# A Hamiltonian Pitchfork in the Self-Consistent Field method

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**Abstract**

In this paper we study a bifurcation in the equilibria of the Self-Consistent Field (SCF) iteration as described using Josephson dynamics. Josephson dynamics characterizes the bonding and anti-bonding states between atoms by describing the bonding as overlap between electron orbitals, and we vary a parameter corresponding to the bond strength to show a Hamiltonian pitchfork bifurcation in the dynamics.

## 1 Introduction

This project examines an approximation of the dynamics for a system of two hydrogen atoms (equivalently, two electrons), by determining the configuration of the spatial orbitals and the electrons that occupy them through a fixed-point problem called a Self-Consistent Field (SCF) iteration. The approximation is constructed by taking the determinant of a matrix with columns indexed by the electron orbital wave-functions and rows indexed by the distance from the center of mass. The value of this determinant is called the Hartree-Fock wave function:

$$\psi^{\mathrm{HF}}(r_1,\ldots,r_N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(r_1) & \psi_2(r_1) & \cdots & \psi_N(r_1)\\ \psi_1(r_2) & \psi_2(r_2) & \cdots & \psi_N(r_2)\\ \vdots & \vdots & \ddots & \vdots\\ \psi_1(r_N) & \psi_2(r_N) & \cdots & \psi_N(r_N)\end{vmatrix}$$

and

$$\langle\psi_i|\psi_j\rangle=\delta_{ij}\quad 1\le i,j\le N$$

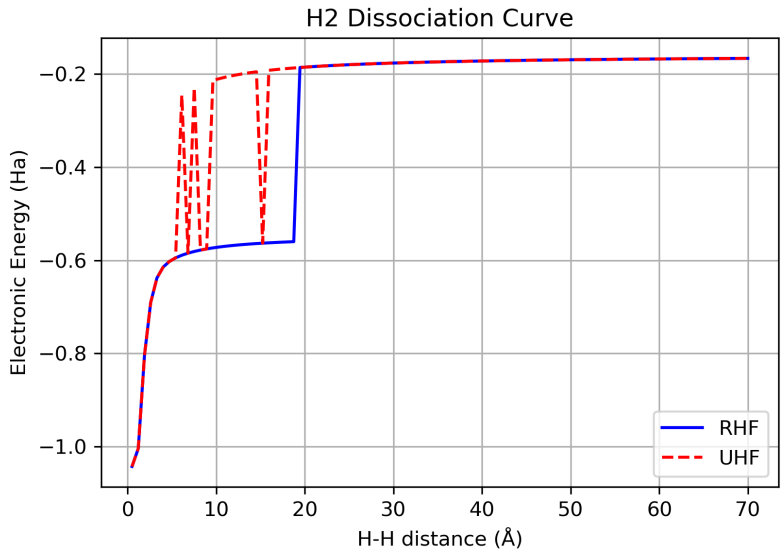
The iteration is performed until the HF determinant remains within a small epsilon distance from the previous iteration. As the iteration progresses, the inputs of the determinant can be modeled using a 2-D system of ordinary differential equations. By tuning the parameters of this system, we observe a Hamiltonian pitchfork bifurcation, where a central equilibrium splits into two centers connected by a saddle with trajectories leading to each center.

(Echenique and Alonso (2007))

## 1.1 Research Goal(s)/Aim(s)/Question(s)

There are two equilibria in this system. In one, the electrons are paired in the same orbital, while in the other, the electrons occupy separate orbitals. A simple way to examine these equilibria is by tuning a parameter corresponding to the bond length between the atoms. Because the dynamics are Hamiltonian, they are divergence-free. In this paper, we show how this divergence-free property shapes the bifurcation of the equilibria as the atomic separation is varied.

The two equilibria corresponding to if the electrons are paired (blue) or separated (red), can be seen in the following graph generated using pySCF:




As the radius between the atoms increase (the horizontal axis), the electrons are less likely to pair, leading to the two separate solutions.

## 1.2 Approach/Methods

The dynamics of the determinant approximation along the SCF iteration can be modeled by the following system:

$$\dot{z} = -2T\sqrt{1-z^2}\sin\theta = f(z,\theta)$$
$$\dot{\theta} = 2T\frac{z}{\sqrt{1-z^2}}\cos\theta + Uz = g(z,\theta).$$

$z$ measures the occupancy of an orbital and $\theta$ measures how the spatial orbitals overlap, which determines how the electrons move between them (i.e. constructive/destructive interference). Our parameters are the "tunneling energy" $T$, whose value determines when an electron moves between orbitals, and $U$, which is the repulsion between two electrons in the same orbital.

This system of equations has the Hamiltonian function

$$H(z,\theta) = \frac{U}{2}z^2 - 2T\sqrt{1-z^2}\cos\theta$$

that computes level sets of the determinant on the domain of inputs $(z,\theta)$.

Then it is easy to see our equilibria of the system are given by

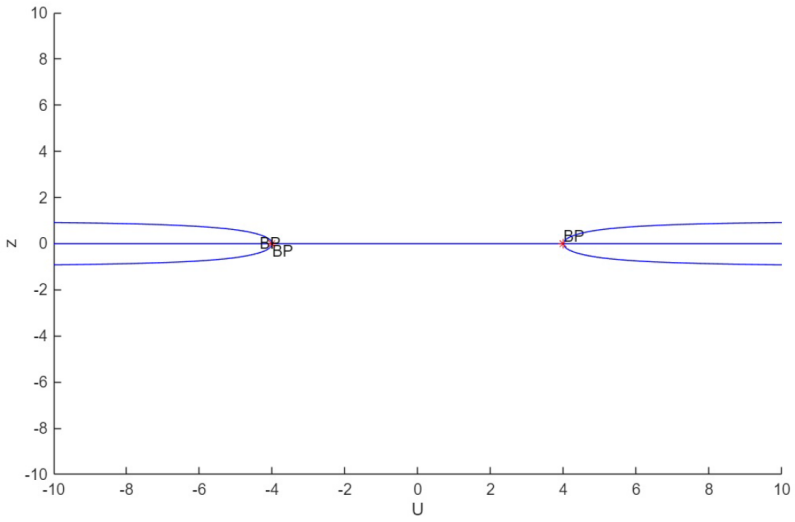
$$f(z,\theta) = 0 \implies \theta = \{0,\pi\}$$
$$g(z,\theta) = 0 \implies z = 0, \quad \text{and} \quad z = \pm\sqrt{1-\frac{4T^2}{U^2}\cos^2\theta}$$

To see our bifurcation, we will vary the parameter electron repulsion, $U$. This is equivalent to varying the radius between atoms, causing the electrons to decouple and exist in different orbitals. This reflects our two different solutions.

(Vianello et al. (2025))

# 2 Results

Using MATCONT, we set $T = 2$ and examine trajectories as $U$ is varied. Since the dynamics of $z$ coordinate are constant at our equilibria values $\theta = \{0,\pi\}$, we examine trajectories in the $(U,z)$ plane. This reveals the pitchfork bifurcation structures at $U = \pm 4$.




# 3 Discussion

Lets focus on the pitchfork corresponding to $U = 4$ by considering only $U > 0$. Using the Routh-Horwitz Criteria, we can determine the stability of our Hamiltonian system using only the determinant of the Jacobian, since the trace (or equivalently, the divergence), will always be zero.
At $(0, 0)$, our system Jacobian evaluates to

$$J|_{(0,0)} = \begin{bmatrix} 0 & 4 \\ U-4 & 0 \end{bmatrix}$$

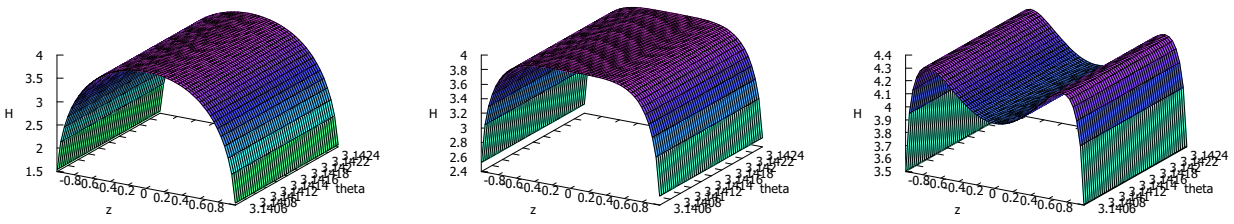
and, $det(J_{(0,0)}) = -4(U-4)$. So if $U < 4$, $\det J|_{(0,0)} > 0$ and $(0, 0)$ must be a center.
If $U > 0$, $\det J|_{(0,0)} < 0$ and the equilibrium must be a saddle. Trajectories around the saddle move toward the upper or lower arcs, which we will now show are centers.

At $(0, \pm\sqrt{1 - \frac{4T^2}{U^2}})$, the Jacobian for $U = 5$ (and $T = 2$) becomes

$$J|_{(0,\pm)} = \begin{bmatrix} 0 & \frac{16}{5} \\ -\frac{45}{16} & 0 \end{bmatrix}.$$

So $\det(J_{(0,\pm)} > 0$, and must have purely imaginary eigenvalues. So our equilibria $(0, \pm\sqrt{1 - \frac{4T^2}{U^2}})$ are centers.

We can highlight the existence of this bifurcation into two different systems of the same total energy in these graphs representing the total Hamiltonian total energy at $U = 3$, $U = 4$, and $U = 5$, respectively:




(a) $U = 3$ (b) $U = 4$ (c) $U = 5$

Figure 1: Trajectories of the SCF determinant approximation for different values of $U$.

# References

Echenique, P., and J. L. Alonso. 2007. A mathematical and computational review of hartree--fock scf methods in quantum chemistry. Molecular Physics 105:3057--3098. Review of Hartree--Fock theory, SCF algorithms, mathematical foundations and computational implementations.

Vianello, C., S. Salvatore, and L. Salasnich. 2025. Quantum action of the josephson dynamics. International Journal of Theoretical Physics 64:315. Derives mean-field Josephson dynamics for phase and population imbalance; includes canonical ODEs for two-mode model.