Physics of Condensed Matter I

1100-4INZ`PC

Chemical bonding and molecules

Faculty of Physics UW

Jacek.Szczytko@fuw.edu.pl

inżynieria nanostruktur

Born Oppenheimer approximation

Full non-relativistic Hamiltonian of the nuclei and electrons:

$$H(\vec{r},\vec{R})\Psi(\vec{r},\vec{R}) = E\Psi(\vec{r},\vec{R})$$

$$H(\vec{r},\vec{R}) = \cdots$$

$m, \vec{r}_i, i$ – electrons
$M_N, \vec{R}_N, Z_N$ - nuclei

Coordinates of electrons subsystem and nuclei subsystem (ions) are mixed, separation of electronic and nuclear variables is impossible.

One should use the Born-Oppenheimer adiabatic approximation

Chemical bonding and molecules

Born Oppenheimer approximation

Full non-relativistic Hamiltonian of the nuclei and electrons:

$$H(\vec{r},\vec{R})\Psi(\vec{r},\vec{R}) = E\Psi(\vec{r},\vec{R})$$

$$\begin{aligned}
&H(\vec{r},\vec{R}) = \\
&= -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_N \frac{\hbar^2}{2M_N}\nabla_N^2 - \frac{1}{4\pi\varepsilon_0}\sum_{N,i}\frac{Z_N e^2}{|\vec{r}_i - \vec{R}_N|} + \\
&+ \frac{1}{4\pi\varepsilon_0}\sum_{N<K}\frac{Z_N Z_K e^2}{|\vec{R}_N - \vec{R}_K|} + \frac{1}{4\pi\varepsilon_0}\sum_{i<j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} = \\
&= \hat{T}_e + \hat{T}_N + V(\vec{r},\vec{R}) + V_e(\vec{r}) + G(\vec{R})
\end{aligned}$$

$m, \vec{r}_i, i$ – electrons
$M_N, \vec{R}_N, Z_N$ - nuclei

Coordinates of electrons subsystem and nuclei subsystem (ions) are mixed, separation of electronic and nuclear variables is impossible.

One should use the Born-Oppenheimer adiabatic approximation

Chemical bonding and molecules

Born Oppenheimer approximation

F … of the nuclei and electrons:

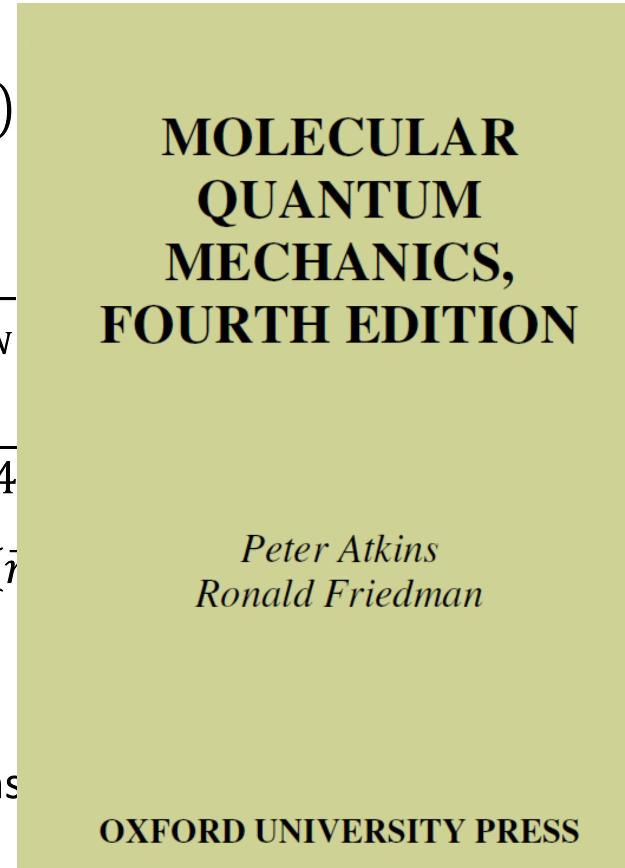
$$H(\vec{r},\vec{R})\Psi(\vec{r},\vec{R}) = E\Psi(\vec{r},\vec{R})$$

$$H(\vec{r},\vec{R}) =$$

$$= -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_N \frac{\hbar^2}{2M_N} \dots$$

$$+\frac{1}{4\pi\varepsilon_0}\sum_{N<K}\frac{Z_N Z_K e^2}{|\vec{R}_N - \vec{R}_K|} + \frac{\dots}{4\dots}$$

$$= \hat{T}_e + \hat{T}_N + V(\vec{r},\vec{R}) + V_e(\dots$$

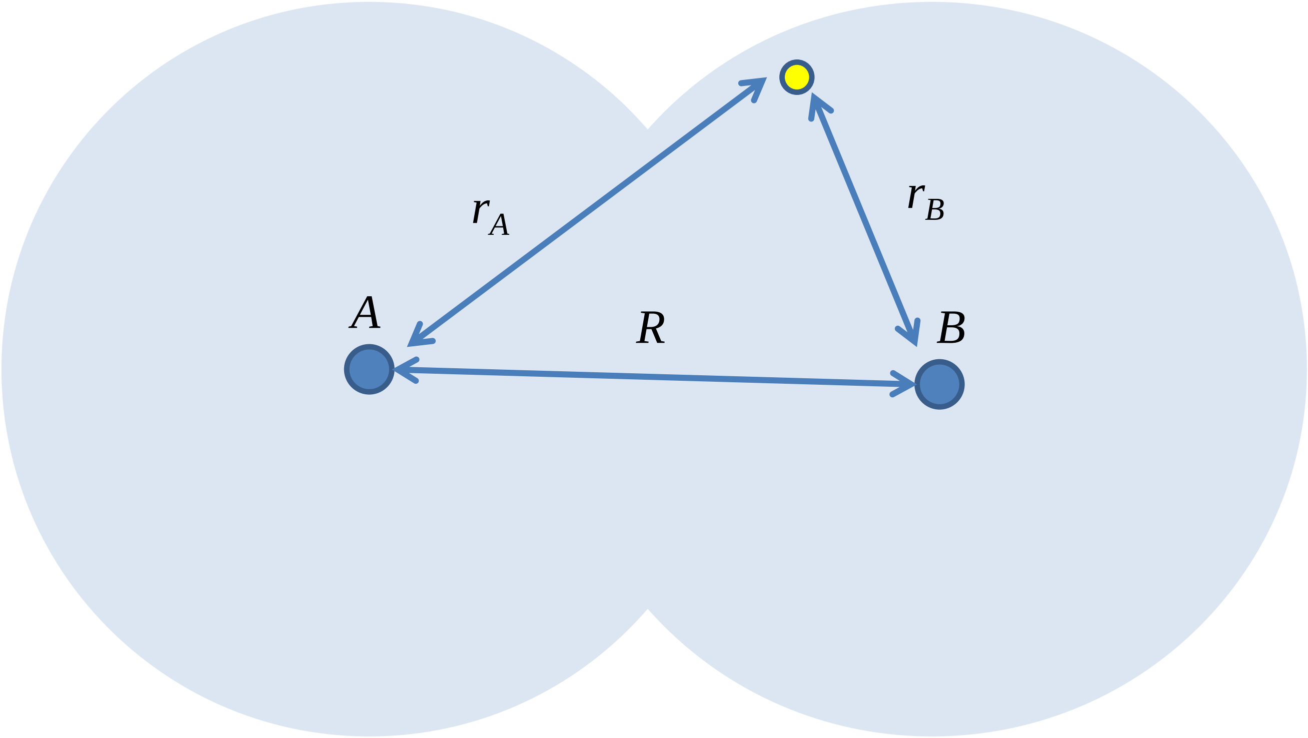


C … em and nuclei subsystem (ions …
e … is impossible.

One should use the Born-Oppenheimer adiabatic approximation

Chemical bonding and molecules

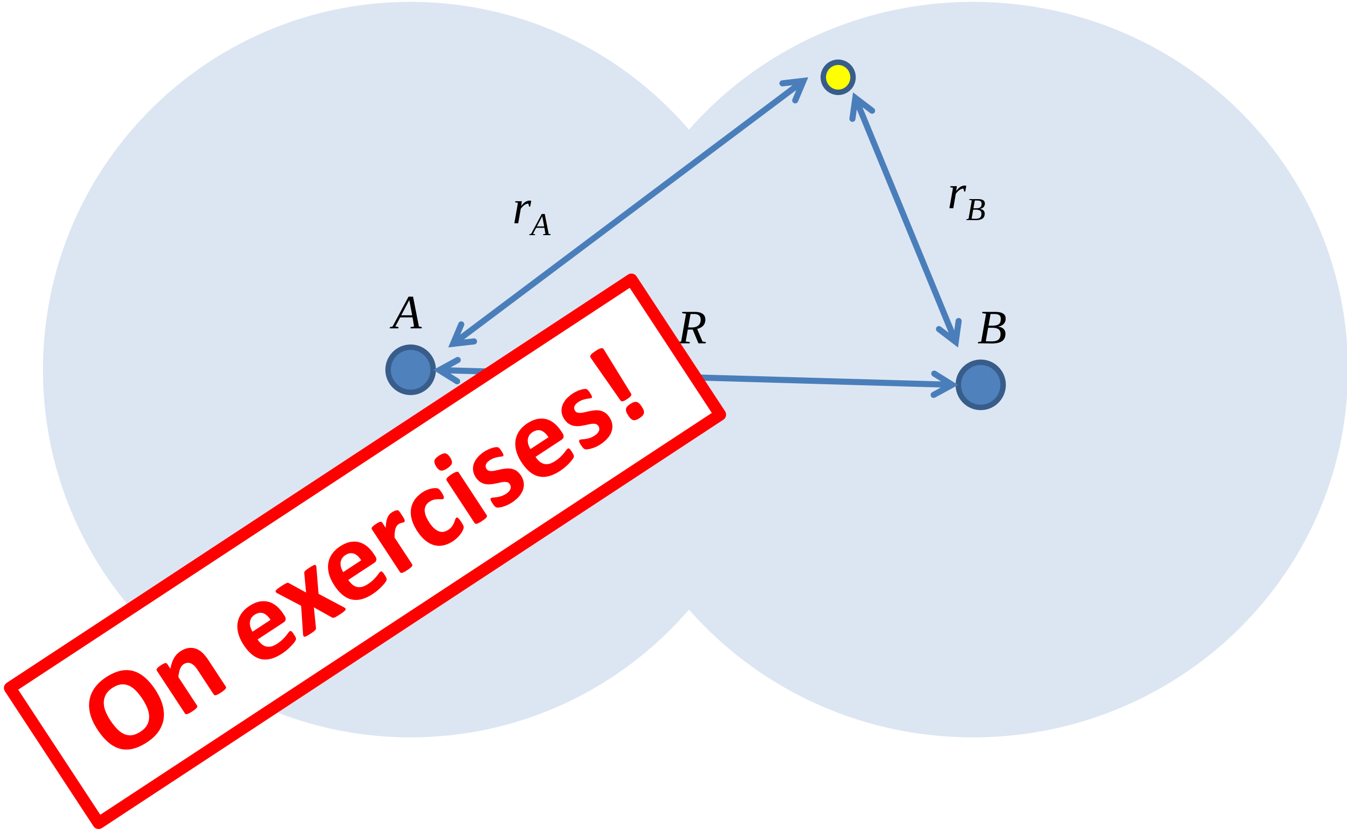
The molecule H_2^+



$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{\hbar^2}{2M}\nabla_A^2 - \frac{\hbar^2}{2M}\nabla_B^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_A} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_B} + \frac{1}{4\pi\varepsilon_0}\frac{e^2}{R}$$

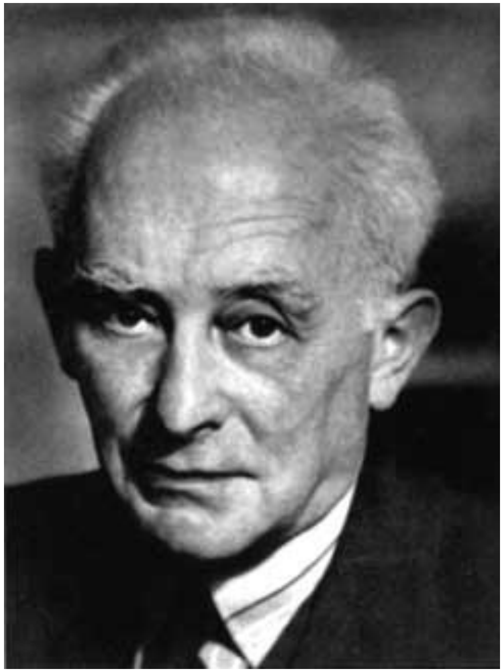
Chemical bonding and molecules

The molecule H_2^+



$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{\hbar^2}{2M}\nabla_A^2 - \frac{\hbar^2}{2M}\nabla_B^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_A} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_B} + \frac{1}{4\pi\varepsilon_0}\frac{e^2}{R}$$

Born Oppenheimer approximation



Max Born
(1882-1970)

Jacob R. Oppenheimer
(1904-1967)

Chemical bonding and molecules

Born Oppenheimer approximation

Full non-relativistic Hamiltonian of the nuclei and electrons:

$$H(\vec{r},\vec{R})\Psi(\vec{r},\vec{R}) = E\Psi(\vec{r},\vec{R})$$

$$H(\vec{r},\vec{R}) =$$
$$= -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_N \frac{\hbar^2}{2M_N}\nabla_N^2 - \frac{1}{4\pi\varepsilon_0}\sum_{N,i}\frac{Z_N e^2}{|\vec{r}_i - \vec{R}_N|} +$$
$$+\frac{1}{4\pi\varepsilon_0}\sum_{N<K}\frac{Z_N Z_K e^2}{|\vec{R}_N - \vec{R}_K|} + \frac{1}{4\pi\varepsilon_0}\sum_{i<j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} =$$
$$= \hat{T}_e + \hat{T}_N + V(\vec{r},\vec{R}) + V_e(\vec{r}) + G(\vec{R})$$

$m, \vec{r}_i, i$ – electrons
$M_N, \vec{R}_N, Z_N$ - nuclei

Observation: atomic nuclei are tens or even hundreds of thousands heavier than electrons, so the nuclei move more slowly than electrons.

Chemical bonding and molecules

Born Oppenheimer approximation

Full non-relativistic Hamiltonian of the nuclei and electrons:

$$H(\vec{r},\vec{R})\Psi(\vec{r},\vec{R}) = E\Psi(\vec{r},\vec{R})$$

$$H(\vec{r},\vec{R}) =$$

$$= -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \cancel{\sum_N \frac{\hbar^2}{2M_N}\nabla_N^2} - \frac{1}{4\pi\varepsilon_0}\sum_{N,i}\frac{Z_N e^2}{|\vec{r}_i - \vec{R}_N|} +$$

$$+ \cancel{\frac{1}{4\pi\varepsilon_0}\sum_{N<K}\frac{Z_N Z_K e^2}{|\vec{R}_N - \vec{R}_K|}} + \frac{1}{4\pi\varepsilon_0}\sum_{i<j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} =$$

$$= \hat{T}_e + \cancel{\hat{T}_K} + V(\vec{r},\vec{R}) + V_e(\vec{r}) + \cancel{G(\vec{R})}$$

$m, \vec{r}_i, i$ – electrons
$M_N, \vec{R}_N, Z_N$ - nuclei

Observation: atomic nuclei are tens or even hundreds of thousands heavier than electrons, so the nuclei move more slowly than electrons.

Chemical bonding and molecules

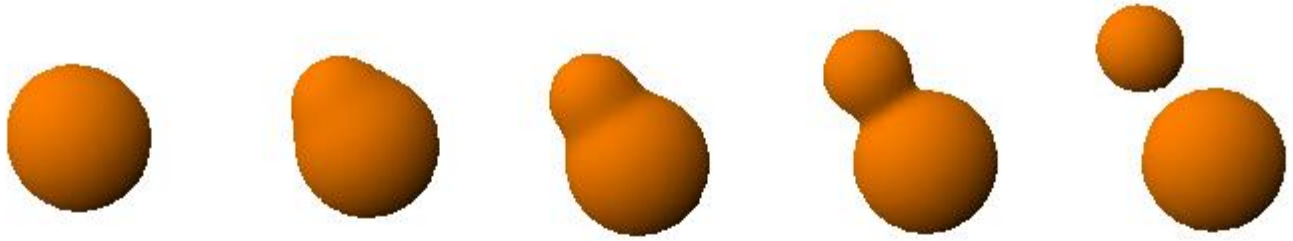
Born Oppenheimer approximation

Atomic nuclei are tens or even hundreds of thousands heavier than electrons, so the nuclei move more slowly than electrons.
Infinitely heavy nuclei - omit the kinetic energy of the nuclei

$$H_{el}(\vec{r},\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R}) = E_{el}^{k}\Psi_{el}^{k}(\vec{r},\vec{R})$$

$$\boxed{\left[\hat{T}_e + V(\vec{r},\vec{R}) + V_e(\vec{r})\right]}$$

$\vec{R}$ – is treated as fixed parameter
k – a set of quantum numbers of a multielectron quantum state
$E_{el}^{k}(\vec{R})$ – electron energies of different states k as a function of the positions of the nuclei
$T_N = 0$



1A 2A 3A 4A 5A

Chemical bonding and molecules

Born Oppenheimer approximation

First we solve simplified Hamiltonian for the fixed configuration of atoms (when nuclei do not move). This is so-called **electronic Hamiltonian or clamped nucleus Hamiltonian** (*hamiltonian elektronowy*)

$$H_{el}(\vec{r},\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R}) = E_{el}^{k}\Psi_{el}^{k}(\vec{r},\vec{R})$$

for each instantaneous (*chwilowa*) position of the ion $\vec{R}$ electrons are in quantum states $\Psi_{el}^{k}(\vec{r},\vec{R})$ corresponding to the global potential of the configuration of ions

$$H_{el}(\vec{r},\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R}) = \left[\hat{T}_e + V(\vec{r},\vec{R}) + V_e(\vec{r})\right]\Psi_{el}^{k}(\vec{r},\vec{R}) = E_{el}^{k}(\vec{R})\,\Psi_{el}^{k}(\vec{r},\vec{R})$$

Multi-electron wave functions $\Psi_{el}^{k}(\vec{r},\vec{R})$ depend on the positions of all the electrons, and are parameterized by instantaneous positions of all nuclei (ions) $\vec{R}$. Index k represents a set of quantum numbers of a multielectron quantum state. Energies $E_{el}^{k}(\vec{R})$ depend on the parameters $\vec{R}$.

These functions will be the base of the final solution – they contain electon-electron kinectic and potential energy $T_e + V(\vec{r},\vec{R}) + V_e(\vec{r})$

Chemical bonding and molecules

Born Oppenheimer approximation

$$H_{el}(\vec{r},\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R}) = [\hat{T}_e + V(\vec{r},\vec{R}) + V_e(\vec{r})]\Psi_{el}^{k}(\vec{r},\vec{R}) = E_{el}^{k}(\vec{R})\,\Psi_{el}^{k}(\vec{r},\vec{R})$$

Expanding the wavefunction $\Psi(\vec{r},\vec{R})$ in basis $\Psi_{el}^{k}(\vec{r},\vec{R})$: $\Psi(\vec{r},\vec{R}) = \sum_k \chi^k(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R})$

$$[\hat{T}_N + \boxed{\hat{T}_e + V(\vec{r},\vec{R}) + V_e(\vec{r})} + G(\vec{R})]\Psi(\vec{r},\vec{R}) = E\,\Psi(\vec{r},\vec{R})$$

$$[\hat{T}_N + \boxed{H_{el}(\vec{r},\vec{R})} + G(\vec{R})]\Psi(\vec{r},\vec{R}) = E\,\Psi(\vec{r},\vec{R})$$

$$[\hat{T}_N + H_{el}(\vec{r},\vec{R}) + G(\vec{R})]\sum_k \chi^k(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R}) = E\sum_k \chi^k(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R})$$

Chemical bonding and molecules

Born Oppenheimer approximation

$$H_{el}(\vec{r},\vec{R})\Psi^k_{el}(\vec{r},\vec{R}) = [\hat{T}_e + V(\vec{r},\vec{R}) + V_e(\vec{r})]\Psi^k_{el}(\vec{r},\vec{R}) = E^k_{el}(\vec{R})\,\Psi^k_{el}(\vec{r},\vec{R})$$

Expanding the wavefunction $\Psi(\vec{r},\vec{R})$ in basis $\Psi^k_{el}(\vec{r},\vec{R})$: $\Psi(\vec{r},\vec{R}) = \sum_k \chi^k(\vec{R})\Psi^k_{el}(\vec{r},\vec{R})$

$$[\hat{T}_N + \boxed{\hat{T}_e + V(\vec{r},\vec{R}) + V_e(\vec{r})} + G(\vec{R})]\Psi(\vec{r},\vec{R}) = E\,\Psi(\vec{r},\vec{R})$$

$$[\hat{T}_N + \boxed{H_{el}(\vec{r},\vec{R})} + G(\vec{R})]\Psi(\vec{r},\vec{R}) = E\,\Psi(\vec{r},\vec{R})$$

$$[\hat{T}_N + H_{el}(\vec{r},\vec{R}) + G(\vec{R})]\sum_k \chi^k(\vec{R})\Psi^k_{el}(\vec{r},\vec{R}) = E\sum_k \chi^k(\vec{R})\Psi^k_{el}(\vec{r},\vec{R})$$

$$[\hat{T}_N + H_{el}(\vec{r},\vec{R}) + \cancel{G(\vec{R})}]\sum_k \chi^k(\vec{R})|\Psi^k_{el}(\vec{r},\vec{R})\rangle = E(\vec{R})\sum_k \chi^k(\vec{R})|\Psi^k_{el}(\vec{r},\vec{R})\rangle \;/*\; \langle\Psi^n_{el}(\vec{r},\vec{R})|$$

$$\langle\Psi^n_{el}(\vec{r},\vec{R})|[\hat{T}_N + H_{el}(\vec{r},\vec{R})]|\textstyle\sum_k \chi^k(\vec{R})|\Psi^k_{el}(\vec{r},\vec{R})\rangle\,\rangle = \langle\Psi^n_{el}(\vec{r},\vec{R})|E(\vec{R})|\textstyle\sum_k \chi^k(\vec{R})|\Psi^k_{el}(\vec{r},\vec{R})\rangle\,\rangle$$

Chemical bonding and molecules

Born Oppenheimer approximation

$$H_{el}(\vec{r},\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R}) = [\hat{T}_e + V(\vec{r},\vec{R}) + V_e(\vec{r})]\Psi_{el}^{k}(\vec{r},\vec{R}) = E_{el}^{k}(\vec{R})\,\Psi_{el}^{k}(\vec{r},\vec{R})$$

Expanding the wavefunction $\Psi(\vec{r},\vec{R})$ in basis $\Psi_{el}^{k}(\vec{r},\vec{R})$: $\Psi(\vec{r},\vec{R}) = \sum_k \chi^k(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R})$

$$\langle\Psi_{el}^{n}(\vec{r},\vec{R})\big|[\hat{T}_N + H_{el}(\vec{r},\vec{R})]\big|\textstyle\sum_k \chi^k(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R})\rangle = \langle\Psi_{el}^{n}(\vec{r},\vec{R})\big|E(\vec{R})\big|\textstyle\sum_k \chi^k(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R})\rangle$$

$$[\hat{T}_N + E_{el}(\vec{r},\vec{R})]\chi^n(\vec{R}) + \sum_k \chi^k(\vec{R})\langle\Psi_{el}^{n}(\vec{r},\vec{R})\big|\hat{T}_N\big|\Psi_{el}^{k}(\vec{r},\vec{R})\rangle = E(\vec{R})\chi^n(\vec{R})$$

Electronic states are mixed!

Chemical bonding and molecules

Born Oppenheimer approximation

$$H_{el}(\vec{r},\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R}) = [\hat{T}_e + V(\vec{r},\vec{R}) + V_e(\vec{r})]\Psi_{el}^{k}(\vec{r},\vec{R}) = E_{el}^{k}(\vec{R})\,\Psi_{el}^{k}(\vec{r},\vec{R})$$

Expanding the wavefunction $\Psi(\vec{r},\vec{R})$ in basis $\Psi_{el}^{k}(\vec{r},\vec{R})$: $\Psi(\vec{r},\vec{R}) = \sum_k \chi^k(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R})$

$$\langle\Psi_{el}^{n}(\vec{r},\vec{R})\big|[\hat{T}_N + H_{el}(\vec{r},\vec{R})]\big|\textstyle\sum_k \chi^k(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R})\rangle = \langle\Psi_{el}^{n}(\vec{r},\vec{R})\big|E(\vec{R})\big|\textstyle\sum_k \chi^k(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R})\rangle$$

$$[\hat{T}_N + E_{el}(\vec{r},\vec{R})]\chi^n(\vec{R}) + \sum_k \chi^k(\vec{R})\langle\Psi_{el}^{n}(\vec{r},\vec{R})\big|\hat{T}_N\big|\Psi_{el}^{k}(\vec{r},\vec{R})\rangle = E(\vec{R})\chi^n(\vec{R})$$

$$[\hat{T}_N + E_{el}(\vec{r},\vec{R})]\chi^n(\vec{R}) + \sum_{k\neq n} \chi^k(\vec{R})\langle\Psi_{el}^{n}(\vec{r},\vec{R})\big|\hat{T}_N\big|\Psi_{el}^{k}(\vec{r},\vec{R})\rangle +$$
$$+\chi^n(\vec{R})\langle\Psi_{el}^{n}(\vec{r},\vec{R})\big|\hat{T}_N\big|\Psi_{el}^{n}(\vec{r},\vec{R})\rangle = E(\vec{R})\chi^n(\vec{R})$$

Electronic states are mixed!

Chemical bonding and molecules

Born Oppenheimer approximation

$$H_{el}(\vec{r},\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R}) = [\hat{T}_e + V(\vec{r},\vec{R}) + V_e(\vec{r})]\Psi_{el}^{k}(\vec{r},\vec{R}) = E_{el}^{k}(\vec{R})\,\Psi_{el}^{k}(\vec{r},\vec{R})$$

Expanding the wavefunction $\Psi(\vec{r},\vec{R})$ in basis $\Psi_{el}^{k}(\vec{r},\vec{R})$: $\Psi(\vec{r},\vec{R}) = \sum_k \chi^k(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R})$

$$\langle\Psi_{el}^{n}(\vec{r},\vec{R})|[\hat{T}_N + H_{el}(\vec{r},\vec{R})]|\textstyle\sum_k \chi^k(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R})\rangle = \langle\Psi_{el}^{n}(\vec{r},\vec{R})|E(\vec{R})|\textstyle\sum_k \chi^k(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R})\rangle$$

$$[\hat{T}_N + E_{el}(\vec{r},\vec{R})]\chi^n(\vec{R}) + \sum_k \chi^k(\vec{R})\langle\Psi_{el}^{n}(\vec{r},\vec{R})|\hat{T}_N|\Psi_{el}^{k}(\vec{r},\vec{R})\rangle = E(\vec{R})\chi^n(\vec{R})$$

$$[\hat{T}_N + E_{el}(\vec{r},\vec{R})]\chi^n(\vec{R}) + \sum_{k\neq n} \chi^k(\vec{R})\langle\Psi_{el}^{n}(\vec{r},\vec{R})|\hat{T}_N|\Psi_{el}^{k}(\vec{r},\vec{R})\rangle +$$

$$+\chi^n(\vec{R})\langle\Psi_{el}^{n}(\vec{r},\vec{R})|\hat{T}_N|\Psi_{el}^{n}(\vec{r},\vec{R})\rangle = E(\vec{R})\chi^n(\vec{R})$$

Approximation 1: **Adiabatic**

The movement of electrons is so fast that during a small change of the nuclei position electrons immediately adapt to the new conditions. This means that the electrons do not change their state Ψ_{el}^{k} upon movement of the nuclei. Mathematically: $\hat{T}_N$ operator acting on Ψ_{el}^{k} does not change it into different function Ψ_{el}^{k}, $n \neq k$

Chemical bonding and molecules

Born Oppenheimer approximation

$$H_{el}(\vec{r},\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R}) = \left[\hat{T}_e + V(\vec{r},\vec{R}) + V_e(\vec{r})\right]\Psi_{el}^{k}(\vec{r},\vec{R}) = E_{el}^{k}(\vec{R})\,\Psi_{el}^{k}(\vec{r},\vec{R})$$

Expanding the wavefunction $\Psi(\vec{r},\vec{R})$ in basis $\Psi_{el}^{k}(\vec{r},\vec{R})$: $\Psi(\vec{r},\vec{R}) = \sum_k \chi^k(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R})$

$$\langle\Psi_{el}^{n}(\vec{r},\vec{R})\big|\left[\hat{T}_N + H_{el}(\vec{r},\vec{R})\right]\big|\sum_k \chi^k(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R})\rangle = \langle\Psi_{el}^{n}(\vec{r},\vec{R})\big|E(\vec{R})\big|\sum_k \chi^k(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R})\rangle$$

$$\left[\hat{T}_N + E_{el}(\vec{r},\vec{R})\right]\chi^n(\vec{R}) + \sum_k \chi^k(\vec{R})\langle\Psi_{el}^{n}(\vec{r},\vec{R})\big|\hat{T}_N\big|\Psi_{el}^{k}(\vec{r},\vec{R})\rangle = E(\vec{R})\chi^n(\vec{R})$$

$$\left[\hat{T}_N + E_{el}(\vec{r},\vec{R})\right]\chi^n(\vec{R}) + \sum_{k\neq n} \chi^k(\vec{R})\langle\Psi_{el}^{n}(\vec{r},\vec{R})\big|\hat{T}_N\big|\Psi_{el}^{k}(\vec{r},\vec{R})\rangle +$$

$$+\chi^n(\vec{R})\langle\Psi_{el}^{n}(\vec{r},\vec{R})\big|\hat{T}_N\big|\Psi_{el}^{n}(\vec{r},\vec{R})\rangle = E(\vec{R})\chi^n(\vec{R})$$

Approximation 1: **Adiabatic**

Thus:

$$\Psi(\vec{r},\vec{R}) = \sum_k \chi^k(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R}) \approx \chi^n(\vec{R})\Psi_{el}^{n}(\vec{r},\vec{R})$$

Chemical bonding and molecules

Born Oppenheimer approximation

$$H_{el}(\vec{r},\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R}) = \left[\hat{T}_e + V(\vec{r},\vec{R}) + V_e(\vec{r})\right]\Psi_{el}^{k}(\vec{r},\vec{R}) = E_{el}^{k}(\vec{R})\,\Psi_{el}^{k}(\vec{r},\vec{R})$$

Expanding the wavefunction $\Psi(\vec{r},\vec{R})$ in basis $\Psi_{el}^{k}(\vec{r},\vec{R})$: $\quad \Psi(\vec{r},\vec{R}) = \sum_{k} \chi^{k}(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R})$

$$\left\langle \Psi_{el}^{n}(\vec{r},\vec{R})\right|\left[\hat{T}_N + H_{el}(\vec{r},\vec{R})\right]\left| \sum_k \chi^{k}(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R})\right\rangle = \left\langle \Psi_{el}^{n}(\vec{r},\vec{R})\right| E(\vec{R}) \left| \sum_k \chi^{k}(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R})\right\rangle$$

$$\left[\hat{T}_N + H_{el}(\vec{r},\vec{R})\right]\chi^{n}(\vec{R}) + \sum_{k} \chi^{k}(\vec{R})\left\langle \Psi_{el}^{n}(\vec{r},\vec{R})\right|\hat{T}_N\left|\Psi_{el}^{k}(\vec{r},\vec{R})\right\rangle = E(\vec{R})\chi^{n}(\vec{R})$$

$$\left[\hat{T}_N + E_{el}(\vec{r},\vec{R})\right]\chi^{n}(\vec{R}) + \sum_{k\neq n} \chi^{k}(\vec{R})\left\langle \Psi_{el}^{n}(\vec{r},\vec{R})\right|\hat{T}_N\left|\Psi_{el}^{k}(\vec{r},\vec{R})\right\rangle +$$

$$+\chi^{n}(\vec{R})\left\langle \Psi_{el}^{n}(\vec{r},\vec{R})\right|\hat{T}_N\left|\Psi_{el}^{n}(\vec{r},\vec{R})\right\rangle = E(\vec{R})\chi^{n}(\vec{R})$$

Approximation 2:
changing position of the nuclei weakly affects the state of electrons.
Mathematically: $\hat{T}_N$ operator acting on Ψ_{el}^{k} gives $\quad \hat{T}_N\left|\Psi_{el}^{n}(\vec{r},\vec{R})\right\rangle \approx 0$

Chemical bonding and molecules

Born Oppenheimer approximation

$$H_{el}(\vec{r},\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R}) = \left[\hat{T}_e + V(\vec{r},\vec{R}) + V_e(\vec{r})\right]\Psi_{el}^{k}(\vec{r},\vec{R}) = E_{el}^{k}(\vec{R})\,\Psi_{el}^{k}(\vec{r},\vec{R})$$

Expanding the wavefunction $\Psi(\vec{r},\vec{R})$ in basis $\Psi_{el}^{k}(\vec{r},\vec{R})$: $\quad \Psi(\vec{r},\vec{R}) = \sum_k \chi^k(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R})$

$$\Psi(\vec{r},\vec{R}) \approx \chi^n(\vec{R})\Psi_{el}^{n}(\vec{r},\vec{R})$$

$$\left[\hat{T}_N + E_{el}(\vec{r},\vec{R})\right]\chi^n(\vec{R}) + \sum_{k\neq n}\chi^k(\vec{R})\left\langle\Psi_{el}^{n}(\vec{r},\vec{R})\middle|\hat{T}_N\middle|\Psi_{el}^{k}(\vec{r},\vec{R})\right\rangle +$$

$$+\chi^n(\vec{R})\left\langle\Psi_{el}^{n}(\vec{r},\vec{R})\middle|\hat{T}_N\middle|\Psi_{el}^{n}(\vec{r},\vec{R})\right\rangle = E(\vec{R})\chi^n(\vec{R})$$

$$E(\vec{R}) \to E^n$$

$$\left[\hat{T}_N + E_{el}(\vec{r},\vec{R}) + G(\vec{R})\right]\chi^n(\vec{R}) = E^n\chi^n(\vec{R})$$

effective potential

Chemical bonding and molecules

Born Oppenheimer approximation

$$H_{el}(\vec{r},\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R}) = [\hat{T}_e + V(\vec{r},\vec{R}) + V_e(\vec{r})]\Psi_{el}^{k}(\vec{r},\vec{R}) = E_{el}^{k}(\vec{R})\,\Psi_{el}^{k}(\vec{r},\vec{R})$$

Expanding the wavefunction $\Psi(\vec{r},\vec{R})$ in basis $\Psi_{el}^{k}(\vec{r},\vec{R})$: $\quad \Psi(\vec{r},\vec{R}) = \sum_k \chi^k(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R})$

$$\Psi(\vec{r},\vec{R}) \approx \chi^n(\vec{R})\Psi_{el}^{n}(\vec{r},\vec{R})$$

$$[\hat{T}_N + E_{el}(\vec{r},\vec{R})]\chi^n(\vec{R}) + \sum_{k\neq n} \chi^k(\vec{R})\langle\Psi_{el}^{n}(\vec{r},\vec{R})|\hat{T}_N|\Psi_{el}^{k}(\vec{r},\vec{R})\rangle +$$

$$+\chi^n(\vec{R})\langle\Psi_{el}^{n}(\vec{r},\vec{R})|\hat{T}_N|\Psi_{el}^{n}(\vec{r},\vec{R})\rangle = E(\vec{R})\chi^n(\vec{R})$$

Does it remind you of something?

$$[\hat{T}_N + E_{el}(\vec{r},\vec{R}) + G(\vec{R})]\chi^n(\vec{R}) = E^n\chi^n(\vec{R})$$

effective potential

Born Oppenheimer approximation

$$H_{el}(\vec{r},\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R}) = [\hat{T}_e + V(\vec{r},\vec{R}) + V_e(\vec{r})]\Psi_{el}^{k}(\vec{r},\vec{R}) = E_{el}^{k}(\vec{R})\,\Psi_{el}^{k}(\vec{r},\vec{R})$$

Expanding the wavefunction $\Psi(\vec{r},\vec{R})$ in basis $\Psi_{el}^{k}(\vec{r},\vec{R})$: $\quad \Psi(\vec{r},\vec{R}) = \sum_k \chi^k(\vec{R})\Psi_{el}^{k}(\vec{r},\vec{R})$

$$\Psi(\vec{r},\vec{R}) \approx \chi^n(\vec{R})\Psi_{el}^{n}(\vec{r},\vec{R})$$

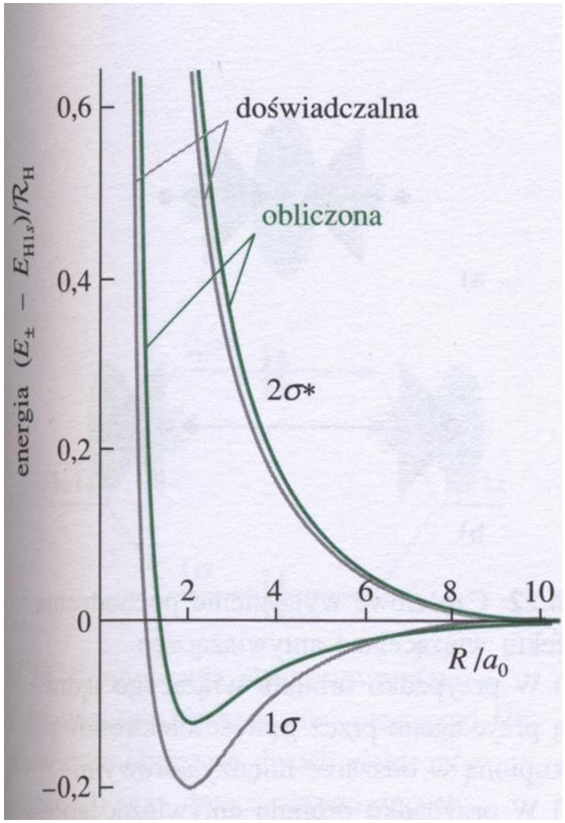
$$[\hat{T}_N + E_{el}(\vec{r},\vec{R})]\chi^n(\vec{R}) + \sum_{k\neq n}\chi^k(\vec{R})\langle\Psi_{el}^{n}(\vec{r},\vec{R})|\hat{T}_N|\Psi_{el}^{k}(\vec{r},\vec{R})\rangle +$$
$$+\chi^n(\vec{R})\langle\Psi_{el}^{n}(\vec{r},\vec{R})|\hat{T}_N|\Psi_{el}^{n}(\vec{r},\vec{R})\rangle = E(\vec{R})\chi^n(\vec{R})$$

Schrodinger equation of the motion of nuclei with repulsive potential $G(\vec{R})$:

$$[\hat{T}_N + E_{el}(\vec{r},\vec{R}) + G(\vec{R})]\chi^n(\vec{R}) = E^n\chi^n(\vec{R})$$

effective potential

Chemical bonding and molecules



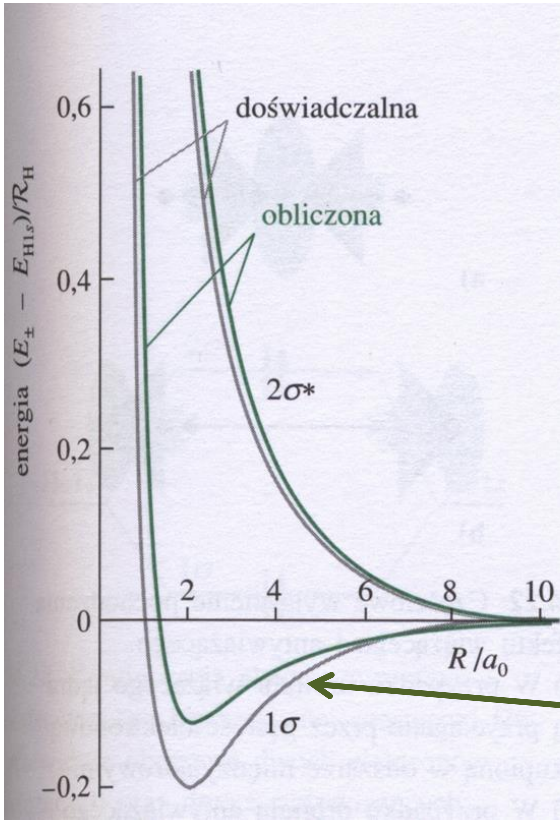
$\chi^n(\vec{R})$ is the wave function describing the motion of nuclei (ions) in their mutual interaction potential $G(\vec{R})$ adiabatic electron contribution to the energy of the motion of nuclei (ions) $E_{el}^k(\vec{R})$

Schrodinger equation of the motion of nuclei with repulsive potential $G(\vec{R})$:

$$\left[\hat{T}_N + E_{el}(\vec{r},\vec{R}) + G(\vec{R})\right]\chi^n(\vec{R}) = E^n\chi^n(\vec{R})$$

effective potential

Chemical bonding and molecules



$\chi^n(\vec{R})$ is the wave function describing the motion of nuclei (ions) in their mutual interaction potential $G(\vec{R})$ adiabatic electron contribution to the energy of the motion of nuclei (ions) $E_{el}^k(\vec{R})$

Born-Oppenheimer approximation **is not fulfilled** when the potential energy surfaces of two electronic states are too close.

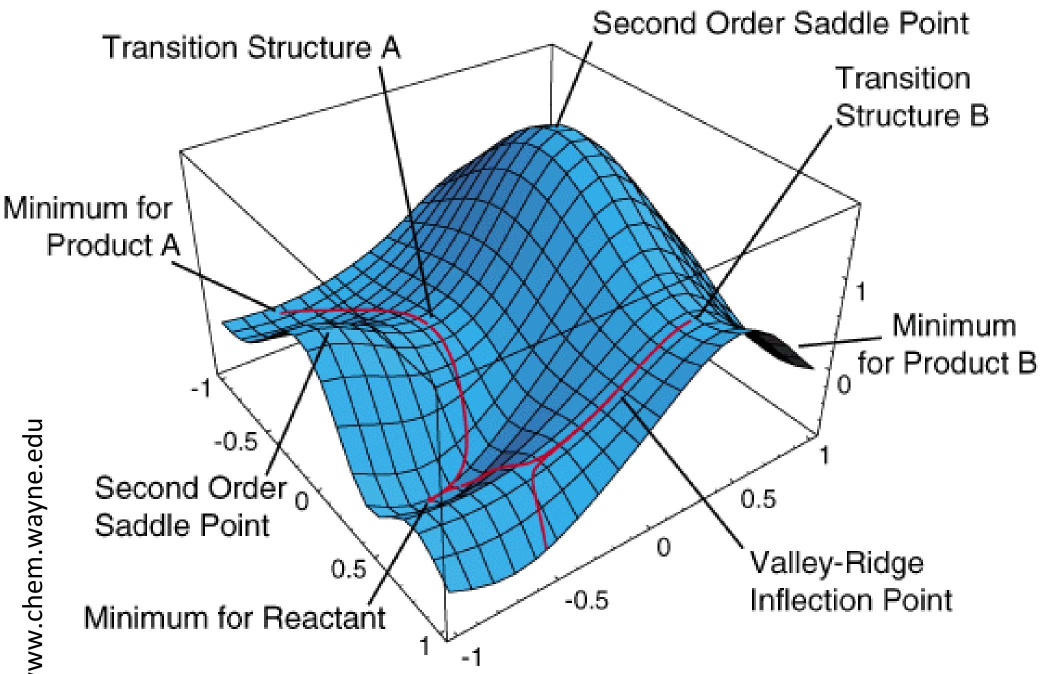
the potential energy surface

Schrodinger equation of the motion of nuclei with repulsive potential $G(\vec{R})$:

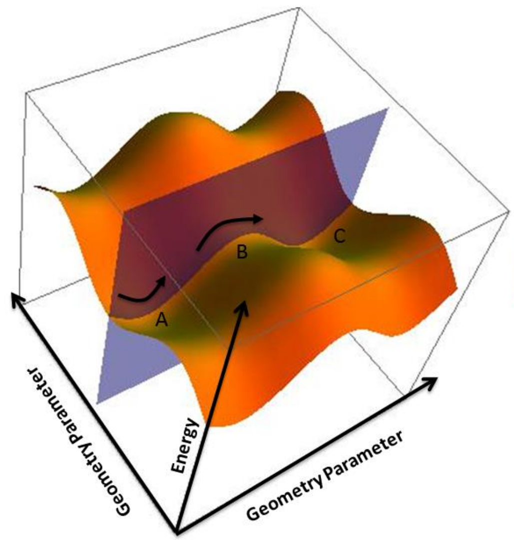
$$\left[\hat{T}_N + E_{el}(\vec{r}, \vec{R}) + G(\vec{R})\right]\chi^n(\vec{R}) = E^n \chi^n(\vec{R})$$

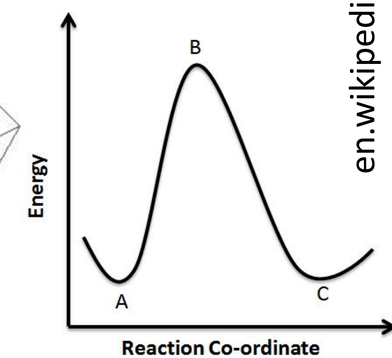
effective potential

Chemical bonding and molecules



www.chem.wayne.edu





en.wikipedia.org

the potential energy surface

<u>Schrodinger equation of the motion of nuclei with repulsive potential</u> $G(\vec{R})$:

$$\left[\hat{T}_N + E_{el}(\vec{r},\vec{R}) + G(\vec{R})\right]\chi^n(\vec{R}) = E^n\chi^n(\vec{R})$$

effective potential

Chemical bonding and molecules

Approximations

$$\left[\hat{T}_N + E_{el}(\vec{r},\vec{R}) + G(\vec{R})\right]\chi^n(\vec{R}) = E^n\chi^n(\vec{R})$$

The kinetic energy separates on vibration (oscillation) and rotation energy – we assume "small" oscillations and slow speed of rotataion.

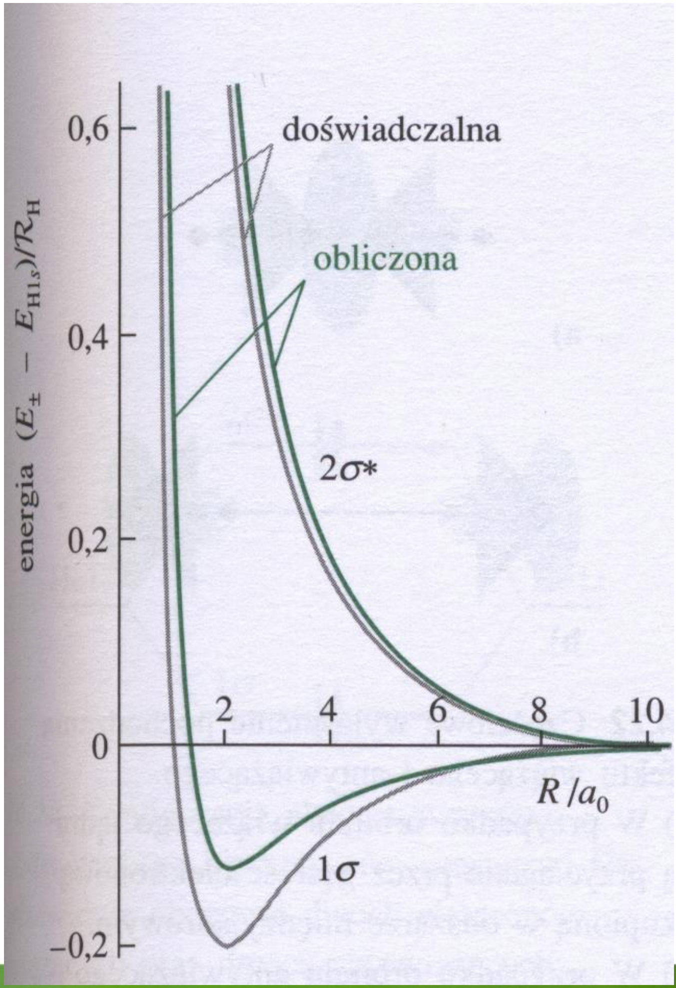
$$\left[\hat{T}_{osc} + \hat{T}_{rot} + E_{el}(\vec{r},\vec{R}) + G(\vec{R})\right]\chi^n(\vec{R}) = E^n\chi^n(\vec{R})$$

Operators act on different coordinates: we can we separate the variables:

$$\chi^n(\vec{R}) = \chi^n_{osc}(R)\chi^n_{rot}(\theta,\varphi)$$
$$E^n = E^n_{osc} + E^n_{rot}$$

Altogether:

$$\Psi(\vec{r},\vec{R}) = \chi^n(\vec{R})\Psi^n_{el}(\vec{r},\vec{R}) = \chi^n_{osc}(R)\chi^n_{rot}(\theta,\varphi)\Psi^n_{el}(\vec{r},\vec{R})$$
$$E^n = E^n_{osc} + E^n_{rot} + E_{el}$$



Chemical bonding and molecules

Approximations

$$\left[\hat{T}_N + E_{el}(\vec{r},\vec{R}) + G(\vec{R})\right]\chi^n(\vec{R}) = E^n\chi^n(\vec{R})$$

The kinetic energy separates on vibration (oscillation) and rotation energy – we assume "small" oscillations and slow speed of rotataion.

$$\left[\hat{T}_{osc} + \hat{T}_{rot} + E_{el}(\vec{r},\vec{R}) + G(\vec{R})\right]\chi^n(\vec{R}) = E^n\chi^n(\vec{R})$$

Operators act on different coordinates: we ca separate the variables:

$$\chi^n(\vec{R}) = \chi^n_{osc}(R)\chi^n_{rot}(\theta,\varphi)$$
$$E^n = E^n_{osc} + E^n_{rot}$$

One by one we will discuss:

- electronic structure
- rotations
- oscillations

Altogether:

$$\Psi(\vec{r},\vec{R}) = \chi^n(\vec{R})\Psi^n_{el}(\vec{r},\vec{R}) = \chi^n_{osc}(R)\chi^n_{rot}(\theta,\varphi)\Psi^n_{el}(\vec{r},\vec{R})$$
$$E^n = E^n_{osc} + E^n_{rot} + E_{el}$$