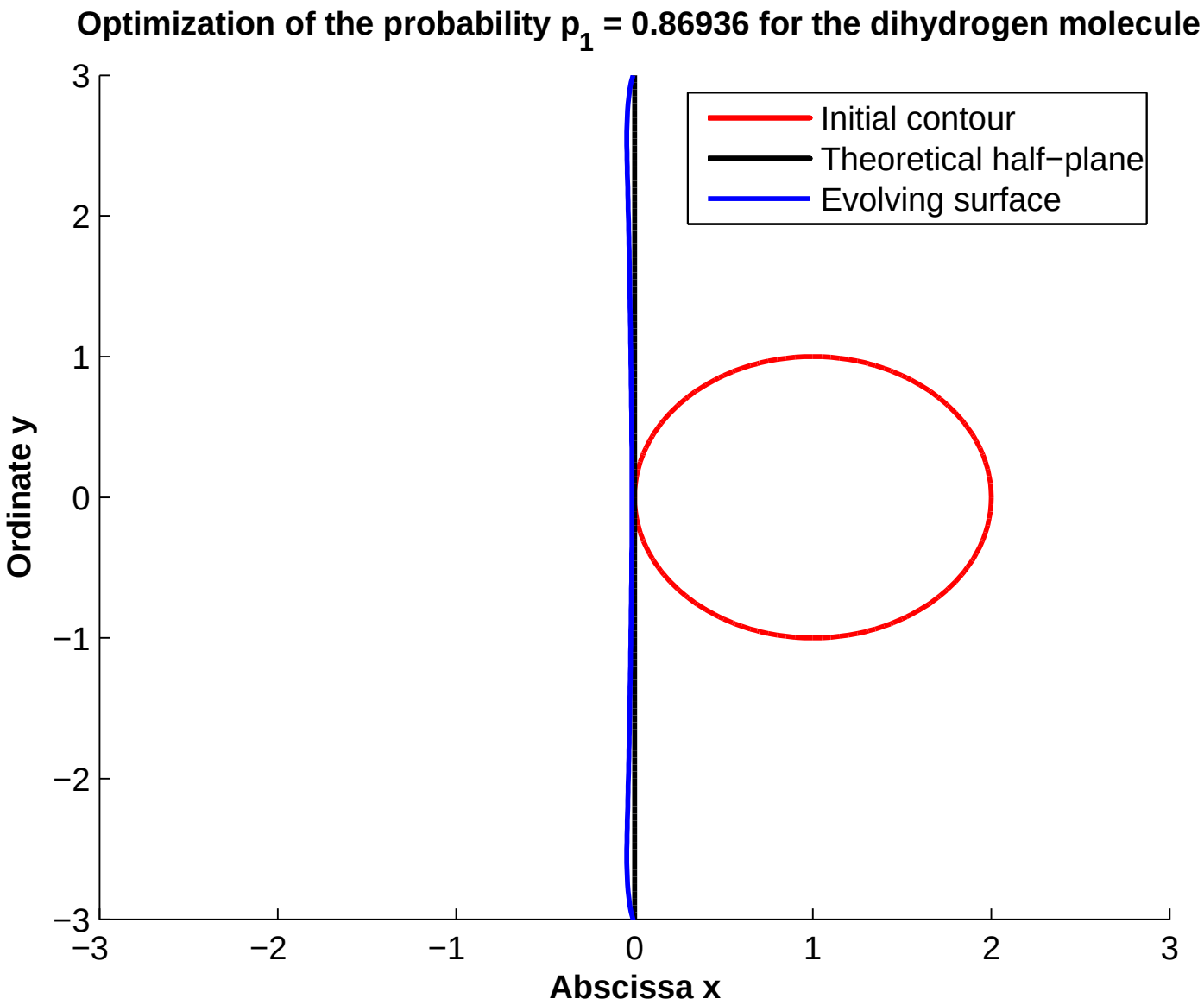

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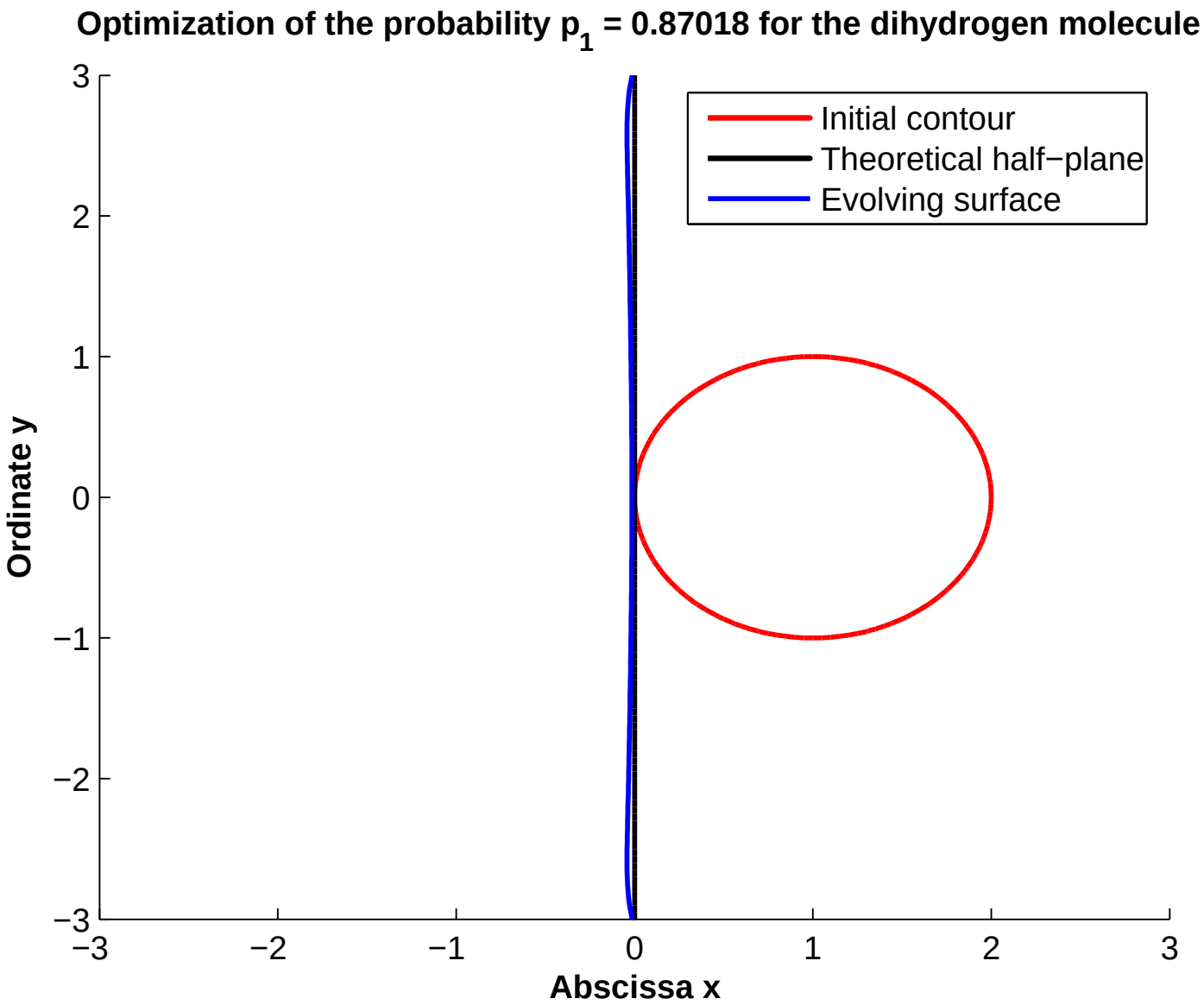

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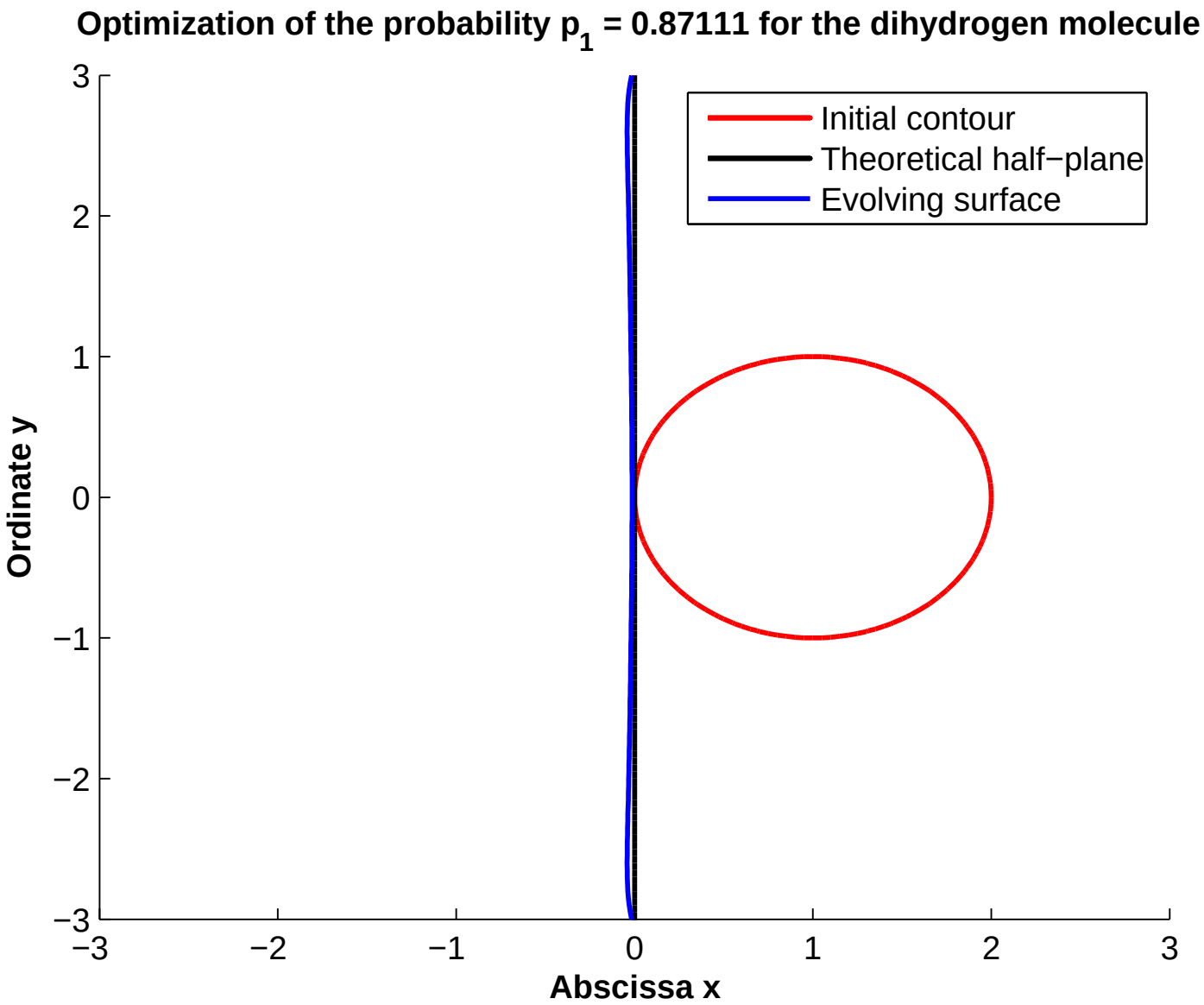

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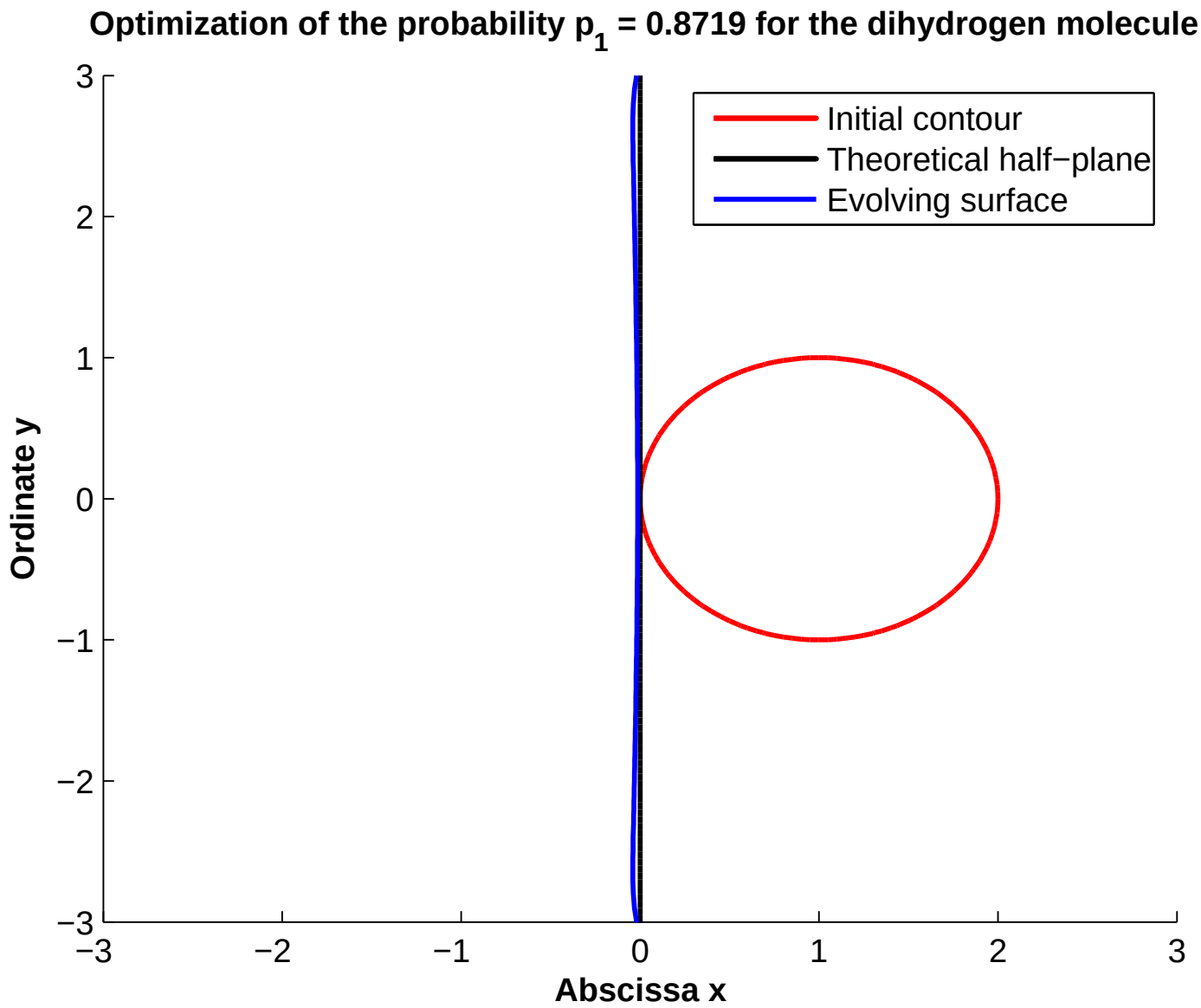

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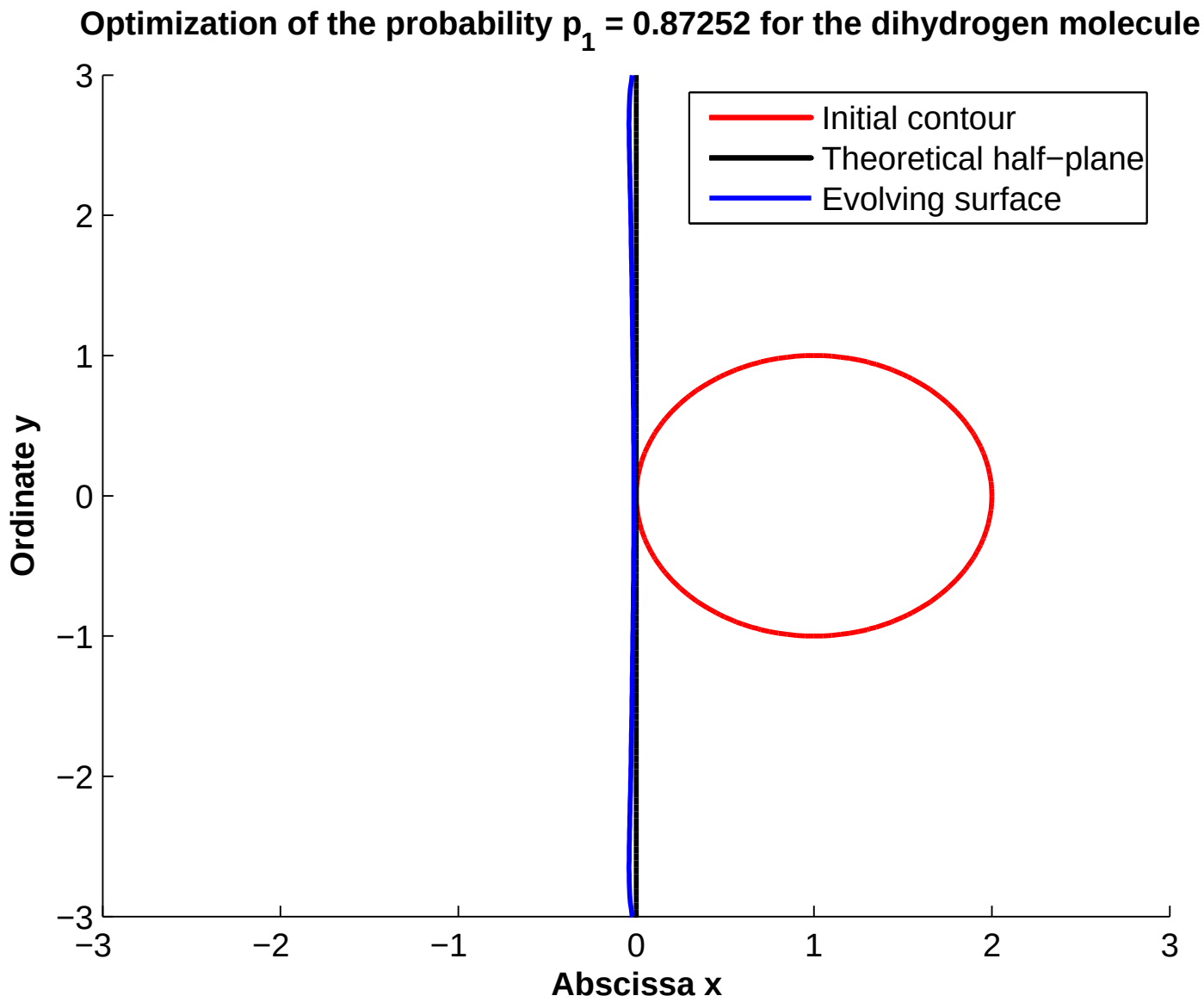

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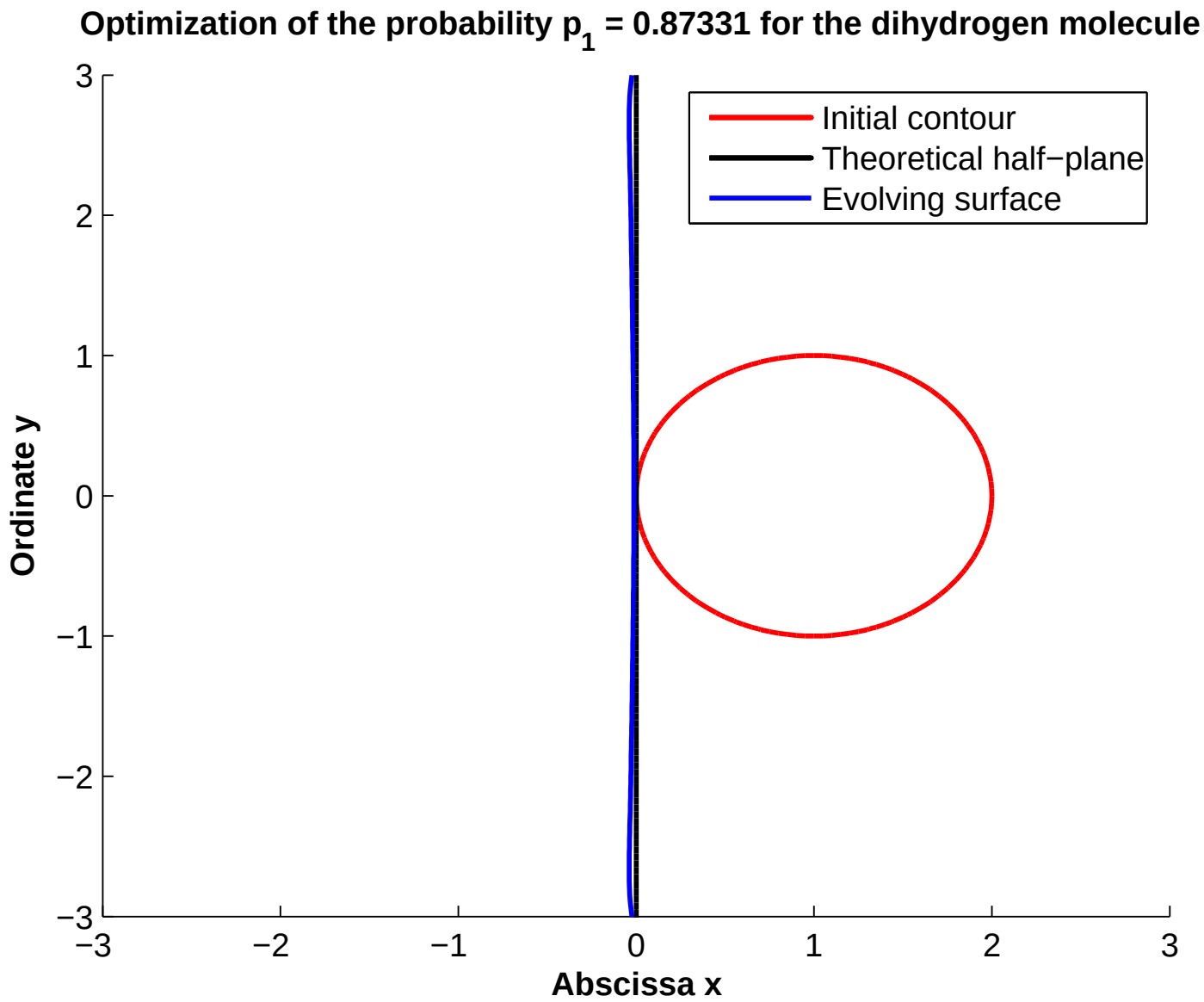

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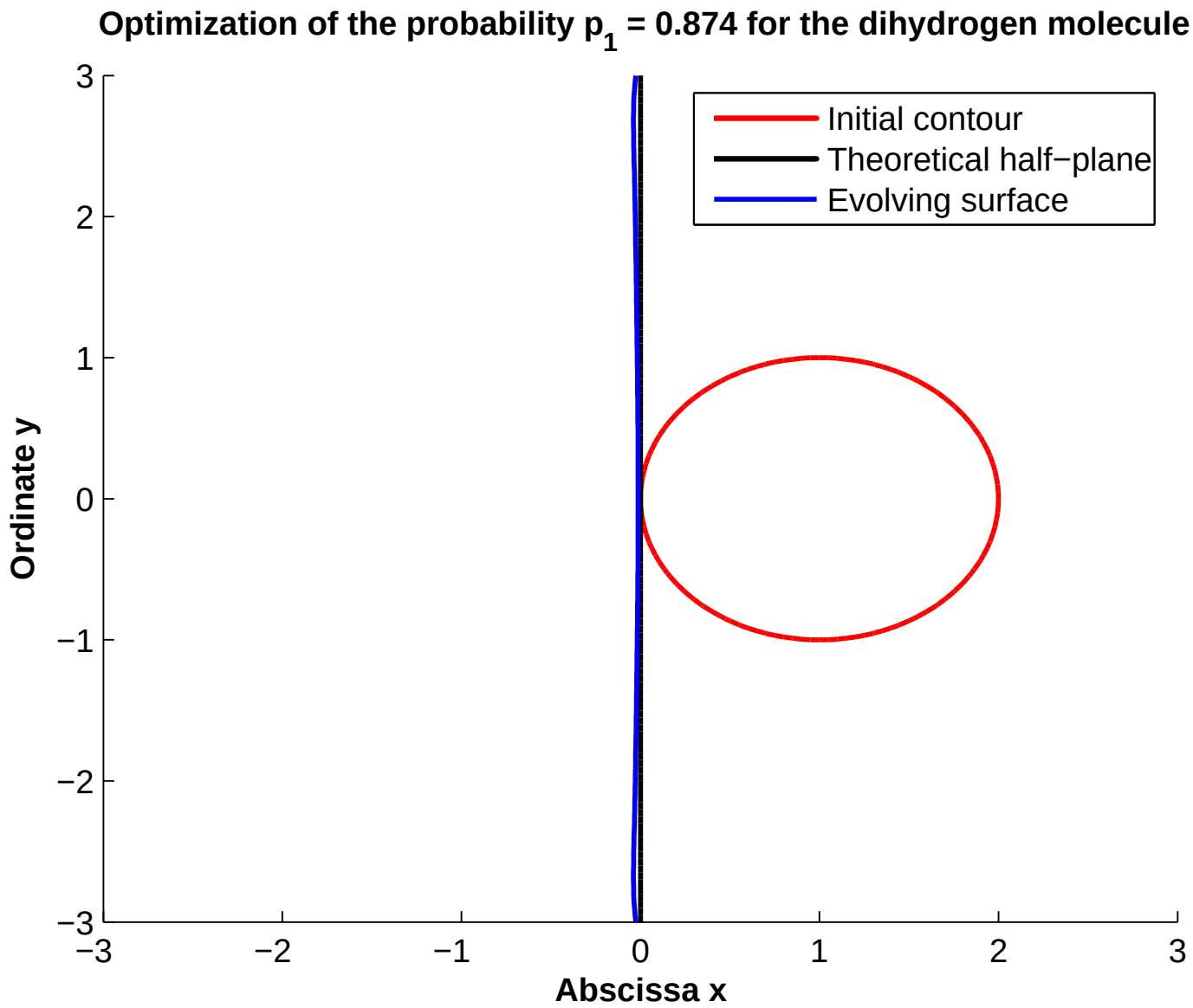

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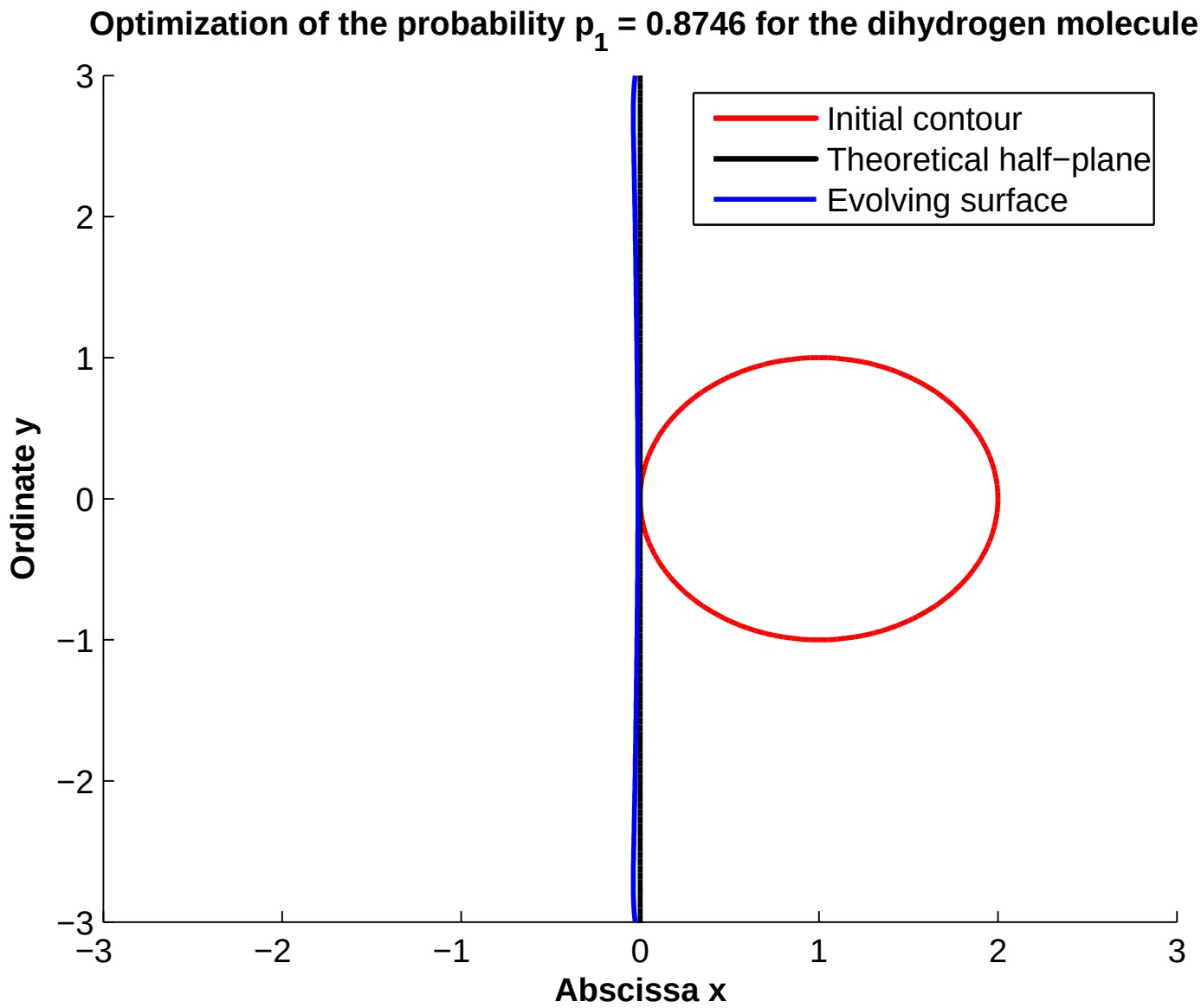

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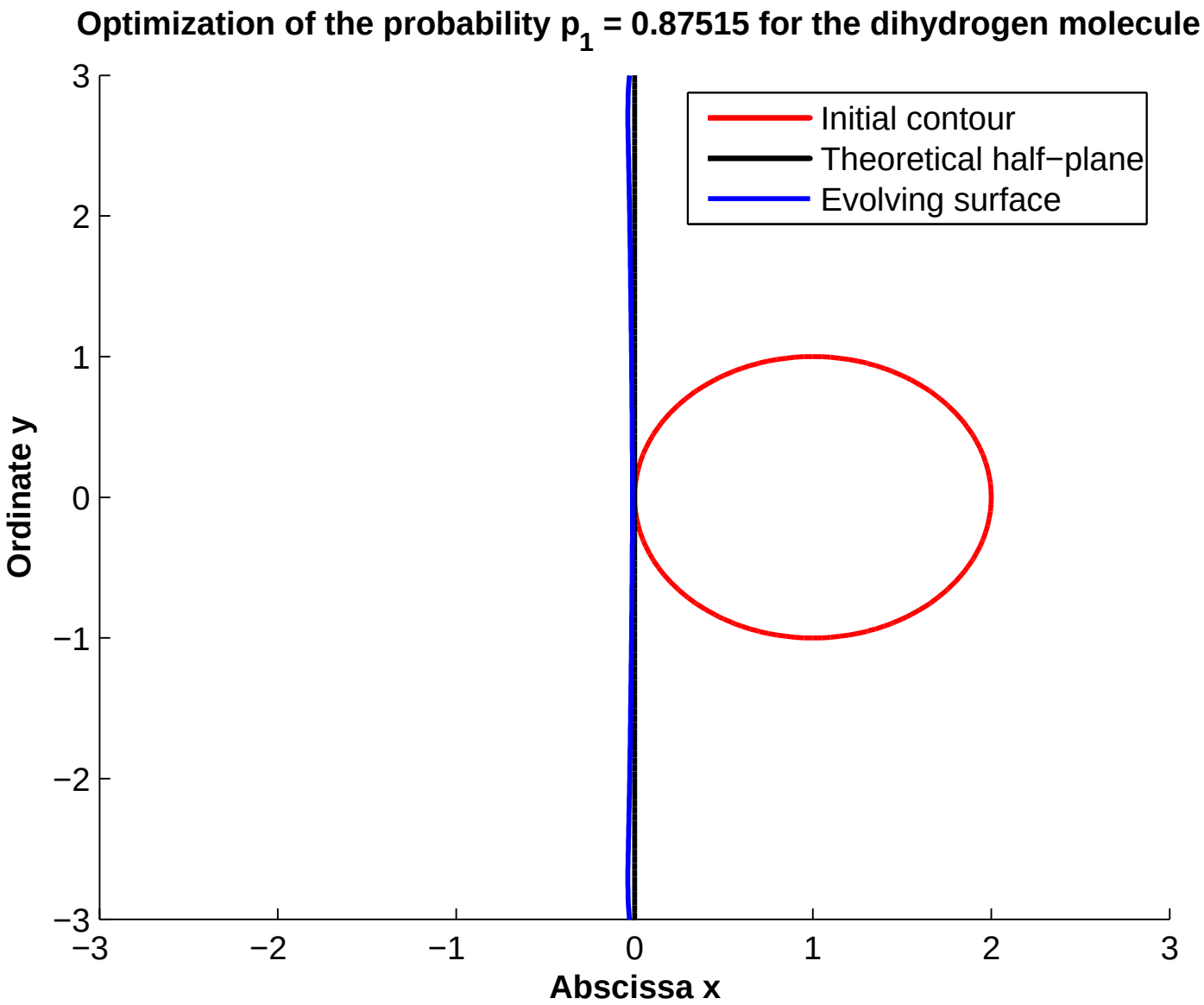

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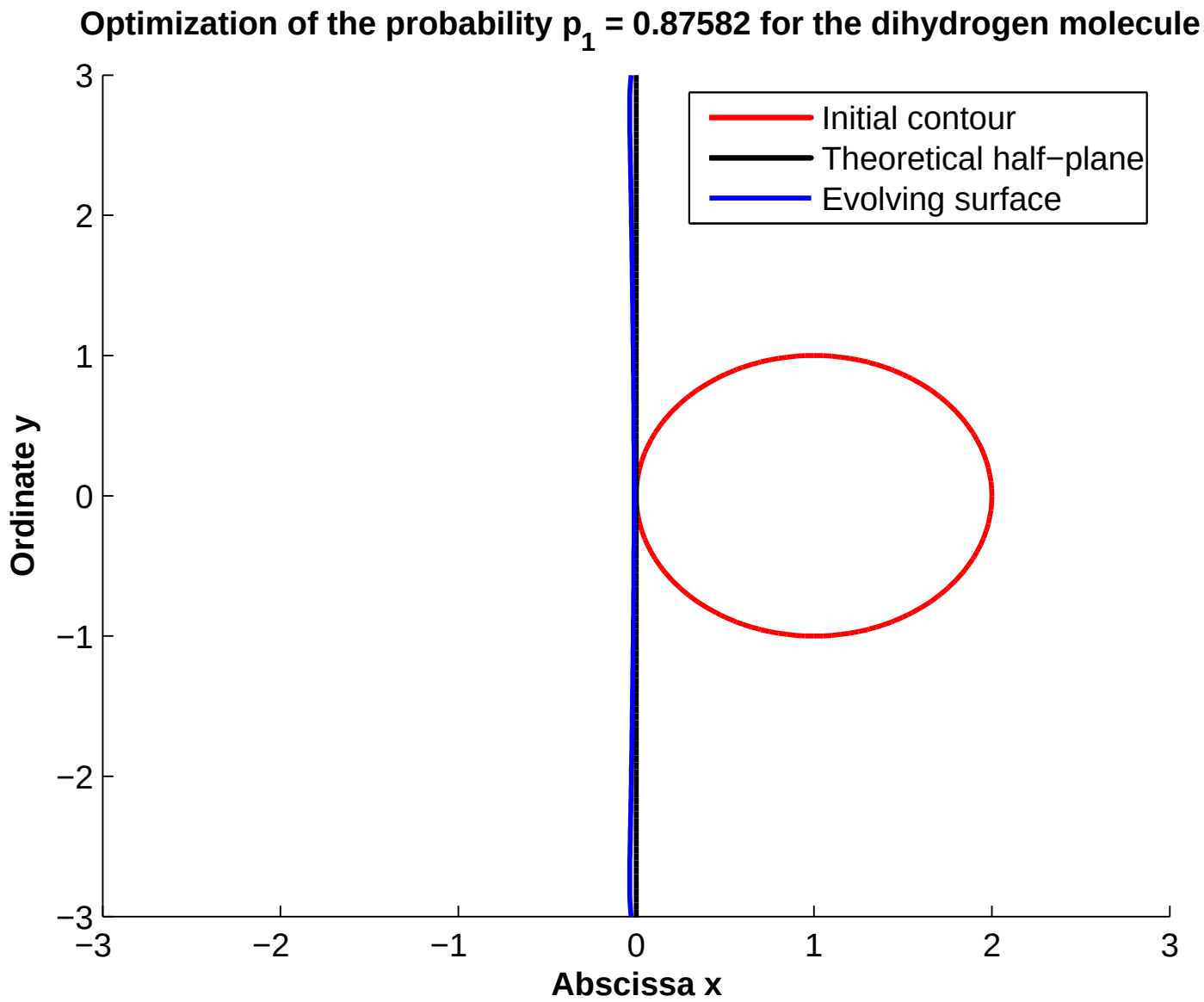

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