

NPTEL ONLINE CERTIFICATION COURSES

Approximate Methods in Quantum Chemistry

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Lecture 17: Perturbation Theory

Perturbation Theory

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}'$$

$$\hat{H}\Psi_n = E_n\Psi_n$$

$$\hat{H}_0\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)}$$

$$\begin{aligned}\Psi_n &= \Psi_n^{(0)} + \lambda\Psi_n^{(1)} + \lambda^2\Psi_n^{(2)} \dots \\ E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} \dots\end{aligned}$$

$$\begin{aligned}(\hat{H}_0 + \lambda\hat{H}')(\Psi_n^{(0)} + \lambda\Psi_n^{(1)} + \lambda^2\Psi_n^{(2)} \dots) = \\ (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} \dots)(\Psi_n^{(0)} + \lambda\Psi_n^{(1)} + \lambda^2\Psi_n^{(2)} \dots)\end{aligned}$$

$$\lambda^0 : \hat{H}_0\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)}$$

$$\lambda^1 : \hat{H}_0\Psi_n^{(1)} + \hat{H}'\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(1)} + E_n^{(1)}\Psi_n^{(0)}$$

$$\lambda^2 : \hat{H}_0\Psi_n^{(2)} + \hat{H}'\Psi_n^{(1)} = E_n^{(0)}\Psi_n^{(2)} + E_n^{(1)}\Psi_n^{(1)} + E_n^{(2)}\Psi_n^{(0)}$$



Perturbation Theory

First Order

$$\lambda^1 : \hat{H}_0 \Psi_n^{(1)} + \hat{H}' \Psi_n^{(0)} = E_n^{(0)} \Psi_n^{(1)} + E_n^{(1)} \Psi_n^{(0)}$$

$$\langle \Psi_m^{(0)} | H_0 | \Psi_n^{(1)} \rangle + \langle \Psi_m^{(0)} | H' | \Psi_n^{(0)} \rangle = \langle \Psi_m^{(0)} | E_n^{(0)} | \Psi_n^{(1)} \rangle + \langle \Psi_m^{(0)} | E_n^{(1)} | \Psi_n^{(0)} \rangle$$

$$\langle \Psi_n^{(1)} | H_0 | \Psi_m^{(0)} \rangle^* + \langle \Psi_m^{(0)} | H' | \Psi_n^{(0)} \rangle = E_n^{(0)} \langle \Psi_m^{(0)} | \Psi_n^{(1)} \rangle + E_n^{(1)} \langle \Psi_m^{(0)} | \Psi_n^{(0)} \rangle$$

$$\langle \Psi_m^{(0)} | H' | \Psi_n^{(0)} \rangle = \left(E_n^{(0)} - E_m^{(0)} \right) \langle \Psi_m^{(0)} | \Psi_n^{(1)} \rangle + E_n^{(1)} \delta_{mn}$$

$$n = m : E_n^{(1)} = \frac{\langle \Psi_n^{(0)} | H' | \Psi_n^{(0)} \rangle}{\langle \Psi_n^{(0)} | \Psi_n^{(0)} \rangle}$$

1st order energy
correction



Perturbation Theory

First Order

$$\left\langle \Psi_m^{(0)} | H' | \Psi_n^{(0)} \right\rangle = \left(E_n^{(0)} - E_m^{(0)} \right) \left\langle \Psi_m^{(0)} | \Psi_n^{(1)} \right\rangle + E_n^{(1)} \delta_{mn}$$

$$n \neq m : \left\langle \Psi_m^{(0)} | \Psi_n^{(1)} \right\rangle = \frac{\left\langle \Psi_m^{(0)} | H' | \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)}$$

$$\Psi_n^{(1)} = \sum_k c_k \Psi_k^{(0)} \quad \text{where, } c_k = \left\langle \Psi_k^{(0)} | \Psi_n^{(1)} \right\rangle$$

$$\left\langle \Psi_m^{(0)} | \sum_k c_k \Psi_k^{(0)} \right\rangle = c_m$$

$$c_m = \frac{\left\langle \Psi_m^{(0)} | H' | \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)}$$

1st Order wave
function correction

$$\Psi_n^{(1)} = \sum_{m \neq n} \frac{\left\langle \Psi_m^{(0)} | H' | \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)} \Psi_m^{(0)}$$



Perturbation Theory

Second Order

$$\lambda^0 : \hat{H}_0 \Psi_n^{(0)} = E_n^{(0)} \Psi_n^{(0)}$$

$$\lambda^1 : \hat{H}_0 \Psi_n^{(1)} + \hat{H}' \Psi_n^{(0)} = E_n^{(0)} \Psi_n^{(1)} + E_n^{(1)} \Psi_n^{(0)}$$

$$E_n^{(1)} = \frac{\langle \Psi_n^{(0)} | \hat{H}' | \Psi_n^{(0)} \rangle}{\langle \Psi_n^{(0)} | \Psi_n^{(0)} \rangle}$$

$$\Psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \Psi_m^{(0)} | \hat{H}' | \Psi_n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})} \Psi_m^{(0)}$$

$$\lambda^2 : \hat{H}_0 \Psi_n^{(2)} + \hat{H}' \Psi_n^{(1)} = E_n^{(0)} \Psi_n^{(2)} + E_n^{(1)} \Psi_n^{(1)} + E_n^{(2)} \Psi_n^{(0)}$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{\left| \langle \Psi_m^{(0)} | \hat{H}' | \Psi_n^{(0)} \rangle \right|^2}{E_n^{(0)} - E_m^{(0)}}$$

2nd order energy
correction



Perturbation Theory

$$E_n^{(1)} = \frac{\langle \Psi_n^{(0)} | H' | \Psi_n^{(0)} \rangle}{\langle \Psi_n^{(0)} | \Psi_n^{(0)} \rangle}$$

$$\Psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \Psi_m^{(0)} | H' | \Psi_n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})} \Psi_m^{(0)}$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \Psi_m^{(0)} | \hat{H}' | \Psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \dots$$

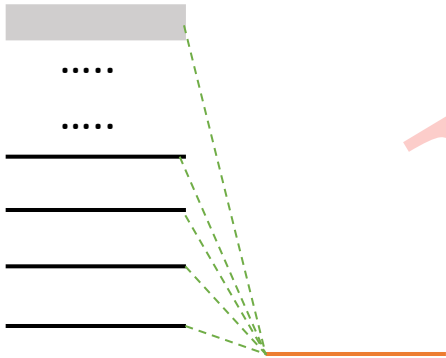
$$\Psi_n = \Psi_n^{(0)} + \Psi_n^{(1)} + \Psi_n^{(2)} + \dots$$

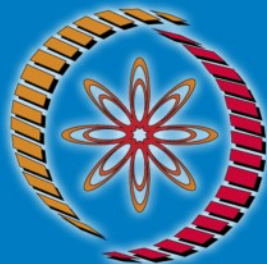
- Wave function correction up to n^{th} order is enough for energy correction up to $2n+1^{\text{th}}$ order.

- Where to truncate the sum?

- Symmetry argument

$$\int \Psi_m^{(0)} \hat{H}' \Psi_n^{(0)} d\tau \equiv \Gamma^{(m)} \Gamma^{(pert)} \Gamma^{(n)}$$





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Lecture 18: Applications of Perturbation Theory

Perturbation Theory

$$E_n^{(1)} = \frac{\langle \Psi_n^{(0)} | H' | \Psi_n^{(0)} \rangle}{\langle \Psi_n^{(0)} | \Psi_n^{(0)} \rangle}$$

$$\Psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \Psi_m^{(0)} | H' | \Psi_n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})} \Psi_m^{(0)}$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \Psi_m^{(0)} | \hat{H}' | \Psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \dots$$

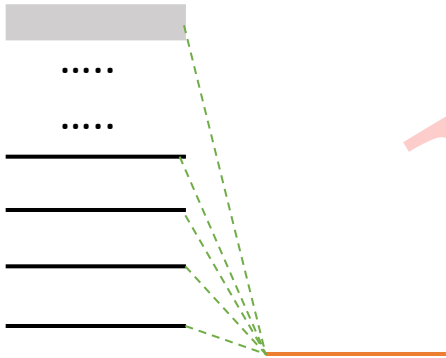
$$\Psi_n = \Psi_n^{(0)} + \Psi_n^{(1)} + \Psi_n^{(2)} + \dots$$

- Wave function correction up to n^{th} order is enough for energy correction up to $2n+1^{\text{th}}$ order.

- Where to truncate the sum?

- Symmetry argument

$$\int \Psi_m^{(0)} \hat{H}' \Psi_n^{(0)} d\tau \equiv \Gamma^{(m)} \Gamma^{(pert)} \Gamma^{(n)}$$



Perturbation Theory: Examples

Particle in a box with a constant perturbation

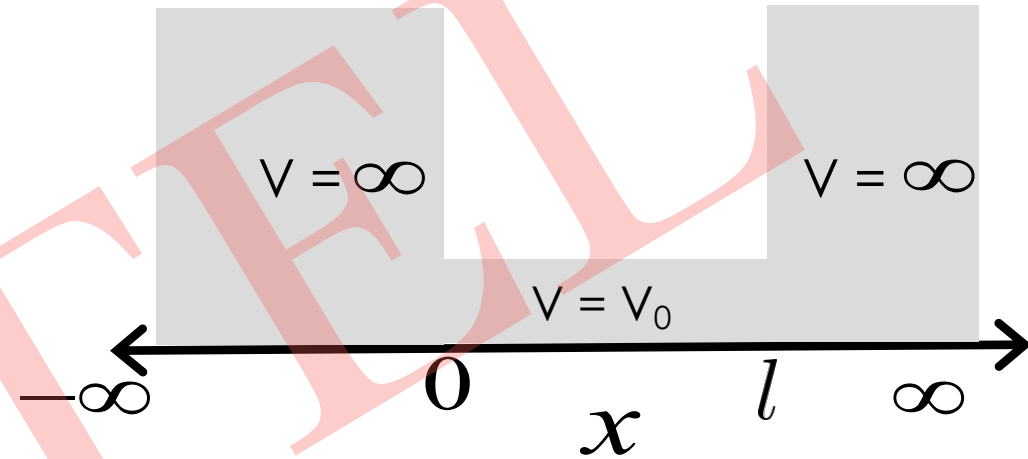
$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

$$E_n^{(0)} = \frac{n^2 \hbar^2}{8ml^2} \quad \Psi_n^{(0)} = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right)$$

$$\hat{H}' = V_0$$

$$E_n^{(1)} = \frac{\langle \Psi_n^{(0)} | H' | \Psi_n^{(0)} \rangle}{\langle \Psi_n^{(0)} | \Psi_n^{(0)} \rangle}$$

$$\Psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \Psi_m^{(0)} | H' | \Psi_n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})} \Psi_m^{(0)}$$



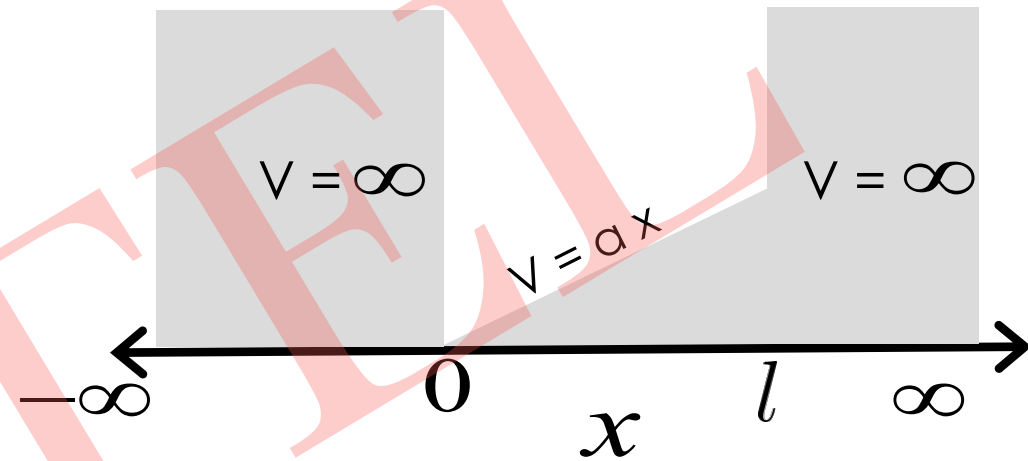
Perturbation Theory: Examples

Particle in a box with a linear perturbation

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

$$E_n^{(0)} = \frac{n^2 \hbar^2}{8ml^2} \quad \Psi_n^{(0)} = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right)$$

$$\begin{aligned} E_n^{(1)} &= \frac{\langle \Psi_n^{(0)} | H' | \Psi_n^{(0)} \rangle}{\langle \Psi_n^{(0)} | \Psi_n^{(0)} \rangle} = \frac{2}{l} \int_0^l \sin\left(\frac{n\pi x}{l}\right) (ax) \sin\left(\frac{n\pi x}{l}\right) dx \\ &= \frac{2a}{l} \int_0^l x \sin^2\left(\frac{n\pi x}{l}\right) dx = \frac{al}{2} \end{aligned}$$



Perturbation Theory: Examples

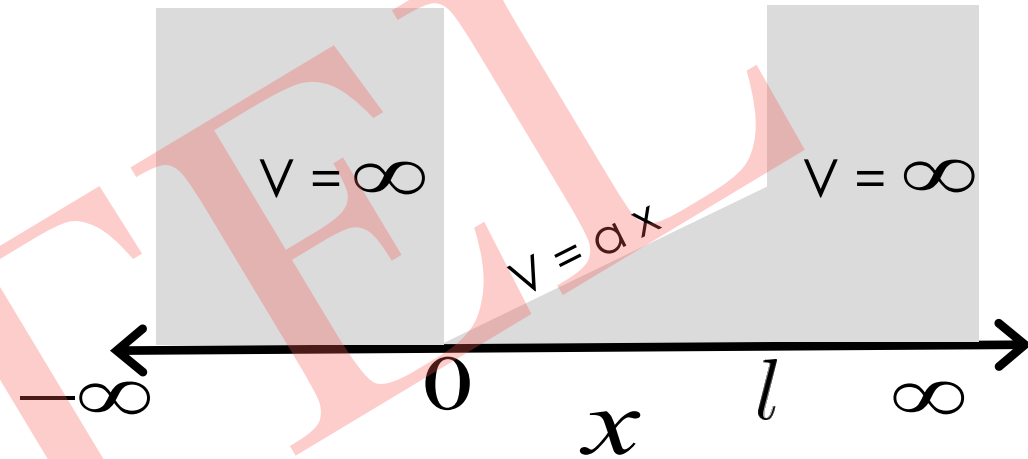
Particle in a box with a linear perturbation

$$\Psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \Psi_m^{(0)} | H' | \Psi_n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})} \Psi_m^{(0)}$$

$$\begin{aligned} \langle \Psi_m^{(0)} | H' | \Psi_n^{(0)} \rangle &= \frac{2a}{l} \int_0^l \sin\left(\frac{m\pi x}{l}\right) x \sin\left(\frac{n\pi x}{l}\right) dx \\ &= \frac{al}{\pi^2} \left(\frac{\cos((m-n)\pi) - 1}{(m-n)^2} - \frac{\cos((m+n)\pi) - 1}{(m+n)^2} \right) \end{aligned}$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \Psi_m^{(0)} | \hat{H}' | \Psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$\begin{aligned} \sin ax \cos bx &= \frac{1}{2} (\cos(a-b)x - \cos(a+b)x) \\ \int x \cos nx \, dx &= \frac{x}{n} \sin nx + \frac{1}{n^2} \cos nx \end{aligned}$$



Perturbation Theory: Examples

Zeeman Effect in Hydrogen Atom

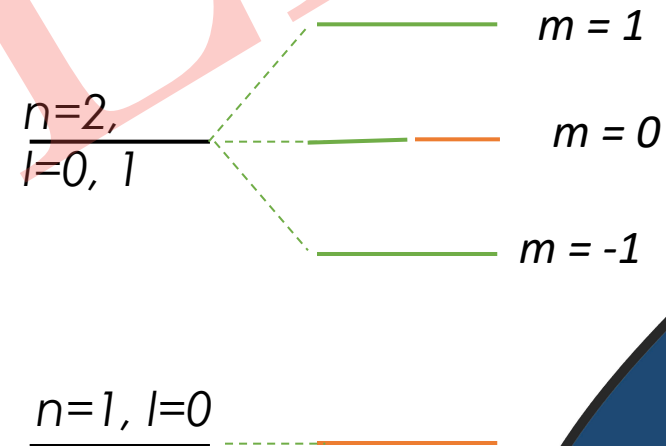
$$\hat{H}_0 = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

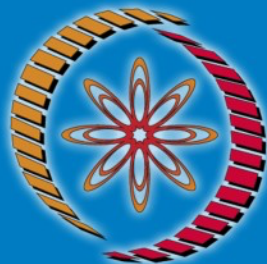
$$\vec{\mu} = \frac{q}{2m_e}\vec{L}$$

$$E_{\text{interaction}} = -\vec{\mu} \cdot \vec{B}_{\text{ext}}$$

$$\hat{H}' = \frac{e}{2m_e}B_{\text{ext}}\hat{L}_z$$

$$\begin{aligned} E_n^{(1)} &= \langle \psi_{nlm} | \hat{H}' | \psi_{nlm} \rangle \\ &= \frac{e}{2m_e}B_{\text{ext}} \langle \psi_{nlm} | \hat{L}_z | \psi_{nlm} \rangle \\ &= \frac{e\hbar}{2m_e}B_{\text{ext}}m = \mu_B B_{\text{ext}}m \end{aligned}$$





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Lecture 19: Applications of Perturbation Theory - II

Perturbation Theory: Examples

Spin-Orbit Coupling in Hydrogen Atom

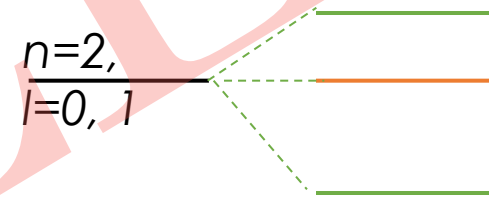
$$\hat{H}_0 = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

$$\hat{H}' = A(r) \hat{L} \cdot \hat{S}$$

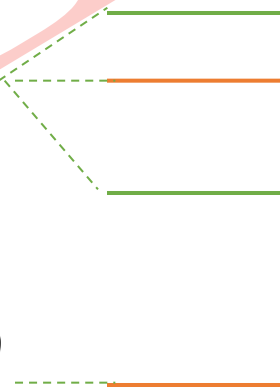
$$\{\psi_{nlm}\} \Rightarrow \{\psi_{nlms}\}$$

$$\hat{J} = \hat{L} + \hat{S} \Rightarrow \hat{L} \cdot \hat{S} = \frac{1}{2} (\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$$

$$E_n = -E_1/n^2$$



$n=1, l=0$



n	l	$E_n^{(0)}$	j	$E_n^{(1)}/A_{nl}$
1	0	$-E_1$	1/2	0
2	0	$-E_1/4$	1/2	0
	1		3/2	+1/2
			1/2	-1

$$E_n^{(1)} = \langle \psi_{nlsjm} | \hat{H}' | \psi_{nlsjm} \rangle$$

$$= \langle \psi_{nlsjm} | \hat{J}^2 - \hat{L}^2 - \hat{S}^2 | \psi_{nlsjm} \rangle \frac{A_{nl}}{2}$$

$$= [j(j+1) - l(l+1) - s(s+1)] \frac{A_{nl}\hbar^2}{2}$$



Perturbation Theory: Examples

Helium Atom

Expt - 79.01 eV

$$\hat{H} = \sum_{i=1}^2 \left(-\frac{\nabla_i^2}{2} - \frac{2}{r_i} \right) + \frac{1}{r_{12}}$$
$$= \sum_{i=1}^2 \hat{H}_i^{(0)} + \frac{1}{r_{12}}$$

$$\psi_{1s}^{(0)} = \psi_{1s}(1) \cdot \psi_{1s}(2) = \frac{1}{\pi} \left(\frac{Z}{a} \right)^3 e^{-Zr_1/a} e^{-Zr_2/a}$$

$$E_{1s}^{(0)} = E_{1s}(1) + E_{1s}(2) = 2 \times Z^2 E_H = 2 \times 4 \times -13.6 \text{ eV} = -108.83 \text{ eV} \quad 38\% \text{ Error}$$

$$E^{(1)} = \langle \psi_{1s}^{(0)} | H | \psi_{1s}^{(0)} \rangle = \frac{5Z}{4} E_1 = \frac{10}{4} 13.6 \text{ eV} = 34.01 \text{ eV} \quad E^{(0)} + E^{(1)} = -74.82 \text{ eV} \quad 5\% \text{ Error}$$

$$E^{(0)} + E^{(1)} + E^{(2)} = -79.17 \text{ eV} \quad 0.2\% \text{ Error}$$

$$E^{(0)} + E^{(1)} + E^{(2)} + \dots + E^{(20)} = -79.002 \text{ eV} \quad 0.01\% \text{ Error}$$



Perturbation Theory: Examples

Hellmann-Feynman Theorem

$$\hat{H} \equiv \hat{H}(p)$$

$$\hat{H}\psi = E\psi$$

$$E = \langle \psi | \hat{H} | \psi \rangle \equiv E(p)$$

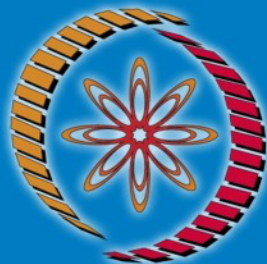
$$\frac{dE}{dp} = \left\langle \frac{d\psi}{dp} | \hat{H} | \psi \right\rangle + \left\langle \psi | \frac{d\hat{H}}{dp} | \psi \right\rangle + \left\langle \psi | \hat{H} | \frac{d\psi}{dp} \right\rangle$$

$$\frac{dE}{dp} = E \left\langle \frac{d\psi}{dp} | \psi \right\rangle + \left\langle \frac{d\hat{H}}{dp} \right\rangle + E \left\langle \psi | \frac{d\psi}{dp} \right\rangle$$

$$\frac{dE}{dp} = \left\langle \frac{d\hat{H}}{dp} \right\rangle + E \frac{d}{dp} \langle \psi | \psi \rangle$$

$$\frac{dE}{dp} = \left\langle \frac{d\hat{H}}{dp} \right\rangle$$





NPTEL ONLINE CERTIFICATION COURSES

Approximate Methods in Quantum Chemistry

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Lecture 20: Molecular Response to Electric Field

Perturbation Theory: Examples

Hellmann-Feynman Theorem

$$\hat{H} \equiv \hat{H}(p)$$

$$\hat{H}\psi = E\psi$$

$$E = \langle \psi | \hat{H} | \psi \rangle \equiv E(p)$$

$$\frac{dE}{dp} = \left\langle \frac{d\hat{H}}{dp} \right\rangle$$

Example

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

$$\psi_n = A_n \mathcal{H}_n(\rho) e^{-\frac{\rho^2}{2}}, \quad \rho = \sqrt{\frac{m\omega}{\hbar}} x$$

$$E_n = \hbar\omega(n + 1/2)$$

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi_n^* x^2 \psi_n dx$$

$$p = \omega \Rightarrow \frac{d\hat{H}}{d\omega} = m\omega x^2$$

$$m\omega \langle x^2 \rangle = \frac{dE_n}{d\omega} = \hbar(n + 1/2)$$

$$\langle x^2 \rangle = \frac{\hbar}{m\omega}(n + 1/2)$$

$$\langle \hat{p}^2 \rangle, \quad \langle \hat{K} \rangle, \quad \langle \hat{V} \rangle$$



Perturbation Theory: Examples

Response to Electric Field

$$\mu = \sum_i q_i r_i \quad \hat{H}' = -\mu \cdot \varepsilon$$
$$= -\mu_z \cdot \varepsilon_z$$

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

$$\frac{\partial E}{\partial \varepsilon} = \left\langle \frac{\partial \hat{H}}{\partial \varepsilon} \right\rangle = -\langle \mu_z \rangle \quad \text{From Hellmann-Feynman Theorem}$$

$$E = E_0 + \left(\frac{dE}{d\varepsilon} \right)_0 \varepsilon + \frac{1}{2!} \left(\frac{d^2 E}{d\varepsilon^2} \right)_0 \varepsilon^2 + \frac{1}{3!} \left(\frac{d^3 E}{d\varepsilon^3} \right)_0 \varepsilon^3 + \dots = E_0 - \mu_{0z} \varepsilon - \frac{1}{2!} \alpha_{zz} \varepsilon^2 - \frac{1}{3!} \beta_{zzz} \varepsilon^3 + \dots$$

$$\langle \mu_z \rangle = - \left(\frac{dE}{d\varepsilon} \right)_0 - \left(\frac{d^2 E}{d\varepsilon^2} \right)_0 \varepsilon - \frac{1}{2!} \left(\frac{d^3 E}{d\varepsilon^3} \right)_0 \varepsilon^2 - \dots$$
$$= \mu_{0z} + \alpha_{zz} \varepsilon + \frac{1}{2} \beta_{zzz} \varepsilon^2 + \dots$$

Molecular Response Parameters

μ_0 Permanent dipole moment

α Polarizability

β Hyperpolarizability



Perturbation Theory: Examples

Response to Electric Field

From perturbation theory,

$$\begin{aligned} E_n &= E_n^{(0)} + \langle \Psi_n^{(0)} | \hat{H}' | \Psi_n^{(0)} \rangle + \sum_{m \neq n} \frac{|\langle \Psi_m^{(0)} | \hat{H}' | \Psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} \\ &= E_n^{(0)} - \langle \Psi_n^{(0)} | \mu_z | \Psi_n^{(0)} \rangle \varepsilon + \sum_{m \neq n} \frac{|\langle \Psi_m^{(0)} | \mu_z | \Psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} \varepsilon^2 \\ &= E_n^{(0)} - \mu_{0z} \varepsilon - \frac{1}{2} \alpha_{zz} \varepsilon^2 \dots \end{aligned}$$

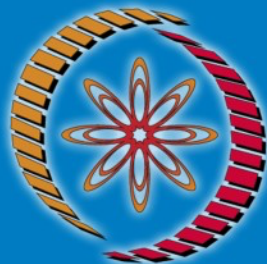
$$\mu_{0z} = \langle \Psi_n^{(0)} | \mu_z | \Psi_n^{(0)} \rangle$$

$$\alpha_{zz} = -2 \sum_{m \neq n} \frac{|\langle \Psi_m^{(0)} | \mu_z | \Psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} = 2 \sum_{m \neq n} \frac{|\langle \Psi_m^{(0)} | \mu_z | \Psi_n^{(0)} \rangle|^2}{E_m^{(0)} - E_n^{(0)}} = 2 \sum_{m \neq n} \frac{|\mu_{z,mn}|^2}{\Delta E_{mn}^{(0)}}$$

$$\alpha = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) = \frac{2}{3} \sum_{m \neq n} \frac{|\mu_{mn}|^2}{\Delta E_{mn}^{(0)}}$$

mean polarizability





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Lecture 21: Molecular Response to Electric Field - II

Perturbation Theory: Examples

Response to Electric Field

$$\mu = \sum_i q_i r_i \qquad \hat{H}' = -\mu \cdot \varepsilon$$
$$= -\mu_z \cdot \varepsilon_z$$

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

$$\frac{\partial E}{\partial \varepsilon} = \left\langle \frac{\partial \hat{H}}{\partial \varepsilon} \right\rangle = -\langle \mu_z \rangle \quad \text{From Hellmann-Feynman Theorem}$$

$$E = E_0 + \left(\frac{dE}{d\varepsilon} \right)_0 \varepsilon + \frac{1}{2!} \left(\frac{d^2 E}{d\varepsilon^2} \right)_0 \varepsilon^2 + \frac{1}{3!} \left(\frac{d^3 E}{d\varepsilon^3} \right)_0 \varepsilon^3 + \dots = E_0 - \mu_{0z} \varepsilon - \frac{1}{2!} \alpha_{zz} \varepsilon^2 - \frac{1}{3!} \beta_{zzz} \varepsilon^3 + \dots$$

$$\langle \mu_z \rangle = - \left(\frac{dE}{d\varepsilon} \right)_0 - \left(\frac{d^2 E}{d\varepsilon^2} \right)_0 \varepsilon - \frac{1}{2!} \left(\frac{d^3 E}{d\varepsilon^3} \right)_0 \varepsilon^2 - \dots$$
$$= \mu_{0z} + \alpha_{zz} \varepsilon + \frac{1}{2} \beta_{zzz} \varepsilon^2 + \dots$$

Molecular Response Parameters

μ_0 Permanent dipole moment

α Polarizability

β Hyperpolarizability

Perturbation Theory: Examples

Response to Electric Field

From perturbation theory,

$$\begin{aligned} E_n &= E_n^{(0)} + \langle \Psi_n^{(0)} | \hat{H}' | \Psi_n^{(0)} \rangle + \sum_{m \neq n} \frac{|\langle \Psi_m^{(0)} | \hat{H}' | \Psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} \\ &= E_n^{(0)} - \langle \Psi_n^{(0)} | \mu_z | \Psi_n^{(0)} \rangle \varepsilon + \sum_{m \neq n} \frac{|\langle \Psi_m^{(0)} | \mu_z | \Psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} \varepsilon^2 \\ &= E_n^{(0)} - \mu_{0z} \varepsilon - \frac{1}{2} \alpha_{zz} \varepsilon^2 \dots \end{aligned}$$

$$\mu_{0z} = \langle \Psi_n^{(0)} | \mu_z | \Psi_n^{(0)} \rangle$$

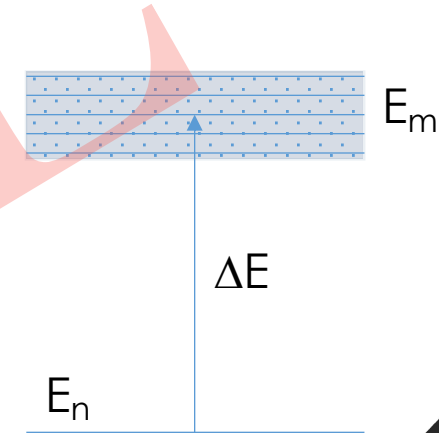
$$\alpha_{zz} = -2 \sum_{m \neq n} \frac{|\langle \Psi_m^{(0)} | \mu_z | \Psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} = 2 \sum_{m \neq n} \frac{|\langle \Psi_m^{(0)} | \mu_z | \Psi_n^{(0)} \rangle|^2}{E_m^{(0)} - E_n^{(0)}} = 2 \sum_{m \neq n} \frac{|\mu_{z,mn}|^2}{\Delta E_{mn}^{(0)}}$$

$$\alpha = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) = \frac{2}{3} \sum_{m \neq n} \frac{|\mu_{mn}|^2}{\Delta E_{mn}^{(0)}} \quad \text{mean polarizability}$$

Perturbation Theory: Examples

Closure Approximation of 2nd order Energy Correction

$$\begin{aligned} E_n^{(2)} &= \sum_{m \neq n} \frac{|\langle \Psi_m^{(0)} | \hat{H}' | \Psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} = - \sum_{m \neq n} \frac{|\langle m | \hat{H}' | n \rangle|^2}{\Delta E_{mn}} \\ &= - \sum_{m \neq n} \frac{\langle n | \hat{H}' | m \rangle \langle m | \hat{H}' | n \rangle}{\Delta E_{mn}} = - \sum_{m \neq n} \frac{H'_{nm} H'_{mn}}{\Delta E_{mn}} \\ &\approx - \frac{1}{\Delta E} \sum_{m \neq n} H'_{nm} H'_{mn} \end{aligned}$$



$$\sum_m A_{nm} B_{mn} = (AB)_{nn}$$

$$\begin{aligned} \sum_{m \neq n} H'_{nm} H'_{mn} &= \left(\sum_m H'_{nm} H'_{mn} \right) - H'_{nn} H'_{nn} \\ &= (H'^2)_{nn} - (H'_{nn})^2 = \langle \Delta \hat{H}' \rangle^2 \end{aligned}$$

Perturbation Theory: Examples

Molecular properties and polarizability

$$\alpha = \frac{2}{3} \sum_{m \neq n} \frac{|\mu_{mn}|^2}{\Delta E_{mn}^{(0)}} \approx \frac{2}{3\Delta E} (\langle \mu^2 \rangle - \langle \mu \rangle^2) \approx \frac{2\Delta\mu^2}{3\Delta E}$$

$$\alpha \approx \frac{\Delta\mu^2}{\Delta E}$$

Polarizability and *fluctuation* in the electric dipole moment

$$\alpha \approx \frac{e^2 \langle r^2 \rangle}{\Delta E}$$

Polarizability and mean square radius of an orbital

$$\alpha \approx \frac{e^2 R_a^2}{\text{IP}}$$

Polarizability and radius of atom/ Ionization potential of atom

$$\alpha \approx \frac{e^2 R_a^2}{e^2/4\pi\epsilon_0 R_a} \approx 4\pi\epsilon_0 R_a^3$$

$$\alpha' = R_a^3$$

Polarizability and volume of atom



Perturbation Theory: Examples

Polarizability in molecular spectroscopy

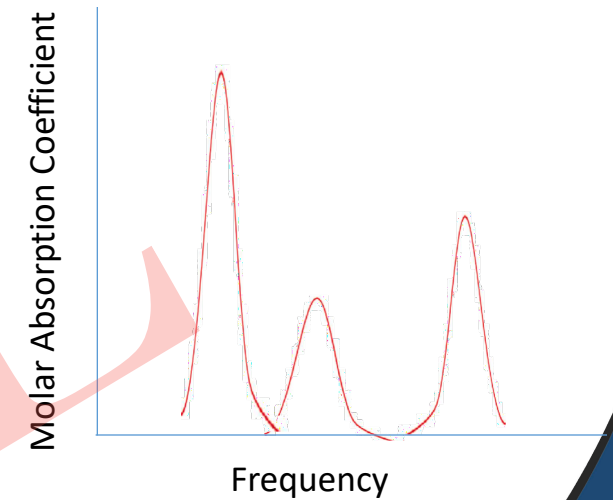
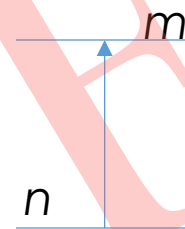
Oscillator Strength

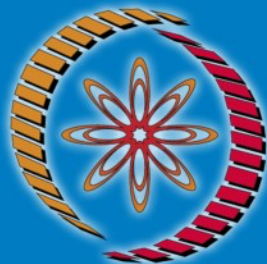
$$f_{mn} = \left(\frac{4\pi m_e}{3e^2 \hbar} \right) \nu_{mn} |\mu_{mn}|^2$$

$$\alpha = \frac{2}{3} \sum_{m \neq n} \frac{|\mu_{mn}|^2}{\Delta E_{mn}}$$

$$\alpha = \frac{e^2 \hbar^2}{m_e} \sum_{m \neq n} \frac{f_{mn}}{\Delta E_{mn}^2}$$

- Molecules showing intense absorption spectrum at low frequency are highly polarizable: *intensely coloured molecules*
- Molecules showing weak absorption spectrum at high frequency are least polarizable: *colourless hydrocarbons*





NPTEL ONLINE CERTIFICATION COURSES

Approximate Methods in Quantum Chemistry

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Lecture 22: Degenerate Perturbation Theory

Perturbation Theory for Degenerate States

$$E_n = E_n^{(0)} + \left\langle \Psi_n^{(0)} \left| \hat{H}' \right| \Psi_n^{(0)} \right\rangle + \sum_{m \neq n} \frac{\left| \left\langle \Psi_m^{(0)} \left| \hat{H}' \right| \Psi_n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$\hat{H}_0 \Psi_n^{(0)} = E_n^{(0)} \Psi_n^{(0)} \quad n = 1, 2, \dots, d$$

$$E_1^{(0)} = E_2^{(0)} = \dots = E_d^{(0)}$$

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}'$$

$$\hat{H} \Psi_n = E_n \Psi_n$$

$$\lambda \rightarrow 0 \quad \Psi_n \rightarrow \Psi_n^{(0)}$$

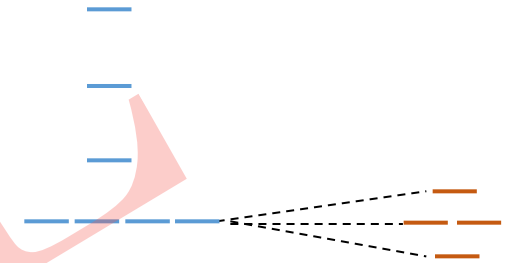
$$\Phi_n^{(0)} = \lim_{\lambda \rightarrow 0} \Psi_n = \sum_{i=1}^d c_i \Psi_i^{(0)} \quad 1 \leq n \leq d$$

$$\Psi_n = \Phi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} \dots$$

$$\left(\hat{H}_0 + \lambda \hat{H}' \right) \left(\Phi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} \dots \right)$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} \dots$$

$$= \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} \dots \right) \left(\Phi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} \dots \right)$$



Perturbation Theory for Degenerate States

$$\left(\hat{H}_0 + \lambda \hat{H}'\right) \left(\Phi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} \dots\right) = \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} \dots\right) \left(\Phi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} \dots\right)$$

$$\lambda^0 : \hat{H}_0 \Phi_n^{(0)} = E_n^{(0)} \Phi_n^{(0)}$$

$$\lambda^1 : \hat{H}_0 \Psi_n^{(1)} + \hat{H}' \Phi_n^{(0)} = E_n^{(0)} \Psi_n^{(1)} + E_n^{(1)} \Phi_n^{(0)}$$

$$\langle \Psi_m^{(0)} | \hat{H}_0 | \Psi_n^{(1)} \rangle + \langle \Psi_m^{(0)} | \hat{H}' | \Phi_n^{(0)} \rangle = \langle \Psi_m^{(0)} | E_n^{(0)} | \Psi_n^{(1)} \rangle + \langle \Psi_m^{(0)} | E_n^{(1)} | \Phi_n^{(0)} \rangle$$

$$\langle \Psi_m^{(0)} | \hat{H}' | \Phi_n^{(0)} \rangle = E_n^{(1)} \langle \Psi_m^{(0)} | \Phi_n^{(0)} \rangle \quad E_n^{(0)} = E_m^{(0)}$$

$$\left\langle \Psi_m^{(0)} \left| \hat{H}' \right| \sum_{i=1}^d c_i \Psi_i^{(0)} \right\rangle = E_n^{(1)} \left\langle \Psi_m^{(0)} \left| \sum_{i=1}^d c_i \Psi_i^{(0)} \right\rangle \right\rangle$$

$$\sum_{i=1}^d \left(\langle \Psi_m^{(0)} | \hat{H}' | \Psi_i^{(0)} \rangle - E_n^{(1)} \langle \Psi_m^{(0)} | \Psi_i^{(0)} \rangle \right) c_i = 0$$

$$\sum_{i=1}^d (H'_{mi} - E_n^{(1)} \delta_{mi}) c_i = 0$$



Perturbation Theory for Degenerate States

$$\begin{vmatrix} H'_{11} - E_n^{(1)} & H'_{12} & \dots & H'_{1d} \\ H'_{12} & H'_{22} - E_n^{(1)} & \dots & H'_{2d} \\ \vdots & \vdots & \ddots & \vdots \\ H'_{d1} & H'_{d2} & \dots & H'_{dd} - E_n^{(1)} \end{vmatrix} \begin{vmatrix} c_1 \\ c_2 \\ \vdots \\ c_d \end{vmatrix} = 0$$

$$\Phi_n^{(0)} = \sum_{i=1}^d c_i \Psi_i^{(0)} \quad 1 \leq n \leq d$$



Perturbation Theory for Degenerate States: Examples

Excited States of Helium Atom

Unperturbed energy of He atom $E_n^{(0)} = -\frac{Z^2}{2} \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right) \text{ au}$

Electronic configuration for the **ground state**: $1s^2$

Electronic configuration for the **excited states**: $1s^1 2s^1, 1s^1 2p_x^1, 1s^1 2p_y^1, 1s^1 2p_z^1, \dots$

Unperturbed wave functions for the excited states:

	1s	2s	2p _x	2p _y	2p _z
$\psi_1^{(0)}$	1	2			
$\psi_2^{(0)}$	2	1			
$\psi_3^{(0)}$	1		2		
$\psi_4^{(0)}$	2		1		
$\psi_5^{(0)}$	1			2	
$\psi_6^{(0)}$	2			1	
$\psi_7^{(0)}$	1				2
$\psi_8^{(0)}$	2				1

$$\phi_n^{(0)} = \sum_i^8 c_i \psi_i^{(0)}$$

$$\begin{vmatrix} H'_{11} - E_n^{(1)} & H'_{12} & \dots & H'_{18} \\ H'_{12} & H'_{22} - E_n^{(1)} & \dots & H'_{28} \\ \vdots & \vdots & \ddots & \vdots \\ H'_{81} & H'_{82} & \dots & H'_{88} - E_n^{(1)} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \\ \vdots \\ c_8 \end{vmatrix} = 0$$

