

9/25/2024

- Time-Independent Perturbation Theory
 - Two-level systems
 - Many-level systems
- Exercise: Approximation Methods
- This lecture is designed to help you achieve the following learning objectives
 - Use perturbation theory to extend analytical models to more realistic situations

Time-Independent Perturbation Theory

- Exact solutions to Schrodinger's equation are only known in a few systems
- For most chemical systems, we need to use approximation methods
- For certain systems $\hat{\mathbf{H}} = \hat{\mathbf{H}}^{(0)} + \hat{\mathbf{H}}^{(1)}$ may describe the Hamiltonian
 - $\hat{\mathbf{H}}^{(0)}$ is a Hamiltonian with a solvable Schrodinger equation
 - $\hat{\mathbf{H}}^{(1)}$ is a perturbation to this Hamiltonian
- For example, if the potential energy is $V(x) = \frac{1}{2}k_f x^2 + ax^3$, then ax^3 can be considered a perturbation to a harmonic oscillator potential energy.

Two-level systems

- Consider a system with two
 - Eigenstates of the Hamiltonian $\hat{\mathbf{H}}^{(0)}$, $|1\rangle$ and $|2\rangle$
 - Corresponding wavefunctions, $\Psi_1^{(0)}$ and $\Psi_2^{(0)}$
 - Energy levels, E_1 and E_2
- Examples are
 - electron or nucleus with spin 1/2
 - many-level system with two predominant states

General solution

- The true wavefunction is $\Psi = c_1 \Psi_1^{(0)} + c_2 \Psi_2^{(0)}$, where c_1 and c_2 are unknown
- How to obtain c_1 and c_2 ?
- Start by inserting wavefunction into the Schrodinger equation,
$$c_1(\hat{\mathbf{H}} - E) |1\rangle + c_2(\hat{\mathbf{H}} - E) |2\rangle = 0$$

- $c_1(\hat{\mathbf{H}} - E) |1\rangle + c_2(\hat{\mathbf{H}} - E) |2\rangle = 0$ is the Schrodinger equation
- Left-multiply by $\langle 1 |$ or $\langle 2 |$,
- $\langle 1 | c_1(\hat{\mathbf{H}} - E) |1\rangle + \langle 1 | c_2(\hat{\mathbf{H}} - E) |2\rangle = c_1(H_{11} - E) + c_2H_{12} = 0$
- $\langle 2 | c_1(\hat{\mathbf{H}} - E) |1\rangle + \langle 2 | c_2(\hat{\mathbf{H}} - E) |2\rangle = c_1H_{21} + c_2(H_{22} - E) = 0$
- Remember that
 - $H_{mn} = \langle m | \hat{\mathbf{H}} | n \rangle$ and that $\langle 1 | 2 \rangle = \langle 2 | 1 \rangle = 0$
 - $|1\rangle$ and $|2\rangle$ are eigenfunctions of $\hat{\mathbf{H}}^{(0)}$, not of $\hat{\mathbf{H}}$
- This is a linear algebra problem,
$$\begin{pmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$
- There is a solution when
$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0$$

- $\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0$
- $(H_{11} - E)(H_{22} - E) - H_{12}H_{21} = 0$
- $E^2 - (H_{11} + H_{22})E + (H_{11}H_{22} - H_{12}H_{21}) = 0$ by expansion
- $E_{\pm} = \frac{1}{2} (H_{11} + H_{22}) \pm \frac{1}{2} \sqrt{(H_{22} - H_{11})^2 - 4H_{12}H_{21}}$ are energies of the *perturbed* system
- Perturbed wavefunctions can be found by substituting energies into $\begin{pmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$ and solving for the coefficients

Many-level systems

- Consider a system with multiple
 - Eigenstates of the Hamiltonian $\hat{\mathbf{H}}^{(0)}: |n\rangle$
 - Corresponding wavefunctions: $\Psi_n^{(0)}$
 - Energy levels: E_n
 - for $n = 0, 1, 2, \dots, n$
- We can write a perturbed
 - Hamiltonian:
$$\hat{\mathbf{H}} = \hat{\mathbf{H}}^{(0)} + \lambda \hat{\mathbf{H}}^{(1)} + \lambda^2 \hat{\mathbf{H}}^{(2)} + \dots$$
 - Wavefunction:
$$\Psi_0^{(0)} = \Psi_0^{(0)} + \lambda \Psi_0^{(1)} + \lambda^2 \Psi_0^{(2)} + \dots$$
 - Energy:
$$E_o = E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \dots$$
 - Superscripts are *orders* of correction
 - The parameter λ
 - tracks order of perturbation
 - ultimately set to 1

Using the power series

We can substitute these power series into the Schrodinger equation and rearrange in terms of λ ,

$$\begin{aligned} & \left(\hat{\mathbf{H}}^{(0)} + \lambda \hat{\mathbf{H}}^{(1)} + \lambda^2 \hat{\mathbf{H}}^{(2)} \right) \left(\Psi_0^{(0)} + \lambda \Psi_0^{(1)} + \lambda^2 \Psi_0^{(2)} \right) - \\ & \left(E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} \right) \left(\Psi_0^{(0)} + \lambda \Psi_0^{(1)} + \lambda^2 \Psi_0^{(2)} \right) = \\ & \left(\hat{\mathbf{H}}^{(0)} \Psi_0^{(0)} - E_0^{(0)} \Psi_0^{(0)} \right) + \\ & \left(\hat{\mathbf{H}}^{(0)} \Psi_0^{(1)} + \hat{\mathbf{H}}^{(1)} \Psi_0^{(0)} - E_0^{(0)} \Psi_0^{(1)} - E_0^{(1)} \Psi_0^{(0)} \right) \lambda + \\ & \left(\hat{\mathbf{H}}^{(0)} \Psi_0^{(2)} + \hat{\mathbf{H}}^{(1)} \Psi_0^{(1)} + \hat{\mathbf{H}}^{(2)} \Psi_0^{(0)} - E_0^{(0)} \Psi_0^{(2)} - E_0^{(1)} \Psi_0^{(1)} - E_0^{(2)} \Psi_0^{(0)} \right) \lambda^2 + O(\lambda^3) = 0 \end{aligned}$$

Determining the perturbation

- Because λ is not zero, the coefficients of each power of λ must equal to zero separately. This gives us a system of equations.
 1. $\hat{\mathbf{H}}^{(0)}\Psi_0^{(0)} - E_0^{(0)}\Psi_0^{(0)} = 0$
 2. $\left(\hat{\mathbf{H}}^{(0)}\Psi_0^{(1)} + \hat{\mathbf{H}}^{(1)}\Psi_0^{(0)} - E_0^{(0)}\Psi_0^{(1)} - E_0^{(1)}\Psi_0^{(0)} \right) = 0$
 3. $\left(\hat{\mathbf{H}}^{(0)}\Psi_0^{(2)} + \hat{\mathbf{H}}^{(1)}\Psi_0^{(1)} + \hat{\mathbf{H}}^{(2)}\Psi_0^{(0)} - E_0^{(0)}\Psi_0^{(2)} - E_0^{(1)}\Psi_0^{(1)} - E_0^{(2)}\Psi_0^{(0)} \right) = 0$
- We already know the solution to Eq 1.
- To solve Eq 2, we use $\Psi_0^{(1)} = \sum_n c_n \Psi_n^{(0)}$, because the wavefunctions are a complete set of basis functions.

First-order correction to energy

- $\left(\hat{\mathbf{H}}^{(0)} \Psi_0^{(1)} + \hat{\mathbf{H}}^{(1)} \Psi_0^{(0)} - E_0^{(0)} \Psi_0^{(1)} - E_0^{(1)} \Psi_0^{(0)} \right) = 0$
- Because the $\Psi_n^{(0)}$ are a complete basis set, $\Psi_0^{(1)} = \sum_n c_n \Psi_n^{(0)}$.
- $\sum_n c_n \left(\hat{\mathbf{H}}^{(0)} - E_0^{(0)} \right) \Psi_n^{(0)} + \left(\hat{\mathbf{H}}^{(1)} - E_0^{(1)} \right) \Psi_0^{(0)} = 0$
- $\sum_n c_n \left(E_n^{(0)} - E_0^{(0)} \right) |n\rangle = - \left(\hat{\mathbf{H}}^{(1)} - E_0^{(1)} \right) |0\rangle$, using ket notation
- $\sum_n c_n \langle 0 | \left(E_n^{(0)} - E_0^{(0)} \right) |n\rangle = - \langle 0 | \left(\hat{\mathbf{H}}^{(1)} - E_0^{(1)} \right) |0\rangle$, left multiplying by $\langle 0 |$
- $E_0^{(1)} = H_{00}^{(1)}$, as l.h.s is zero.

Example: Gravitational Well

- $$V(x) = \begin{cases} \infty & x < 0 \\ \frac{V_o x}{a} & 0 < x < a \\ \infty & x > a \end{cases}$$
- The PIB solution is $|n^{(0)}\rangle = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi a}{x}\right)$ with energy $E_n^{(0)} = \frac{n^2 h^2}{8ma^2}$
- $$E_n^{(1)} = \left\langle n^{(0)} \left| \frac{V_o x}{a} \right| n^{(0)} \right\rangle = \frac{2V_o}{a} \int_0^a x \sin^2\left(\frac{n\pi x}{a}\right) dx = \frac{V_o}{2}$$
- $$E_1 = E_1^{(0)} + E_1^{(1)} = \frac{h^2}{8ma^2} + \frac{V_o}{2}$$

First-order correction to the wavefunction

- $\sum_n c_n \left(E_n^{(0)} - E_0^{(0)} \right) |n\rangle = - \left(\hat{\mathbf{H}}^{(1)} - E_0^{(1)} \right) |0\rangle$ came from using the linear

combination of wavefunctions in the first-order term

- $\sum_n \langle k | c_n \left(E_n^{(0)} - E_0^{(0)} \right) |n\rangle = - \langle k | \left(\hat{\mathbf{H}}^{(1)} - E_0^{(1)} \right) |0\rangle$, left multiplying by $\langle k |$,

where $k \neq 0$

- $c_k \left(E_k^{(0)} - E_0^{(0)} \right) = - \langle k | \left(\hat{\mathbf{H}}^{(1)} - E_0^{(1)} \right) |0\rangle = - \langle k | \hat{\mathbf{H}}^{(1)} |0\rangle$

- If there are no degenerate states, $c_k = \frac{H_{k0}^{(1)}}{E_0^{(0)} - E_k^{(0)}}$ and therefore

$$\Psi_0 \approx \Psi_0^{(0)} + \sum_{k \neq 0} \left\{ \frac{H_{k0}^{(1)}}{E_0^{(0)} - E_k^{(0)}} \right\} \Psi_k^{(0)}$$

First-order correction to the wavefunction

- $\Psi_0 \approx \Psi_0^{(0)} + \sum_{k \neq 0} \left\{ \frac{H_{k0}^{(1)}}{E_0^{(0)} - E_k^{(0)}} \right\} \Psi_k^{(0)}$
 - Proportional to the extent of the first-order perturbation
 - Inversely proportional to the energy gap

Second-order correction to the energy

- Starting from,

$$\left(\hat{\mathbf{H}}^{(0)}\Psi_0^{(2)} + \hat{\mathbf{H}}^{(1)}\Psi_0^{(1)} + \hat{\mathbf{H}}^{(2)}\Psi_0^{(0)} - E_0^{(0)}\Psi_0^{(2)} - E_0^{(1)}\Psi_0^{(1)} - E_0^{(2)}\Psi_0^{(0)} \right) = 0,$$

follow a similar procedure of substituting a linear combination of eigenfunctions and left-multiplying by a ket $\langle 0 |$.

- $E_0^{(2)} = H_{00}^{(2)} + \sum_{n \neq 0} \frac{H_{0n}^{(1)} H_{n0}^{(1)}}{E_0^{(0)} - E_n^{(0)}}$ is the second-order correction to the energy

Exercise: Approximation Methods

https://colab.research.google.com/github/daveminh/Chem550-2024F/blob/main/exercises/02-Approximation_Methods.ipynb

Review Questions

- Does perturbation theory provide any bounds to the ground-state energy?
- How are perturbation theory energies and wavefunctions made more accurate?