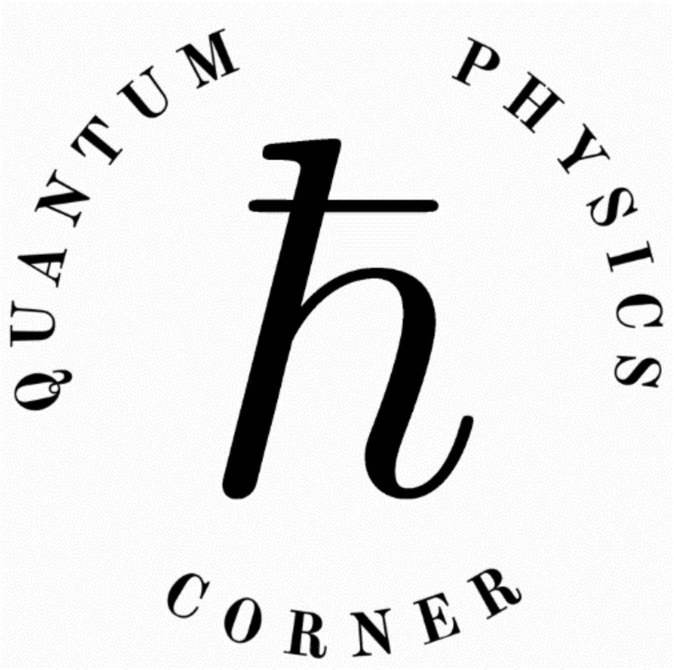
L1 - Quantum Mechanics 1

The Born-Oppenheimer approximation

Wave functions and the Schrödinger equation



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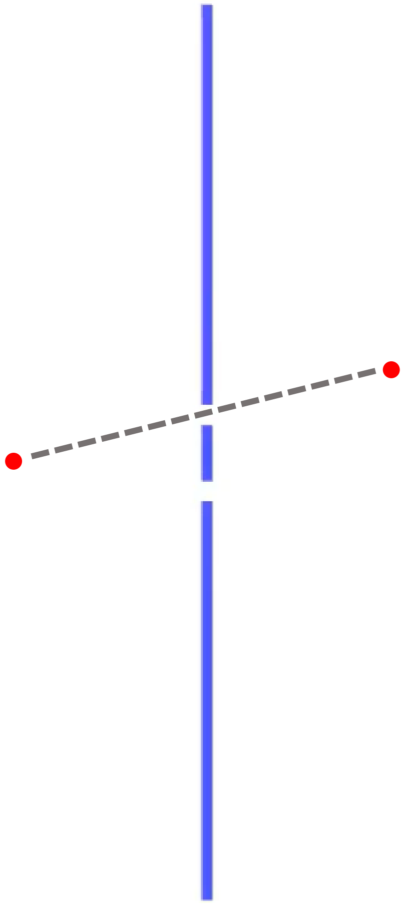
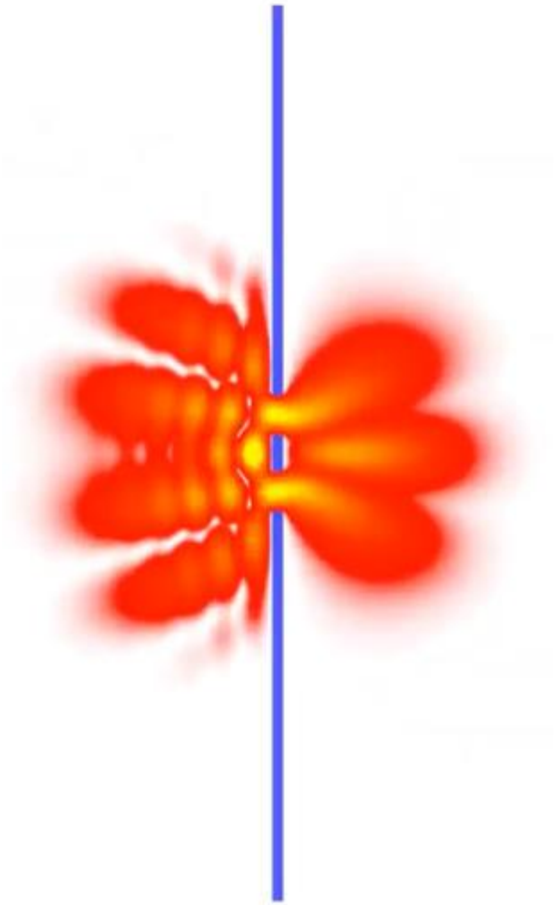


A **classical particle**
is a particle (!)



A **quantum particle**
delocalizes over space

The delocalization pattern is determined by the environment.

QUANTUM PHYSICS

$\hbar$

CORNER

▶ youtu.be/04zbUVSb6xE

QUANTUM PHYSICS

$\hbar$

CORNER

youtu.be/ff48yjUqrsM

The **quantum delocalization** looks like a wave.

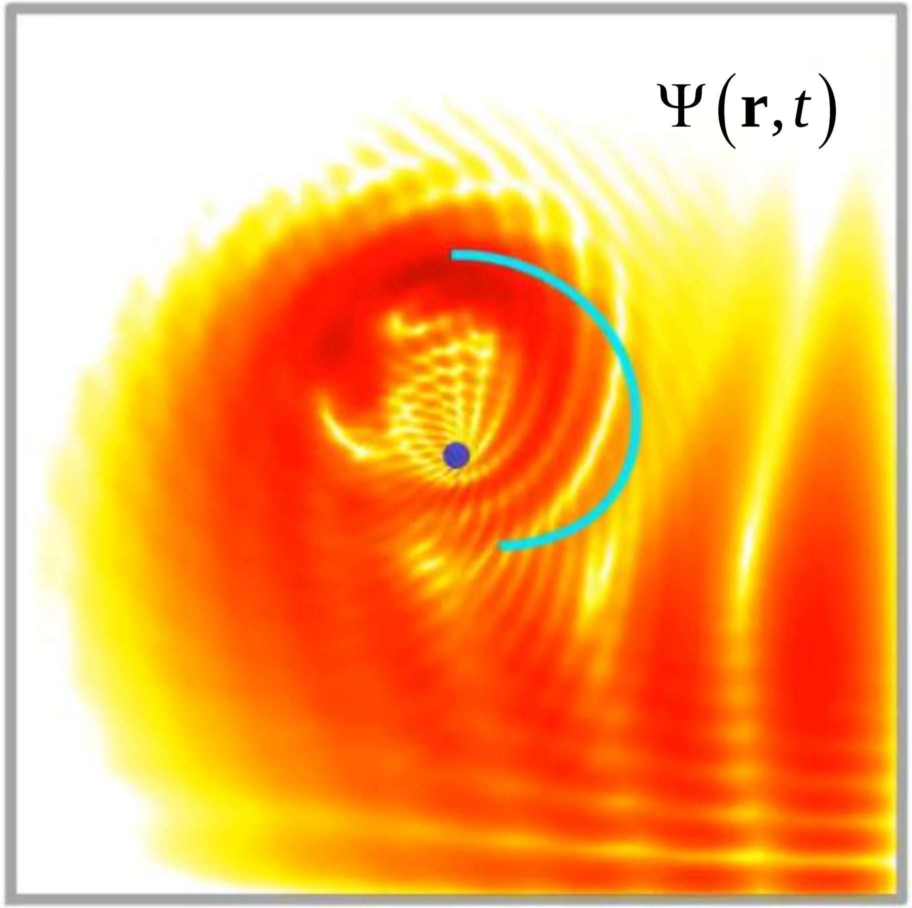
It is mathematically described by a wave function $\Psi(\mathbf{r},t)$.

$\Psi(\mathbf{r},t)$ attributes a value for each point **r** at each time *t*.

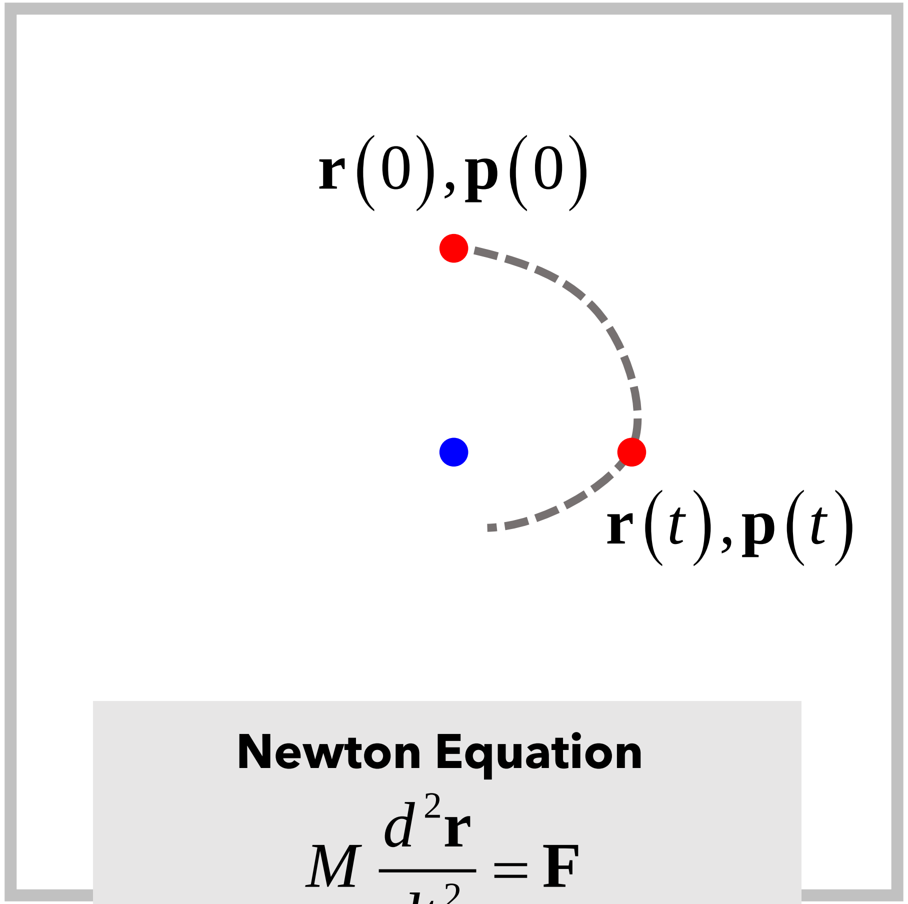
The value of $\Psi(\mathbf{r},t)$ is a complex number in the form of

$$a + ib$$

where $i^2 = -1$.



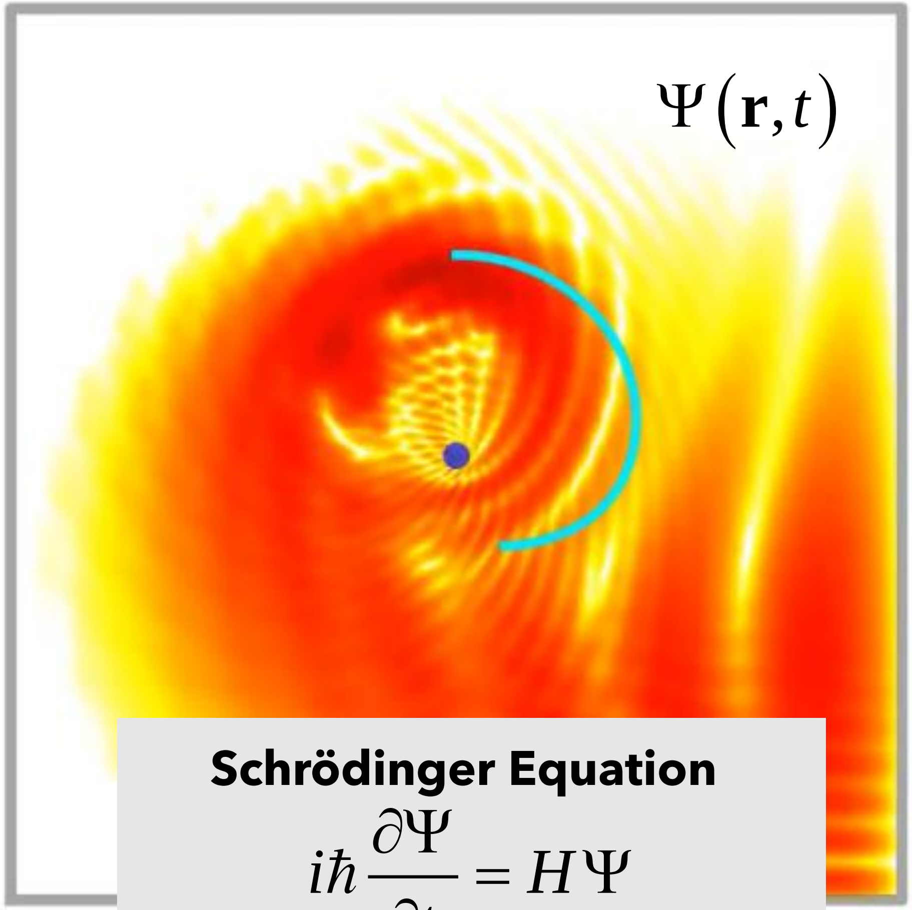
The **classical state** is determined by position and momentum at each time.



Newton Equation

$$M\frac{d^2\mathbf{r}}{dt^2}=\mathbf{F}$$

The **quantum state** is determined by the wave function of position and time.



Schrödinger Equation

$$i\hbar\frac{\partial\Psi}{\partial t}=H\Psi$$

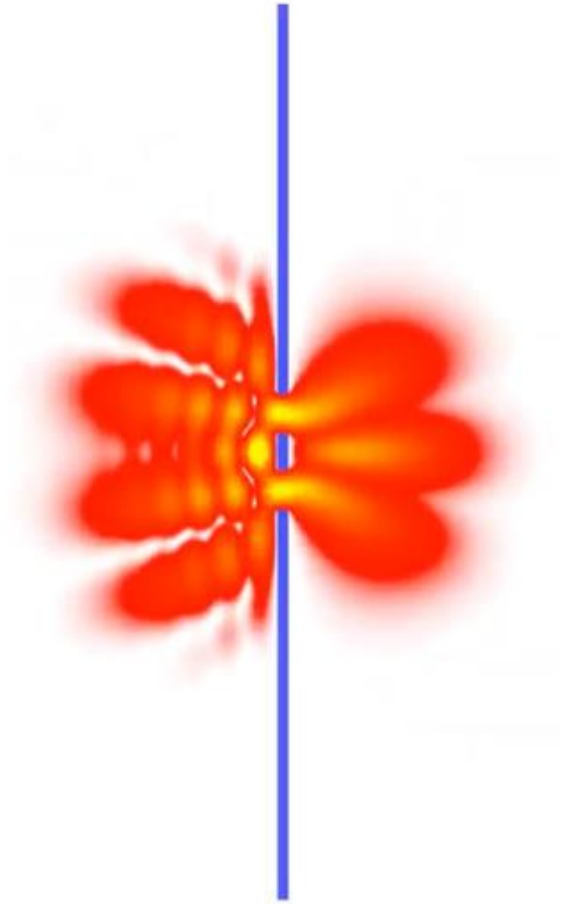
Schrödinger Equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$$

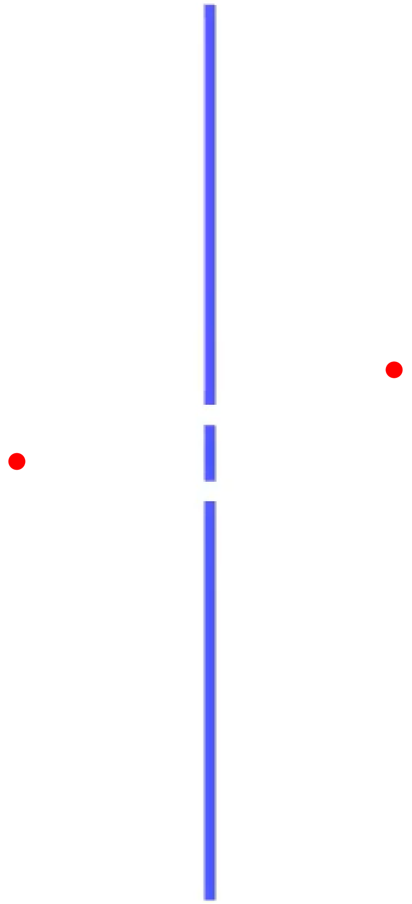
H is the Hamiltonian operator

$\hbar = 6.582 \times 10^{-16}$ eV.s is the Planck constant

We do not directly observe $\Psi(\mathbf{r},t)$.

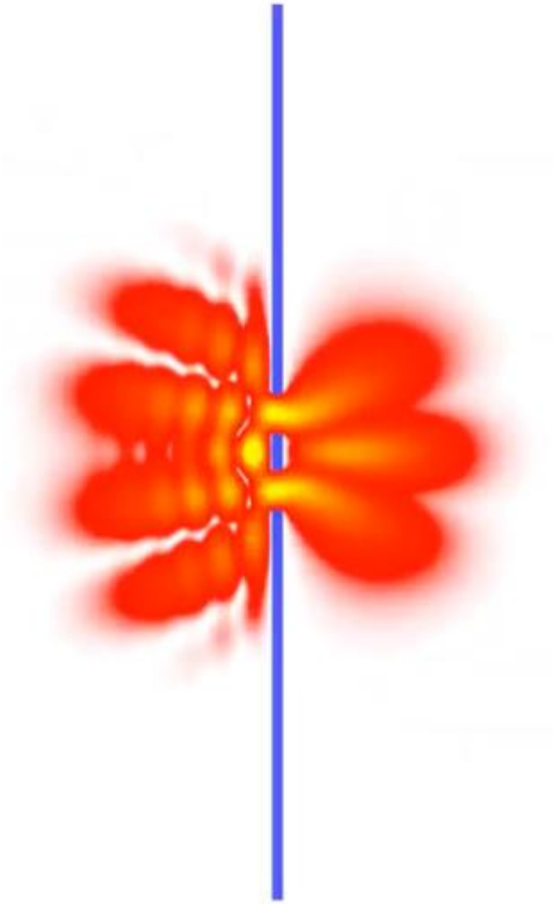


Wave function
$\Psi(\mathbf{r},t) = a + ib$

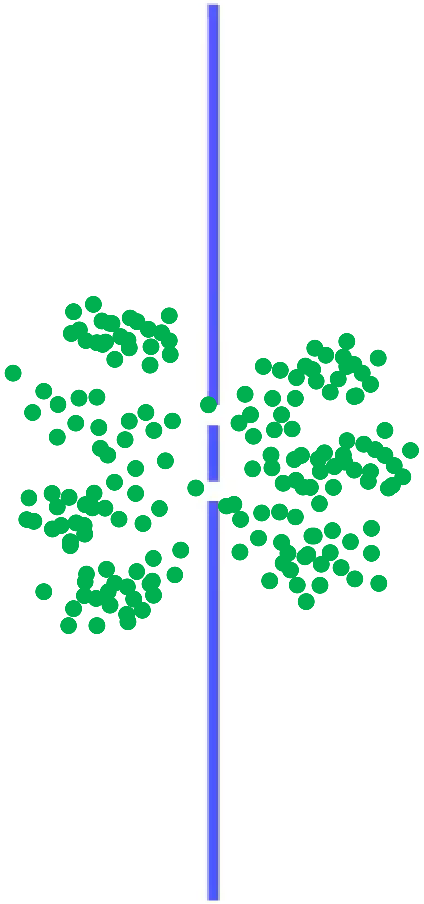


Each measure yields a classical particle.

We do not directly observe $\Psi(\mathbf{r},t)$.



Wave function
$\Psi(\mathbf{r},t) = a + ib$



Repeated measurements tend to
$|\Psi(\mathbf{r},t)|^2 = a^2 + b^2$

The Born rule

$$\left|\Psi\left(\mathbf{r},t\right)\right|^2 d^3\mathbf{r} = \Psi\left(\mathbf{r},t\right)^* \Psi\left(\mathbf{r},t\right) d^3\mathbf{r}$$

This quantity is the probability of finding the particle in a volume d^3**r** around **r** at time *t*.

The probability the particle will be somewhere is 1.

$$\int\left|\Psi\left(\mathbf{r},t\right)\right|^2 d^3\mathbf{r} = \int\Psi\left(\mathbf{r},t\right)^* \Psi\left(\mathbf{r},t\right) d^3\mathbf{r} = 1$$

Ψ* is the complex conjugate of Ψ

$$\Psi \quad = a + ib$$

$$\Psi^* = a - ib$$

WAVE
PARTICLE DUALITY

youtu.be/qCmtegdqOOA

The mean value of any observable A is given as

$$\begin{aligned}\langle A\rangle &= \int d\mathbf{r}\Psi^*(\mathbf{r},t)A\Psi(\mathbf{r},t)\\ &= \langle\Psi|A|\Psi\rangle\end{aligned}$$

Bra ⟨bra| and ket |ket⟩ symbols are Dirac’s notation to simplify long integral expressions.

The mean value of the position **r**

$$\begin{aligned}\langle \mathbf{r} \rangle &= \int d\mathbf{r}\,\Psi^*(\mathbf{r},t)\,\mathbf{r}\,\Psi(\mathbf{r},t)\\ &= \langle \Psi | \mathbf{r} | \Psi \rangle\end{aligned}$$

Mean value of component *x*

$$\langle x \rangle = \langle \Psi | x | \Psi \rangle = \int dx\,dy\,dz\,\Psi^*(\mathbf{r},t)\,x\,\Psi(\mathbf{r},t)$$

The mean value of the momentum $p_x = -i\hbar \frac{\partial}{\partial x}$

$$\begin{aligned}\left\langle p_x \right\rangle &= -i\hbar \int d\mathbf{r}\, \Psi^*\left(\mathbf{r},t\right) \frac{\partial \Psi\left(\mathbf{r},t\right)}{\partial x} \\ &= -i\hbar \left\langle \Psi \middle| \frac{\partial}{\partial x} \middle| \Psi \right\rangle \\ &= -i\hbar \left\langle \Psi \middle| \frac{\partial \Psi}{\partial x} \right\rangle\end{aligned}$$

Nabla operator

$$\nabla = \begin{pmatrix} \partial_x \\ \partial_y \\ \partial_z \end{pmatrix} \rightarrow \left\langle \mathbf{p} \right\rangle = -i\hbar \left\langle \Psi \middle| \nabla \Psi \right\rangle$$

The mean value Hamiltonian *H* is the energy

$$
\begin{aligned}
\langle H \rangle &= \int d\mathbf{r}\, \Psi^*(\mathbf{r},t)\, H\, \Psi(\mathbf{r},t) \\
&= \langle \Psi | H | \Psi \rangle \\
&= E
\end{aligned}
$$

Suppose time-independent Hamiltonian $H(\mathbf{r})$.

We can separate **r** and *t* in the wave function:

$$\Psi\left(\mathbf{r},t\right)=\psi\left(\mathbf{r}\right)\phi\left(t\right)$$

Replace in the Schrödinger equation

$$i\hbar\frac{\partial\Psi}{\partial t}=H\left(\mathbf{r}\right)\Psi\rightarrow i\hbar\frac{\partial\psi\left(\mathbf{r}\right)\phi\left(t\right)}{\partial t}=H\left(\mathbf{r}\right)\psi\left(\mathbf{r}\right)\phi\left(t\right)$$

$$i\hbar\psi\left(\mathbf{r}\right)\frac{d\phi\left(t\right)}{dt}=H\left(\mathbf{r}\right)\psi\left(\mathbf{r}\right)\phi\left(t\right)$$

Separate the variables:

$$i\hbar\frac{1}{\phi\left(t\right)}\frac{d\phi\left(t\right)}{dt}=\frac{H\left(\mathbf{r}\right)\psi\left(\mathbf{r}\right)}{\psi\left(\mathbf{r}\right)}=E$$

$$\begin{cases} i\hbar\dfrac{d\phi\left(t\right)}{dt}=E\phi\left(t\right) \\ H\left(\mathbf{r}\right)\psi\left(\mathbf{r}\right)=E\psi\left(\mathbf{r}\right) \end{cases}$$

The first equation

$$i\hbar \frac{d\phi(t)}{dt} = E\phi(t)$$

gives

$$\phi(t) = \exp\left(-i\frac{Et}{\hbar}\right)$$

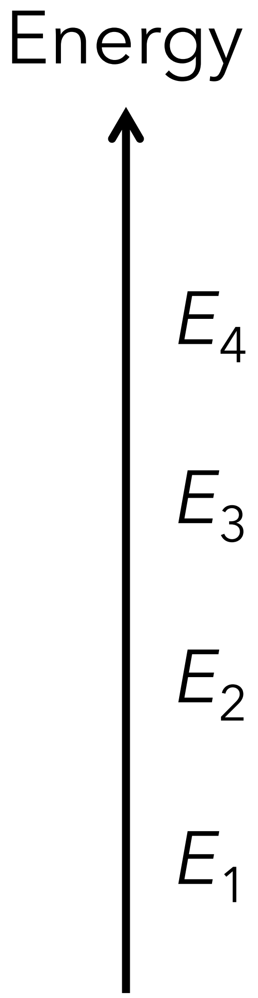
The second equation

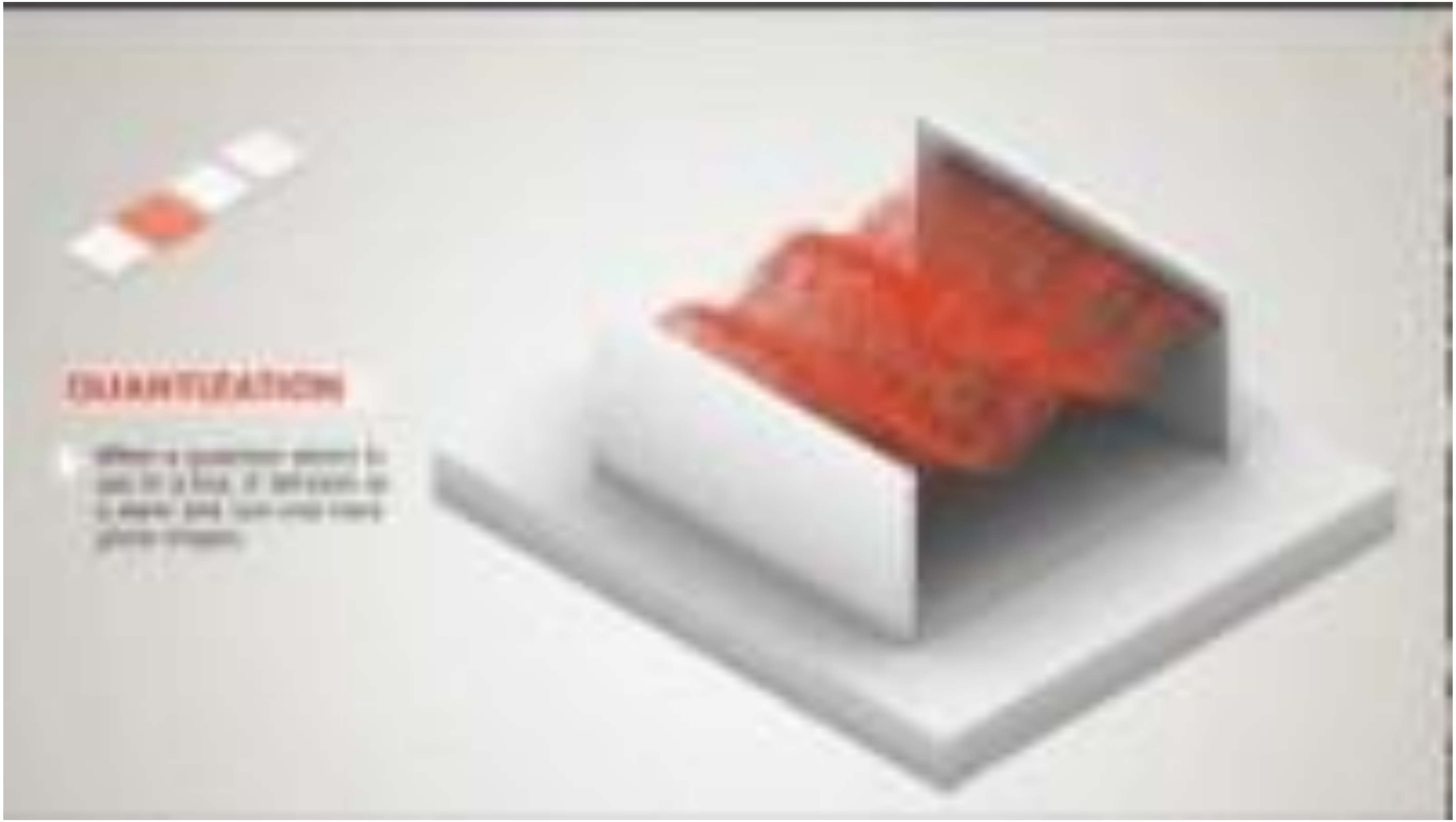
$$H(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

is called the Time-Independent Schrödinger equation.

$$H(\mathbf{r})\overset{\overset{\text{Eigenvector}}{\downarrow}}{\psi}(\mathbf{r}) = \underset{\underset{\text{Eigenvalue}}{\uparrow}}{E}\psi(\mathbf{r})$$

$$\begin{array}{ll} H(\mathbf{r})\psi_1(\mathbf{r}) = E_1\psi_1(\mathbf{r}) & \text{Ground state} \\ \left.\begin{array}{l} H(\mathbf{r})\psi_2(\mathbf{r}) = E_2\psi_2(\mathbf{r}) \\ \vdots \\ H(\mathbf{r})\psi_N(\mathbf{r}) = E_N\psi_N(\mathbf{r}) \end{array}\right\} & \text{Excited states} \end{array}$$





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If H is time-independent and $\Psi(\mathrm{r}, t=0)$ is an eigenvector of H,
the system is in a *stationary state*.

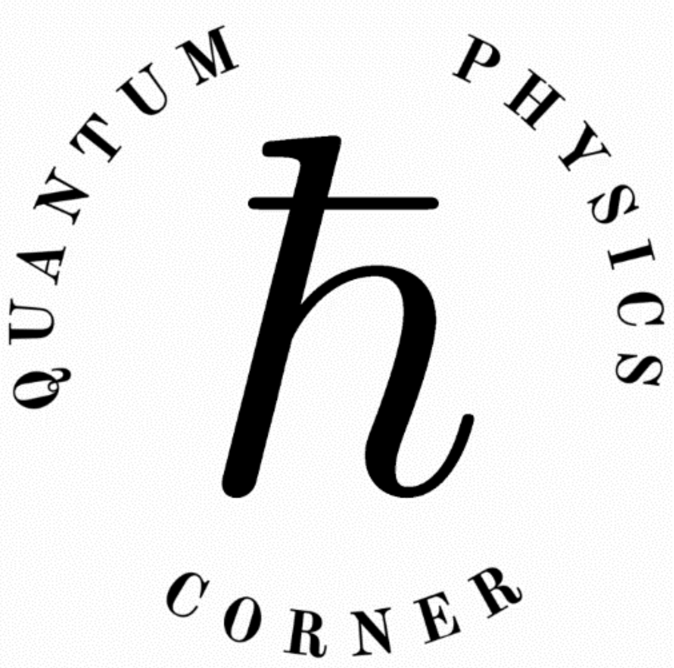
That means that $|\Psi|^2$ remains constant with time.

Oscillations between real and imaginary parts occur with frequency $E/\hbar$.

If H is time-independent and $\Psi(\mathrm{r}, t=0)$ is NOT an eigenvector of H, the system is not *stationary*.

In this case, $|\Psi|^2$ changes with time.

A standard procedure to solve non-stationary states is to first solve a stationary case, and use the eigenvectors to expand the time-dependent Ψ.



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If we have more than one particle, we still write a single wave function.

However, the wave function now depends on the coordinates of all particles.

For two particles:

$$\Psi\left(\mathbf{r}_1, \mathbf{r}_2, t\right)$$

For *N* particles:

$$\Psi\left(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N, t\right)$$

The molecular roller coaster

“The Born-Oppenheimer idea is one of those wonderful approximations that even in failure forms the basis for discussion and systematic corrections.

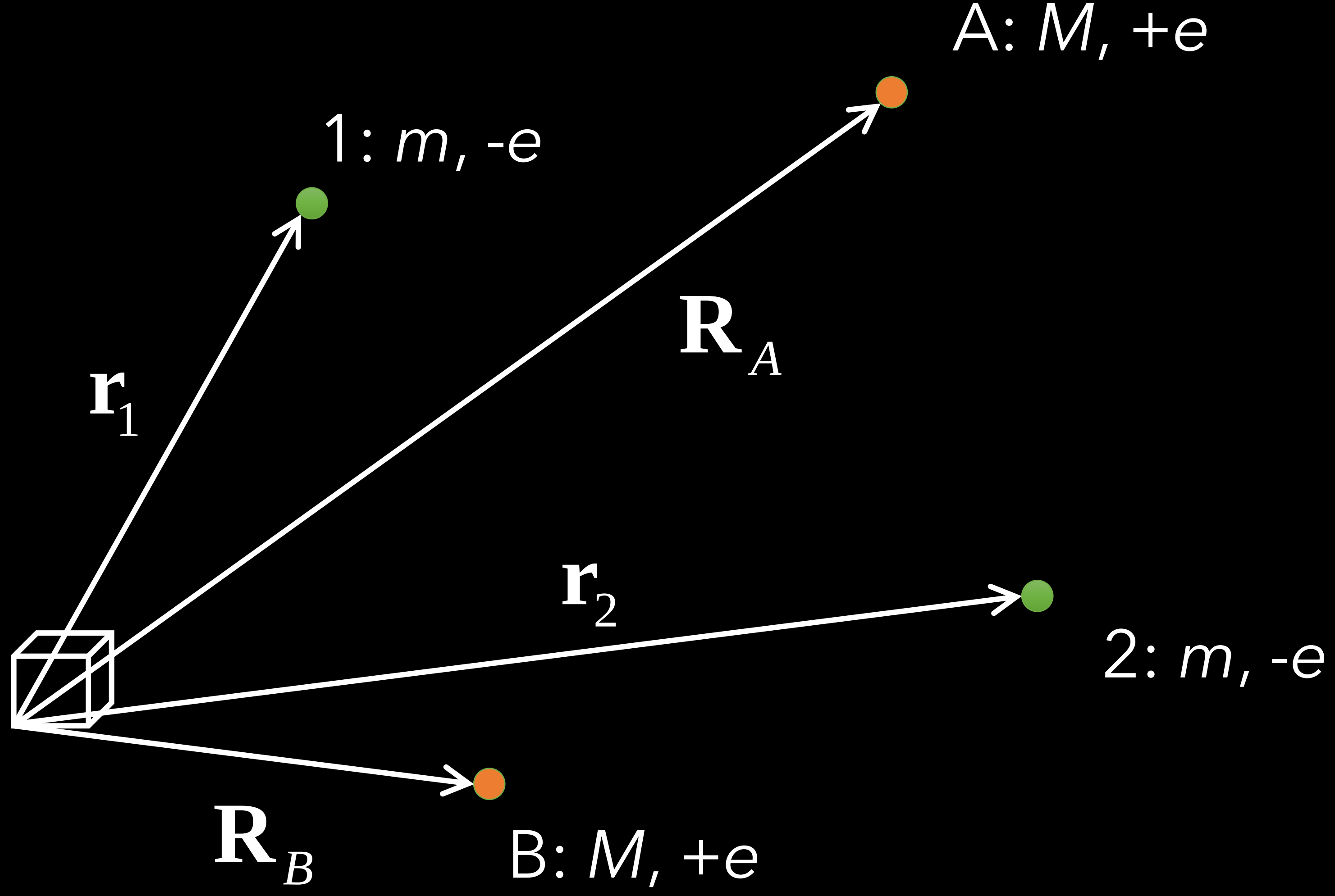
“Without the Born-Oppenheimer approximation as a foundation, there would be no molecular structure, solid-state crystal structure, molecular vibrations, phonons, electronic band structure, and so on.

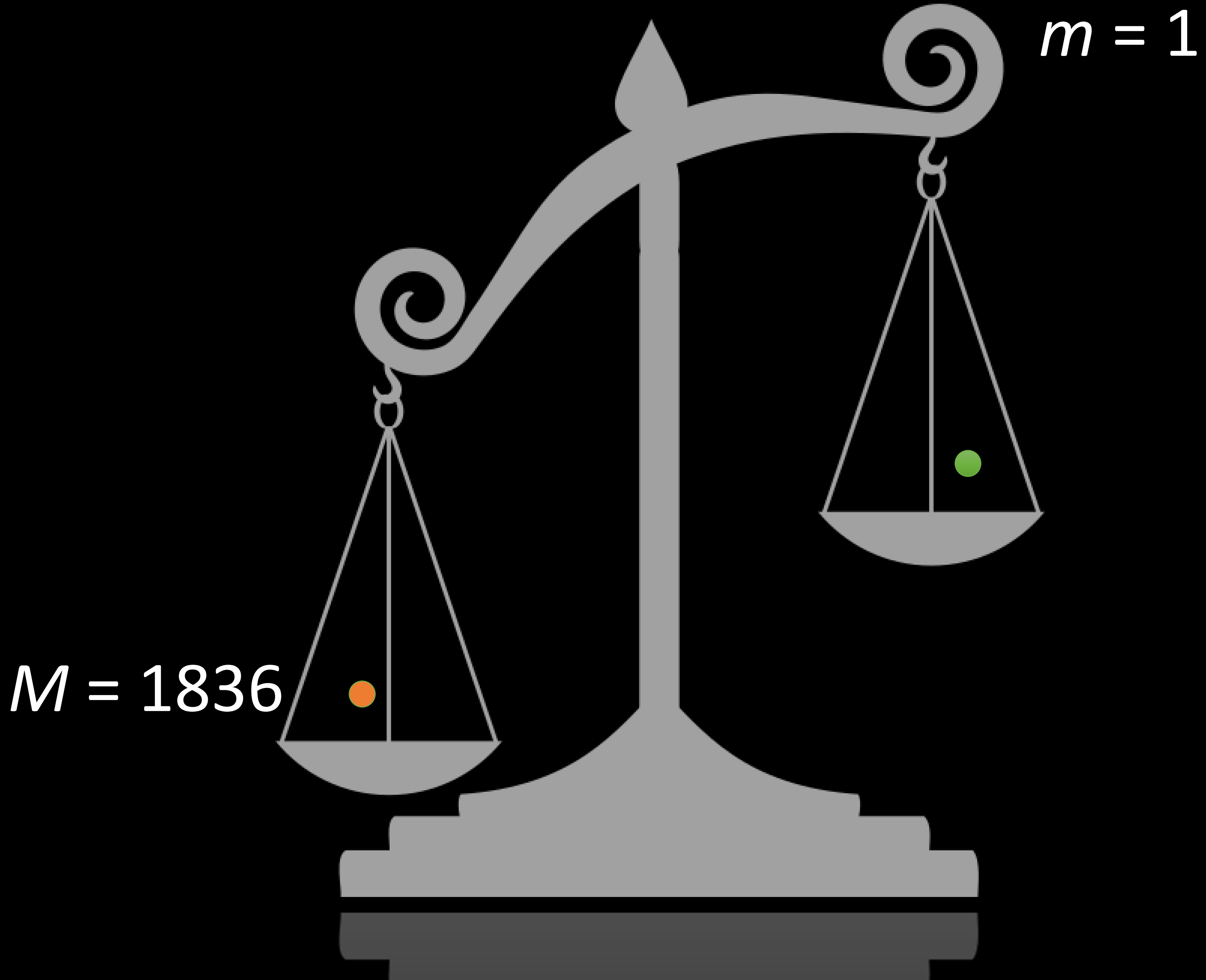
“Why? Because it is the Born-Oppenheimer approximation that allows separation of electronic from nuclear motion. Without it, we appear to be lost in a soggy many-body ‘pea soup’ or plasma of electrons and nuclei, where there is seemingly no structure at all, save the kind of structure one finds in a two-component liquid.”

Eric J Heller- The semiclassical way to dynamics and spectroscopy, 2018

$$\Psi\left(\mathbf{R}_A, \mathbf{R}_B, \mathbf{r}_1, \mathbf{r}_2\right)$$

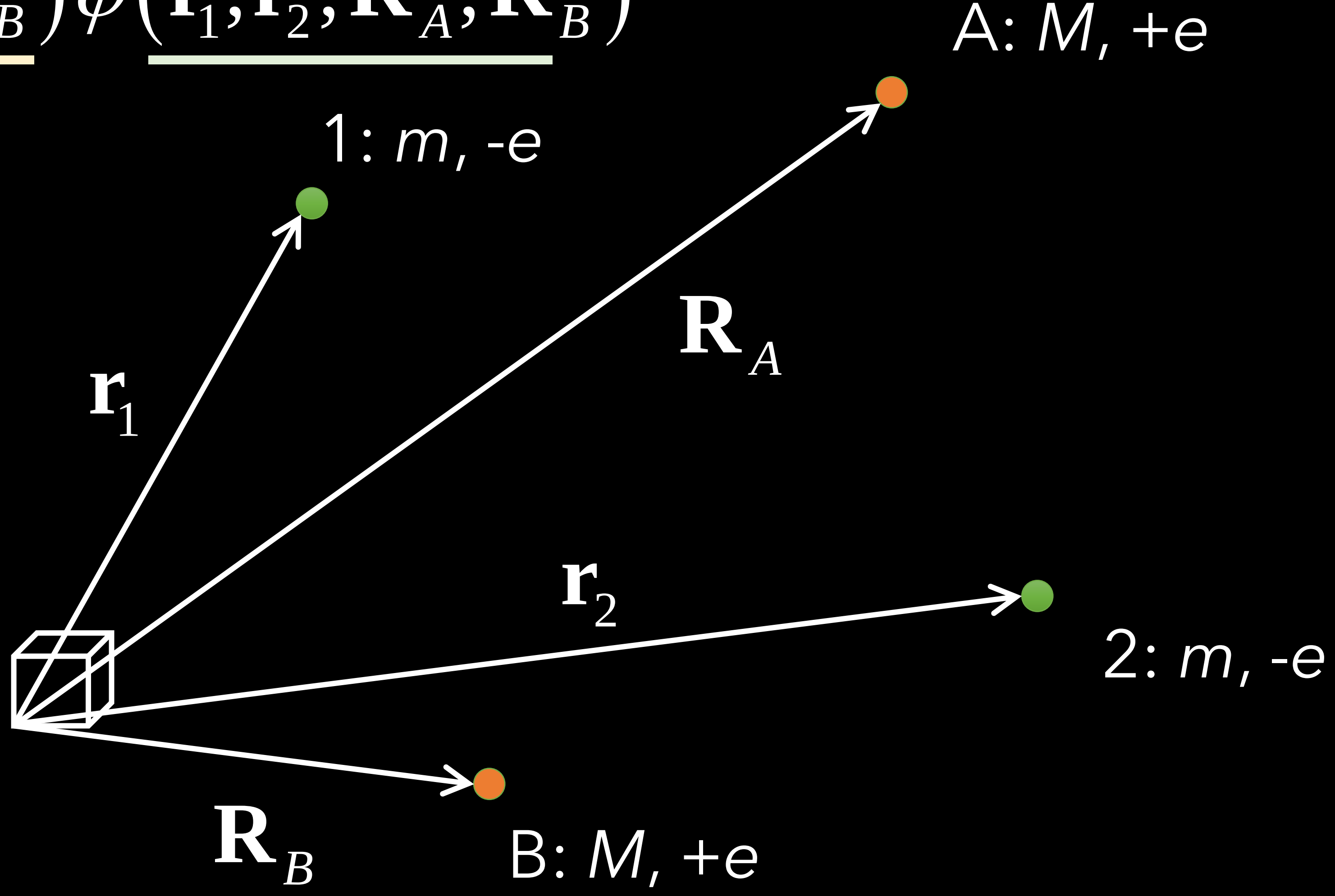
$$\mathbf{H}\Psi = \varepsilon\Psi$$

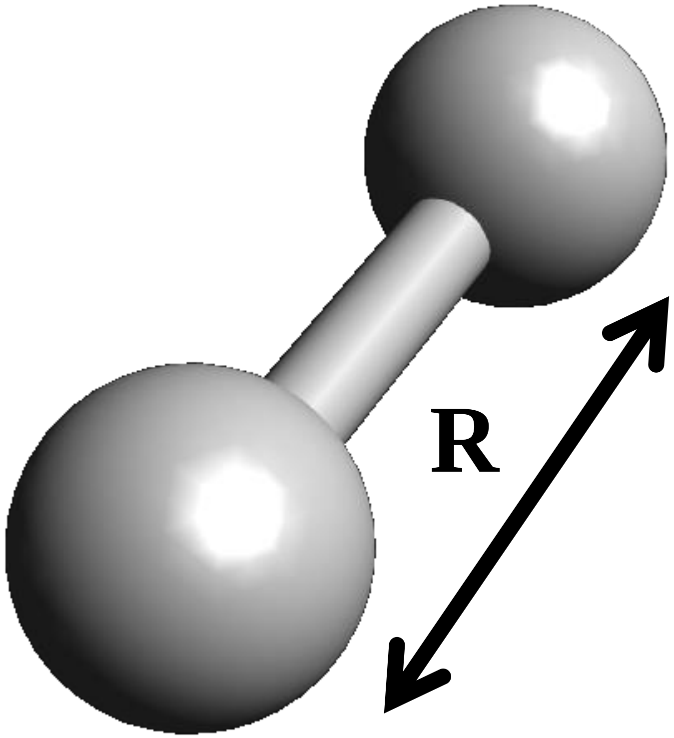


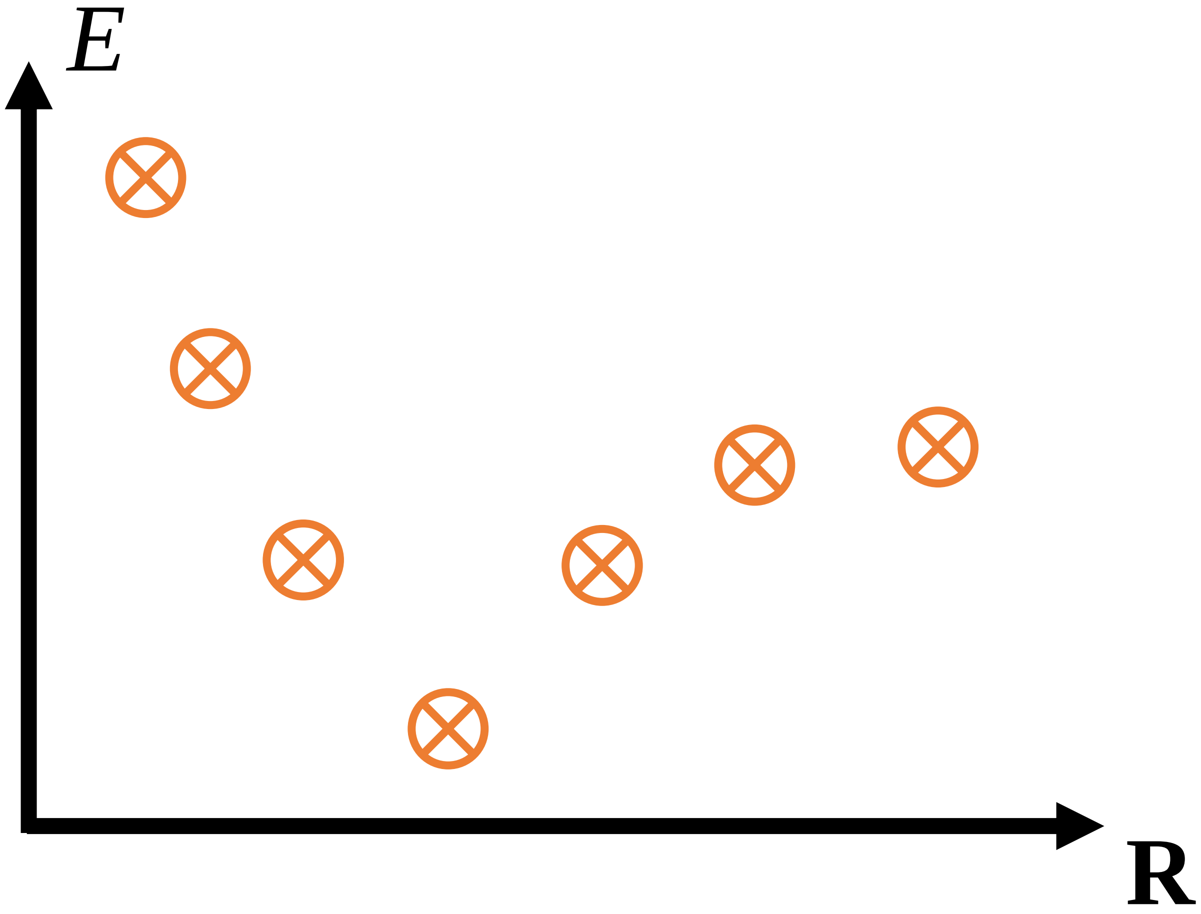

$m = 1$
$M = 1836$

$$\Psi\left(\mathbf{R}_A,\mathbf{R}_B,\mathbf{r}_1,\mathbf{r}_2\right)$$

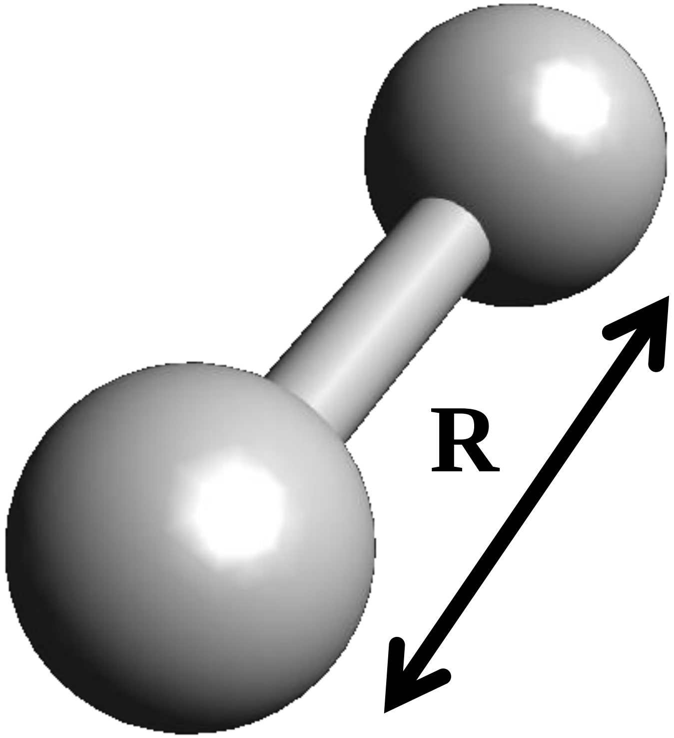
$$=\chi\underline{\left(\mathbf{R}_A,\mathbf{R}_B\right)}\varphi\underline{\left(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R}_A,\mathbf{R}_B\right)}$$

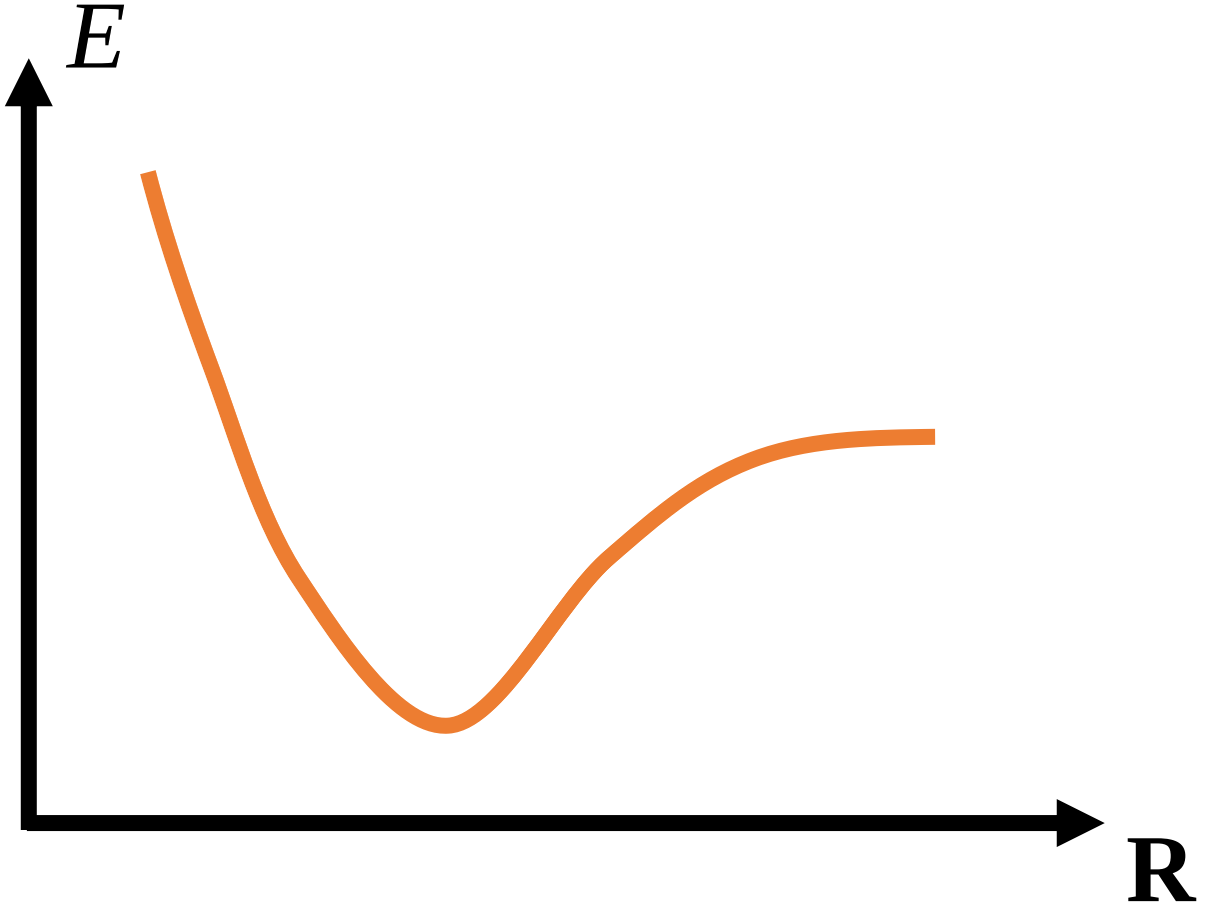






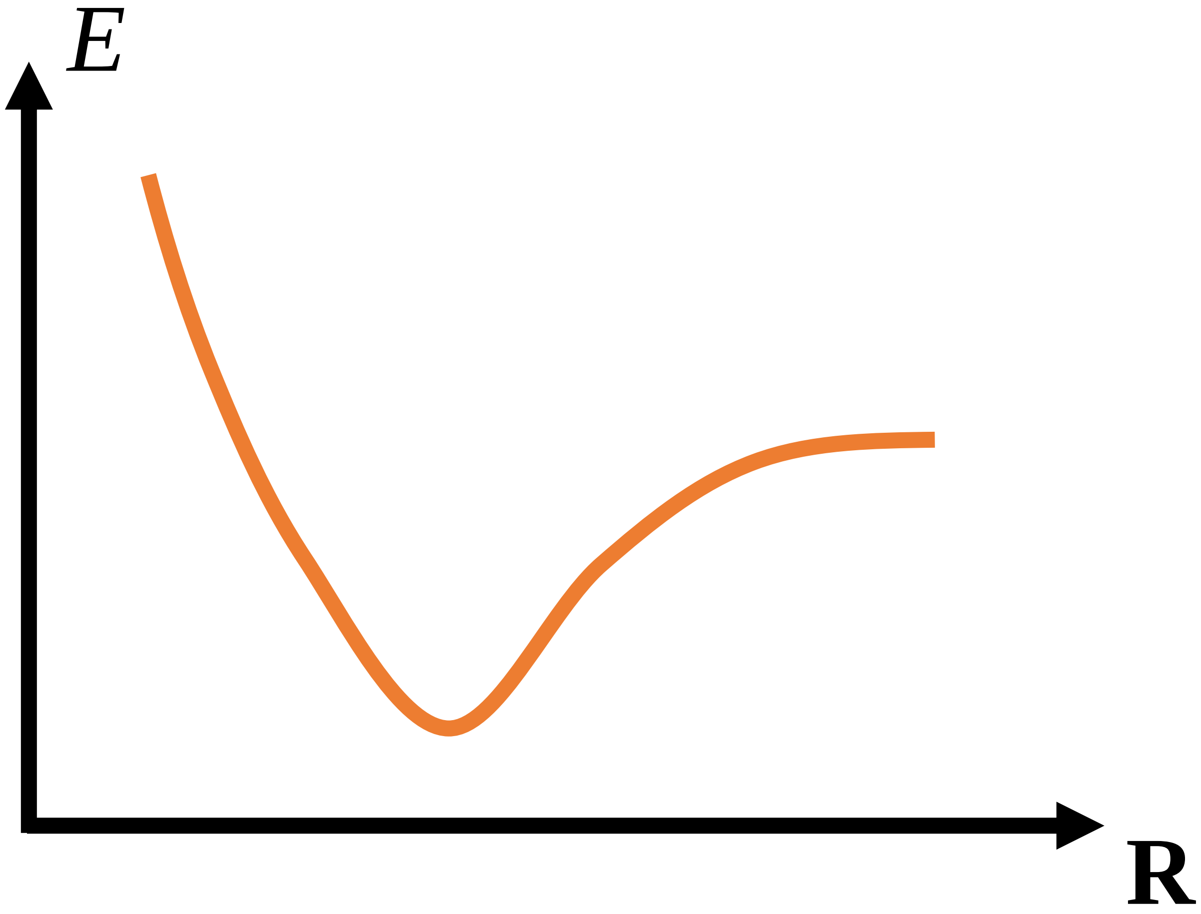
$$H_{elec}\varphi\left(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R}\right)=E\varphi\left(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R}\right)$$

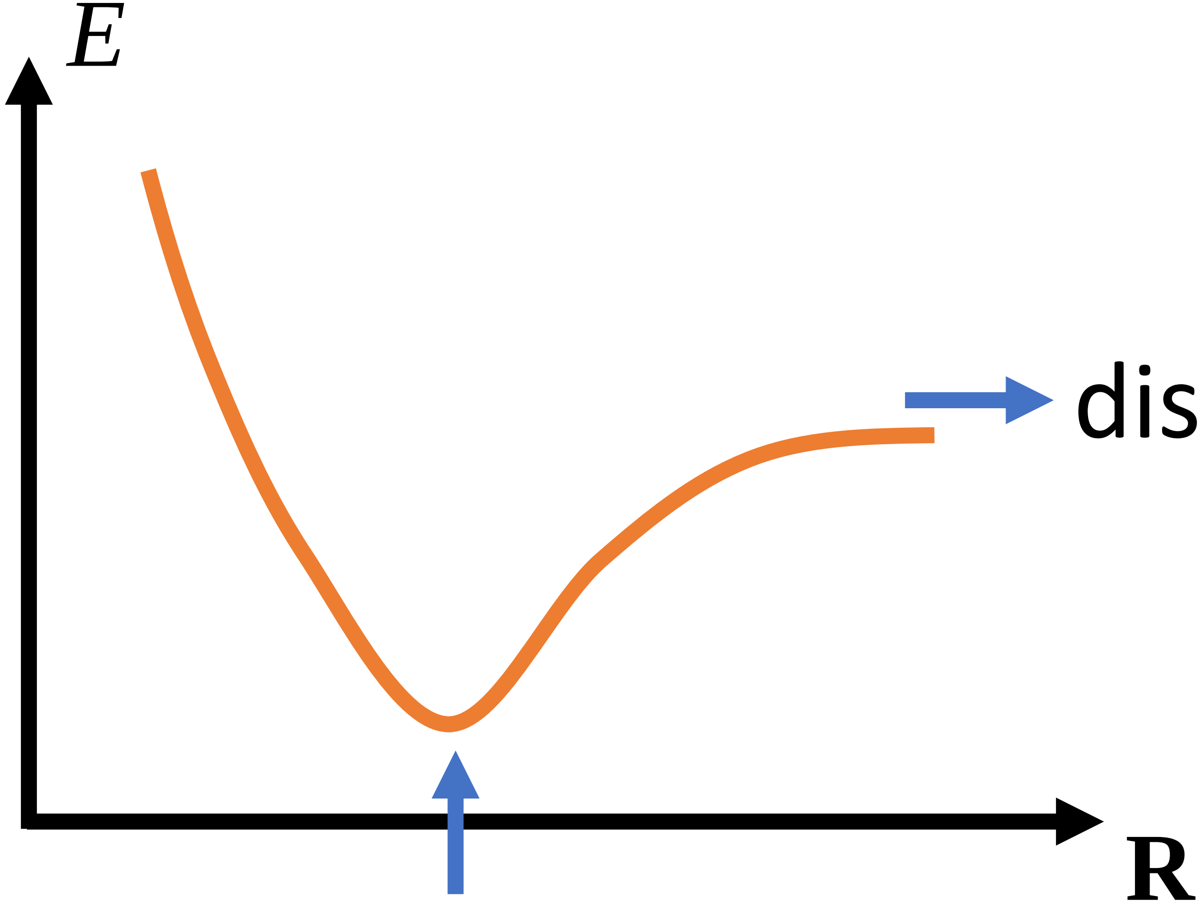




$$H_{elec}\varphi\left(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R}\right)=E\varphi\left(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R}\right)$$

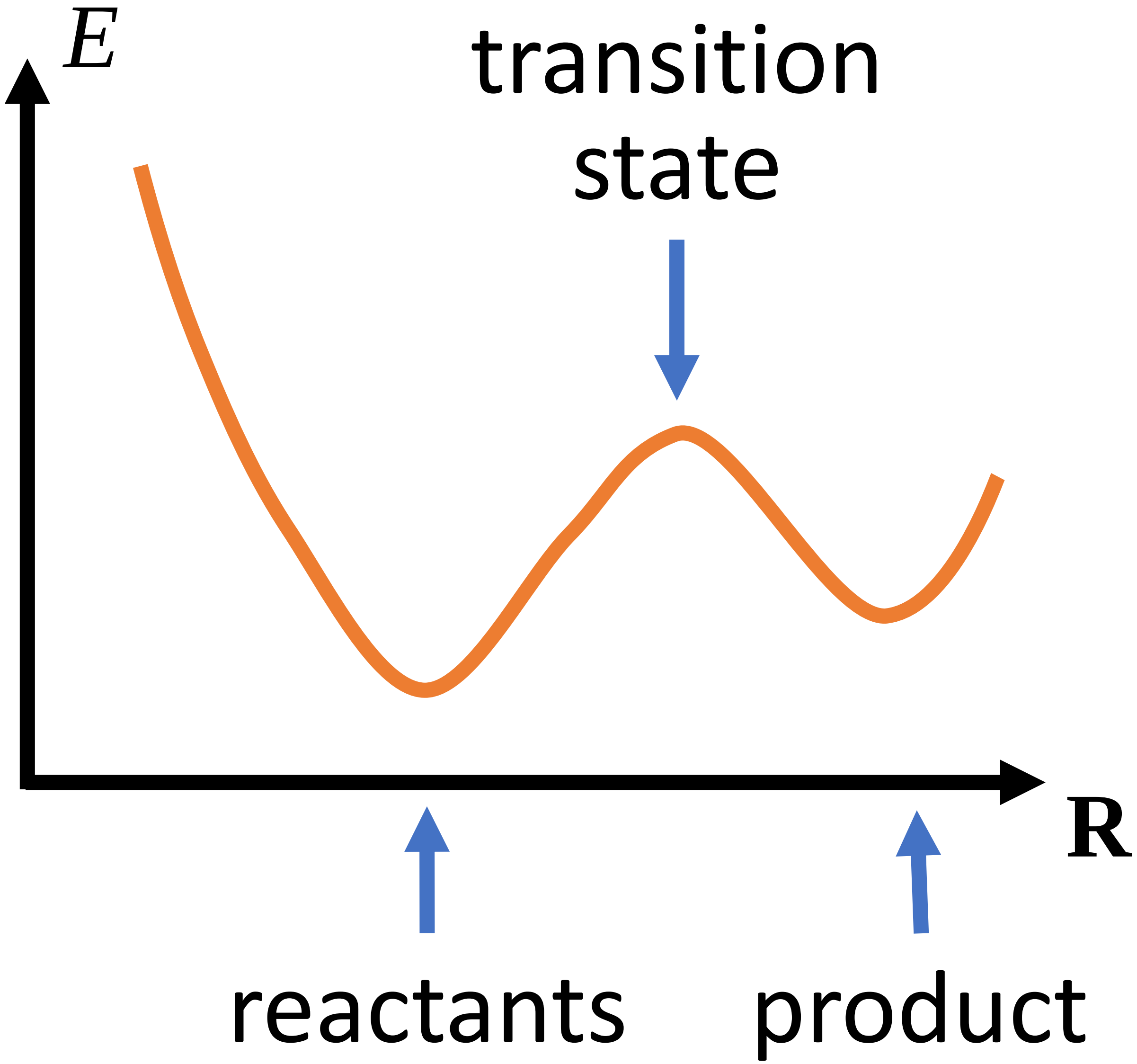
Potential energy surface





dissociation

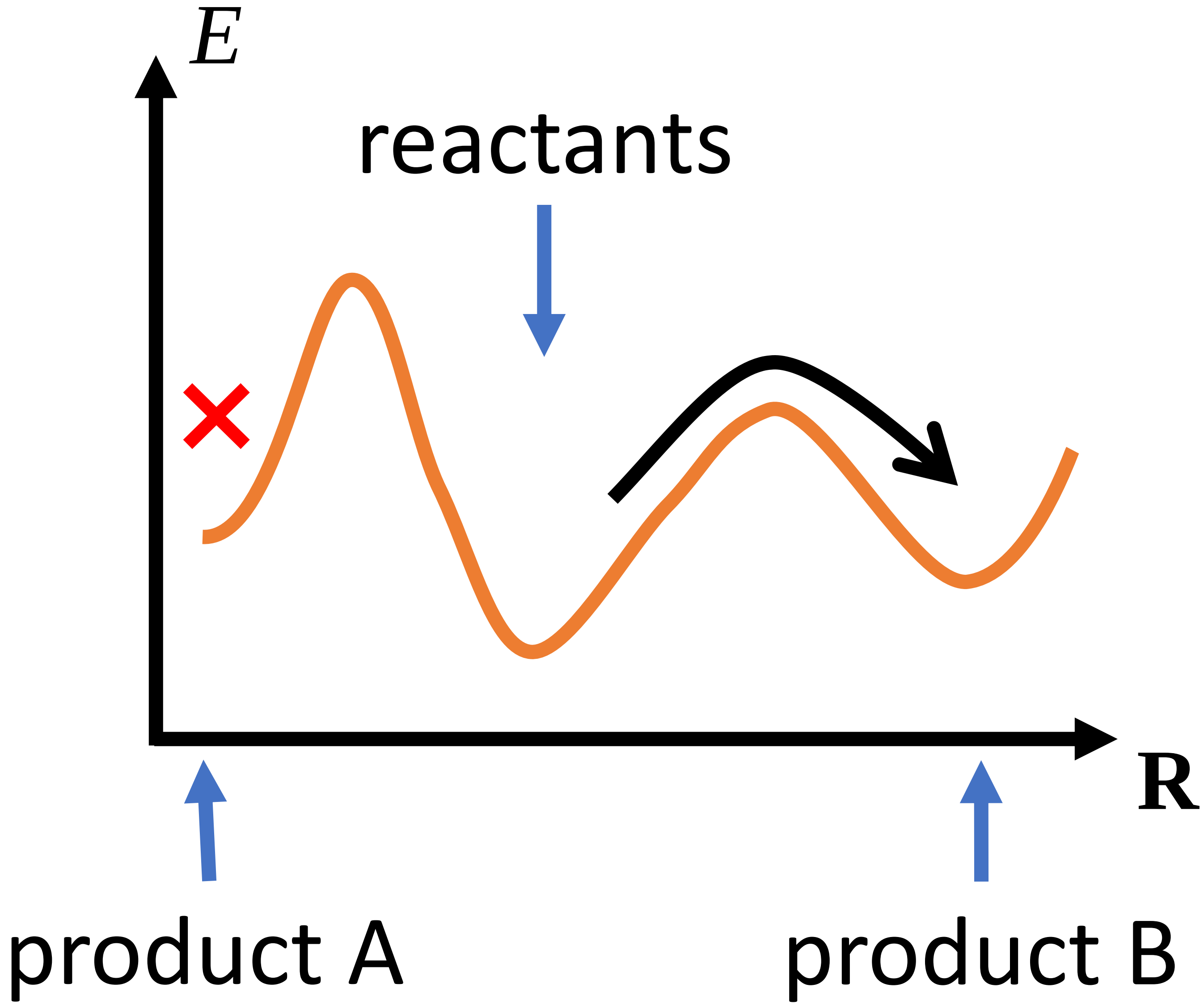
equilibrium



transition state

reactants

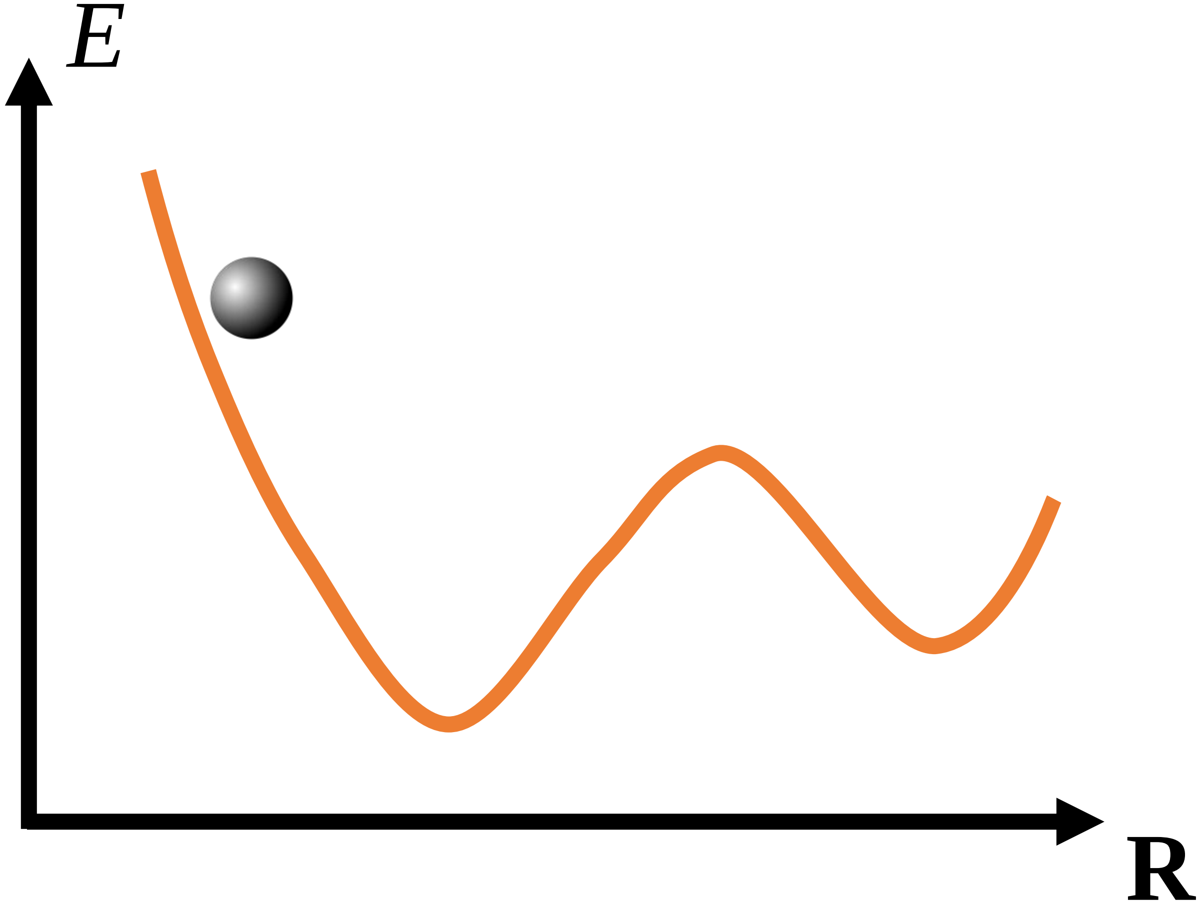
product



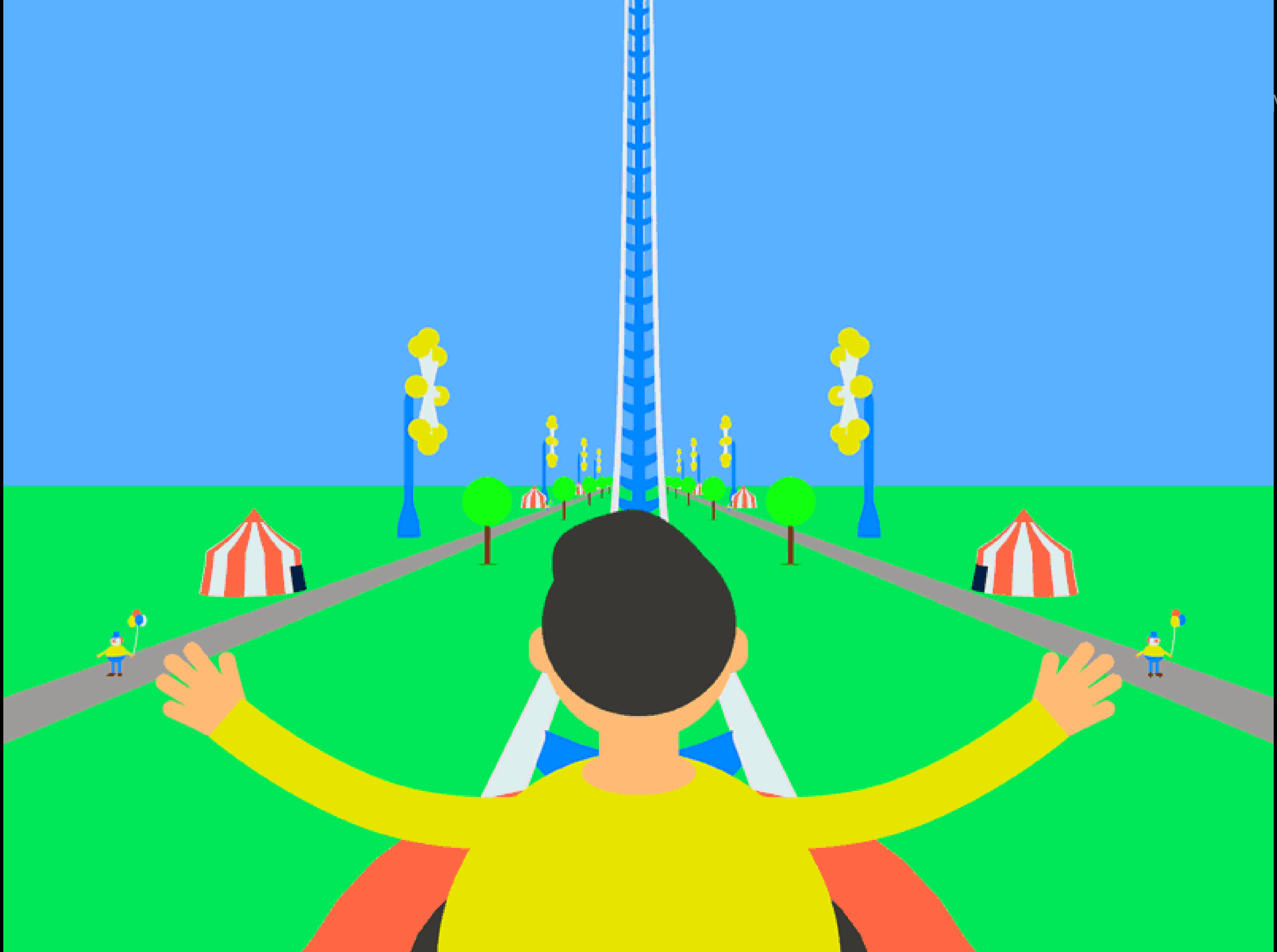
reactants

product A

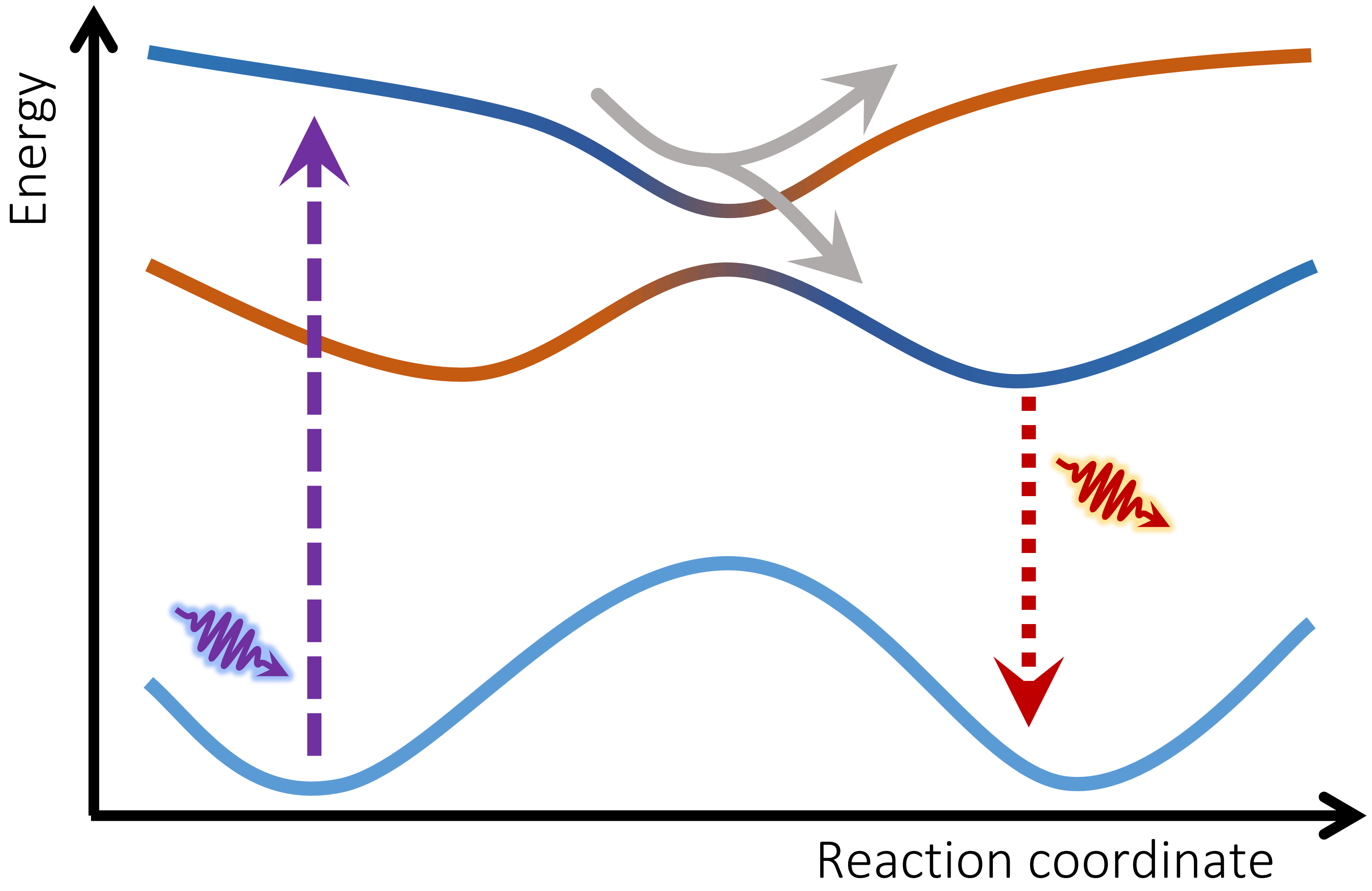
product B



E
R



LIGHT AND
MOLECULES



- EM fields (photoabsorption, stimulated emission)
- Diabatic mixing (internal conversion, intersystem crossing)
- Vacuum fluctuations (fluorescence, phosphorescence)

A math reminder

Electronic equation

$$\Psi(r,R) \qquad \hat{A}(r,R)\Psi(r,R)=b\Psi(r,R)$$

expand

$$\Psi(r,R)=\sum_n \chi_n(R)\varphi_n(r)$$

replace

$$\hat{A}(r,R)\sum_n \chi_n(R)\varphi_n(r)=b\sum_n \chi_n(R)\varphi_n(r)$$

project

$$\chi_m^*(R)\hat{A}(r,R)\sum_n \chi_n(R)\varphi_n(r)=\chi_m^*(R)b\sum_n \chi_n(R)\varphi_n(r)$$

integrate

$$\int dR\chi_m^*(R)\hat{A}(r,R)\sum_n \chi_n(R)\varphi_n(r)=b\int dR\chi_m^*(R)\sum_n \chi_n(R)\varphi_n(r)$$

group

$$\sum_n \underbrace{\left[\int dR\chi_m^*(R)\hat{A}(r,R)\chi_n(R)\right]}_{C_{mn}(r)}\varphi_n(r)=b\sum_n \underbrace{\left[\int dR\chi_m^*(R)\chi_n(R)\right]}_{D_{mn}}\varphi_n(r)$$

$$\boxed{\sum_n C_{mn}(r)\varphi_n(r)=b\sum_n D_{mn}\varphi_n(r)}$$

Electronic equation

$$\Psi(r,R) \qquad \hat{A}(r,R)\Psi(r,R) = b\Psi(r,R)$$

expand

$$\Psi(r,R) = \sum_n \chi_n(R)\varphi_n(r)$$

replace

$$\hat{A}(r,R)\sum_n \chi_n(R)\varphi_n(r) = b\sum_n \chi_n(R)\varphi_n(r)$$

project & integrate

$$\left\langle \chi_m(R)\middle|\hat{A}(r,R)\sum_n\middle|\chi_n(R)\varphi_n(r)\right\rangle_R = b\left\langle \chi_m(R)\middle|\sum_n\middle|\chi_n(R)\varphi_n(r)\right\rangle_R$$

group

$$\sum_n \underbrace{\left\langle \chi_m(R)\middle|\hat{A}(r,R)\middle|\chi_n(R)\right\rangle_R}_{C_{mn}(r)} \varphi_n(r) = b\sum_n \underbrace{\left\langle \chi_m(R)\middle|\chi_n(R)\right\rangle_R}_{D_{mn}} \varphi_n(r)$$

$$\boxed{\sum_n C_{mn}(r)\varphi_n(r) = b\sum_n D_{mn}\varphi_n(r)}$$

Try yourself to find the electronic equation!

For $\hat{A}(r,R)\Psi(r,R) = b\Psi(r,R)$ (1)

$\Psi(r,R) = \sum_n \chi_n(R)\varphi_n(r)$ (2)

show that

$$\sum_n \left\langle \chi_m(R) \middle| \hat{A}(r,R) \middle| \chi_n(R) \right\rangle_R \varphi_n(r) = b\sum_n \left\langle \chi_m(R) \middle| \chi_n(R) \right\rangle_R \varphi_n(r)$$

Hint:

- Replace Eq. (2) in (1)
- Project: multiply by $\left\langle \chi_m(R) \right|$ at left of both sides

Nuclear equation

$$\Psi(r,R) \qquad \hat{A}(r,R)\Psi(r,R)=b\Psi(r,R)$$

expand

$$\Psi(r,R)=\sum_n \chi_n(R)\varphi_n(r)$$

replace

$$\hat{A}(r,R)\sum_n \chi_n(R)\varphi_n(r)=b\sum_n \chi_n(R)\varphi_n(r)$$

project & integrate

$$\left\langle \varphi_m(r)\middle|\hat{A}(r,R)\sum_n\middle|\chi_n(R)\varphi_n(r)\right\rangle_r = b\left\langle \varphi_m(r)\middle|\sum_n\middle|\chi_n(R)\varphi_n(r)\right\rangle_r$$

group

$$\sum_n \underbrace{\left\langle \varphi_m(r)\middle|\hat{A}(r,R)\middle|\varphi_n(r)\right\rangle_r}_{E_{mn}(R)}\chi_n(R)=b\sum_n \underbrace{\left\langle \varphi_m(r)\middle|\varphi_n(r)\right\rangle_r}_{F_{mn}}\chi_n(R)$$

$$\boxed{\sum_n E_{mn}(R)\chi_n(R)=b\sum_n F_{mn}\chi_n(R)}$$

$$\hat{A}(r,R)\Psi(r,R) = b\Psi(r,R)$$

~~$\sum_n C_{mn}(r)\varphi_n(r) = b\sum_n D_{mn}\varphi_n(r)$~~

$$\sum_n E_{mn}(R)\chi_n(R) = b\sum_n F_{mn}\chi_n(R)$$

$$\Psi(r,R) = \sum_n \chi_n(R)\varphi_n(r)$$

$$b = \left\langle \Psi(r,R) \middle| \hat{A}(r,R) \middle| \Psi(r,R) \right\rangle_{r,R}$$

$$\hat{A}(r,R)\Psi(r,R)=b\Psi(r,R)$$

$$\hat{A}^{(0)}(r,R)\varphi(r;R)=\varepsilon\varphi(r;R)$$

$$\sum_n E_{mn}(R)\chi_n(R)=b\sum_n F_{mn}\chi_n(R)$$

$$\Psi(r,R)=\sum_n \chi_n(R)\varphi_n(r)$$

$$b=\left\langle \Psi(r,R)\middle|\hat{A}(r,R)\middle|\Psi(r,R)\right\rangle_{r,R}$$

The Born-Oppenheimer approximation

Field-free non-relativistic molecular problem

$$H\left(\mathbf{R},\mathbf{r}\right)\Psi^{k}\left(\mathbf{R},\mathbf{r}\right)=\varepsilon_{k}\Psi^{k}\left(\mathbf{R},\mathbf{r}\right)$$

with

$$H\left(\mathbf{R},\mathbf{r}\right)=T_{nuc}\left(\mathbf{R}\right)+T_{elec}\left(\mathbf{r}\right)+V\left(\mathbf{r},\mathbf{R}\right)$$

Born-Huang wave function

$$\Psi_{k}\left(\mathbf{R},\mathbf{r}\right)=\sum_{nj}c_{nj}^{k}\varphi_{n}\left(\mathbf{r};\mathbf{R}\right)\chi_{nj}\left(\mathbf{R}\right)$$

$$\begin{aligned}\Psi_{k}\left(\mathbf{R},\mathbf{r}\right)&=\sum_{n}\varphi_{n}\left(\mathbf{r};\mathbf{R}\right)\left(\sum_{j}c_{nj}^{k}\chi_{nj}\left(\mathbf{R}\right)\right)\\&=\sum_{n}\varphi_{n}\left(\mathbf{r};\mathbf{R}\right)h_{n}^{k}\left(\mathbf{R}\right)\end{aligned}$$

Solving the **electronic** part

$$\Psi_k\left(\mathbf{R},\mathbf{r}\right)=\sum_n \varphi_n\left(\mathbf{r};\mathbf{R}\right)h_n^k\left(\mathbf{R}\right)$$

$$\left(T_{elec}\left(\mathbf{r}\right)+V\left(\mathbf{r},\mathbf{R}\right)\right)\varphi_n\left(\mathbf{r};\mathbf{R}\right)=E_n\left(\mathbf{R}\right)\varphi_n\left(\mathbf{r};\mathbf{R}\right)$$

Solving the **nuclear** part

$$H\left(\mathbf{R},\mathbf{r}\right)\Psi^k\left(\mathbf{R},\mathbf{r}\right)=\varepsilon_k\Psi^k\left(\mathbf{R},\mathbf{r}\right)$$

with

$$H=T_{nuc}\left(\mathbf{R}\right)+T_{elec}\left(\mathbf{r}\right)+V\left(\mathbf{r},\mathbf{R}\right)$$

$$\Psi^k\left(\mathbf{R},\mathbf{r}\right)=\sum_n\varphi_n\left(\mathbf{r};\mathbf{R}\right)h_n^k\left(\mathbf{R}\right)$$

$$\left(T_{nuc}\left(\mathbf{R}\right)+T_{elec}\left(\mathbf{r}\right)+V\left(\mathbf{r},\mathbf{R}\right)\right)\left(\sum_n\varphi_n\left(\mathbf{r};\mathbf{R}\right)h_n^k\left(\mathbf{R}\right)\right)=\varepsilon_k\left(\sum_n\varphi_n\left(\mathbf{r};\mathbf{R}\right)h_n^k\left(\mathbf{R}\right)\right)$$

$$\left(T_{nuc}\left(\mathbf{R}\right)+T_{elec}\left(\mathbf{r}\right)+V\left(\mathbf{r},\mathbf{R}\right)\right)\left(\sum_n \varphi_n\left(\mathbf{r};\mathbf{R}\right)h_n^k\left(\mathbf{R}\right)\right)=\varepsilon_k\left(\sum_n \varphi_n\left(\mathbf{r};\mathbf{R}\right)h_n^k\left(\mathbf{R}\right)\right)$$

Working on the left-side term

$$T_{nuc}\left(\sum_n \varphi_n h_n^k\right)+\left(T_{elec}+V\right)\left(\sum_n \varphi_n h_n^k\right)=$$

$$-\frac{\hbar^2}{2\mathbf{M}}\nabla_{\mathbf{R}}^2\left(\sum_n \varphi_n h_n^k\right)+\sum_n E_n\varphi_n h_n^k$$

$$\boxed{\frac{1}{\mathbf{M}}f\left(\mathbf{R}\right)\rightarrow\sum_\alpha \frac{1}{M_\alpha}f\left(\mathbf{R}_\alpha\right)}$$

$$-\frac{\hbar^2}{2\mathbf{M}}\nabla^2_{\mathbf{R}}\left(\sum_n \varphi_n(\mathbf{r};\mathbf{R})h_n^k(\mathbf{R})\right)+\sum_n E_n\varphi_n h_n^k=\varepsilon_k\left(\sum_n \varphi_n h_n^k\right)$$

Expanding the blue term

$$-\frac{\hbar^2}{2\mathbf{M}}\nabla^2_{\mathbf{R}}\left(\sum_n \varphi_n h_n^k\right)=$$

$$-\frac{\hbar^2}{2\mathbf{M}}\sum_n\left[\left(\nabla^2_{\mathbf{R}}\varphi_n\right)h_n^k+2\nabla_{\mathbf{R}}\varphi_n\cdot\nabla_{\mathbf{R}}h_n^k+\varphi_n\nabla^2_{\mathbf{R}}h_n^k\right]$$

$$-\frac{\hbar^2}{2\mathbf{M}}\sum_n\left[\left(\nabla^2_{\mathbf{R}}\varphi_n\right)h_n^k+2\nabla_{\mathbf{R}}\varphi_n\cdot\nabla_{\mathbf{R}}h_n^k+\varphi_n\nabla^2_{\mathbf{R}}h_n^k\right]$$

$$+\sum_n E_n\varphi_n h_n^k=\varepsilon_k\left(\sum_n\varphi_n h_n^k\right)$$

Projecting on n′

$$-\left\langle\varphi_{n'}\middle|\frac{\hbar^2}{2\mathbf{M}}\sum_n\left[\left(\nabla^2_{\mathbf{R}}\varphi_n\right)h_n^k+2\nabla_{\mathbf{R}}\varphi_n\cdot\nabla_{\mathbf{R}}h_n^k+\varphi_n\nabla^2_{\mathbf{R}}h_n^k\right]\right\rangle_{\mathbf{r}}$$

$$+\left\langle\varphi_{n'}\middle|\sum_n E_n\varphi_n h_n^k\right\rangle_{\mathbf{r}}=\left\langle\varphi_{n'}\middle|\varepsilon_k\left(\sum_n\varphi_n h_n^k\right)\right\rangle_{\mathbf{r}}$$

$$-\left\langle \varphi_{n'} \middle| \frac{\hbar^2}{2\mathbf{M}} \sum_n \left[\left(\nabla_{\mathbf{R}}^2 \varphi_n \right) h_n^k + 2\nabla_{\mathbf{R}} \varphi_n \cdot \nabla_{\mathbf{R}} h_n^k + \varphi_n \nabla_{\mathbf{R}}^2 h_n^k \right] \right\rangle_{\mathbf{r}}$$

$$+\left\langle \varphi_{n'} \middle| \sum_n E_n \varphi_n h_n^k \right\rangle_{\mathbf{r}} = \left\langle \varphi_{n'} \middle| \varepsilon_k \left(\sum_n \varphi_n h_n^k \right) \right\rangle_{\mathbf{r}}$$

Using orthonormality

$$\left\langle \varphi_{n'} \middle| \varphi_n \right\rangle_{\mathbf{r}} = \delta_{nn'}$$

$$-\frac{\hbar^2}{2\mathbf{M}} \sum_n \left[\left\langle \varphi_{n'} \middle| \nabla_{\mathbf{R}}^2 \varphi_n \right\rangle_{\mathbf{r}} h_n^k + 2 \left\langle \varphi_{n'} \middle| \nabla_{\mathbf{R}} \varphi_n \right\rangle_{\mathbf{r}} \cdot \nabla_{\mathbf{R}} h_n^k \right]$$

$$-\frac{\hbar^2}{2\mathbf{M}} \nabla_{\mathbf{R}}^2 h_{n'}^k + E_{n'} h_{n'}^k = \varepsilon_k h_{n'}^k$$

Time-independent Born-Huang formulation

$$H_{n'}h_{n'}^{k}-\varepsilon_k h_{n'}^{k}+\sum_n N_{n'n}=0$$

$$H_{n'}=-\frac{\hbar^2}{2\mathbf{M}}\nabla_{\mathbf{R}}^2+E_{n'}$$

$$N_{n'n}=-\frac{\hbar^2}{2\mathbf{M}}\left[\left\langle\varphi_{n'}\middle|\nabla_{\mathbf{R}}^2\varphi_n\right\rangle_{\mathbf{r}}h_n^k+2\left\langle\varphi_{n'}\middle|\nabla_{\mathbf{R}}\varphi_n\right\rangle_{\mathbf{r}}\cdot\nabla_{\mathbf{R}}h_n^k\right]$$

$$\begin{pmatrix} H_1(\mathbf{R})-\varepsilon_k & N_{12}(\mathbf{R}) & N_{13}(\mathbf{R}) & \cdots \\ N_{21}(\mathbf{R}) & H_2(\mathbf{R})-\varepsilon_k & N_{23}(\mathbf{R}) & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{pmatrix}\begin{pmatrix} h_1^k(\mathbf{R}) \\ h_2^k(\mathbf{R}) \\ h_3^k(\mathbf{R}) \\ \vdots \end{pmatrix}=\begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \end{pmatrix}$$

Adiabatic approximation

$$\boxed{N_{n'n}(\mathbf{R}) = 0}$$

$$\begin{pmatrix} H_1(\mathbf{R}) - \varepsilon_k & 0 & 0 & \cdots \\ 0 & H_2(\mathbf{R}) - \varepsilon_k & 0 & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{pmatrix} \begin{pmatrix} h_1^k(\mathbf{R}) \\ h_2^k(\mathbf{R}) \\ h_3^k(\mathbf{R}) \\ \vdots \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \end{pmatrix}$$

$$H_n(\mathbf{R}) h_n^k(\mathbf{R}) - \varepsilon_k h_n^k(\mathbf{R}) = 0$$

$$-\frac{\hbar^2}{2\mathbf{M}} \nabla_{\mathbf{R}}^2 h_n^k(\mathbf{R}) + E_n(\mathbf{R}) h_n^k(\mathbf{R}) = \varepsilon_k h_n^k(\mathbf{R})$$

$$-\frac{\hbar^2}{2\mathbf{M}}\nabla^2_{\mathbf{R}}h_n^k\left(\mathbf{R}\right)+E_n\left(\mathbf{R}\right)h_n^k\left(\mathbf{R}\right)=\varepsilon_k h_n^k\left(\mathbf{R}\right)$$

$$h_n^k\left(\mathbf{R}\right)=\sum_j c_{nj}^k\chi_{nj}\left(\mathbf{R}\right)$$

Returning to χ

$$-\frac{\hbar^2}{2\mathbf{M}}\nabla^2_{\mathbf{R}}\left(\sum_j c_{nj}^k\chi_{nj}\left(\mathbf{R}\right)\right)+E_n\left(\mathbf{R}\right)\left(\sum_j c_{nj}^k\chi_{nj}\left(\mathbf{R}\right)\right)=\varepsilon_k\left(\sum_j c_{nj}^k\chi_{nj}\left(\mathbf{R}\right)\right)$$

$$-\frac{\hbar^2}{2\mathbf{M}}\nabla^2_{\mathbf{R}}c_{nj}^k\chi_{nj}\left(\mathbf{R}\right)+E_n\left(\mathbf{R}\right)c_{nj}^k\chi_{nj}\left(\mathbf{R}\right)=\varepsilon_k c_{nj}^k\chi_{nj}\left(\mathbf{R}\right)$$

$$-\frac{\hbar^2}{2\mathbf{M}}\nabla^2_{\mathbf{R}}\chi_{nj}\left(\mathbf{R}\right)+E_n\left(\mathbf{R}\right)\chi_{nj}\left(\mathbf{R}\right)=\varepsilon_{nj}\chi_{nj}\left(\mathbf{R}\right)$$

Time-independent BO adiabatic formulation

Nuclear Schrödinger equation

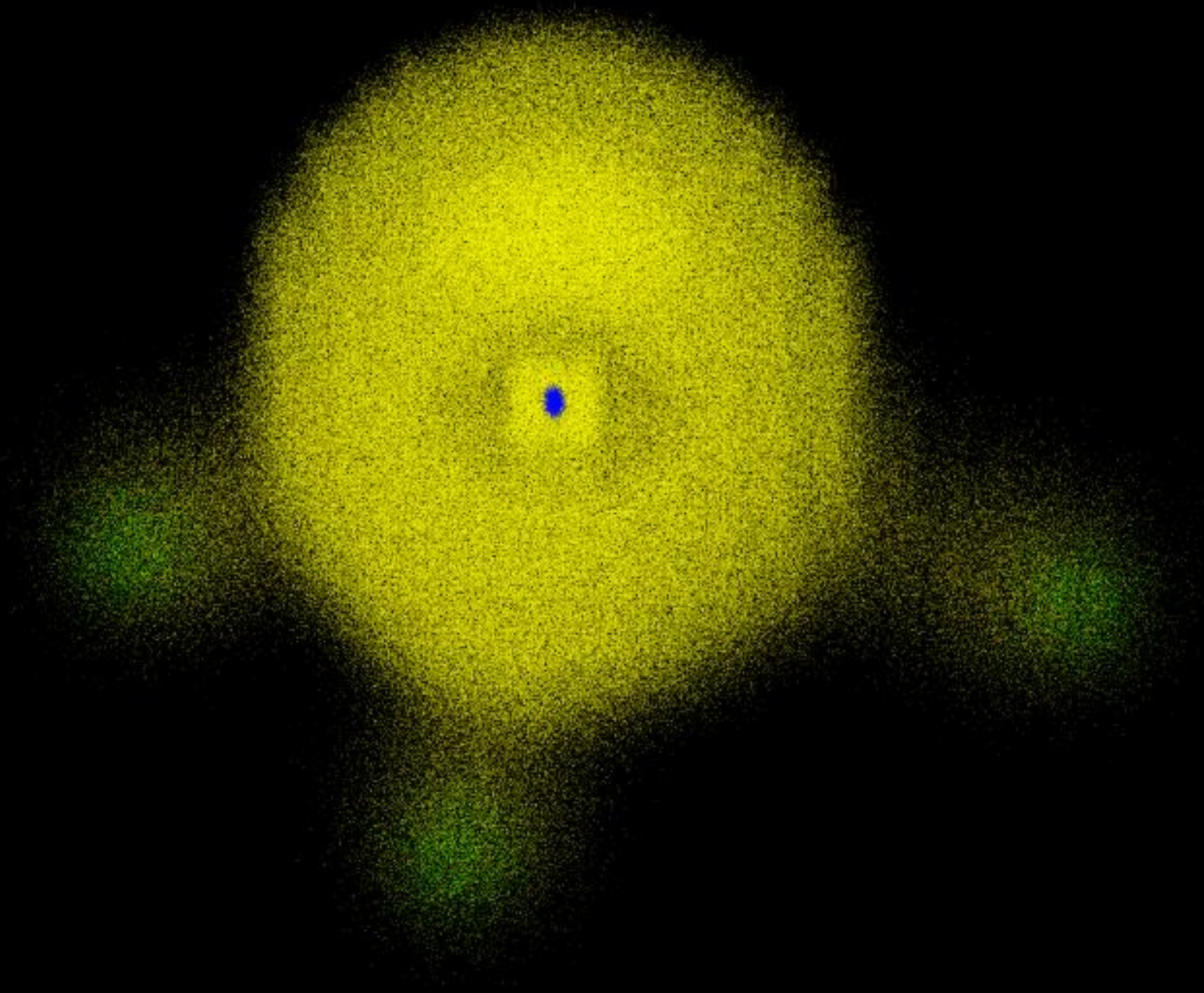
$$\left(T_{nuc}(\mathbf{R})+E_n(\mathbf{R})\right)\chi_{nj}(\mathbf{R})=\varepsilon_{nj}\chi_{nj}(\mathbf{R})$$

Electronic Schrödinger equation

$$\left(T_{elec}(\mathbf{r})+V(\mathbf{r},\mathbf{R})\right)\varphi_n(\mathbf{r};\mathbf{R})=E_n(\mathbf{R})\varphi_n(\mathbf{r};\mathbf{R})$$

BO molecular wave function

$$\Psi_{nj}^{BO}(\mathbf{R},\mathbf{r})=\varphi_n(\mathbf{r};\mathbf{R})\chi_{nj}(\mathbf{R})$$



To know more:

Wave functions and the Schrödinger equation
- McQuarrie; Simon, *Physical chemistry*. **1997**. Ch 3

BO approximation

A math reminder:
- Szabo; Ostlund, *Modern quantum chemistry*. **1989**. Ch 1

The BO approximation
- Eric J Heller, *The semiclassical way*, **2018**. Ch 16

Available for download at:
amubox.univ-amu.fr/s/xXAiMZrDPb9RMRX
The password will be given in class.