Approximate methods II
Perturbation methods

Quantum Chemistry

Lesson 6

Contents

1. General idea
2. Illustrative example
3. Stationary perturbation method in quantum chemistry (quantum mechanics)

General idea

Task to solve

- task P_0 (unperturbed problem), known solution y_0
- find $y(\varepsilon)$, a solution of task $P(\varepsilon) = P_0 + \Delta P(\varepsilon)$ (perturbed problem)
  - where $\Delta P(\varepsilon) \to 0$ for $\varepsilon \to 0$ is (considered) “small” (perturbation)
  - $\Delta P(\varepsilon) = \varepsilon P'$ (“smallness” parameter)

Solution

- *assumption:* $y(\varepsilon)$ is an analytic function of ε, $y(\varepsilon) = \sum_{k=0}^{+\infty} Y_k\, \varepsilon^k \approx \sum_{k=0}^{n} Y_k\, \varepsilon^k$ (Taylor series / polynomial)
- coefficients Y_k are obtained by inserting the series/polynomial in $P(\varepsilon) \to$ set of equations $y_0 \to Y_1, \{y_0, Y_1\} \to Y_2$
- perturbation orders of $y(\varepsilon)$
  - $y(\varepsilon) \approx Y_0 = y_0$ (0^{th} order approximation)
  - $y(\varepsilon) \approx y_1 = \sum_{k=0}^{1} Y_k\, \varepsilon^k = Y_0 + Y_1\varepsilon = y_0 + Y_1\varepsilon$ (1^{st} order / linear approximation)
  - $y(\varepsilon) \approx y_2 = \sum_{k=0}^{2} Y_k\, \varepsilon^k = Y_0 + Y_1\varepsilon + Y_2\varepsilon^2 = y_0 + Y_1\varepsilon + Y_2\varepsilon^2$ (2^{nd} order / quadratic approximation)
  - *etc.*

General idea

Applications

- quantum mechanics
    - stationary perturbation theory (to solve perturbed time-independent Schrödinger equation)
        - quantum chemistry (mechanics)
        - scattering theory
    - non-stationary perturbation theory (to solve perturbed time-dependent Schrödinger equation)
        - interaction of molecules, molecular complexes, nanoparticles, *etc.* with electromagnetic radiation (laser radiation)
- quantum field theory
    - elementary particles collisions (Feynman diagrams)
- many other branches of science ...

General idea

Applications

- quantum mechanics
  - stationary perturbation theory (to solve perturbed time-independent Schrödinger equation)
    - quantum chemistry (mechanics)
    - scattering theory
  - non-stationary perturbation theory (to solve perturbed time-dependent Schrödinger equation)
    - interaction of molecules, molecular complexes, nanoparticles, *etc.* with electromagnetic radiation (laser radiation)
- quantum field theory
  - elementary particles collisions (Feynman diagrams)
- many other branches of science ...

Illustrative example

Task to solve

- perturbed problem $P(\varepsilon)$: $y^3 - y + \varepsilon = 0$
- unperturbed problem P_0: $y^3 - y = 0$
  - three (known) solutions: $y_0 = 0$, $y_0 = \pm 1$

Solution of $P(\varepsilon)$ corresponding to $y_0 = 0$

- $y(\varepsilon) = \sum_{k=0}^{+\infty} Y_k\, \varepsilon^k = y_0 + \sum_{k=1}^{+\infty} Y_k \varepsilon^k = \sum_{k=1}^{+\infty} Y_k \varepsilon^k$
  - $y(\varepsilon) = Y_1\varepsilon + Y_2\varepsilon^2 + Y_3\varepsilon^3 + \cdots$
  - $y^2(\varepsilon) = (Y_1\varepsilon + Y_2\varepsilon^2 + Y_3\varepsilon^3 + \cdots)(Y_1\varepsilon + Y_2\varepsilon^2 + Y_3\varepsilon^3 + \cdots) = Y_1^2\varepsilon^2 + 2Y_1Y_2\varepsilon^3 + \cdots$
  - $y^3(\varepsilon) = (Y_1^2\varepsilon^2 + 2Y_1Y_2\varepsilon^3 + \cdots)(Y_1\varepsilon + Y_2\varepsilon^2 + Y_3\varepsilon^3 + \cdots) = Y_1^3\varepsilon^3 + \cdots$
- $(Y_1^3\varepsilon^3 + \cdots) - (Y_1\varepsilon + Y_2\varepsilon^2 + Y_3\varepsilon^3 + \cdots) + \varepsilon = 0$
- $(Y_1^3 - Y_3)\varepsilon^3 - Y_2\varepsilon^2 + (1 - Y_1)\varepsilon + \cdots = 0$

Illustrative example

Continuation ...

- $(Y_1^3 - Y_3)\varepsilon^3 - Y_2\varepsilon^2 + (1 - Y_1)\varepsilon + \cdots = 0$
  - $Y_1^3 - Y_3 = 0$
  - $-Y_2 \quad\quad = 0$
  - $1 - Y_1 \quad = 0$
  - $Y_1 = 1, Y_2 = 0, Y_3 = 1$ (and $y_0 = 0$)
- $y(\varepsilon) = y_0 + Y_1\varepsilon + Y_2\varepsilon^2 + Y_3\varepsilon^3 + \cdots = \varepsilon + \varepsilon^3 + \cdots$
  - 0th order solution: $y_0 = 0$ (l.h.s. $\equiv y^3 - y + \varepsilon = \varepsilon = [\varepsilon = 0.1] = 0.1 = 10^{-1}$)
  - 1st order solution: $y_1 = \varepsilon$ (l.h.s. $= \cdots = \varepsilon^3 = [\varepsilon = 0.1] = 0.001 = 10^{-3} \approx 0$)
  - 2nd order solution: $y_2 = \varepsilon$
  - 3rd order solution: $y_3 = \varepsilon + \varepsilon^3$ (l.h.s. $= \cdots = 3\varepsilon^5 + 3\varepsilon^7 = [\varepsilon = 0.1] = 0.0000303 \approx 3 \times 10^{-5} \approx 0$)
  - ...

Stationary perturbation method in QC

Task to solve

- perturbed problem $P(\varepsilon)$: $\hat{H}|\psi_\alpha\rangle = E_\alpha|\psi_\alpha\rangle, \quad \hat{H} = \hat{H}_0 + \hat{H}_{\mathrm{P}} = \hat{H}_0 + \varepsilon\hat{H}_1$
- unperturbed problem P_0: $\hat{H}_0|\psi_{0\alpha}\rangle = E_{0\alpha}|\psi_{0\alpha}\rangle$ (non-degenerate spectrum)

Solution

- $|\psi_\alpha\rangle = |\psi_\alpha(\varepsilon)\rangle = \sum_{k=0}^{+\infty} \varepsilon^k |\Psi_{k\alpha}\rangle$
- $E_\alpha = E_\alpha(\varepsilon) = \sum_{k=0}^{+\infty} \varepsilon^k \mathcal{E}_{k\alpha}$
- $\left(\hat{H}_0 + \varepsilon\hat{H}_1\right)\left(\sum_{k=0}^{+\infty} \varepsilon^k |\Psi_{k\alpha}\rangle\right) = \left(\sum_{k=0}^{+\infty} \varepsilon^k \mathcal{E}_{k\alpha}\right)\left(\sum_{k=0}^{+\infty} \varepsilon^k |\Psi_{k\alpha}\rangle\right)$

  $\left(\hat{H}_0 + \varepsilon\hat{H}_1\right)(|\Psi_{0\alpha}\rangle + \varepsilon|\Psi_{1\alpha}\rangle + \cdots) = (\mathcal{E}_{0\alpha} + \varepsilon\mathcal{E}_{1\alpha} + \cdots)(|\Psi_{0\alpha}\rangle + \varepsilon|\Psi_{1\alpha}\rangle + \cdots)$

[wiki]

Stationary perturbation method in QC

Continuation ...

- $(\hat{H}_0 + \varepsilon\hat{H}_1)(|\Psi_{0\alpha}\rangle + \varepsilon|\Psi_{1\alpha}\rangle + \cdots) = (\mathcal{E}_{0\alpha} + \varepsilon\mathcal{E}_{1\alpha} + \cdots)(|\Psi_{0\alpha}\rangle + \varepsilon|\Psi_{1\alpha}\rangle + \cdots)$
- $\hat{H}_0|\Psi_{0\alpha}\rangle + (\hat{H}_0|\Psi_{1\alpha}\rangle + \hat{H}_1|\Psi_{0\alpha}\rangle)\varepsilon + \cdots = \mathcal{E}_{0\alpha}|\Psi_{0\alpha}\rangle + (\mathcal{E}_{0\alpha}|\Psi_{1\alpha}\rangle + \mathcal{E}_{1\alpha}|\Psi_{0\alpha}\rangle)\varepsilon + \cdots$
  - 0^{th} order solution: $\hat{H}_0|\Psi_{0\alpha}\rangle = \mathcal{E}_{0\alpha}|\Psi_{0\alpha}\rangle$ $\{|\Psi_{0\alpha}\rangle = |\psi_{0\alpha}\rangle,\ \mathcal{E}_{0\alpha} = E_{0\alpha}\}$ (assumingly known)
  - 1^{st} order solution : $\hat{H}_0|\Psi_{1\alpha}\rangle + \hat{H}_1|\Psi_{0\alpha}\rangle = E_{0\alpha}|\Psi_{1\alpha}\rangle + \mathcal{E}_{1\alpha}|\Psi_{0\alpha}\rangle$
  - ...

Stationary perturbation method in QC

1st order solution - energy

- $\hat{H}_0|\Psi_{1\alpha}\rangle + \hat{H}_1|\psi_{0\alpha}\rangle = E_{0\alpha}|\Psi_{1\alpha}\rangle + \mathcal{E}_{1\alpha}|\psi_{0\alpha}\rangle \quad , \langle\psi_{0\alpha}| \rightarrow$
- $\underbrace{\langle\psi_{0\alpha}|\hat{H}_0|\Psi_{1\alpha}\rangle}_{E_{0\alpha}\langle\psi_{0\alpha}|\Psi_{1\alpha}\rangle} + \langle\psi_{0\alpha}|\hat{H}_1|\psi_{0\alpha}\rangle = E_{0\alpha}\langle\psi_{0\alpha}|\Psi_{1\alpha}\rangle + \mathcal{E}_{1\alpha}\underbrace{\langle\psi_{0\alpha}|\psi_{0\alpha}\rangle}_{1}$
- $\mathcal{E}_{1\alpha} = \langle\psi_{0\alpha}|\hat{H}_1|\psi_{0\alpha}\rangle,$ or $\mathcal{E}_{1\alpha} = \frac{\langle\psi_{0\alpha}|\hat{H}_1|\psi_{0\alpha}\rangle}{\langle\psi_{0\alpha}|\psi_{0\alpha}\rangle}$
- $E_\alpha \approx E_{1\alpha} = E_{0\alpha} + \varepsilon\mathcal{E}_{1\alpha} = E_{0\alpha} + \varepsilon\langle\psi_{0\alpha}|\hat{H}_1|\psi_{0\alpha}\rangle = E_{0\alpha} + \langle\psi_{0\alpha}|\hat{H}_\mathrm{P}|\psi_{0\alpha}\rangle$

Stationary perturbation method in QC

1st order solution – wave function

- $\hat{H}_0|\Psi_{1\alpha}\rangle + \hat{H}_1|\psi_{0\alpha}\rangle = E_{0\alpha}|\Psi_{1\alpha}\rangle + \mathcal{E}_{1\alpha}|\psi_{0\alpha}\rangle$
- $|\Psi_{1\alpha}\rangle = \sum_{\beta=0}^{+\infty} c_{\alpha\beta}^{(1)}|\psi_{0\beta}\rangle$
  - without any loss of generality: $c_{\alpha\alpha}^{(1)} = 0 \Leftrightarrow \langle\Psi_{1\alpha}|\psi_{0\alpha}\rangle = 0$ (why?)

- $\hat{H}_0 \sum_{\beta=0}^{+\infty} c_{\alpha\beta}^{(1)}|\psi_{0\beta}\rangle + \hat{H}_1|\psi_{0\alpha}\rangle = E_{0\alpha} \sum_{\beta=0}^{+\infty} c_{\alpha\beta}^{(1)}|\psi_{0\beta}\rangle + \mathcal{E}_{1\alpha}|\psi_{0\alpha}\rangle$, $\langle\psi_{0\gamma}| \rightarrow, \gamma \neq \alpha$
- $\underbrace{\langle\psi_{0\gamma}|\hat{H}_0 \sum_{\beta=0}^{+\infty} c_{\alpha\beta}^{(1)}|\psi_{0\beta}\rangle}_{E_{0\gamma} \sum_{\beta=0}^{+\infty} c_{\alpha\beta}^{(1)} \underbrace{\langle\psi_{0\gamma}|\psi_{0\beta}\rangle}_{\delta_{\beta\gamma}}} + \langle\psi_{0\gamma}|\hat{H}_1|\psi_{0\alpha}\rangle = E_{0\alpha} \sum_{\beta=0}^{+\infty} c_{\alpha\beta}^{(1)} \underbrace{\langle\psi_{0\gamma}|\psi_{0\beta}\rangle}_{\delta_{\beta\gamma}} + \mathcal{E}_{1\alpha} \underbrace{\langle\psi_{0\gamma}|\psi_{0\alpha}\rangle}_{\delta_{\alpha\gamma}=0}$

Stationary perturbation method in QC

Continuation ...

- $\underbrace{\langle\psi_{0\gamma}|\hat{H}_0\sum_{\beta=0}^{+\infty}c_{\alpha\beta}^{(1)}|\psi_{0\beta}\rangle}_{E_{0\gamma}\sum_{\beta=0}^{+\infty}c_{\alpha\beta}^{(1)}\underbrace{\langle\psi_{0\gamma}|\psi_{0\beta}\rangle}_{\delta_{\beta\gamma}}} + \langle\psi_{0\gamma}|\hat{H}_1|\psi_{0\alpha}\rangle = E_{0\alpha}\sum_{\beta=0}^{+\infty}c_{\alpha\beta}^{(1)}\underbrace{\langle\psi_{0\gamma}|\psi_{0\beta}\rangle}_{\delta_{\beta\gamma}} + \mathcal{E}_{1\alpha}\underbrace{\langle\psi_{0\gamma}|\psi_{0\alpha}\rangle}_{\delta_{\alpha\gamma}=0}$
    - $c_{\alpha\gamma}^{(1)}E_{0\gamma} + \langle\psi_{0\gamma}|\hat{H}_1|\psi_{0\alpha}\rangle = c_{\alpha\gamma}^{(1)}E_{0\alpha}$
    - $c_{\alpha\gamma}^{(1)} = \frac{\langle\psi_{0\gamma}|\hat{H}_1|\psi_{0\alpha}\rangle}{E_{0\alpha}-E_{0\gamma}}$
- $|\Psi_{1\alpha}\rangle = \sum_{\gamma=0}^{+\infty}c_{\alpha\gamma}^{(1)}|\psi_{0\gamma}\rangle = \sum_{\gamma=0,\ \gamma\neq\alpha}^{+\infty}\frac{\langle\psi_{0\gamma}|\hat{H}_1|\psi_{0\alpha}\rangle}{E_{0\alpha}-E_{0\gamma}}|\psi_{0\gamma}\rangle$
- $|\psi_\alpha\rangle \approx |\psi_{1\alpha}\rangle \equiv |\psi_{0\alpha}\rangle + \varepsilon|\Psi_{1\alpha}\rangle = |\psi_{0\alpha}\rangle + \varepsilon|\Psi_{1\alpha}\rangle = \cdots = |\psi_{0\alpha}\rangle + \sum_{\gamma=0,\ \gamma\neq\alpha}^{+\infty}\frac{\langle\psi_{0\gamma}|\hat{H}_\mathrm{P}|\psi_{0\alpha}\rangle}{E_{0\alpha}-E_{0\gamma}}|\psi_{0\gamma}\rangle$

The end of lesson 6.