Computational Materials Physics

Center for Molecular Modeling

Department of Materials Science and Engineering

Born-Oppenheimer approximation

Stefaan.Cottenier@ugent.be
Technologiepark 903, Zwijnaarde

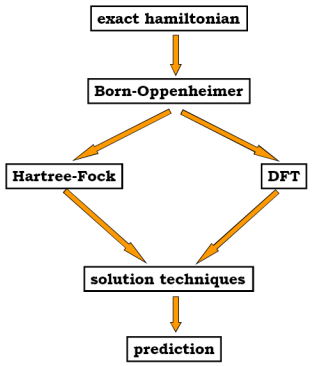
http://molmod.ugent.be
http://www.ugent.be/ea/dmse/en
my talks on Youtube: http://goo.gl/P2b1Hs

three levels of approximations

level 1:

level 2:

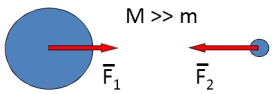
level 3:



Born-Oppenheimer approximation

(a.k.a. the adiabatic principle)

Classical picture:



nucleus | electron

$F_1=-F_2=F$

$a_1=F/M$ | $a_2=-F/m$

$v_1=F\Delta t/M$ | $v_2=F\Delta t/m$

$v_1 << v_2$

Born-Oppenheimer approximation

(a.k.a. the adiabatic principle)

Therefore, let us freeze the nuclear positions = Born-Oppenheimer approximation

Consequence 1: from $4(N_e+N_n)$ to $4N_e$ variables.

$$\Psi(\underbrace{x_1, y_1, z_1, \alpha_1, \ldots, x_{N_e}, y_{N_e}, z_{N_e}, \alpha_{N_e}}_{\text{variables of the function}}; \underbrace{\left[\vec{R}_1, \ldots, \vec{R}_{N_n}\right]}_{\text{parameters}})$$

Born-Oppenheimer approximation

(a.k.a. the adiabatic principle)

$$H = \cancel{-\sum_i \frac{\nabla^2}{M_i}} - \sum_i \frac{\nabla^2}{m_i} - \sum_{i,j} \frac{(eZ_i)\ e}{\left|\vec{R}_i - \vec{r}_j\right|} + \frac{1}{2}\sum_{i \neq j} \frac{e^2}{\left|\vec{r}_i - \vec{r}_j\right|} + \underbrace{\frac{1}{2}\sum_{i \neq j} \frac{(eZ_i)(eZ_j)}{\left|\vec{R}_i - \vec{R}_j\right|}}_{\text{constant}}$$

Consequence 2: simplified Hamiltonian

➔ The BO-approximation is a major simplification, but still the resulting equation is way too hard to solve. More is needed...

Born-Oppenheimer approximation

(a.k.a. the adiabatic principle)

Advanced optional reading on Born-Oppenheimer and beyond :

Yonehara et al. (2012)
Fundamental Approaches to Nonadiabaticity:
Toward a Chemical Theory beyond the Born–Oppenheimer Paradigm
http://dx.doi.org/10.1021/cr200096s

Schmidt (2013)
Quantum characteristics of the hydrogen bond
http://dx.doi.org/10.1080/00268976.2012.728636