Key concepts and challenges in quantum chemistry:
A (very) general introduction

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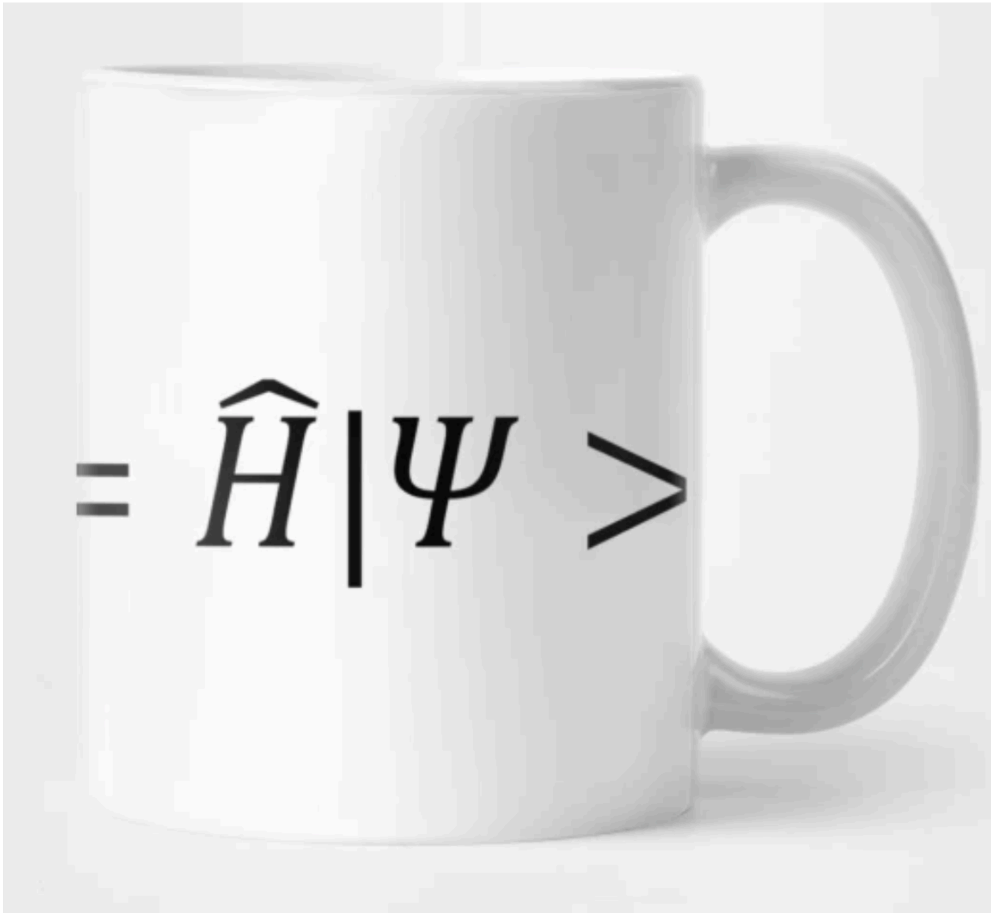
Time-independent ***Schrödinger equation***

$$E|\Psi\rangle$$



Time-independent ***Schrödinger equation***

$$\hat{H}\Psi = E\Psi$$

Schrödinger equation

I am the ***fundamental differential equation*** of quantum mechanics

$$\hat{H}\Psi = E\Psi$$

Schrödinger equation

$$\hat{H}\Psi = E\Psi$$

I am the ***electronic wave function***
(unknown in the equation)

Electronic wave function

$$\Psi$$

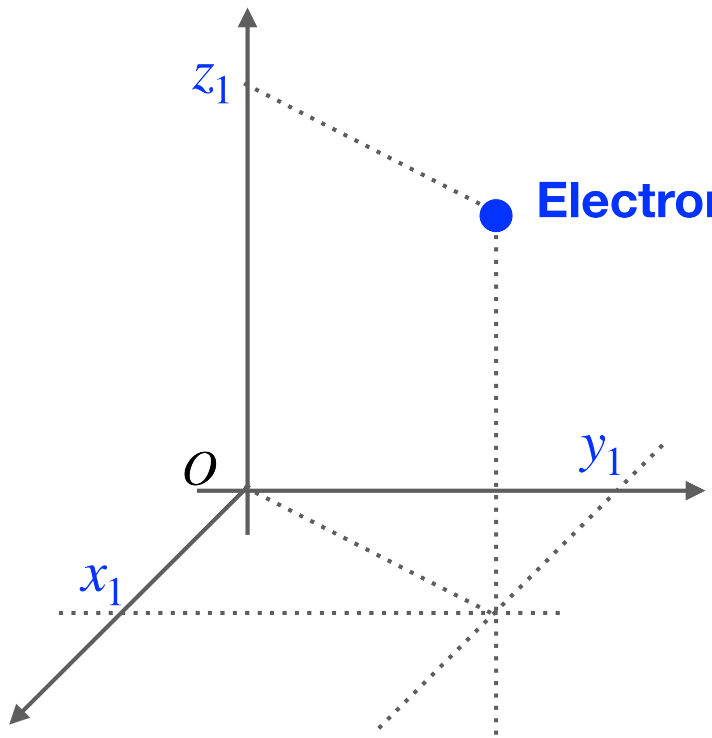
Electronic wave function

$$\Psi \equiv \Psi(x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N)$$

Electronic wave function

$$\Psi \equiv \Psi(x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N)$$

Cartesian coordinates
*that the **first electron** can take*



Electronic wave function

$$\Psi \equiv \Psi(x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N)$$

Cartesian coordinates
that the ***first electron*** *can take*

Cartesian coordinates
that the ***second electron*** *can take*

Electronic wave function

$$\Psi \equiv \Psi(x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N)$$

*Cartesian coordinates that the **first electron** can take*

*Cartesian coordinates that the **second electron** can take*

*Cartesian coordinates that the **Nth electron** can take*

Schrödinger equation

$$\hat{H}\Psi = E\Psi$$

I am a ***known differential operator***
(I transform the wave function)

Schrödinger equation

$$\hat{H}\Psi = E\Psi$$

I am the ***Hamiltonian operator***

Schrödinger equation

$$\hat{H} \equiv ?$$

Schrödinger equation

$$\hat{H} \equiv -\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}\right)$$

I ***differentiate twice*** the wave function
with respect to the coordinates of the ***first electron***

Schrödinger equation

$$\hat{H} \equiv -\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}\right) \quad \Longleftrightarrow$$

Kinetic energy of the first electron

Schrödinger equation

$$\hat{H} \equiv -\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right)-\frac{1}{2}\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right)$$

*Same for the **second electron***

Schrödinger equation

$$\hat{H} \equiv -\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right)-\frac{1}{2}\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right)-\ldots-\frac{1}{2}\left(\frac{\partial^2}{\partial x_N^2}+\frac{\partial^2}{\partial y_N^2}+\frac{\partial^2}{\partial z_N^2}\right)$$

Schrödinger equation

$$\hat{H} \equiv -\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right)-\frac{1}{2}\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right)-\ldots-\frac{1}{2}\left(\frac{\partial^2}{\partial x_N^2}+\frac{\partial^2}{\partial y_N^2}+\frac{\partial^2}{\partial z_N^2}\right)$$

$$\left(-\sum_{A}^{nuclei}\frac{\mathcal{Z}_A}{\sqrt{(x_1-X_A)^2+(y_1-Y_A)^2+(z_1-Z_A)^2}}\right.$$

Attraction of the first electron ***to the nuclei***

Schrödinger equation

$$\hat{H} \equiv -\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right)-\frac{1}{2}\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right)-\ldots-\frac{1}{2}\left(\frac{\partial^2}{\partial x_N^2}+\frac{\partial^2}{\partial y_N^2}+\frac{\partial^2}{\partial z_N^2}\right)$$

$$\left(-\sum_{A}^{nuclei}\frac{\mathcal{Z}_A}{\sqrt{(x_1-X_A)^2+(y_1-Y_A)^2+(z_1-Z_A)^2}}\right.$$

Atomic number of nucleus *A*

Schrödinger equation

$$\hat{H} \equiv -\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right)-\frac{1}{2}\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right)-\dots-\frac{1}{2}\left(\frac{\partial^2}{\partial x_N^2}+\frac{\partial^2}{\partial y_N^2}+\frac{\partial^2}{\partial z_N^2}\right)$$

$$\left(-\sum_{A}^{nuclei}\frac{\mathscr{Z}_A}{\sqrt{(x_1-X_A)^2+(y_1-Y_A)^2+(z_1-Z_A)^2}}\right.$$

Cartesian coordinates of nucleus A

Schrödinger equation

$$\hat{H} \equiv -\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right)-\frac{1}{2}\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right)-\ldots-\frac{1}{2}\left(\frac{\partial^2}{\partial x_N^2}+\frac{\partial^2}{\partial y_N^2}+\frac{\partial^2}{\partial z_N^2}\right)$$

$$\left(-\sum_{A}^{nuclei}\frac{\mathcal{Z}_A}{\sqrt{(x_1-X_A)^2+(y_1-Y_A)^2+(z_1-Z_A)^2}}-\sum_{A}^{nuclei}\frac{\mathcal{Z}_A}{\sqrt{(x_2-X_A)^2+(y_2-Y_A)^2+(z_2-Z_A)^2}}\right.$$

Same for the **second electron**

Schrödinger equation

$$\hat{H} \equiv -\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right)-\frac{1}{2}\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right)-\ldots-\frac{1}{2}\left(\frac{\partial^2}{\partial x_N^2}+\frac{\partial^2}{\partial y_N^2}+\frac{\partial^2}{\partial z_N^2}\right)$$

$$\left(-\sum_{A}^{nuclei}\frac{\mathcal{Z}_A}{\sqrt{(x_1-X_A)^2+(y_1-Y_A)^2+(z_1-Z_A)^2}}-\sum_{A}^{nuclei}\frac{\mathcal{Z}_A}{\sqrt{(x_2-X_A)^2+(y_2-Y_A)^2+(z_2-Z_A)^2}}\right.$$

$$-\ldots-\sum_{A}^{nuclei}\frac{\mathcal{Z}_A}{\sqrt{(x_N-X_A)^2+(y_N-Y_A)^2+(z_N-Z_A)^2}}$$

Schrödinger equation

$$\hat{H} \equiv -\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right)-\frac{1}{2}\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right)-\ldots-\frac{1}{2}\left(\frac{\partial^2}{\partial x_N^2}+\frac{\partial^2}{\partial y_N^2}+\frac{\partial^2}{\partial z_N^2}\right)$$

$$\left(-\sum_A^{nuclei}\frac{\mathcal{Z}_A}{\sqrt{(x_1-X_A)^2+(y_1-Y_A)^2+(z_1-Z_A)^2}}-\sum_A^{nuclei}\frac{\mathcal{Z}_A}{\sqrt{(x_2-X_A)^2+(y_2-Y_A)^2+(z_2-Z_A)^2}}\right.$$

$$-\ldots-\sum_A^{nuclei}\frac{\mathcal{Z}_A}{\sqrt{(x_N-X_A)^2+(y_N-Y_A)^2+(z_N-Z_A)^2}}$$

$$+\frac{1}{\sqrt{(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2}}$$

⟷ ***Repulsion** between the first two electrons*

Schrödinger equation

$$\hat{H} \equiv -\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right)-\frac{1}{2}\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right)-\dots-\frac{1}{2}\left(\frac{\partial^2}{\partial x_N^2}+\frac{\partial^2}{\partial y_N^2}+\frac{\partial^2}{\partial z_N^2}\right)$$

$$\left(-\sum_{A}^{noyaux}\frac{\mathcal{Z}_A}{\sqrt{(x_1-X_A)^2+(y_1-Y_A)^2+(z_1-Z_A)^2}}-\sum_{A}^{noyaux}\frac{\mathcal{Z}_A}{\sqrt{(x_2-X_A)^2+(y_2-Y_A)^2+(z_2-Z_A)^2}}\right.$$

$$-\dots-\sum_{A}^{noyaux}\frac{\mathcal{Z}_A}{\sqrt{(x_N-X_A)^2+(y_N-Y_A)^2+(z_N-Z_A)^2}}$$

$$\left.+\frac{1}{\sqrt{(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2}}+\dots\right)\times$$

← **to-be-multiplied** *by the wave function*

Schrödinger equation

$$\hat{H}\Psi = E \times \Psi$$

↓

Unchanged wave function!

Schrödinger equation

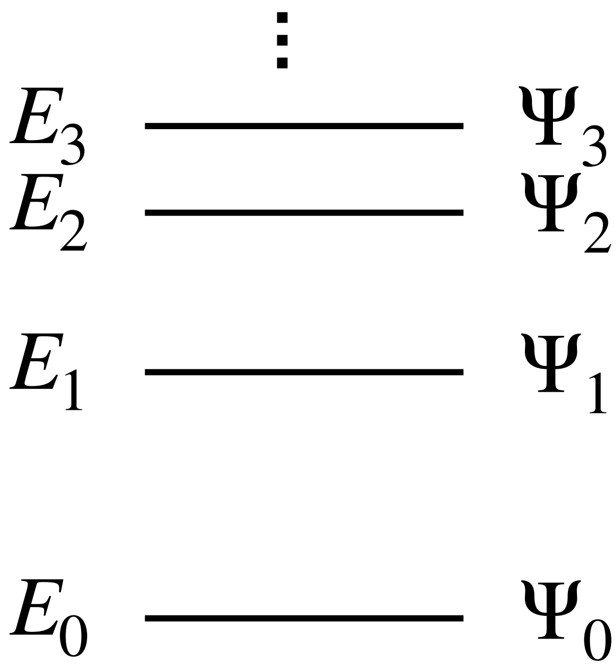
I am the ***energy of the electrons***
(unknown in the equation)

$$\hat{H}\Psi = E \times \Psi$$

Schrödinger equation

There is an infinite number of solutions $(I = 0,1,2,3,\ldots)$

$$\hat{H}\Psi_I = E_I \times \Psi_I$$

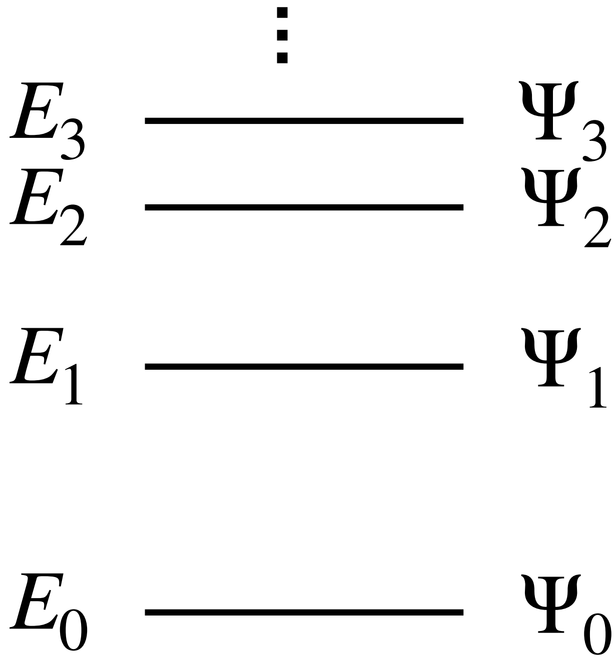


Schrödinger equation

There is an infinite number of solutions $(I = 0,1,2,3,\ldots)$

$$\hat{H}\Psi_I = E_I \times \Psi_I$$

UV/visible **spectroscopy**,
photochemistry, …



Schrödinger equation

$$\hat{H}\Psi = E \times \Psi$$

$$\cdots - \sum_{A}^{nuclei} \frac{\mathcal{Z}_A}{\sqrt{(x_1 - X_A)^2 + (y_1 - Y_A)^2 + (z_1 - Z_A)^2}} - \cdots$$

Determined for a given geometry R

Computation of reaction paths

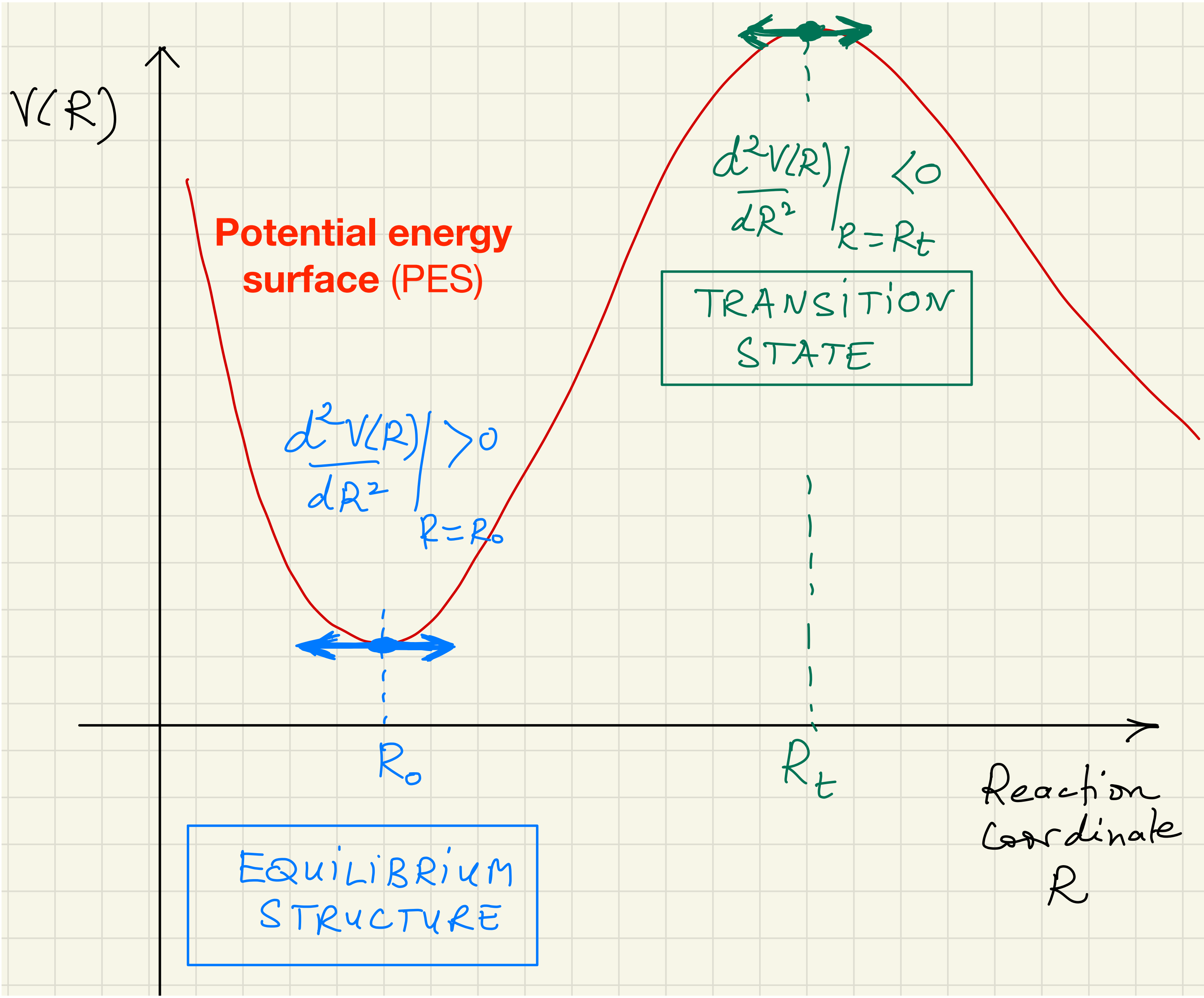
$$V(R) = E(R) + \sum_{A<B}^{nuclei} \frac{\mathcal{Z}_A \mathcal{Z}_B}{\sqrt{(X_A - X_B)^2 + (Y_A - Y_B)^2 + (Z_A - Z_B)^2}}$$

Total potential energy

Quantum **electronic energy**

Classical **nuclear repulsion energy**

Computation of reaction paths



Approximate N-electron wave functions

$$\Psi \equiv \Psi(x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N)$$

$$\approx \varphi_1(x_1, y_1, z_1) \times \varphi_2(x_2, y_2, z_2) \times \ldots \times \varphi_N(x_N, y_N, z_N)$$

↓

Uncorrelated wave function:

Each electron is disentangled from the others

Approximate N-electron wave functions

$$\Psi \equiv \Psi(x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N)$$

$$\approx \varphi_1(x_1, y_1, z_1) \times \varphi_2(x_2, y_2, z_2) \times \ldots \times \varphi_N(x_N, y_N, z_N)$$

↓

Wave function of the first electron

Approximate N-electron wave functions

$$\Psi \equiv \Psi(x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N)$$

$$\approx \varphi_1(x_1, y_1, z_1) \times \varphi_2(x_2, y_2, z_2) \times \ldots \times \varphi_N(x_N, y_N, z_N)$$

↓

Wave function of the first electron

↓

"orbital φ_1"

Approximate N-electron wave functions

$$\Psi \equiv \Psi(x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N)$$

$$\approx \varphi_1(x_1, y_1, z_1) \times \varphi_2(x_2, y_2, z_2) \times \ldots \times \varphi_N(x_N, y_N, z_N)$$

↓

Wave function of the second electron

↓

"orbital φ_2"

Approximate N-electron wave functions

$$\Psi \equiv \Psi(x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N)$$

$$\approx \varphi_1(x_1, y_1, z_1) \times \varphi_2(x_2, y_2, z_2) \times \ldots \times \varphi_N(x_N, y_N, z_N)$$

Cannot be the exact solution to the Schrödinger equation

Approximate N-electron wave functions

$$\Psi \equiv \Psi(x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N)$$

$$\approx \varphi_1(x_1, y_1, z_1) \times \varphi_2(x_2, y_2, z_2) \times \ldots \times \varphi_N(x_N, y_N, z_N)$$

Cannot be the exact solution to the Schrödinger equation

Density-functional exactification: $$\sum_{i=1}^{N} \varphi_i^2(x, y, z) = n_{\Psi_0}(x, y, z)$$

Exact electron density

Approximate N-electron wave function
in quantum embedding theory

$$\Psi \equiv \Psi(x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N)$$

$$\approx \psi(x_1, y_1, z_1, x_2, y_2, z_2) \times \varphi_3(x_3, y_3, z_3) \times \ldots \times \varphi_N(x_N, y_N, z_N)$$

Correlated two-electron *wave function*

Core electrons

To be continued…