# RELATIONSHIP BETWEEN CHEMISTRY AND PHYSICS FROM BOHMIAN MECHANICS

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# ORGANIZATION OF THE TALK

- Some difficulties in foundations of quantum chemistry:

  These difficulties arise from the absence of trajectories in orthodox quantum mechanics.

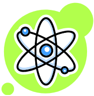
- The Quantum Theory of Motion (Bohmian quantum mechanics).

- Examples: The fact that there are trajectories in QTM can help us to solve the foundational difficulties in quantum chemistry.

- Conclusions.

# QUANTUM MECHANICS

A physical system has an associated wavefunction $\psi(x)$.



$$\longrightarrow \psi(x)$$

The wavefunction carries all the information about the system. There is no definite position and no definite momentum, only probabilities.

$$P\left(x \in (a,b)\right) = \int_a^b \psi(x)\psi^*(x)dx$$

Probability of finding the particle in the interval $(a,b)$.

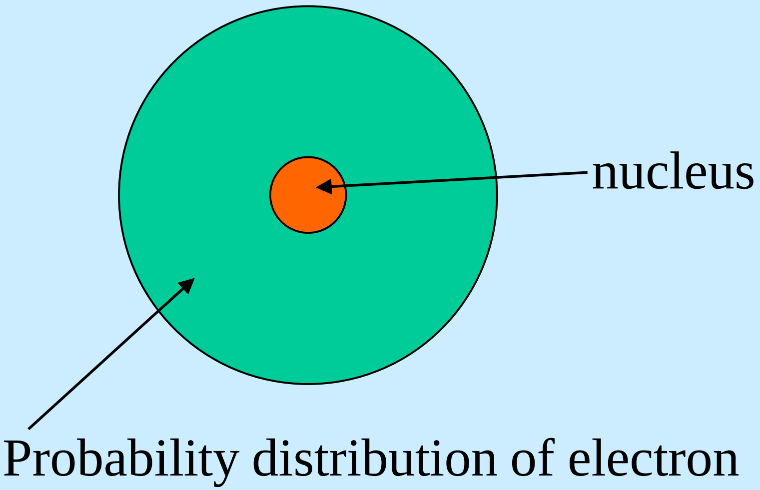
According to the Kochen-Specker theorem, one cannot simultaneously assign position and momentum to a particle.

# ORBITAL "s"

The state "s" of the electron in a hydrogen atom is:

$$\psi = f(r)e^{i\frac{\alpha - Et}{\hbar}}$$

Where is the electron? Nowhere, it is not anywhere.



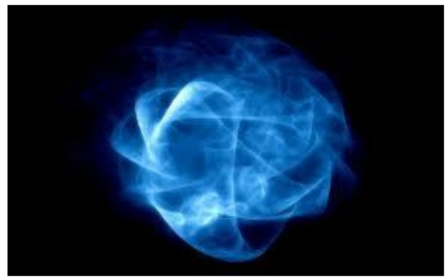

The orbital is a region with high probability of finding the electron.

# STRUCTURE AND BORN-OPPENHEIMER

The quantum Hamiltonian of a molecule is

$$\hat{H} = \sum_{g}^{A} \frac{\hat{\bar{p}}_g^{\,2}}{2m_g} + e^2 \sum_{g<h}^{A} Z_g Z_h \hat{\bar{r}}_{gh}^{\,-1} + \sum_{i}^{N} \left( \frac{\hat{\bar{p}}_i^{\,2}}{2m_i} - e \sum_{g}^{A} Z_g \hat{\bar{r}}_{ig}^{\,-1} \right) + e^2 \sum_{i<j}^{N} \hat{\bar{r}}_{ij}^{\,-1}$$

There are no nuclei positions



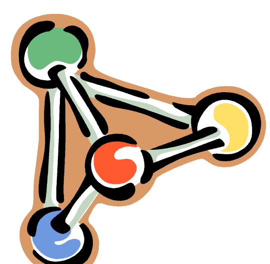
There is no structure

The Born-Oppenheimer Hamiltonian of a molecule is

Now they are numbers

$$\hat{H} = \sum_{g}^{A} \frac{\bar{p}_g^{\,2}}{2m_g} + e^2 \sum_{g<h}^{A} Z_g Z_h \bar{r}_{gh}^{\,-1} + \sum_{i}^{N} \left( \frac{\hat{\bar{p}}_i^{\,2}}{2m_i} - e \sum_{g}^{A} Z_g \hat{\bar{r}}_{ig}^{\,-1} \right) + \cancel{e^2 \sum_{i<j}^{N} \hat{\bar{r}}_{ij}^{\,-1}}$$

$$\hat{H} = \sum_{i}^{N} \left( \frac{\hat{\bar{p}}_i^{\,2}}{2m_i} - e \sum_{g}^{A} Z_g \hat{\bar{r}}_{ig}^{\,-1} \right) \longrightarrow$$



There are nuclear positions

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# STRUCTURE AND BORN-OPPENHEIMER

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There are no nuclei

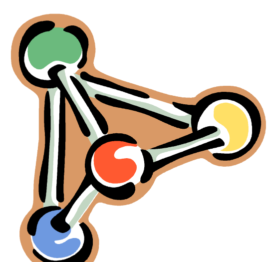
There is no

1. Structure appears after this approximation. Before it, structure does not even make sense.

2. The approximation contradicts the theory postulates.

$$\hat{H} = \sum_{g}^{A} \frac{\hat{\bar{p}}_g^{2}}{2m_g} + e^2 \sum_{g<h}^{A} Z_g Z_h \bar{r}_{gh}^{-1} + \sum_{i}^{N} \left( \frac{\hat{\bar{p}}_i^{2}}{2m_i} - e \sum_{g}^{A} Z_g \hat{\bar{r}}_{ig}^{-1} \right) + \cancel{e^2 \sum_{i<j}^{N} \hat{\bar{r}}_{ij}^{-1}}$$

$$\hat{H} = \sum_{i}^{N} \left( \frac{\hat{\bar{p}}_i^{2}}{2m_i} - e \sum_{g}^{A} Z_g \hat{\bar{r}}_{ig}^{-1} \right) \longrightarrow$$

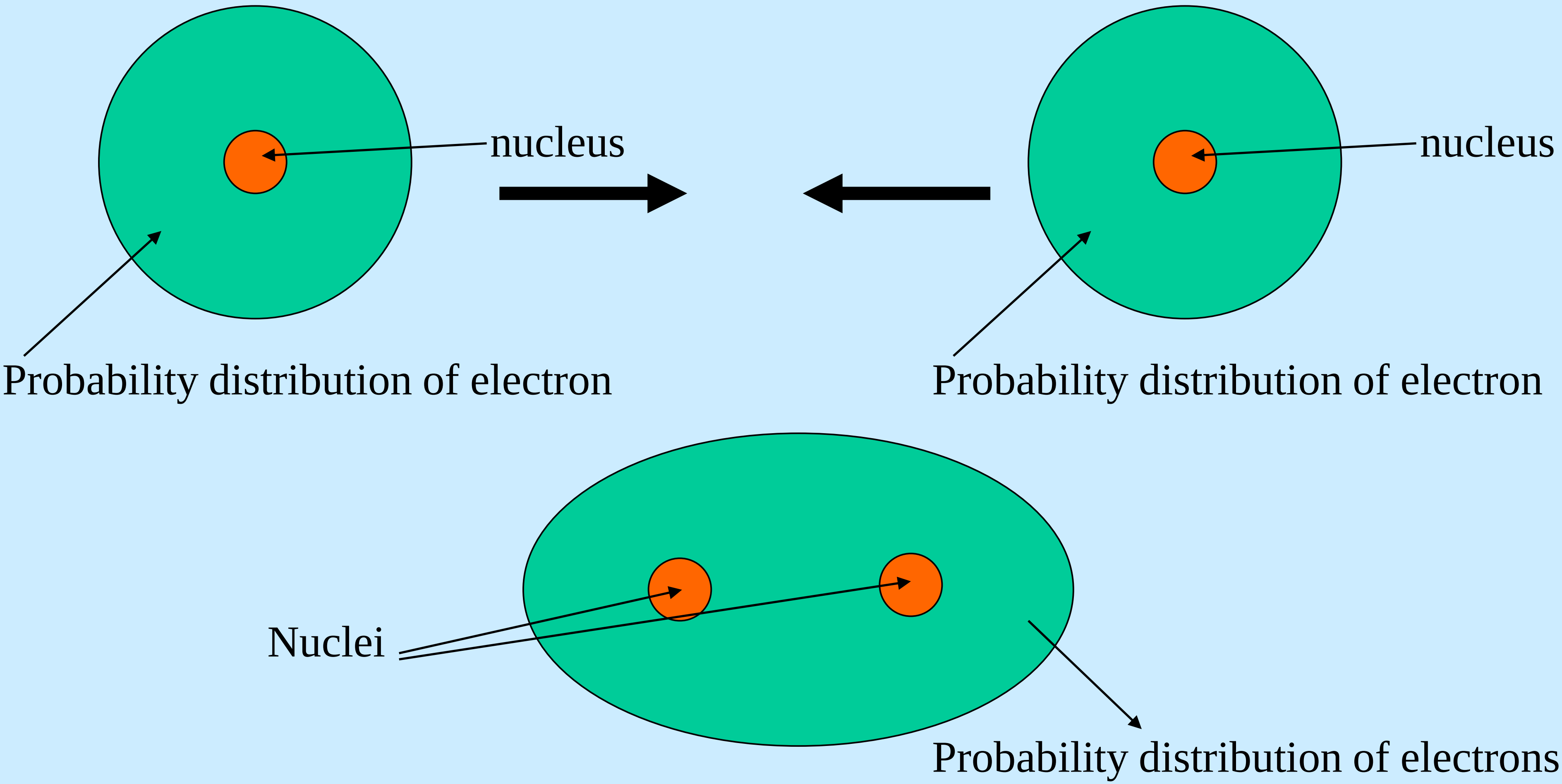


There are nuclear positions

There is structure

# COVALENT BOND

Consider two hydrogen atoms initially far apart, and gradually bring them closer together.




There is a molecular orbital, but the notion of chemical bond is fuzzy.

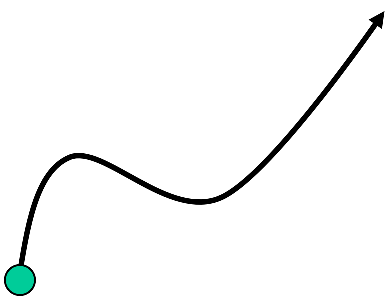
# CLASSICAL MECHANICS

There are many equivalent formulations for classical mechanics.

### Newton

$$\bar{F}_1 + \bar{F}_2 + \ldots = m\ddot{\bar{x}}$$

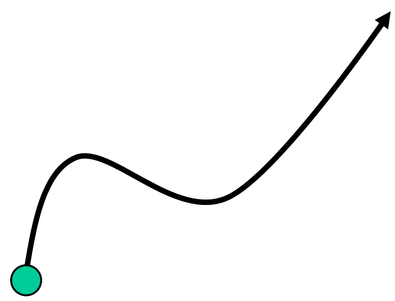
$$\bar{x}(t) = \ldots$$



### Hamilton

$$H = \frac{\bar{p}^2}{2m} + V(x)$$

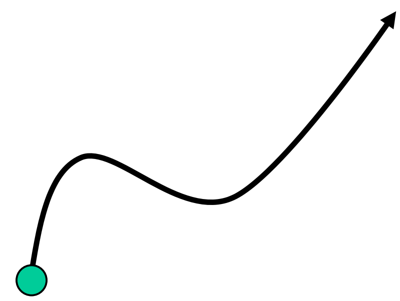
$$\bar{x}(t) = \ldots$$



### Hamilton-Jacobi

$$\frac{\partial S}{\partial t} + \frac{1}{2m}\left(\bar{\nabla} S\right)^2 + V(\bar{x}) = 0$$

$$\bar{x}(t) = \ldots$$



$$\bar{p} = \bar{\nabla} S$$

With the initial conditions, we can compute the trajectory.

# THE SCHRÖDINGER EQUATION

The Schrödinger equation determines the wave function

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

The wave function is complex, so it can be written:

$$\psi = \sqrt{P} \cdot e^{i\frac{S}{\hbar}}$$

Then, substituting in the equation we have obtained equations:

$$\frac{\partial P}{\partial t} + \overline{\nabla} \cdot \left( P \frac{\overline{\nabla} S}{m} \right) = 0 \rightarrow$$ continuity equation (probability is conserved)

$$\frac{\partial S}{\partial t} + \frac{\left(\overline{\nabla} S\right)^2}{2m} + V(\overline{x}) - \frac{\hbar^2}{4m}\left( \frac{\overline{\nabla}^2 P}{P} - \frac{1}{2}\frac{\left(\overline{\nabla} P\right)^2}{P^2} \right) = 0 \rightarrow \quad ?$$

# BOHM'S EQUATION

Let us see the second equation

$$\frac{\partial S}{\partial t}+\frac{\left(\bar{\nabla}S\right)^2}{2m}+V(\bar{x})-\boxed{\frac{\hbar^2}{4m}\left(\frac{\bar{\nabla}^2 P}{P}-\frac{1}{2}\frac{\left(\bar{\nabla}P\right)^2}{P^2}\right)}=0$$

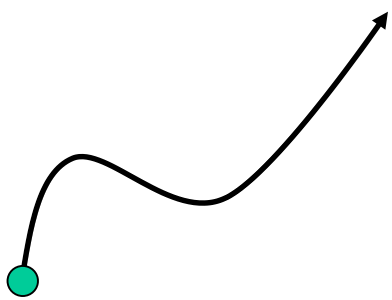
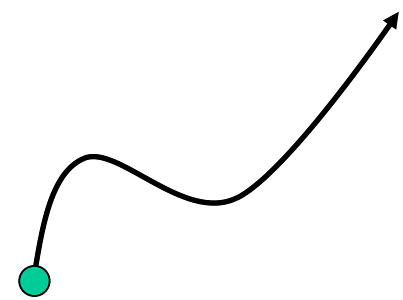
*Quantum Potential*

$$\frac{\partial S}{\partial t}+\frac{\left(\bar{\nabla}S\right)^2}{2m}+V(\bar{x})+\mathrm{U}_q(\bar{x})=0$$

$$\frac{\partial S}{\partial t}+\frac{\left(\bar{\nabla}S\right)^2}{2m}+\tilde{V}(\bar{x})=0$$

# BOHM'S MECHANICS

In analogy with the formulation of Hamilton-Jacobi...

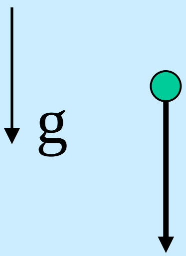
| **Bohm** | **Hamilton-Jacobi** |
|---|---|
| $\frac{\partial S}{\partial t}+\frac{\left(\bar{\nabla} S\right)^2}{2m}+\tilde{V}(\bar{x})=0$ | $\frac{\partial S}{\partial t}+\frac{1}{2m}\left(\bar{\nabla} S\right)^2+V(\bar{x})=0$ |
| $\bar{x}(t)=\ldots$ | $\bar{x}(t)=\ldots$ |
|  |  |
| $\bar{p}=\bar{\nabla} S$ | $\bar{p}=\bar{\nabla} S$ |

With the initial conditions, we can compute the trajectory.

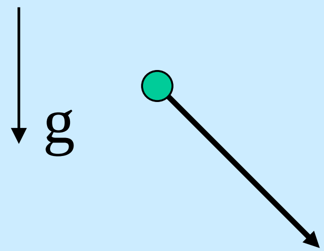
# WHAT IS THE TRICK?

## Free particle

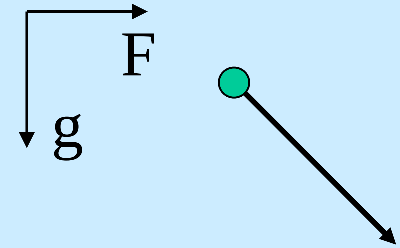
I expect




I see

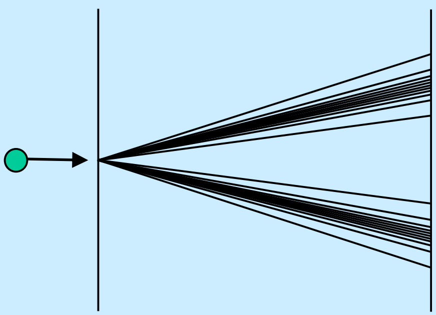



I say: the particle is not free, there is another force

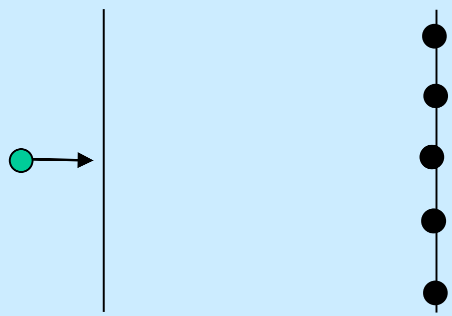



## Double slit

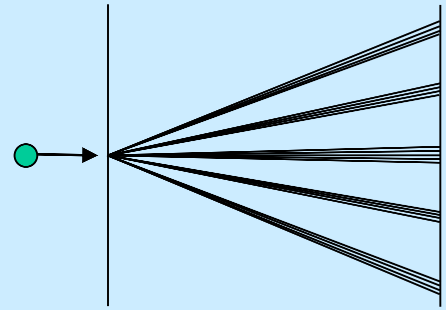
I expect



I see

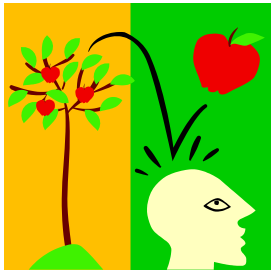


I say: there is another force



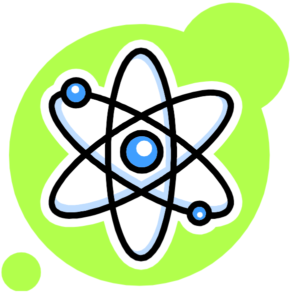
# QUANTUM FORCE

There are diferent forces in nature



Gravity

Electromagnetism



Strong force

…

We can postulate the existence of a new force:

The ***Quantum Force***

$$F_q(\overline{x}) = \frac{\hbar^2}{2m}\overline{\nabla}\left(\frac{\overline{\nabla}^2 R}{R}\right)$$

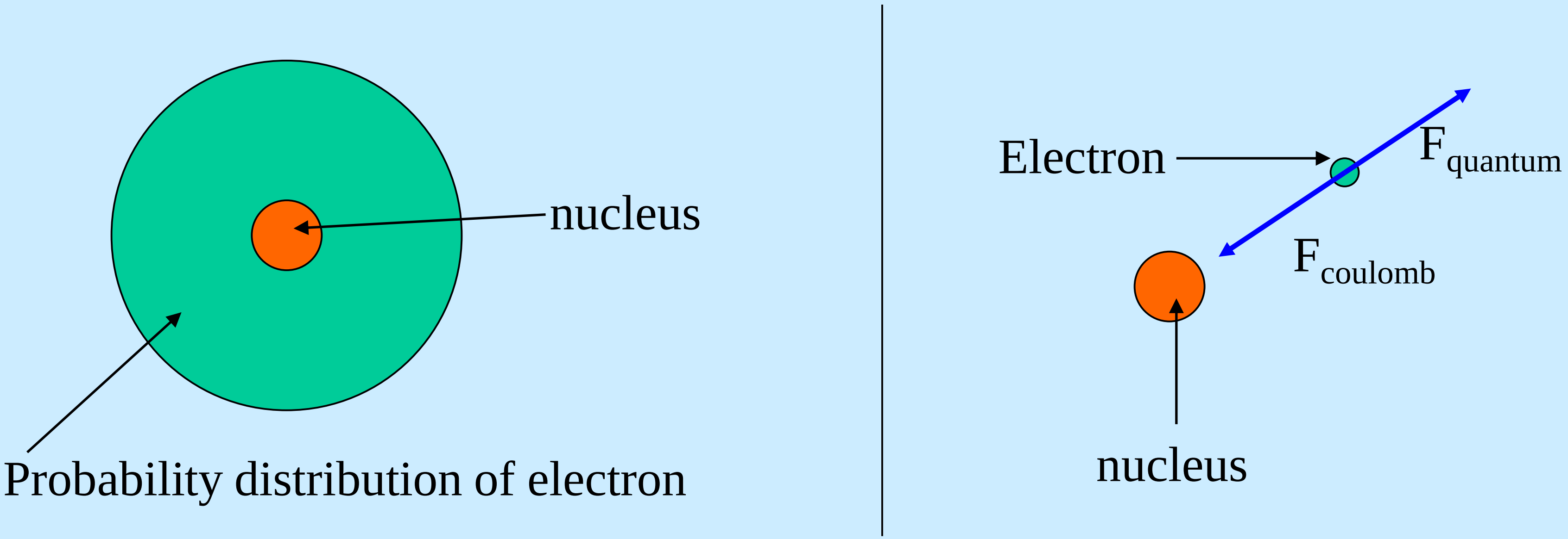
The Quantum Force is responsible for the quantum behavior

# ORBITAL “s”

The state “s” of an electron in a hydrogen atom is reinterpreted.

$$\psi = f(r)e^{i\frac{\alpha - Et}{\hbar}} \Rightarrow S = \alpha - Et \Rightarrow \bar{p} = \bar{\nabla} S = 0$$

**THE ELECTRON IS AT REST!!!**




I cannot *know* where it is, but it is still at a distance $r = r_{Bohr}$

# OTHER ORBITALS

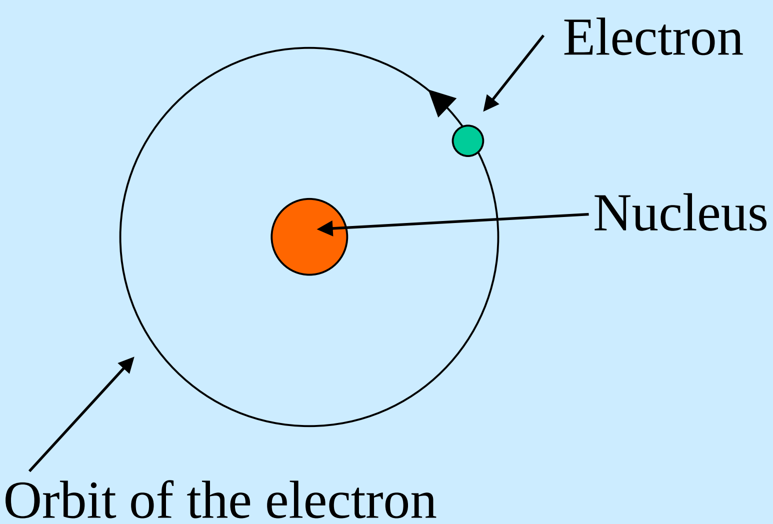
The other states of an electron in a hydrogen atom are also reinterpreted

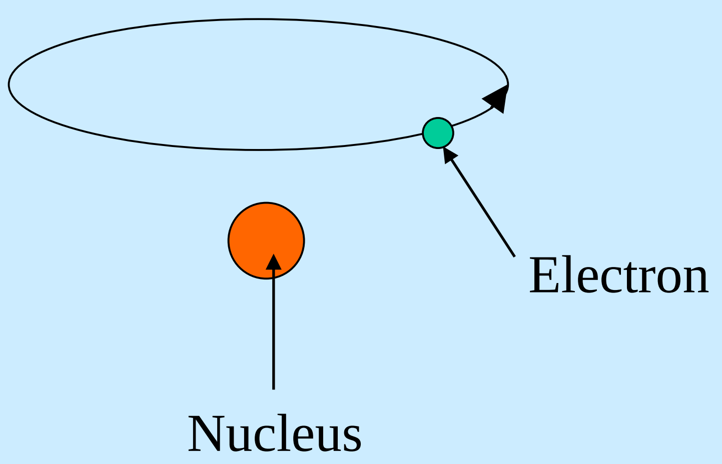
$$\psi = f(r)e^{i\left(m\phi - \frac{Et}{\hbar}\right)} \Rightarrow S = m\phi - \frac{Et}{\hbar} \Rightarrow \bar{p} = \bar{\nabla} S \neq 0$$

The solution is

$$r = r_0 \quad \theta = \theta_0 \quad \phi = \phi_0 + t\frac{m\hbar}{m_0} r_0^2 \sin(\theta_0)$$

**THE ELECTRON IS IN AN ORBIT!!!**



# STRUCTURE AND BORN-OPPENHEIMER

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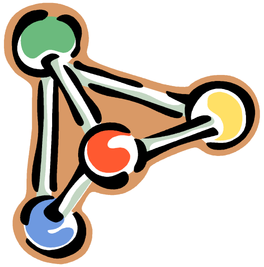
The Hamiltonian is a mere calculation tool. Bohm's equations give the position and momentum of all particles.

The Born-Oppenheimer Hamiltonian of a molecule is

$$\hat{H} = \sum_{g}^{A} \frac{\bar{p}_g^{\,2}}{2m_g} + e^2 \sum_{g<h}^{A} Z_g Z_h \bar{r}_{gh}^{\,-1} + \sum_{i}^{N} \left( \frac{\hat{\bar{p}}_i^{\,2}}{2m_i} - e \sum_{g}^{A} Z_g \hat{\bar{r}}_{ig}^{\,-1} \right) + \cancel{e^2 \sum_{i<j}^{N} \hat{\bar{r}}_{ij}^{\,-1}}$$

$$\hat{H} = \sum_{i}^{N} \left( \frac{\hat{\bar{p}}_i^{\,2}}{2m_i} - e \sum_{g}^{A} Z_g \hat{\bar{r}}_{ig}^{\,-1} \right) \longrightarrow$$



There are nuclear positions

There is structure

# STRUCTURE AND BORN-OPPENHEIMER

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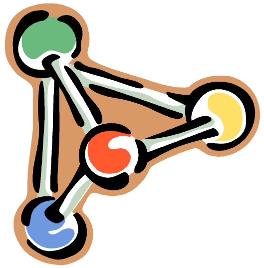
The Hamiltonian is a mere calculation tool. Bohm's equations give the position and momentum of all particles.

1. The structure is always there.
2. The approximation does not contradict the theory postulates.

$$\hat{H} = \sum_{g} \frac{\hat{\bar{p}}_g^2}{2m_g} + e^2 \sum_{g<h} Z_g Z_h \hat{\bar{r}}_{gh}^{-1} + \sum_{i} \left( \frac{\hat{\bar{p}}_i^2}{2m_i} - e \sum_{g} Z_g \hat{\bar{r}}_{ig}^{-1} \right) \cancel{+ e^2 \sum_{i<j} \hat{\bar{r}}_{ij}^{-1}}$$

$$\hat{H} = \sum_{i}^{N} \left( \frac{\hat{\bar{p}}_i^2}{2m_i} - e \sum_{g}^{A} Z_g \hat{\bar{r}}_{ig}^{-1} \right) \longrightarrow$$

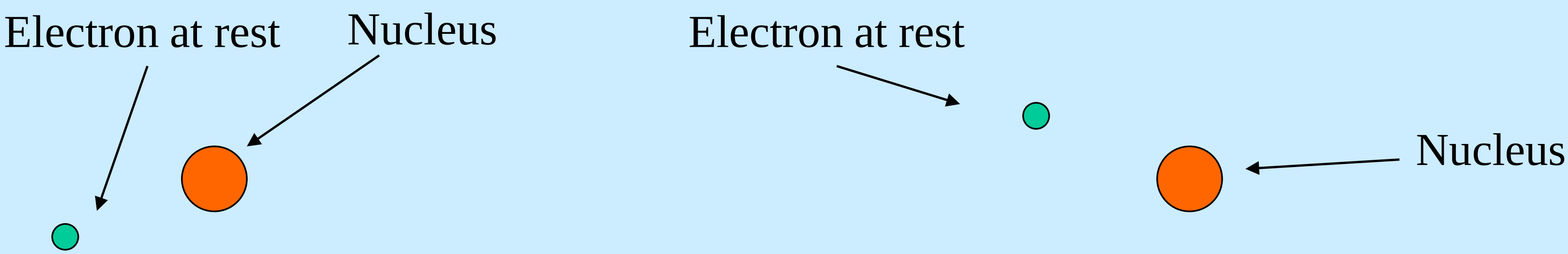


There are nuclear positions

There is structure

# COVALENT BOND

Consider two hydrogen atoms initially far apart, and gradually bring them closer together.




$$\psi_A = f(r_A) e^{i\frac{\alpha - Et}{\hbar}} \qquad \psi_B = f(r_B) e^{i\frac{\alpha - Et}{\hbar}}$$

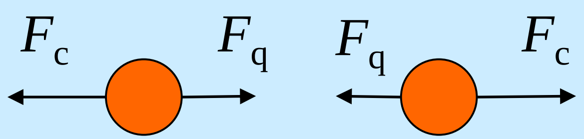
$$\Psi = \Psi\left(\overline{x}_1, \overline{x}_2, \overline{r}_A, \overline{r}_B\right)$$

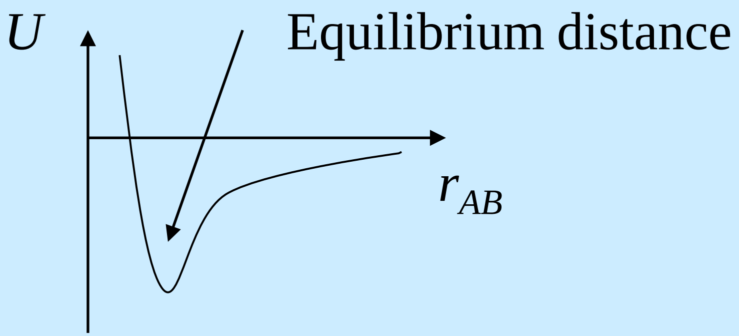
The total Hamiltonian is

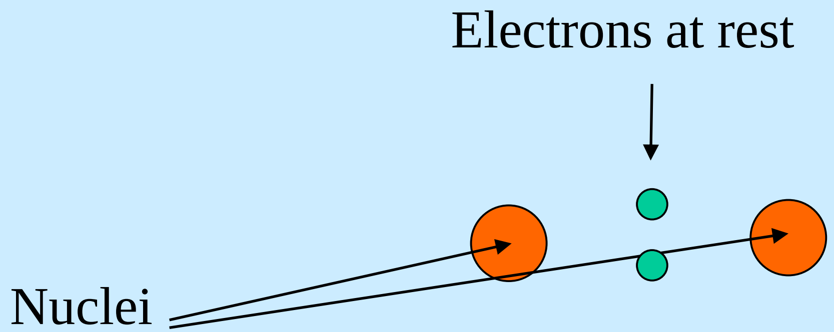
$$\hat{H} = -\frac{\hbar^2}{2m_e}\left(\overline{\nabla}_1^2 + \overline{\nabla}_2^2\right) - \frac{\hbar^2}{2M_n}\left(\overline{\nabla}_A^2 + \overline{\nabla}_B^2\right) - \frac{e^2}{r_{A1}} - \frac{e^2}{r_{A2}} - \frac{e^2}{r_{B1}} - \frac{e^2}{r_{B2}} + \frac{e^2}{r_{12}} + \frac{e^2}{r_{AB}}$$

# COVALENT BOND

Electrons and nuclei have definite positions.




There are two electrons at rest in the middle point,
in a way similar to the Lewis bond.

# CONCLUSIONS

In this talk we argued that:

➔ Some difficulties in the foundations of quantum chemistry arise from the absence of trajectories in orthodox quantum mechanics.

➔ Since there are trajectories in the QTM, this theory can help us to solve the difficulties in the foundations of quantum chemistry.

➔ The QTM is a more adequate quantum theory for chemistry.