

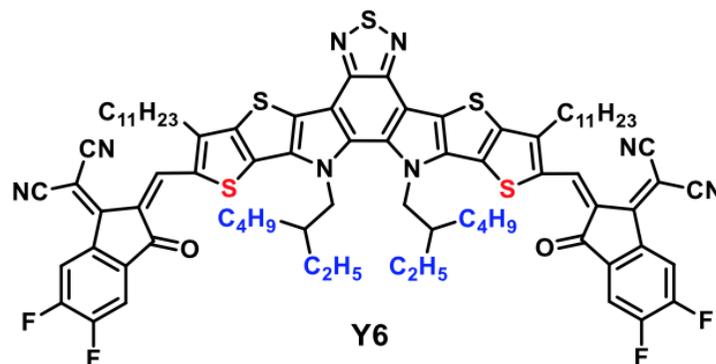
# Overview

## “From Statics to Dynamics: Let’s Make the Atoms Move”

- Born-Oppenheimer approximation
- Classical approximation of nuclear motion
- Molecular Dynamics
- Time Stepping Algorithms
- DFT-based Born-Oppenheimer molecular dynamics
- Hellmann-Feynman Theorem
- Ensembles and Thermostats
- Property calculation

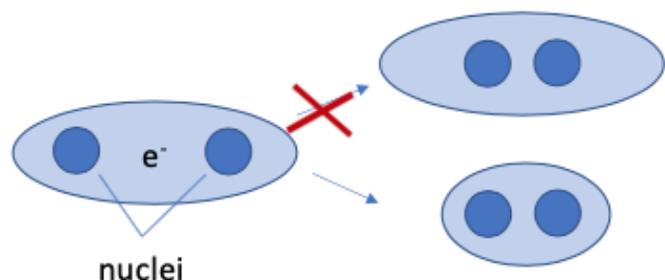
## Born-Oppenheimer (BO) approximation - preliminary considerations

When we draw a molecule we usually indicate the positions of the nuclei but not the ones of the electrons. Why?



We usually think of electrons zipping around nuclei, not the other way round. Why is that?

There is an intuitive answer: nuclei are heavy, electrons are light, therefore electrons are faster than nuclei and will “instantly” adjust to nuclear motion.



Hence, the position of the nuclei determine where the electrons are and we only need to draw nuclei, not electrons.

## Schrödinger equation of interacting electrons and nuclei

Consider the stationary Schrödinger equation of the full coupled nuclear-electronic problem of a molecule comprised of  $M$  electrons and  $N$  nuclei:

$$\hat{H}\Psi(\mathbf{R}, \mathbf{r}) = E_{\text{tot}}\Psi(\mathbf{R}, \mathbf{r}) \quad (1)$$

$$\hat{H} = \hat{T}_n(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + V_{en}(\mathbf{R}, \mathbf{r}) + V_{ee}(\mathbf{r}) + V_{nn}(\mathbf{R}) \quad (2)$$

$\mathbf{R}$  all nuclear coordinates,  $3N$ -dimensional vector

$\mathbf{r}$  all electronic coordinates,  $3M$ -dimensional vector (omitting spin)

$M_I$  mass of nucleus  $I$

$m$  mass of electron

$\hat{T}_n = \sum_I -\frac{1}{2M_I} \nabla_{\mathbf{R}_I}^2$  kinetic energy of nuclei

$\hat{T}_e = \sum_i -\frac{1}{2m} \nabla_{\mathbf{r}_i}^2$  kinetic energy of electrons

$V_{en}, V_{ee}, V_{nn}$  the usual Coulomb interactions between electron-nuclei ( $en$ ), electron-electron ( $ee$ ) and nuclei-nuclei ( $nn$ ).

$\Psi(\mathbf{R}, \mathbf{r})$  total electron-nuclear wavefunction

*How does the picture of electrons tracking nuclear motion arise from this equation?*

Not obvious! The **BO approximation** leads to this picture.

## BO approximation - the physical picture

BO approximation:

The total wave function of electrons and nuclei is assumed separable into a nuclear wavefunction that depends only upon the nuclear coordinates and an electronic part that depends on the electronic coordinates, but only parametrically on the nuclear coordinates.

$$\Psi(\mathbf{R}, \mathbf{r}) = \Psi_{\mathbf{R}}(\mathbf{r})\Phi(\mathbf{R}) \quad (3)$$

$\Psi(\mathbf{R}, \mathbf{r})$  total electron-nuclear wavefunction

$\Psi_{\mathbf{R}}(\mathbf{r})$  electronic wavefunction

$\Phi(\mathbf{R})$  nuclear wavefunction

As we show below, inserting the product Eq. 3 in the SE Eq. 1 and assuming  $M_I \gg m$ , one obtains a “simple” Schrödinger for the nuclei only:

$$[\hat{T}_n(\mathbf{R}) + E_{\mathbf{R}}]\Phi(\mathbf{R}) = E_{\text{tot}}\Phi(\mathbf{R}). \quad (4)$$

$\hat{T}_n$  the kinetic energy operator for the nuclei

$E_{\mathbf{R}}$  the potential energy (hyper) surface

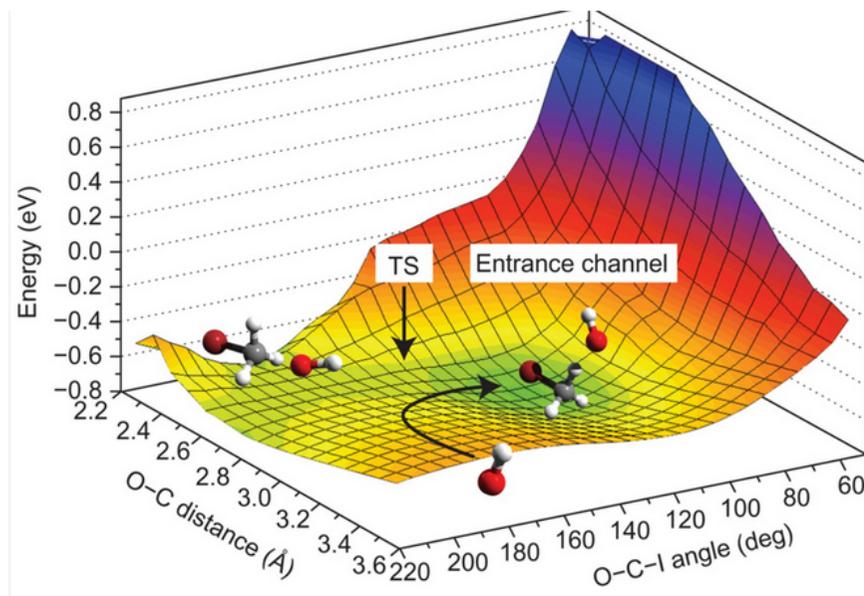
$E_{\text{tot}}$  the total (electronic + nuclear) energy

Notice, all electronic terms in the full SE 1 (electronic kinetic energy, electron-electron energy, electron-nuclear energy), the nuclear-nuclear energy as well as the electronic wavefunction are “condensed” into a single, scalar energy term, the potential energy hyper surface, or short, the **potential energy surface (PES)**,  $E_{\mathbf{R}}$ .

$E_{\mathbf{R}}$  is a complicated multidimensional scalar function that depends on all  $3N$  nuclear coordinates:

$$E_{\mathbf{R}} = E(\mathbf{R}) \quad (5)$$

All nuclear motion (vibrations, chemical reactions etc) occur on the PES:



In the BO approximation, Eq. 4, the electronic wavefunction no longer appears explicitly, only the nuclear wavefunction does giving some rationale why we only indicate nuclear positions when drawing molecular structures.

It is straightforward to formally define the conditions required to arrive at the SE in the BO approximation, Eq. 4, from Eq. 1.

It is much more difficult to justify these conditions mathematically!

It is indeed an empirical observation that the BO approximation is a very good approximation in many situations - not in all.

Exceptions where BO approximation breaks down:

- photo-excited molecule/material
- very high temperatures
- (near) degeneracy of electronic states,.....

## BO approximation - outline of derivation

1. Expand total wavefunction in product of electronic and nuclear wavefunctions (**Born Ansatz**, exact):

$$\Psi(\mathbf{R}, \mathbf{r}) = \sum_i \Psi_{\mathbf{R}}^i(\mathbf{r}) \Phi^i(\mathbf{R}), \quad (6)$$

where  $\Psi_{\mathbf{R}}^i(\mathbf{r})$  are solutions of the electronic Schrödinger equation for a fixed set of nuclear coordinates  $\mathbf{R}$ :

$$[\hat{T}_e(\mathbf{r}) + V_{en}(\mathbf{R}, \mathbf{r}) + V_{ee}(\mathbf{r}) + V_{nn}(\mathbf{R})] \Psi_{\mathbf{R}}^i(\mathbf{r}) = E_{\mathbf{R}}^i \Psi_{\mathbf{R}}^i(\mathbf{r}). \quad (7)$$

Note that  $\Psi_{\mathbf{R}}^i$  and the corresponding eigenvalues  $E_{\mathbf{R}}^i$  depend parametrically on the nuclear positions which is indicated by the subscript  $\mathbf{R}$ .

2. **Neglect all electronic excitations in the expansion Eq. 6 (Approx. 1)**

$$\Psi(\mathbf{R}, \mathbf{r}) = \Psi_{\mathbf{R}}^0(\mathbf{r}) \Phi^0(\mathbf{R}) \quad (8)$$

$\Psi_{\mathbf{R}}^0$  electronic ground state wavefunction with energy  $E_{\mathbf{R}}^0$   
 $\Phi^0(\mathbf{R})$  nuclear wavefunction on the electronic groundstate.

We drop the superscript “0” in the following.

Insertion of Eq. 8 in Eq. 1 gives:

$$(\hat{T}_n + \hat{T}_e + V_{en} + V_{ee} + V_{nn})\Psi_{\mathbf{R}}\Phi(\mathbf{R}) = E_{tot}\Psi_{\mathbf{R}}\Phi(\mathbf{R}) \quad (9)$$

### 3. Mass difference - neglect nuclear derivative of electronic wavefunction (Approx. 2)

Consider action of nuclear and electronic kinetic energy operators:

$$(\hat{T}_n + \hat{T}_e)\Psi_{\mathbf{R}}\Phi(\mathbf{R}) = \Phi(\mathbf{R})\hat{T}_n\Psi_{\mathbf{R}} + \Psi_{\mathbf{R}}\hat{T}_n\Phi(\mathbf{R}) + \Phi(\mathbf{R})\hat{T}_e\Psi_{\mathbf{R}} \quad (10)$$

Remember,  $\hat{T}_n = \sum_I -\frac{1}{2M_I}\nabla_{\mathbf{R}_I}^2$  and  $\hat{T}_e = \sum_i -\frac{1}{2m}\nabla_{\mathbf{r}_i}^2$ . The difference in mass between nuclei and electrons,  $M_I \gg m$ , implies that

$$\hat{T}_n(\mathbf{R})\Psi_{\mathbf{R}}(\mathbf{r}) \ll \hat{T}_e(\mathbf{r})\Psi_{\mathbf{R}}(\mathbf{r}) \quad (11)$$

could be a good approximation.

In the BO approximation one neglects the action of  $\hat{T}_n$  on  $\Psi_{\mathbf{R}}$  altogether:

$$\mathbf{T}_n(\mathbf{R})\Psi_{\mathbf{R}}(\mathbf{r}) = 0 \quad (12)$$

4. Some final algebraic manipulations....

Inserting the approximation Eq. 12 and the electronic SE Eq. 9 in Eq. 1 one obtains the stationary SE of coupled electrons and nuclei in the Born-Oppenheimer approximation,

$$[\hat{T}_n(\mathbf{R}) + E_{\mathbf{R}}]\Phi(\mathbf{R}) = E_{\text{tot}}\Phi(\mathbf{R}). \quad (13)$$

The above arguments imply that the BO-approximation is exact in the limit of infinitely heavy nuclei, but it is usually a good approximation for physically relevant systems in the electronic ground state as a consequence of the large proton to electron mass ratio. See above for situations where the BO approximation breaks down.