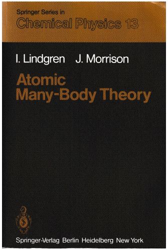
Perturbation TheoriES

ISTPC
Summer School
June 18th - 30th 2017 Aussois

Vincent Robert, vrobert@unistra.fr



UdS - UMR 7177 Laboratoire de Chimie Quantique

UNIVERSITÉ DE STRASBOURG

FRC
International Center for
Frontier Research in Chemistry

Institut de Chimie
de Strasbourg
UMR 7177

1. Perturbation Theory From Quantum Mechanics
2. Two-level Problem (exercise session)
3. Brillouin-Wigner and Rayleigh-Schrödinger
   - Hamiltonian partitioning - Projection Operators
   - Resolvent - Wave Operator
   - Model Space - Bloch Equation
4. Møller-Plesset Theory : MP2
   - Correlation Energy
   - Hamiltonian Partitioning
5. Conclusions and References

Perturbation from Quantum Mechanics

Hamiltonian partitioning

One wants to solve :

$$\hat{\mathcal{H}}|\Psi^{\alpha}\rangle = E^{\alpha}|\Psi^{\alpha}\rangle$$

writing

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{V}}$$

$$\hat{\mathcal{H}}_0|\alpha\rangle = E_0^{\alpha}|\alpha\rangle \quad \text{with} \quad \langle\alpha|\beta\rangle = \delta_{\alpha\beta}$$

non-degenerate case: $\hat{\mathcal{V}} = \lambda\hat{\mathcal{W}}$ with $|\lambda| \ll 1$

$\hat{\mathcal{V}}$ as a perturbation

Perturbation from Quantum Mechanics

Let us recall some general results : $\hat{\mathcal{V}} = \lambda \hat{\mathcal{W}}$ with $|\lambda| \ll 1$

Energy and wavefunction expansions in power series of λ

$$E^\alpha = \epsilon_0^\alpha + \lambda \epsilon_1^\alpha + \lambda^2 \epsilon_2^\alpha + \cdots$$

and

$$|\Psi^\alpha\rangle = |0^\alpha\rangle + \lambda |1^\alpha\rangle + \lambda^2 |2^\alpha\rangle + \cdots$$

$\rightarrow$ identification of λ^n terms in Schrödinger's equation

- zeroth order : $|0^\alpha\rangle = |\alpha\rangle$ and $\epsilon_0^\alpha = E_0^\alpha$
- first order : $|1^\alpha\rangle = \sum_{\beta \neq \alpha} \frac{|\beta\rangle\langle\beta|\hat{\mathcal{W}}|\alpha\rangle}{E_0^\alpha - E_0^\beta}$ and $\epsilon_1^\alpha = \langle\alpha|\hat{\mathcal{W}}|\alpha\rangle$
- second order : $\epsilon_2^\alpha = \sum_{\beta \neq \alpha} \frac{\langle\alpha|\hat{\mathcal{W}}|\beta\rangle\langle\beta|\hat{\mathcal{W}}|\alpha\rangle}{E_0^\alpha - E_0^\beta}$
- etc.

Remarks on second-order energy correction

$$E^{\alpha} = E_0^{\alpha} + \langle\alpha|\hat{\mathcal{V}}|\alpha\rangle + \sum_{\beta\neq\alpha} \frac{\langle\alpha|\hat{\mathcal{V}}|\beta\rangle\langle\beta|\hat{\mathcal{V}}|\alpha\rangle}{E_0^{\alpha} - E_0^{\beta}} + O\left(\lambda^3\right)$$

- all corrections are given by the *unperturbed* eigen-values and eigen-functions $\{|\alpha\rangle\}$ and $\{E_0^{\alpha}\}$
- if $E_0^{\alpha} < E_0^{\beta}$, "*$\alpha$ state is stabilized*"
  $\rightarrow$ avoided crossing, core-valence separation $E_0^{\text{core}} \ll E_0^{\text{valence}}$

Perturbation from Quantum Mechanics

closure relation or identity resolution

let us assume that $E_0^\alpha - E_0^\beta \approx \Delta = cte$ for all α

$$\sum_{\beta \neq \alpha} \frac{\langle\alpha|\hat{\mathcal{V}}|\beta\rangle\langle\beta|\hat{\mathcal{V}}|\alpha\rangle}{E_0^\alpha - E_0^\beta} \approx \frac{1}{\Delta}\left[\left(\sum_\beta \left|\langle\alpha|\hat{\mathcal{V}}|\beta\rangle\right|^2\right) - \left|\langle\alpha|\hat{\mathcal{V}}|\alpha\rangle\right|^2\right]$$

$$\approx \frac{1}{\Delta}\left[\langle\alpha|\hat{\mathcal{V}}| \left(\sum_\beta |\beta\rangle\langle\beta|\right) \hat{\mathcal{V}}|\alpha\rangle - \langle\mathcal{V}\rangle_\alpha^2\right]$$

$$E_2^\alpha \approx \frac{1}{\Delta}\left[\ \langle\hat{\mathcal{V}}^2\rangle_\alpha - \langle\hat{\mathcal{V}}\rangle_\alpha^2\right] \sim \sigma^2$$

second-order is a measure of fluctuations : correlation energy

Hamiltonian partitioning :

$$\begin{aligned}\hat{\mathcal{H}} &= -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} \\ &= \hat{\mathcal{H}}_0 + \hat{\mathcal{V}}\end{aligned}$$

example : monoelectronic reference

$$\hat{\mathcal{H}}_0 = \sum_i \hat{\mathcal{F}}(i)$$

and

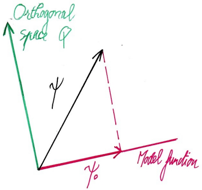
$$\hat{\mathcal{V}} = \sum_{j>i}\frac{1}{r_{ij}} - \sum_i \hat{v}_{HF}(i)$$

Definitions and Notations

$$\hat{\mathcal{H}}_0|\alpha\rangle = E_0^\alpha|\alpha\rangle$$
$$\text{with } \langle\alpha|\beta\rangle = \delta_{\alpha\beta}$$

If $|\alpha\rangle$ is a good approximation to the exact function $|\Psi\rangle$
definition 1 : $|\Psi_0\rangle = |\alpha\rangle$ is the **reference function**

If not, several configurations may be mixed in by the perturbation, or in the presence of quasi-degeneracies
definition 2 : a subspace is defined from the entire space and is referred to as the **model space** P



definition 3 : **projection operators**

$$\hat{P} = \sum_{\alpha\in P} |\alpha\rangle\langle\alpha| \quad \text{and} \quad \hat{Q} = \sum_{\beta\notin P} |\beta\rangle\langle\beta|$$

$$\hat{P} + \hat{Q} = \mathbb{1} \quad \text{and} \quad \left[\hat{\mathcal{H}}_0, \hat{P}\right] = \left[\hat{\mathcal{H}}_0, \hat{Q}\right] = 0$$

and Q is the **outer space**

Model Space ↔ P
Orthogonal Space ↔ Q
$\hat{P}|\psi\rangle = |\psi_0\rangle$

Resolvent - Wave Operator

Brillouin-Wigner : $\hat{P} = |\Psi_0\rangle\langle\Psi_0|$

Given a reference function Ψ_0 :
Fixing $\langle\Psi_0|\Psi\rangle = 1$,

$$\hat{P}|\Psi\rangle = |\Psi_0\rangle\langle\Psi_0|\Psi\rangle = |\Psi_0\rangle$$

and

$$|\Psi\rangle = \left(\hat{P} + \hat{Q}\right)|\Psi\rangle = |\Psi_0\rangle + \hat{Q}|\Psi\rangle$$

definition 4 : $\hat{Q}|\Psi_0\rangle$ is the correlation function (Sinanoğlu)

If $|\Psi_0\rangle$ is known, can be get back to Ψ ?

Resolvent - Wave Operator

Brillouin-Wigner : $\hat{P} = |\Psi_0\rangle\langle\Psi_0|$

Let us start from : $\left(E - \hat{\mathcal{H}}_0\right)|\Psi\rangle = \hat{\mathcal{V}}|\Psi\rangle$

$$\hat{Q}\left(E - \hat{\mathcal{H}}_0\right)|\Psi\rangle = \left(E - \hat{\mathcal{H}}_0\right)\hat{Q}|\Psi\rangle = \hat{Q}\hat{\mathcal{V}}|\Psi\rangle$$

resolvent operator : $\boxed{\hat{T}(E) = \frac{\hat{Q}}{E - \hat{\mathcal{H}}_0}}$

"inverse of $E - \hat{\mathcal{H}}_0$ in the Q space"

Note : strong similarities with Green's function (coming up lectures)

$$\hat{T}(E)\,|\alpha\rangle = 0 \quad \text{and} \quad \hat{T}(E)\,|\beta\rangle = \frac{\hat{Q}}{E - E_0^\beta}|\beta\rangle$$

$$\hat{T}(E) = \sum_{\beta\neq\alpha} \frac{|\beta\rangle\langle\beta|}{E - E_0^\beta}$$

$\boxed{\hat{T}(E) \text{ depends on the exact energy } E \text{ !}}$

Brillouin-Wigner Expansion : Wave Operator

Acting on the right with $\hat{T}(E)$:

$$\hat{T}(E)\,(\,E - \hat{\mathcal{H}}_0)|\Psi\rangle = \boxed{\hat{Q}|\Psi\rangle = \hat{T}(E)\,\hat{\mathcal{V}}|\Psi\rangle}$$

Thus, $|\Psi\rangle = |\Psi_0\rangle + \hat{Q}|\Psi\rangle = |\Psi_0\rangle + \left(\hat{T}\,(E)\,\hat{\mathcal{V}}\right)|\Psi\rangle$

$$|\Psi\rangle = |\Psi_0\rangle + \left(\hat{T}(E)\,\hat{\mathcal{V}}\right)|\Psi_0\rangle + \left(\hat{T}(E)\,\hat{\mathcal{V}}\right)\left(\hat{T}(E)\,\hat{\mathcal{V}}\right)|\Psi\rangle$$

By iterating

$$|\Psi\rangle = \sum_n \left(\frac{\hat{Q}}{E - \hat{\mathcal{H}}_0}\hat{\mathcal{V}}\right)^n |\Psi_0\rangle$$

wave operator definition :

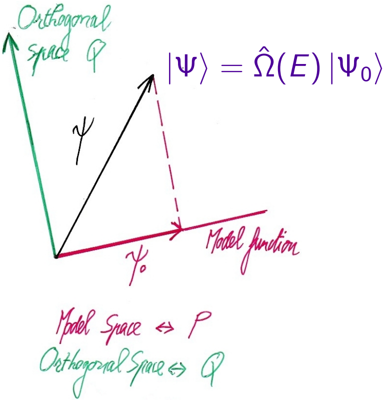
$$\boxed{\hat{\Omega}\,(E) = 1 + \frac{\hat{Q}}{E-\hat{\mathcal{H}}_0}\hat{\mathcal{V}} + \frac{\hat{Q}}{E-\hat{\mathcal{H}}_0}\hat{\mathcal{V}}\frac{\hat{Q}}{E-\hat{\mathcal{H}}_0}\hat{\mathcal{V}} + \ldots}$$

Brillouin-Wigner Expansion

"reciprocal" actions of $\hat{P}$ and $\hat{\Omega}(E)$

$$\hat{\Omega}(E) = \mathbb{1} + \hat{T}(E)\,\hat{\mathcal{V}}\hat{\Omega}(E)$$

"from $|\Psi_0\rangle$, $\hat{\Omega}(E)$ takes us back to $|\Psi\rangle$"



Brillouin-Wigner Expansion : Effective Interaction

Let us evaluate the exact energy E :

$$\begin{aligned} E &= \langle \Psi_0 | \hat{\mathcal{H}} | \Psi \rangle \\ &= \langle \Psi_0 | \hat{\mathcal{H}}_0 | \Psi \rangle + \langle \Psi_0 | \hat{\mathcal{V}} | \Psi \rangle \end{aligned}$$

$$\boxed{E = E_0 + \langle \Psi_0 | \hat{\mathcal{V}} \hat{\Omega}(E) \, | \Psi_0 \rangle}$$

effective interaction definition : $\boxed{\hat{W}(E) = \hat{\mathcal{V}} \hat{\Omega}(E)}$

$\boxed{\hat{W}(E) \, |\Psi_0\rangle = \hat{\mathcal{V}} |\Psi\rangle}$ essence of *effective*

The action of $\hat{W}(E)$ on $|\Psi_0\rangle$ is the same as the perturbation $\hat{\mathcal{V}}$ on $|\Psi\rangle$

Brillouin-Wigner Expansion : Energy Expression

Remembering that :

$$\hat{\Omega}(E) = 1 + \hat{T}(E)\,\hat{\mathcal{V}} + \hat{T}(E)\,\hat{\mathcal{V}}\,\hat{T}(E)\,\hat{\mathcal{V}} + \ldots$$

we get : $$\hat{W}(E) = \hat{\mathcal{V}} + \hat{\mathcal{V}}\,\hat{T}(E)\,\hat{\mathcal{V}} + \hat{\mathcal{V}}\,\hat{T}(E)\,\hat{\mathcal{V}} + \ldots$$

Going back to the exact energy E :

$$E = E_0 + \langle\Psi_0|\hat{\mathcal{V}}\hat{\Omega}(E)\,|\Psi_0\rangle = E_0 + \langle\Psi_0|\hat{W}(E)\,|\Psi_0\rangle$$

$$\boxed{E = E_0 + \langle\Psi_0|\hat{\mathcal{V}} + \hat{\mathcal{V}}\frac{\hat{Q}}{E-\hat{\mathcal{H}}_0}\hat{\mathcal{V}} + \hat{\mathcal{V}}\left(\frac{\hat{Q}}{E-\hat{\mathcal{H}}_0}\hat{\mathcal{V}}\right)^2 + \cdots|\Psi_0\rangle}$$

- first order : $E^{(1)} = \langle\Psi_0|\hat{\mathcal{V}}|\Psi_0\rangle$
- second order : $E^{(2)} = \sum_{\beta\in Q} \frac{\langle\Psi_0|\hat{\mathcal{V}}|\beta\rangle\langle\beta|\hat{\mathcal{V}}|\Psi_0\rangle}{E - E_0^{\beta}}$
- etc.

$\rightarrow$ iterative procedure since $E^{(i)} = f(E)$, E being unknown !

Brillouin-Wigner Expansion : Wavefunction Expansion

From previous slides :

$$|\Psi\rangle = |\Psi_0\rangle + \hat{Q}|\Psi\rangle = |\Psi_0\rangle + \hat{T}(E)\,\hat{\mathcal{V}}|\Psi\rangle$$

$$|\Psi\rangle = \sum_n \left(\frac{\hat{Q}}{E - \hat{\mathcal{H}}_0} \hat{\mathcal{V}} \right)^n |\Psi_0\rangle$$

and the spectral resolution of the resolvent lead to :

- first order : $|\Psi^{(1)}\rangle = \sum_{\beta \in Q} \frac{|\beta\rangle\langle\beta|\hat{\mathcal{V}}|\Psi_0\rangle}{E - E_0^\beta}$
- second order : $|\Psi^{(2)}\rangle = \sum_{\beta,\gamma \in Q} \frac{|\beta\rangle\langle\beta|\hat{\mathcal{V}}|\gamma\rangle\langle\gamma|\hat{\mathcal{V}}|\Psi_0\rangle}{\left(E - E_0^\beta\right)\left(E - E_0^\gamma\right)}$
- etc.

again, note the E-dependency !

Brillouin-Wigner Perturbation Theory

- rather *simple* approach, though iterative
- targeted energies
- **effective Hamiltonian**
  operate $\hat{P}$ on $\left(\hat{\mathcal{H}}_0 + \hat{\mathcal{V}}\right)|\Psi\rangle = E|\Psi\rangle$

$$\hat{P}\hat{\mathcal{H}}_0|\Psi\rangle + \hat{P}\hat{\mathcal{V}}\hat{\Omega}(E)\,|\Psi_0\rangle = E|\Psi_0\rangle$$

$$\left(\hat{\mathcal{H}}_0 + \hat{P}\hat{\mathcal{V}}\hat{\Omega}(E)\right)|\Psi_0\rangle = E|\Psi_0\rangle$$

$$\boxed{\hat{\mathcal{H}}_{\text{eff}} = \hat{\mathcal{H}}_0 + \hat{P}\hat{\mathcal{V}}\hat{\Omega}(E)}$$

$\hat{\mathcal{H}}_{\text{eff}}$ acts in the model space with $\underline{E \text{ as an eigen-value}}$

- size-extensivity problem : $N \to \infty$
- one energy E at a time...

Rayleigh Schrödinger Perturbation Theory

the model space consists of more than one function, dimension is n

$$\hat{P} = \sum_{i=1}^{n} |\alpha_i\rangle\langle\alpha_i| = \sum_{\alpha\in P} |\alpha\rangle\langle\alpha|$$

$$\hat{\mathcal{H}}_0|\alpha\rangle = E_0^{\alpha}|\alpha\rangle$$

<u>*definition 5*</u> : the wavefunctions of the full Hamiltonian having their main projections in the P-space define the **target space** $\{|\Psi^a\rangle\}_{a=1,n}$

important : the P-projection of $|\Psi^a\rangle$ is not necessarily a given $|\alpha\rangle$!

a one-to-one correspondance between target and model spaces :

$$|\Psi_0^a\rangle = \hat{P}|\Psi^a\rangle \qquad a = 1, 2, \cdots n$$

$$|\Psi^a\rangle = \hat{\Omega}|\Psi_0^a\rangle \qquad a = 1, 2, \cdots n$$

important : the wave operator $\hat{\Omega}$ is the same for all n states

Bloch Theory

non-orthogonality
model functions are not necessarily orthogonal !

definition 6 : **dual functions** satisfy the bi-orthogonality condition
$\langle \Psi_0'^b | \Psi_0^a \rangle = \delta_{ab}$

$$\hat{P} = \sum_{b=1}^{n} |\Psi_0^b\rangle\langle\Psi_0'^b|$$

property 1 : One can verify the action of $\hat{P}$ in the P-space :

$$\hat{P}|\Psi_0^a\rangle = \sum_{b=1}^{n} |\Psi_0^b\rangle\langle\Psi_0'^b|\Psi_0^a\rangle = |\Psi_0^a\rangle$$

property 2 : From $\hat{P}$ and $\hat{\Omega}$ definitions, $|\Psi_0^a\rangle = \hat{P}\hat{\Omega}|\Psi_0^a\rangle$

$$\hat{P}\hat{\Omega}\sum_{b=1}^{n} |\Psi_0^b\rangle\langle\Psi_0'^b| = \sum_{b=1}^{n} \hat{P}\hat{\Omega}|\Psi_0^b\rangle\langle\Psi_0'^b| = \sum_{b=1}^{n} |\Psi_0^b\rangle\langle\Psi_0'^b| = \hat{P}$$

which leads to $\boxed{\hat{P}\hat{\Omega}\hat{P} = \hat{P}}$

Generalized Bloch Equation

As in Brillouin-Wigner theory, $\hat{\Omega} = \hat{P} + \hat{\chi}$: **correlation operator**

$$\hat{\chi}|\Psi_0^a\rangle = \left(\hat{\Omega} - \hat{P}\right)|\Psi_0^a\rangle = |\Psi^a\rangle - \hat{P}|\Psi^a\rangle = \hat{Q}|\Psi^a\rangle$$

From $\left(E^a - \hat{\mathcal{H}}_0\right)|\Psi^a\rangle = \hat{\mathcal{V}}|\Psi^a\rangle$, we operate with $\hat{P}$:

$$\left(E^a - \hat{\mathcal{H}}_0\right)|\Psi_0^a\rangle = \hat{P}\hat{\mathcal{V}}|\Psi^a\rangle$$

and then with $\hat{\Omega}$:

$$E^a|\Psi^a\rangle - \hat{\Omega}\hat{H}_0|\Psi_0^a\rangle = \hat{\Omega}\hat{P}\hat{\mathcal{V}}\hat{\Omega}|\Psi_0^a\rangle$$

Combined with Schrödinger equation to eleminate E^a,

$$\left(\hat{\Omega}\hat{H}_0 - \hat{H}_0\hat{\Omega}\right)|\Psi_0^a\rangle = \left(\hat{\mathcal{V}}\hat{\Omega} - \hat{\Omega}\hat{P}\hat{\mathcal{V}}\hat{\Omega}\right)|\Psi_0^a\rangle$$

$$\left[\hat{\Omega}, \hat{H}_0\right]\hat{P} = \hat{\mathcal{V}}\hat{\Omega}\hat{P} - \hat{\Omega}\hat{P}\hat{\mathcal{V}}\hat{\Omega}\hat{P}$$

or equivalently $$\boxed{\left[\hat{\Omega}, \hat{H}_0\right]\hat{P} = \hat{Q}\hat{\mathcal{V}}\hat{\Omega}\hat{P} - \hat{\chi}\hat{P}\hat{\mathcal{V}}\hat{\Omega}\hat{P}}$$

$\rightarrow$ generalized Bloch equation, equivalent to Schrödinger equation convenient for a perturbation treatment : Rayleigh-Schrödinger expansion

Order-by-order expansion

$\hat{\chi}$ "pushes back" $|\Psi_0^a\rangle$ into the Q-space

Let us write $\hat{\chi} = \hat{\Omega}^{(1)} + \hat{\Omega}^{(2)} + \cdots$ where order n, $\hat{\Omega}^{(n)}$, contains n interactions with $\hat{\mathcal{V}}$.

$$\begin{aligned}
\hat{\Omega}^{(0)} &= \hat{P} \\
\left[\hat{\Omega}^{(1)}, \hat{H}_0\right] \hat{P} &= \hat{Q}\hat{\mathcal{V}}\hat{P} \\
\left[\hat{\Omega}^{(2)}, \hat{H}_0\right] \hat{P} &= \hat{Q}\hat{\mathcal{V}}\hat{P}\hat{\Omega}^{(1)}\hat{P} - \hat{\Omega}^{(1)}\hat{P}\hat{\mathcal{V}}\hat{P}
\end{aligned}$$

and so on...

note : iterative procedure can be used as well

Rayleigh-Schrödinger into matrix form

Matrix representation : $|\alpha\rangle, |\alpha'\rangle \in P$ and $|\beta\rangle, |\beta'\rangle \in Q$

general relation : $\langle\beta\left|\left[\hat{\Omega}, \hat{H}_0\right]\right|\alpha\rangle = \left(E_0^\alpha - E_0^\beta\right)\langle\beta|\hat{\Omega}|\alpha\rangle$

$$\langle\beta|\hat{Q}\hat{\mathcal{V}}\hat{P}|\alpha\rangle = \langle\beta|\hat{\mathcal{V}}|\alpha\rangle$$

First orders of the Rayleigh-Schrödinger expansion :

$$\langle\beta|\hat{\Omega}^{(1)}|\alpha\rangle = \frac{\langle\beta|\hat{\mathcal{V}}|\alpha\rangle}{E_0^\alpha - E_0^\beta}$$

$$\langle\beta|\hat{\Omega}^{(2)}|\alpha\rangle = \sum_{\beta'\in Q} \frac{\langle\beta|\hat{\mathcal{V}}|\beta'\rangle\langle\beta'|\hat{\mathcal{V}}|\alpha\rangle}{\left(E_0^\alpha - E_0^\beta\right)\left(E_0^\alpha - E_0^{\beta'}\right)} - \sum_{\alpha'\in P} \frac{\langle\beta|\hat{\mathcal{V}}|\alpha'\rangle\langle\alpha'|\hat{\mathcal{V}}|\alpha\rangle}{\left(E_0^\alpha - E_0^\beta\right)\left(E_0^{\alpha'} - E_0^\beta\right)}$$

still, we do not know the $\{|\Psi_0^a\rangle\}$!

Rayleigh-Schrödinger : effective Hamiltonian

effect of $\hat{\mathcal{V}}$ in the model space P : $\langle \Psi_0^b | \hat{\mathcal{V}} | \Psi_0^a \rangle$?
note : quasi-degeneracy, correlation energy partitioning

Operate with $\hat{P}$ on Schrödinger equation :

$$\hat{P}\hat{\mathcal{H}}\hat{\Omega}|\Psi_0^a\rangle = E^a|\Psi_0^a\rangle$$

$$\boxed{\hat{\mathcal{H}}_{\text{eff}} = \hat{P}\hat{\mathcal{H}}\hat{\Omega}\hat{P}}$$

and

$$\boxed{\hat{\mathcal{H}}_{\text{eff}}|\Psi_0^a\rangle = E^a|\Psi_0^a\rangle}$$

eigenvectors = model functions and eigenvalues = exact energies

$$\hat{\mathcal{H}}_{\text{eff}} = \hat{P}\left(\hat{\mathcal{H}}_0 + \hat{\mathcal{V}}\right)\hat{\Omega}\hat{P} = \hat{P}\hat{\mathcal{H}}_0\hat{P} + \hat{P}\hat{\mathcal{V}}\hat{\Omega}\hat{P}$$

$\hat{\mathcal{H}}_{\text{eff}}$ must be constructed and diagonalize simultaneously !

Case of study : Degenerate Model Space

$$\hat{\mathcal{H}}_{\text{eff}} = \hat{P}\hat{\mathcal{H}}_0\hat{P} + \hat{P}\hat{\mathcal{V}}\hat{\Omega}\hat{P}$$

Let us assume degeneracy in the model space :

$$E_0^a = E_0 \text{ for all } a = 1, n$$

examples: $|a\bar{b}|$ and $|\bar{a}b|$ in H_2 or any magnetic system

Then $\left[\hat{\Omega}, \hat{\mathcal{H}}_0\right]\hat{P} = \left(E_0 - \hat{\mathcal{H}}_0\right)\hat{\Omega}\hat{P}$

and

$$\boxed{\left(E_0 - \hat{\mathcal{H}}_0\right)\hat{\Omega}\hat{P} = \hat{Q}\hat{\mathcal{V}}\hat{\Omega}\hat{P} - \hat{\chi}\hat{P}\hat{\mathcal{V}}\hat{\Omega}\hat{P}}$$

The first term suggests the use of the resolvent $\hat{R} = \frac{\hat{Q}}{E_0 - \hat{\mathcal{H}}_0}$

$$\hat{R} = \sum_{\beta \in Q} \frac{|\beta\rangle\langle\beta|}{E_0 - E_0^\beta}$$

Case of study : Degenerate Model Space

$$\hat{\mathcal{H}}_{\text{eff}} = \hat{P}\hat{\mathcal{H}}_0\hat{P} + \hat{P}\hat{\mathcal{V}}\hat{\Omega}\hat{P}$$

Order-by-order expansion : $\hat{\Omega} = \mathbb{1} + \hat{\Omega}^{(1)} + \hat{\Omega}^{(2)} \dots$

$$\begin{aligned} \hat{\Omega}^{(1)}\hat{P} &= \hat{R}\hat{\mathcal{V}}\hat{P} \\ \hat{\Omega}^{(2)}\hat{P} &= \hat{R}\hat{\mathcal{V}}\hat{R}\hat{\mathcal{V}}\hat{P} - \hat{R}^2\hat{\mathcal{V}}\hat{P}\hat{\mathcal{V}}\hat{P} \end{aligned}$$

<u>if the model functions are known</u> :

$$|\Psi^{a,(1)}\rangle = \hat{\Omega}^{(1)}|\Psi_0^a\rangle = \sum_{\beta} \frac{|\beta\rangle\langle\beta|\hat{\mathcal{V}}|\Psi_0^a\rangle}{E_0 - E_0^\beta}$$

$$\begin{aligned} |\Psi^{a,(2)}\rangle = \hat{\Omega}^{(2)}|\Psi_0^a\rangle &= \sum_{\beta,\beta'} \frac{|\beta\rangle\langle\beta|\hat{\mathcal{V}}|\beta'\rangle\langle\beta'|\hat{\mathcal{V}}|\Psi_0^a\rangle}{\left(E_0 - E_0^\beta\right)\left(E_0 - E_0^{\beta'}\right)} \\ &- \sum_{\alpha,\beta} \frac{|\beta\rangle\langle\beta|\hat{\mathcal{V}}|\alpha\rangle\langle\alpha|\hat{\mathcal{V}}|\Psi_0^a\rangle}{\left(E_0 - E_0^\beta\right)^2} \end{aligned}$$

very similar to Brillouin-Wigner, energy denominator is different !

Effective Hamiltonian Construction

$$
\begin{aligned}
\hat{\mathcal{H}}_{\text{eff}}^{(0)} &= \hat{P}\hat{\mathcal{H}}_0\hat{P} \\
\hat{\mathcal{H}}_{\text{eff}}^{(1)} &= \hat{P}\hat{\mathcal{V}}\hat{P} \\
\hat{\mathcal{H}}_{\text{eff}}^{(2)} &= \hat{P}\hat{\mathcal{V}}\hat{R}\hat{\mathcal{V}}\hat{P}
\end{aligned}
$$

Therefore, the energy corrections are :

$$
\begin{aligned}
E^{a,(1)} &= \langle \Psi_0^a | \hat{\mathcal{H}}_{\text{eff}}^{(1)} | \Psi_0^a \rangle = \langle \Psi_0^a | \hat{\mathcal{V}} | \Psi_0^a \rangle \\
E^{a,(2)} &= \langle \Psi_0^a | \hat{\mathcal{H}}_{\text{eff}}^{(2)} | \Psi_0^a \rangle = \sum_{\beta \in Q} \frac{\langle \Psi_0^a | \hat{\mathcal{V}} | \beta \rangle \langle \beta | \hat{\mathcal{V}} | \Psi_0^a \rangle}{E_0 - E_0^\beta}
\end{aligned}
$$

and the energies read :

$$
\langle \Psi_0^a | \hat{\mathcal{H}} | \Psi_0^a \rangle = \langle \Psi_0^a | \hat{\mathcal{H}}_0 | \Psi_0^a \rangle + \langle \Psi_0^a | \hat{\mathcal{V}} | \Psi_0^a \rangle
$$

$$
\boxed{\langle \Psi_0^a | \hat{\mathcal{H}} | \Psi_0^a \rangle = E_0 + E^{a,(1)}}
$$

Quasi Degenerate Perturbation Theory

Let us lift the strict degeneracy condition : *QDPT*

$|\alpha\rangle$ and $|\alpha'\rangle$ functions of the model space P, $E_0^\alpha \neq E_0^{\alpha'}$
and β in the Q space.

Remembering that $\left[\hat{\Omega}^{(1)}, \hat{H}_0\right] \hat{P} = \hat{Q}\hat{\mathcal{V}}\hat{P}$,

$$\langle\alpha|[\hat{\Omega}^{(1)}, \hat{H}_0]|\alpha'\rangle = \left(E_0^{\alpha'} - E_0^{\alpha}\right) \langle\alpha|\hat{\Omega}^{(1)}|\alpha'\rangle = \langle\alpha|\hat{Q}\hat{\mathcal{V}}|\alpha'\rangle = 0$$

Therefore $\boxed{\langle\alpha|\hat{\Omega}^{(1)}|\alpha'\rangle = 0}$

$\rightarrow$ no direct coupling through $\hat{\Omega}^{(1)}$ in the model space

Quasi Degenerate Perturbation Theory

$$\hat{\Omega} = \hat{P} + \hat{\Omega}^{(1)} + \hat{\Omega}^{(2)} + \cdots$$

Let us represent $\hat{\mathcal{H}}_{\text{eff}} = \hat{P}\hat{\mathcal{H}}_0\hat{P} + \hat{P}\hat{\mathcal{V}}\hat{\Omega}\hat{P}$

$$\begin{aligned}
\langle\alpha|\hat{\mathcal{H}}^{(0)}_{\text{eff}}|\alpha'\rangle &= 0 \\
\langle\alpha|\hat{\mathcal{H}}^{(1)}_{\text{eff}}|\alpha'\rangle &= \langle\alpha|\hat{\mathcal{V}}|\alpha'\rangle \\
\langle\alpha|\hat{\mathcal{H}}^{(2)}_{\text{eff}}|\alpha'\rangle &= \langle\alpha|\hat{\mathcal{V}}\hat{\Omega}^{(1)}|\alpha'\rangle \\
&= \langle\alpha|\hat{\mathcal{V}}| \sum_{\gamma\in P\bigoplus Q} |\gamma\rangle\langle\gamma|\hat{\Omega}^{(1)}|\alpha'\rangle \\
&= \langle\alpha|\hat{\mathcal{V}}| \sum_{\beta\in Q} |\beta\rangle\langle\beta|\hat{\Omega}^{(1)}|\alpha'\rangle
\end{aligned}$$

$$\langle\alpha|\hat{\mathcal{H}}^{(2)}_{\text{eff}}|\alpha'\rangle = \sum_{\beta\in Q} \frac{\langle\alpha\hat{\mathcal{V}}|\beta\rangle\langle\beta|\hat{\mathcal{V}}|\alpha\rangle}{E_0^{\alpha'} - E_0^{\beta}}$$

Quasi Degenerate Perturbation Theory

$\boxed{\text{non hermiticity of } \hat{\mathcal{H}}_{\text{eff}}}$

$$\langle\alpha|\hat{\mathcal{H}}^{(2)}_{\text{eff}}|\alpha'\rangle \neq \langle\alpha'|\hat{\mathcal{H}}^{(2)}_{\text{eff}}|\alpha\rangle$$

examples : if $|\alpha\rangle$ and $|\alpha'\rangle$ are different in nature, the interactions with the outer space are different

$\boxed{\text{full representation of } \hat{\mathcal{H}}_{\text{eff}}}$

Starting from n calculations, CASSCF type : model space
example : 2 electrons in 2 MOs, $M_S = 0$: 4 configurations

- n eigenvalues $\{E_0^a\}_{a=1,n} \rightarrow n$ quantities
- n *normalized* projections $\{|\Psi_0^a\rangle\}_{a=1,n} \rightarrow n\,(n-1)$ quantities

n^2 quantities to define the non-hermitian $n \times n$ effective Hamiltonian

$\rightarrow$ *model Hamiltonians validation and construction*

Möller-Plesset Perturbation Theory

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{V}}$$

$$\text{with} \quad \hat{\mathcal{H}}_0 = \sum_{i=1}^{N} \hat{\mathcal{F}}(i) \quad \text{and} \quad \hat{\mathcal{V}} = \frac{1}{2}\sum_{i\neq j} \frac{1}{r_{ij}} - \sum_i \hat{u}_{HF}(i)$$

$$\text{reminder}: \; \Psi_0^0 = \Psi_{HF} \qquad \langle \Psi_a^r | \hat{\mathcal{H}} | \Psi_0^0 \rangle = 0 \qquad E_0 = \sum_{a,occ} \epsilon_a$$

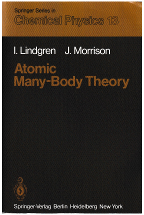
$$\begin{aligned} E^{(1)} &= \langle \Psi_{HF} | \hat{\mathcal{V}} | \Psi_{HF} \rangle \\ &= -\frac{1}{2}\sum_{a,b} \Big((aa, bb) - (ab, ba) \Big) \quad \text{double counting} \end{aligned}$$

$$E^{(2)} = \sum_{\beta \neq HF} \frac{\langle \Psi_{HF} | \hat{\mathcal{V}} | \beta \rangle \langle \beta | \hat{\mathcal{V}} | \Psi_{HF} \rangle}{E_0 - E_0^{\beta}} \quad \text{with} \quad |\beta\rangle = |\Psi_a^r\rangle, |\Psi_{ab}^{rs}\rangle \cdots$$

$$E^{(2)} = -\frac{1}{4}\sum_{ab,rs} \frac{\langle \Psi_{HF} | \hat{\mathcal{H}} | \Psi_{ab}^{rs} \rangle}{\epsilon_r + \epsilon_s - \epsilon_a - \epsilon_b} \approx E_{corr}$$

Conclusion and References

- perturbation as an *inspection* and *rationalization* tool
- rigorous expansions
- low cost as compared to variational methods
- parameters extraction t, U, J



see Nathalie Guihéry and Emmanuel Fromager's lectures

Calzado *et al.* *J. Chem. Phys.* **2002**, 116, 2728-2747
Calzado *et al.* *J. Chem. Phys.* **2002**, 116, 3985-4000