

- Outline

1. Born-Huang Representation (exact)
 2. Adiabatic, Born-Oppenheimer approximation
 3. Hierarchy of EST methodology
- reference
 1. L. Pielas, Ideas of Quantum Chemistry, Ch 6.
 2. J. Olsen, Molecular Electronic Structure Theory
 3. Basile Curchod's slides.

<https://in-silico-photochem.com/lectures/>

1. Born-Huang Representation (exact)

- From a general perspective, dynamics is a topic of solving TDSE, $i\hbar \nabla_t |\Psi\rangle = \hat{H} |\Psi\rangle$. There are different way to postulate molecular wavefunction.

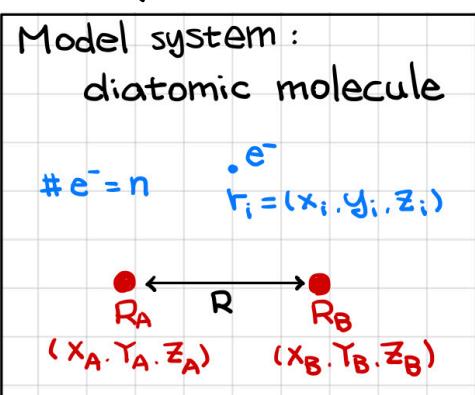
$$\text{Exact} \left[\begin{array}{l} \text{Born-Huang} \\ \text{Exact factorization: } |\Psi(\vec{r}, \vec{R}, t)\rangle = \phi(\vec{r}; \vec{R}, t) \chi(\vec{R}, t) \end{array} \right] : |\Psi(\vec{r}, \vec{R}, t)\rangle = \sum_i^{\infty} \Phi_i(\vec{r}; \vec{R}) \chi_i(\vec{R}, t)$$

Approximation: adiabatic, Born-Oppenheimer, Ehrenfest...

- For molecular electronic structure theory, it solves the TISE, $\hat{H} |\Psi\rangle = E |\Psi\rangle$, and usually starts from Born-Huang representation

$$\begin{aligned} \hat{H} |\Psi\rangle &= E |\Psi\rangle \\ f(\text{Neu}) + f(\text{ele}) + f(\text{Neu,ele}) & \quad \text{BH rep} \\ \rightarrow \hat{T}_N + \hat{V}_{NN} + \hat{T}_{ee} + \hat{V}_{ee} + \hat{V}_{Ne} & \quad \cdot \{ \Phi_j(\vec{r}; \vec{R}) \} \text{ complete and} \\ \rightarrow \text{Separate translational motion} & \quad \text{orthonormal set for ele.} \\ & \quad \cdot |\Psi(\vec{r}, \vec{R})\rangle = \sum_j \Phi_j(\vec{r}; \vec{R}) \cdot \chi_j(\vec{R}) \end{aligned}$$

|



$$R = R_A - R_B$$

Center-of-mass (C.O.M.)

$$: (X, Y, Z)$$

$$\downarrow X = \frac{1}{M} (M_A x_A + M_B x_B + \sum_i^n m_e x'_i)$$

C.O.M. Kinetic operator

$$\rightarrow \hat{H} = -\frac{\hbar^2}{2M} \nabla_{XYZ}^2 + \hat{H}_0 + \hat{H}'$$

electronic Hamiltonian
(clamped nuclei Hamiltonian)

relative motion of nuclei

$$\hat{H}_0 = \hat{T}_e + \hat{V} = \sum_{i=1}^n -\frac{\hbar^2}{2m_e} \nabla_i^2 + \hat{V}$$

$$\hat{H}' = -\frac{\hbar^2}{2\mu} \nabla_R^2 + \underbrace{\hat{H}''}_{\substack{\text{reduced mass} \\ \frac{1}{\mu} = \frac{1}{M_A} + \frac{1}{M_B}}}$$

$$\hat{H}'' = -\frac{\hbar^2}{8\mu} \left(\sum_{i=1}^n \nabla_i \right)^2 - \frac{\hbar^2}{2} \left(\frac{1}{M_A} - \frac{1}{M_B} \right) \nabla_R \sum_{i=1}^n \nabla_i$$

couples the motions of nuclei and electrons

→ After separate the C.O.M. (remove the first term; remove the translational motion).

$$\hat{H} = -\frac{\hbar^2}{2M} \nabla_{XYZ}^2 + \hat{H}_0 + \hat{H}' \rightarrow \hat{H} = \hat{H}_0 + \hat{H}' \quad (\text{still exact})$$

d.o.f. = $3N - 3$

Similarly, remove rotation

$$\text{d.o.f.} = 3N - 5/6.$$

→ Now, plug-in BHT rep. in this TISE

$$\hat{H} |4\rangle = E |4\rangle$$

$$(\hat{H}_0 + \hat{H}') (\sum_j^{\infty} \phi_j \chi_j) = E \sum_j \phi_j \chi_j$$

- $\{\phi_j\}$ complete and orthonormal set for electrons.

- $\langle \phi_i | \phi_j \rangle = \delta_{ij}$. $\hat{H}_0 \phi_i = E_i \phi_i$

$$\rightarrow (\hat{H}^0 - \frac{\hbar^2}{2M} \nabla_R^2 + \hat{H}'') (\sum_j^{\infty} \phi_j \chi_j) = E \sum_j \phi_j \chi_j$$

$$\nabla_R (\nabla_R \phi_j \chi_j + \phi_j \nabla_R \chi_j)$$

$$= \nabla_R^2 \phi_j \chi_j + 2 \nabla_R \phi_j \nabla_R \chi_j + \phi_j \nabla_R^2 \chi_j$$

^{2nd derivative}
coupling

^{1st derivative}
coupling

$$\langle \phi_I | \rightarrow \sum_j \underbrace{\langle \phi_I | \hat{H}^0 | \phi_j \rangle}_{E_j \phi_j} \chi_j - \frac{\hbar^2}{2M} \cancel{\langle \phi_I | \nabla_R^2 \phi_j \rangle} \chi_j - \frac{\hbar^2}{M} \cancel{\langle \phi_I | \nabla_R \phi_j \rangle} \nabla_R \chi_j$$

$$0 \quad \because \nabla_R \phi_j \gg \nabla_R^2 \phi_j$$

$$\therefore \langle \phi_I | \phi_I \rangle = 1$$

$$\therefore \nabla_R \langle \phi_I | \phi_I \rangle = 0$$

$$- \frac{\hbar^2}{2M} \langle \phi_I | \phi_j \rangle \nabla_R^2 \chi_j + \langle \phi_I | \hat{H}'' | \phi_j \rangle \chi_j = \sum_j E \langle \phi_I | \phi_j \rangle \chi_j$$

$$\xrightarrow{S_{IJ}} E_I^0 \chi_I - \frac{\hbar^2}{2M} \nabla_R^2 \chi_I - E \chi_I + H''_{II} \chi_I$$

L.h.S. $J=I$

r.h.s. $J \neq I$

$$= - \sum_{J \neq I} - \frac{\hbar^2}{M} \cancel{\langle \phi_I | \nabla_R \phi_j \rangle} \nabla_R \chi_J + \cancel{H''_{IJ}} \chi_J$$

C_{IJ}
non-adiabatic coupling
vibronic coupling
derivative coupling

$$\rightarrow (E_I^0 - \frac{\hbar^2}{2M} \nabla_R^2 + H''_{II} - E) \cdot \chi_I = - \sum_{J \neq I} C_{IJ} \chi_J$$

$$C_{IJ} = - \frac{\hbar^2}{M} \cancel{\langle \phi_I | \nabla_R \phi_j \rangle} \nabla_R \chi_J + \cancel{H''_{IJ}}$$

#

2.1. Adiabatic approximation

$\therefore M_A \gg m_e \rightarrow$ time-separation approximation

$\therefore C_{IJ} = 0.$

$$\rightarrow \left(E_I^0 - \frac{\hbar^2}{2M} \nabla_R^2 + H''_{II} \right) \chi_J = E \chi_J, \text{ nuclear SE.}$$

$\underbrace{\qquad\qquad}_{f(M_A)}$

the resulting PES = $E_I^0(R) + H''_{II}(M_A)$,
depends on the mass of nuclei.

2.2. Born-Oppenheimer approximation

$$H''_{II} = 0$$

$$\rightarrow \left(-\frac{\hbar^2}{2M} \nabla_R^2 + E_I^0 \right) \chi_J = E \chi_J$$

the resulting PES = $E_I^0(R)$.

* Summary of part 2.

Exact TISE base on BH rep.

$$(E_I^0 - \frac{\hbar^2}{2M} \nabla_R^2 + H'_{II} - E) \cdot \chi_I = - \sum_{J \neq I} C_{IJ} \chi_J$$

coupling matrix

adiabatic approx.

$$C_{IJ} = 0.$$

$$\text{off-diag.} = 0$$

B.O. approx.

$$C_{IJ} = 0, H''_{II} = 0$$

$$\text{diag.} = 0$$

3. Hierarchy of EST methodology

From B.O. approximation (decouple nuclei and electrons)

, the nuclear SE is $(-\frac{\hbar^2}{2M} \nabla_R^2 + E_I^0) \chi_J = E \chi_J$

\rightarrow How to get this term? $E_I^0(R)$

→ Electronic structure theory.

review: $\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{NN} + \hat{V}_{ee} + \hat{V}_{ee}$

① 0. ② vibration only const.

, then the electronic Schrödinger equation is

- electronic Hamiltonian

$$\hat{H}_e |\Psi\rangle = E |\Psi\rangle \quad \hat{H}_e = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{Ne} + \hat{V}_{NN}$$

(const)

- pure electronic Hamiltonian

- $\hat{H}_e = \hat{T}_e + \hat{V}_{Ne} + \underbrace{\hat{V}_{ee}}$
difficult. $\because \frac{1}{r_{ij}}$

→ Hartree-Fock self-consistent-field average this term

→ mean-field approximation.

the resulting error is called electronic correlation.

① dynamic ② static

→ Standard methods in EST

$ \Psi\rangle = \Psi(\vec{r}; \vec{R})\rangle$, d.o.f. = $3Ne$		$P = \Psi ^2$, d.o.f. = 3
MR	$ \Psi\rangle = \sum_i C_i \Psi_{CSF}\rangle$	
SR	<p>CC</p> $\hat{T} = \hat{T}_1 + \hat{T}_2$ $ \Psi\rangle = e^{\hat{T}} \Psi_0\rangle$ $\hat{H} = \hat{H}_0 + \lambda V$ <p>MBPT</p> $ \Psi\rangle = \Psi_0\rangle + \lambda^{(1)} \Psi^{(1)}\rangle + \dots$ $CI \quad \Psi\rangle = \Psi_0\rangle + \sum_{i,a} c_i^a \Psi_i^a\rangle + \dots$ $HF \quad \Psi\rangle = \Psi_0\rangle = \phi_1 \phi_2 \dots\rangle$	$\hat{H}_e = \hat{H}_{KS}[P]$ <p>Jacob's Ladder</p>