

The Born-Oppenheimer approximation

Quantum Chemistry

Lesson 8

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Born-Oppenheimer approximation

Hamilton operator of a polyatomic system (X -representation)

$$\hat{H} = \sum_{K=1}^N \left(-\frac{\hbar^2}{2M_K} \Delta_K \right) + \sum_{k=1}^n \left(-\frac{\hbar^2}{2m_e} \Delta_k \right) + \hat{V}(\vec{r}_1, \dots, \vec{r}_n, \vec{R}_1, \dots, \vec{R}_N)$$

Born-Oppenheimer approximation

$$M_K \rightarrow +\infty \Rightarrow \hat{H} \rightarrow \hat{H}_e = \sum_{k=1}^n \left(-\frac{\hbar^2}{2m_e} \Delta_k \right) + \hat{V}(\vec{r}_1, \dots, \vec{r}_n, \vec{R}_1, \dots, \vec{R}_N) \text{ (electronic Hamiltonian)}$$

Electronic Schrödinger equation

$$\hat{H}_e \Phi_e(\vec{r}_1, \dots, \vec{r}_n; \vec{R}_1, \dots, \vec{R}_N) = E_e(\vec{R}_1, \dots, \vec{R}_N) \Phi_e(\vec{r}_1, \dots, \vec{r}_n; \vec{R}_1, \dots, \vec{R}_N)$$

Remark: Attention! In \hat{V} (and consequently in E_e as well), mutual (Coulombic) interactions of nuclei are included.

Potential energy surface

PES (*Potential Energy Surface*)

- $W(\vec{R}_1, \dots, \vec{R}_N) = E_e(\vec{R}_1, \dots, \vec{R}_N)$
- E_e is obtained by solving the electronic Schrödinger equation
 - the ground state, excited states \rightarrow (infinitely) many PESs
- interpretation
 - the nuclei move in an “external” field represented by a potential of $W(\vec{R}_1, \dots, \vec{R}_N)$
 - the electronic state (usually the ground state) does not change during the motion of nuclei
- how to use?
 - on-the-fly (quantum chemical) calculations
 - quantum chemical calculations on a “representative” grid of nuclear configurations, $\vec{R}_1, \dots, \vec{R}_N$, and a subsequent analytic representation
 - least-squares fitting (regression models)
 - machine learning methods (neural networks, support-vector-machines, kernel regression, symbolic regression + genetic programming, ...)
 - combined methods: on-the-fly (lower accuracy) and machine learning (refinement)

Potential energy surface

“Motion” of nuclei

- quantum picture

- $\hat{H}_{\text{nuc}} = \sum_{K=1}^N \left(-\frac{\hbar^2}{2M_K} \Delta_K \right) + W(\vec{R}_1, \dots, \vec{R}_N) \rightarrow$ time-dependent/independent Schrödinger equation

- classical picture

- $\vec{F}_K = -\nabla_K W \rightarrow$ classical equations of motion (e.g., the Newton ones: $\vec{F}_K = M_K \ddot{\vec{R}}_K$)

PES application I: stationary points

Stationary points

- for each K : $\nabla_K W = 0$
- classified by the definiteness of the Hessian matrix, $\mathcal{H}_{ij} = \frac{\partial^2 W}{\partial q_i \partial q_j}$ ($\mathbf{q} = [\vec{R}_1, \dots, \vec{R}_N] \in \mathbb{R}^{3N}$)
 - local maximum („negative definite“ \mathcal{H})
 - local minimum („positive definite“ \mathcal{H}) – equilibrium structures
 - saddle point („indefinite“ \mathcal{H}) – transition structures (states)

The “definiteness” of Hessian matrices

- eigenvalues
- 6 (5) eigenvalues are equal to zero (translations and rotations)
- others (molecular deformations = vibrations)
 - negative – „negative definite“
 - positive – „positive definite“
 - both positive and negative – „indefinite“
 - one negative, the other positive – 1st order transition point (reaction path)

PES application I: stationary points

Local minima

- optimization problem
 - local (descent) methods – e.g., gradient-based methods
 - global (usually stochastic) methods – e.g., simulated annealing, bio-inspired (genetic, evolutionary, swarm) algorithms
- exploitation of results
 - molecular structures
 - thermodynamics of gas-phase systems at rigid-body approximation level
 - (rigid) geometric structure → **electronic state sum**
 - → inertia momentum tensor → **rotational state sum**

PES application I: stationary points

Local minima

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State sum of N indistinguishable (non-interacting) molecules

$$Z = \frac{1}{N!} z^N$$

$$z = z_e z_t z_r z_v$$

$$z_* = \sum_j g_j^* \exp(-E_j^*/k_B T)$$

Electronic state sum

$$z_e \approx \exp(-E_{GS}^e/k_B T), E_{GS}^e = \text{the value of } W \text{ corresponding to the equilibrium configuration of nuclei and the electronic ground-state}$$

onary, swarm)

PES application I: station

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Rotational state sum

diatomic (linear) molecules

$$z_r = \sum_J (2J + 1) \exp(-E_J^r/k_B T), E_J^r = J(J + 1)\hbar^2/2I$$

$$z_r \approx (k_B T)/(\hbar^2/2I) \quad (\text{classical approximation})$$

polyatomic (non-linear) molecules

$$z_r \approx \frac{\sqrt{\pi}}{\sigma} \sqrt{\frac{(k_B T)^3}{(\hbar^2/2I_1)(\hbar^2/2I_2)(\hbar^2/2I_3)}} \quad (\text{classical approximation})$$

PES application I: stationary points

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Saddle points (1st order)

- more complex optimization-like task
 - many sophisticated methods available in the literature
- exploitation of results
 - energetic barriers between reactants and products of a chemical reaction
 - reaction rates

PES application II: molecular vibrations

Small vibrations (around an equilibrium configuration)

- second-order (quadratic) approximation of W (**harmonic approximation**)

$$W(\mathbf{q}_0 + \mathbf{u}) \approx W(\mathbf{q}_0) + \sum_{k=1}^{3N} \frac{\partial W}{\partial q_k}(\mathbf{q}_0) u_k + \frac{1}{2} \sum_{j,k=1}^{3N} \frac{\partial^2 W}{\partial q_j \partial q_k}(\mathbf{q}_0) u_j u_k \rightarrow \frac{1}{2} \sum_{j,k=1}^{3N} W_{jk} u_j u_k$$

- vibrational eigenmodes
 - $\mathbf{Q}^T \cdot \mathbf{W} \cdot \mathbf{Q} = \text{diag}(\lambda_1, \dots, \lambda_{3N-6}, 0, 0, 0, 0, 0, 0)$,
or $\mathbf{Q}^T \cdot \mathbf{W} \cdot \mathbf{Q} = \text{diag}(\lambda_1, \dots, \lambda_{3N-5}, 0, 0, 0, 0, 0)$ for linear molecules
 - $W(\mathbf{q}_0 + \mathbf{u}) \approx \frac{1}{2} \sum_{k=1}^{3N-6(5)} \lambda_k v_k^2$, where $\mathbf{v} = \mathbf{Q}^T \cdot \mathbf{u}$ (system of independent linear harmonic oscillators)

Exploitation

- vibrational energies (\rightarrow vibrational spectrum), vibrational wave functions
- thermodynamics of gas-phase ensembles of “weakly” non-rigid molecules
 - Hessian matrix \rightarrow vibrational eigenfrequencies \rightarrow **vibrational state sum**

PES application II: molecular vibrations

Small vibrations (around an equilibrium configuration)

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$$W(\mathbf{q}_0 + \mathbf{u}) \approx W(\mathbf{q}_0) + \sum_{k=1}^{3N} \frac{\partial W}{\partial q_k}(\mathbf{q}_0) u_k + \frac{1}{2} \sum_{j,k=1}^{3N} \frac{\partial^2 W}{\partial q_j \partial q_k}(\mathbf{q}_0) u_j u_k \rightarrow \frac{1}{2} \sum_{j,k=1}^{3N} W_{jk} u_j u_k$$

- vibrational eigenmodes

- $\mathbf{Q}^T \cdot \mathbf{W} \cdot \mathbf{Q} = \text{diag}(\lambda_1, \dots, \lambda_{3N-6}, 0, 0, 0, 0, 0, 0)$,

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Exploitation

- vibrational energies (\rightarrow vibrational spectrum)
- thermodynamics of gas-phase ensembles of “weakly interacting” molecules
 - Hessian matrix \rightarrow vibrational eigenfrequencies \rightarrow **vibrational state sum**

$$z_v = \exp(-E_0/k_B T) \prod_k \frac{1}{1 - \exp(-\hbar\omega_k/k_B T)}$$

Context (beyond the B-O approximation)

General Schrödinger equation

$$\hat{H}\varphi(\vec{r}_k, \vec{R}_K, t) = i\hbar \frac{\partial \varphi(\vec{r}_k, \vec{R}_K, t)}{\partial t}$$

- $\varphi(\vec{r}_k, \vec{R}_K, t) \equiv \varphi(\vec{r}_1, \dots, \vec{r}_n, \vec{R}_1, \dots, \vec{R}_N, t)$
- $\hat{H} = \underbrace{\sum_{K=1}^N \left(-\frac{\hbar^2}{2M_K} \Delta_K\right)}_{\hat{T}_{\text{nuc}}} + \underbrace{\sum_{k=1}^n \left(-\frac{\hbar^2}{2m_e} \Delta_k\right) + \hat{V}(\vec{r}_1, \dots, \vec{r}_n, \vec{R}_1, \dots, \vec{R}_N)}_{\hat{H}_e} \equiv \hat{T}_{\text{nuc}} + \hat{H}_e$
- $\hat{H}_e \Phi_{e\alpha}(\vec{r}_k, \vec{R}_K) = E_{e\alpha}(\vec{R}_K) \Phi_{e\alpha}(\vec{r}_k, \vec{R}_K)$

B-O separation ...

$$\varphi(\vec{r}_k, \vec{R}_K, t) = \sum_{\alpha} \chi_{\alpha}(\vec{R}_K, t) \Phi_{e\alpha}(\vec{r}_k, \vec{R}_K)$$

Context (beyond the B-O approximation)

... inserted in the general Schrödinger equation

$$\hat{T}_{\text{jad}}\chi_\beta + \sum_\alpha (\hat{c}_{\beta\alpha} + \delta_{\beta\alpha} E_{e\alpha})\chi_\alpha = i\hbar \frac{\partial \chi_\beta}{\partial t}$$

$$\hat{c}_{\beta\alpha} = \langle \Phi_{e\beta} | \hat{T}_{\text{jad}} | \Phi_{e\alpha} \rangle - \sum_{K=1}^N \frac{\hbar^2}{M_K} \langle \Phi_{e\beta} | \nabla_K \Phi_{e\alpha} \rangle \cdot \nabla_K$$

Approximations

- $\hat{c}_{\beta\alpha} = 0$ (**Born-Oppenheimer**)

$$(\hat{T}_{\text{jad}} + E_{e\beta})\chi_\beta = i\hbar \frac{\partial \chi_\beta}{\partial t} \rightarrow \left[\sum_{K=1}^N \left(-\frac{\hbar^2}{2M_K} \Delta_K \right) + W_\beta \right] \chi_\beta = i\hbar \frac{\partial \chi_\beta}{\partial t}$$

- $\hat{c}_{\beta\alpha} = 0$ pro $\beta \neq \alpha$ (**adiabatic**)

$$(\hat{T}_{\text{jad}} + E_{e\beta} + c_{\beta\beta})\chi_\beta = i\hbar \frac{\partial \chi_\beta}{\partial t} \rightarrow \left[\sum_{K=1}^N \left(-\frac{\hbar^2}{2M_K} \Delta_K \right) + (W_\beta + c_{\beta\beta}) \right] \chi_\beta = i\hbar \frac{\partial \chi_\beta}{\partial t}$$

$$\hat{c}_{\beta\beta} = \langle \Phi_{e\beta} | \hat{T}_{\text{jad}} | \Phi_{e\beta} \rangle = c_{\beta\beta} \quad (\text{real-valued corrections to } W_\beta)$$

Context (beyond the adiabatic approximation)

electronic state
changes with time

... inserted in the general Schrödinger equation

$$\hat{T}_{\text{jad}}\chi_{\beta} + \sum_{\alpha} (\hat{c}_{\beta\alpha} + \delta_{\beta\alpha} E_{e\alpha})\chi_{\alpha} = i\hbar \frac{\partial \chi_{\beta}}{\partial t}$$

$$\hat{c}_{\beta\alpha} = \langle \Phi_{e\beta} | \hat{T}_{\text{jad}} | \Phi_{e\alpha} \rangle - \sum_{K=1}^N \frac{\hbar^2}{M_K} \langle \Phi_{e\beta} | \nabla_K \Phi_{e\alpha} \rangle \cdot \nabla_K$$

Approximations

- $\hat{c}_{\beta\alpha} = 0$ (**Born-Oppenheimer**)

$$(\hat{T}_{\text{jad}} + E_{e\beta})\chi_{\beta} = i\hbar \frac{\partial \chi_{\beta}}{\partial t} \rightarrow \left[\sum_{K=1}^N \left(-\frac{\hbar^2}{2M_K} \Delta_K \right) + W_{\beta} \right] \chi_{\beta} = i\hbar \frac{\partial \chi_{\beta}}{\partial t}$$

- $\hat{c}_{\beta\alpha} = 0$ pro $\beta \neq \alpha$ (**adiabatic**)

$$(\hat{T}_{\text{jad}} + E_{e\beta} + c_{\beta\beta})\chi_{\beta} = i\hbar \frac{\partial \chi_{\beta}}{\partial t} \rightarrow \left[\sum_{K=1}^N \left(-\frac{\hbar^2}{2M_K} \Delta_K \right) + (W_{\beta} + c_{\beta\beta}) \right] \chi_{\beta} = i\hbar \frac{\partial \chi_{\beta}}{\partial t}$$

$$\hat{c}_{\beta\beta} = \langle \Phi_{e\beta} | \hat{T}_{\text{jad}} | \Phi_{e\beta} \rangle = c_{\beta\beta} \quad (\text{real-valued corrections to } W_{\beta})$$

electronic state does
not change with time

The end of lesson 8.