Georgia Institute of Technology:

Summer Lecture Series in Electronic Structure Theory

Many-Body Perturbation Theory

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Outline

- Why we need MBPT
- Rayleigh-Schrödinger PT
- Møller-Plesset PT
- Applications of MBPT
- MBPT failures

Other methods:

- You have been taught the following methods:
  - Hartree-Fock
  - Density Functional Theory
  - Coupled-Cluster Methods
  - Configuration Interaction

Why we need MBPT

- You have been taught the following methods:
  - **Hartree-Fock**
  - Density Functional Theory
  - Coupled-Cluster Methods
  - Configuration Interaction

Does not account for dynamic electron correlation

Why we need MBPT

- You have been taught the following methods:
  - Hartree-Fock
  - **Density Functional Theory**
  - Coupled-Cluster Methods
  - Configuration Interaction

1) No way to systematically improve results
2) No long range dynamic e- correlation

*Actual size may vary!

Why we need MBPT

- You have been taught the following methods:
  - Hartree-Fock
  - Density Functional Theory
  - **Coupled-Cluster Methods**
  - Configuration Interaction

Steep scaling
CCSD - $O(N^6)$
CCSDT - $O(N^7)$

Why we need MBPT

- You have been taught the following methods:
  - Hartree-Fock
  - Density Functional Theory
  - Coupled-Cluster Methods
  - **Configuration Interaction**

Steep scaling
CISD - O(N^6)
FCI - O(N!)

Why we need MBPT

- You have been taught the following methods:
  - Hartree-Fock
  - Density Functional Theory
  - **MBPT**
  - Coupled-Cluster Methods
  - Configuration Interaction

O(N^5) theory that can account for short and long range dynamic electron correlation and can be improved upon

Rayleigh-Schrödinger PT

- Consider the anharmonic oscillator:

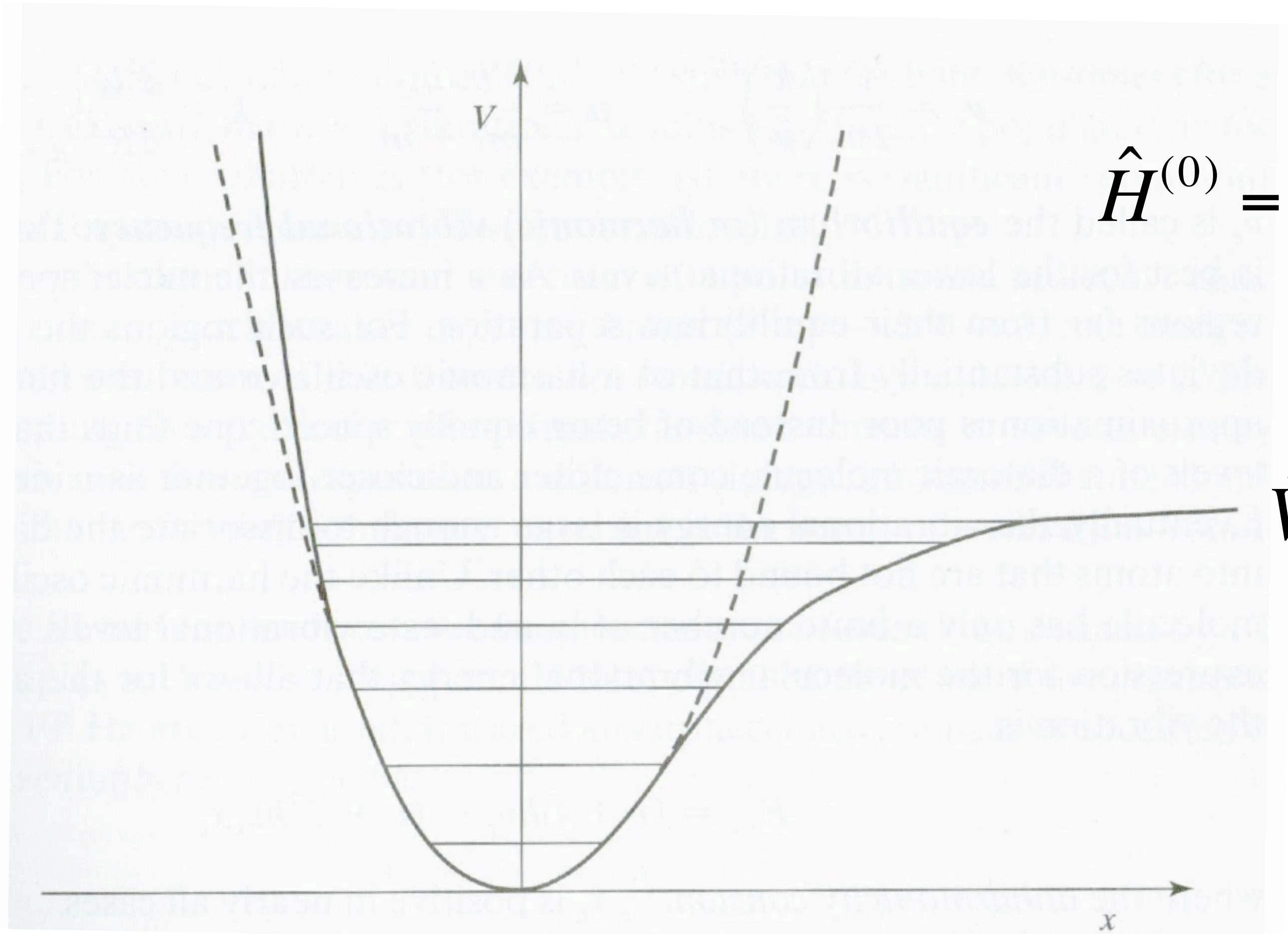
$$\hat{H} = -\frac{\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + cx^3 + dx^4$$

- Need to solve:

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

Rayleigh-Schrödinger PT

$$\hat{H} = -\frac{\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + cx^3 + dx^4$$



$$\hat{H}^{(0)} = -\frac{\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

$$\hat{V} = cx^3 + dx^4$$

$$\hat{H} = \hat{H}^{(0)} + \lambda\hat{V}$$

Rayleigh-Schrödinger PT

$$\hat{H}\left|\Psi_n\right\rangle = \left(\hat{H}^{(0)} + \lambda\hat{V}\right)\left|\Psi_n\right\rangle = E_n\left|\Psi_n\right\rangle$$

$$\left|\Psi_n\right\rangle = \left|\Psi_n(\lambda)\right\rangle \quad \& \quad E_n = E_n(\lambda)$$

Expansion via Taylor Series around lambda=0:

$$\left|\Psi_n\right\rangle = \left|\Psi_n\right\rangle\Big|_{\lambda=0} + \left.\frac{\partial\left|\Psi_n\right\rangle}{\partial\lambda}\right|_{\lambda=0}\lambda + \left.\frac{\partial^2\left|\Psi_n\right\rangle}{\partial\lambda^2}\right|_{\lambda=0}\frac{\lambda^2}{2!} + \cdots$$

$$E_n = E_n\Big|_{\lambda=0} + \left.\frac{\partial E_n}{\partial\lambda}\right|_{\lambda=0}\lambda + \left.\frac{\partial^2 E_n}{\partial\lambda^2}\right|_{\lambda=0}\frac{\lambda^2}{2!} + \cdots$$

Rayleigh-Schrödinger PT

$$\left|\Psi_n^{(k)}\right\rangle = \frac{1}{k!}\frac{\partial^k \left|\Psi_n\right\rangle}{\partial\lambda^k}\bigg|_{\lambda=0}$$

$$E_n^{(k)} = \frac{1}{k!}\frac{\partial^k E_n}{\partial\lambda^k}\bigg|_{\lambda=0}$$

$$\left|\Psi_n\right\rangle = \left|\Psi_n^{(0)}\right\rangle + \lambda\left|\Psi_n^{(1)}\right\rangle + \lambda^2\left|\Psi_n^{(2)}\right\rangle + \cdots$$

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

Rayleigh-Schrödinger PT

$$\hat{H}\left|\Psi_n\right\rangle = E_n\left|\Psi_n\right\rangle$$

$$\left(\hat{H}^{(0)} + \lambda\hat{V}\right)\left(\left|\Psi_n^{(0)}\right\rangle + \lambda\left|\Psi_n^{(1)}\right\rangle + \lambda^2\left|\Psi_n^{(2)}\right\rangle + \cdots\right) =$$

$$\left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)}\cdots\right)\left(\left|\Psi_n^{(0)}\right\rangle + \lambda\left|\Psi_n^{(1)}\right\rangle + \lambda^2\left|\Psi_n^{(2)}\right\rangle + \cdots\right)$$

Must hold true for all $\lambda \in [0,1]$

l.h.s. must equal r.h.s. for a given power of lambda

$$\left(\hat{H}^{(0)} + \lambda\hat{V}\right)\left(\left|\Psi_n^{(0)}\right\rangle + \lambda\left|\Psi_n^{(1)}\right\rangle + \lambda^2\left|\Psi_n^{(2)}\right\rangle + \cdots\right) =$$

$$\left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)}\cdots\right)\left(\left|\Psi_n^{(0)}\right\rangle + \lambda\left|\Psi_n^{(1)}\right\rangle + \lambda^2\left|\Psi_n^{(2)}\right\rangle + \cdots\right)$$

$$\lambda^0 : \quad \hat{H}^{(0)}\left|\Psi_n^{(0)}\right\rangle = E_n^{(0)}\left|\Psi_n^{(0)}\right\rangle$$

$$\left(\hat{H}^{(0)} + \lambda\hat{V}\right)\left(\left|\Psi_n^{(0)}\right\rangle + \lambda\left|\Psi_n^{(1)}\right\rangle + \lambda^2\left|\Psi_n^{(2)}\right\rangle + \cdots\right) =$$

$$\left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)}\cdots\right)\left(\left|\Psi_n^{(0)}\right\rangle + \lambda\left|\Psi_n^{(1)}\right\rangle + \lambda^2\left|\Psi_n^{(2)}\right\rangle + \cdots\right)$$

$$\lambda^0 : \quad \hat{H}^{(0)}\left|\Psi_n^{(0)}\right\rangle = E_n^{(0)}\left|\Psi_n^{(0)}\right\rangle$$

$$\lambda^1 : \quad H^{(0)}\left|\Psi_n^{(1)}\right\rangle + \hat{V}\ \left|\Psi_n^{(0)}\right\rangle = E_n^{(0)}\left|\Psi_n^{(1)}\right\rangle + E_n^{(1)}\left|\Psi_n^{(0)}\right\rangle$$

$$\left(\hat{H}^{(0)} + \lambda\hat{V}\right)\left(\left|\Psi_n^{(0)}\right\rangle + \lambda\left|\Psi_n^{(1)}\right\rangle + \lambda^2\left|\Psi_n^{(2)}\right\rangle + \cdots\right) =$$

$$\left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)}\cdots\right)\left(\left|\Psi_n^{(0)}\right\rangle + \lambda\left|\Psi_n^{(1)}\right\rangle + \lambda^2\left|\Psi_n^{(2)}\right\rangle + \cdots\right)$$

$$\lambda^0 : \quad \hat{H}^{(0)}\left|\Psi_n^{(0)}\right\rangle = E_n^{(0)}\left|\Psi_n^{(0)}\right\rangle$$

$$\lambda^1 : \quad H^{(0)}\left|\Psi_n^{(1)}\right\rangle + \hat{V}\left|\Psi_n^{(0)}\right\rangle = E_n^{(0)}\left|\Psi_n^{(1)}\right\rangle + E_n^{(1)}\left|\Psi_n^{(0)}\right\rangle$$

$$\lambda^2 : \quad H^{(0)}\left|\Psi_n^{(2)}\right\rangle + \hat{V}\left|\Psi_n^{(1)}\right\rangle = E_n^{(0)}\left|\Psi_n^{(2)}\right\rangle + E_n^{(1)}\left|\Psi_n^{(1)}\right\rangle + E_n^{(2)}\left|\Psi_n^{(0)}\right\rangle$$

$$\left(\hat{H}^{(0)} + \lambda\hat{V}\right)\left(\left|\Psi_n^{(0)}\right\rangle + \lambda\left|\Psi_n^{(1)}\right\rangle + \lambda^2\left|\Psi_n^{(2)}\right\rangle + \cdots\right) =$$

$$\left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} \cdots\right)\left(\left|\Psi_n^{(0)}\right\rangle + \lambda\left|\Psi_n^{(1)}\right\rangle + \lambda^2\left|\Psi_n^{(2)}\right\rangle + \cdots\right)$$

_k_th order Schrödinger equations

$$\lambda^0 : \quad \hat{H}^{(0)}\left|\Psi_n^{(0)}\right\rangle = E_n^{(0)}\left|\Psi_n^{(0)}\right\rangle$$

$$\lambda^1 : \quad H^{(0)}\left|\Psi_n^{(1)}\right\rangle + \hat{V}\left|\Psi_n^{(0)}\right\rangle = E_n^{(0)}\left|\Psi_n^{(1)}\right\rangle + E_n^{(1)}\left|\Psi_n^{(0)}\right\rangle$$

$$\lambda^2 : \quad H^{(0)}\left|\Psi_n^{(2)}\right\rangle + \hat{V}\left|\Psi_n^{(1)}\right\rangle = E_n^{(0)}\left|\Psi_n^{(2)}\right\rangle + E_n^{(1)}\left|\Psi_n^{(1)}\right\rangle + E_n^{(2)}\left|\Psi_n^{(0)}\right\rangle$$

$$\vdots$$

$$\lambda^k : \quad H^{(0)}\left|\Psi_n^{(k)}\right\rangle + \hat{V}\left|\Psi_n^{(k-1)}\right\rangle = \sum_{i=0}^{k} E_n^{(i)}\left|\Psi_n^{(k-i)}\right\rangle$$

Rayleigh-Schrödinger PT

- Zeroth Order Energy Correction:

$$\lambda^0 : \hat{H}^{(0)}\left|\Psi_n^{(0)}\right\rangle = E_n^{(0)}\left|\Psi_n^{(0)}\right\rangle$$

$$\left\langle\Psi_n^{(0)}\middle|\hat{H}^{(0)}\middle|\Psi_n^{(0)}\right\rangle = \left\langle\Psi_n^{(0)}\middle|E_n^{(0)}\middle|\Psi_n^{(0)}\right\rangle$$

$$E_n^{(0)} = \left\langle\Psi_n^{(0)}\middle|\hat{H}^{(0)}\middle|\Psi_n^{(0)}\right\rangle$$

Eigenvalues, eigenvectors we already know (this is our reference)

Rayleigh-Schrödinger PT

- First Order Energy Correction:

$$\lambda^1: \quad H^{(0)}\left|\Psi_n^{(1)}\right\rangle + \hat{V}\left|\Psi_n^{(0)}\right\rangle = E_n^{(0)}\left|\Psi_n^{(1)}\right\rangle + E_n^{(1)}\left|\Psi_n^{(0)}\right\rangle$$

$$\left\langle\Psi_n^{(0)}\middle|H^{(0)}\middle|\Psi_n^{(1)}\right\rangle + \left\langle\Psi_n^{(0)}\middle|\hat{V}\middle|\Psi_n^{(0)}\right\rangle =$$

$$\left\langle\Psi_n^{(0)}\middle|E_n^{(0)}\middle|\Psi_n^{(1)}\right\rangle + \left\langle\Psi_n^{(0)}\middle|E_n^{(1)}\middle|\Psi_n^{(0)}\right\rangle$$

$$\left\langle\Psi_n^{(0)}\middle|\hat{V}\middle|\Psi_n^{(0)}\right\rangle = E_n^{(1)}$$

Averaging perturbation over unperturbed wavefunction

Rayleigh-Schrödinger PT

- Second Order Energy Correction:

$$\lambda^2 : H^{(0)}\left|\Psi_n^{(2)}\right\rangle + \hat{V}\left|\Psi_n^{(1)}\right\rangle = E_n^{(0)}\left|\Psi_n^{(2)}\right\rangle + E_n^{(1)}\left|\Psi_n^{(1)}\right\rangle + E_n^{(2)}\left|\Psi_n^{(0)}\right\rangle$$

$$\left\langle\Psi_n^{(0)}\middle|H^{(0)}\middle|\Psi_n^{(2)}\right\rangle + \left\langle\Psi_n^{(0)}\middle|\hat{V}\middle|\Psi_n^{(1)}\right\rangle =$$

$$\left\langle\Psi_n^{(0)}\middle|E_n^{(0)}\middle|\Psi_n^{(2)}\right\rangle + \left\langle\Psi_n^{(0)}\middle|E_n^{(1)}\middle|\Psi_n^{(1)}\right\rangle + \left\langle\Psi_n^{(0)}\middle|E_n^{(2)}\middle|\Psi_n^{(0)}\right\rangle$$

$$E_n^{(0)}\left\langle\Psi_n^{(0)}\middle|\Psi_n^{(2)}\right\rangle + \left\langle\Psi_n^{(0)}\middle|\hat{V}\middle|\Psi_n^{(1)}\right\rangle =$$

$$E_n^{(0)}\left\langle\Psi_n^{(0)}\middle|\Psi_n^{(2)}\right\rangle + E_n^{(1)}\left\langle\Psi_n^{(0)}\middle|\Psi_n^{(1)}\right\rangle + E_n^{(2)}\left\langle\Psi_n^{(0)}\middle|\Psi_n^{(0)}\right\rangle$$

$$\left\langle\Psi_n^{(0)}\middle|\hat{V}\middle|\Psi_n^{(1)}\right\rangle = E_n^{(2)}$$

Rayleigh-Schrödinger PT

- k^{th} Order Energy Correction:

$$\lambda^k : \qquad H^{(0)}\left|\Psi_n^{(k)}\right\rangle + \hat{V}\left|\Psi_n^{(k-1)}\right\rangle = \sum_{i=0}^{k} E_n^{(i)}\left|\Psi_n^{(k-i)}\right\rangle$$

$$\left\langle\Psi_n^{(0)}\middle|H^{(0)}\middle|\Psi_n^{(k)}\right\rangle + \left\langle\Psi_n^{(0)}\middle|\hat{V}\middle|\Psi_n^{(k-1)}\right\rangle = \sum_{i=0}^{k}\left\langle\Psi_n^{(0)}\middle|E_n^{(i)}\middle|\Psi_n^{(k-i)}\right\rangle$$

$$E_n^{(0)}\left\langle\Psi_n^{(0)}\middle|\Psi_n^{(k)}\right\rangle + \left\langle\Psi_n^{(0)}\middle|\hat{V}\middle|\Psi_n^{(k-1)}\right\rangle = \sum_{i=0}^{k} E_n^{(i)}\left\langle\Psi_n^{(0)}\middle|\Psi_n^{(k-i)}\right\rangle$$

$$\left\langle\Psi_n^{(0)}\middle|\hat{V}\middle|\Psi_n^{(k-1)}\right\rangle = E_n^{(k)}$$

Rayleigh-Schrödinger PT

- Perturbed Wavefunctions:

$$\left|\Psi_n^{(k)}\right\rangle = \sum_{\mu} C_{\mu}^{(k)}\left|\Psi_{\mu}^{(0)}\right\rangle$$

Complete basis constructed (typically) from a linear combination of unperturbed wavefunctions.

- 1st Order Wavefunction Correction:

$$\lambda^1 : \quad H^{(0)}\left|\Psi_n^{(1)}\right\rangle + \hat{V}\left|\Psi_n^{(0)}\right\rangle = E_n^{(0)}\left|\Psi_n^{(1)}\right\rangle + E_n^{(1)}\left|\Psi_n^{(0)}\right\rangle$$

$$\sum_{\mu\neq n} C_\mu^{(1)} H^{(0)}\left|\Psi_\mu^{(0)}\right\rangle + \hat{V}\left|\Psi_n^{(0)}\right\rangle = \sum_{\mu\neq n} C_\mu^{(1)} E_n^{(0)}\left|\Psi_\mu^{(0)}\right\rangle + E_n^{(1)}\left|\Psi_n^{(0)}\right\rangle$$

$$\sum_{\mu\neq n} C_\mu^{(1)} E_\mu^{(0)}\left\langle\Psi_\nu^{(0)}\middle|\Psi_\mu^{(0)}\right\rangle + \left\langle\Psi_\nu^{(0)}\middle|\hat{V}\middle|\Psi_n^{(0)}\right\rangle =$$

$$\sum_{\mu\neq n} C_\mu^{(1)} E_n^{(0)}\left\langle\Psi_\nu^{(0)}\middle|\Psi_\mu^{(0)}\right\rangle + E_n^{(1)}\left\langle\Psi_\nu^{(0)}\middle|\Psi_n^{(0)}\right\rangle$$

$$C_\nu^{(1)} E_\nu^{(0)} + \left\langle\Psi_\nu^{(0)}\middle|\hat{V}\middle|\Psi_n^{(0)}\right\rangle = C_\nu^{(1)} E_n^{(0)}$$

$$C_\nu^{(1)} = \frac{\left\langle\Psi_\nu^{(0)}\middle|\hat{V}\middle|\Psi_n^{(0)}\right\rangle}{\left(E_n^{(0)} - E_\nu^{(0)}\right)} \qquad \therefore \quad \left|\Psi_n^{(1)}\right\rangle = \sum_{\mu\neq n} \frac{\left\langle\Psi_\mu^{(0)}\middle|\hat{V}\middle|\Psi_n^{(0)}\right\rangle}{\left(E_n^{(0)} - E_\mu^{(0)}\right)}\left|\Psi_\mu^{(0)}\right\rangle$$

Back to the anharmonic oscillator

$$\hat{H} = -\frac{\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + cx^3 + dx^4$$

$$E_0^{(1)} = \left\langle \Psi_0^{(0)} \middle| \hat{V} \middle| \Psi_0^{(0)} \right\rangle = \left\langle \Psi_0^{(0)} \middle| cx^3 + dx^4 \middle| \Psi_0^{(0)} \right\rangle$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2}\left(cx^3 + dx^4\right)dx = 2d\left(\frac{\alpha}{\pi}\right)^{1/2} \int_0^{\infty} e^{-\alpha x^2} x^4 dx$$

$$= \frac{3dh^2}{64\pi^4 \upsilon^2 m^2}$$

$$E_0^{Total} = E_0^{(0)} + E_0^{(1)} = \frac{1}{2}h\upsilon + \frac{3dh^2}{64\pi^4 \upsilon^2 m^2}$$

Møller-Plesset PT

$$\hat{H} = \sum_{i}^{N} h_i - \sum_{i<j}^{N} r_{ij}^{-1}$$

- RSPT does not restrict H, $H^{(0)}$, or V.
- MPPT takes RSPT and applies it to electronic structure theory via the following choices:

$$\hat{H}^{(0)} = \sum_{i}^{N} \hat{f}(i) = \sum_{i}^{N} \left[h(i) + \upsilon^{HF}(i) \right]$$

$$\hat{V} = \hat{H}^{(0)} - \hat{H} = \sum_{i<j}^{N} r_{ij}^{-1} - \sum_{i<j}^{N} \upsilon^{HF}(i)$$

Difference of true e-e and the mean field appr.

Møller-Plesset PT

- Quick Notation Reminder:

$$\int dx_1 dx_2 \chi_i^*(x_1)\chi_j^*(x_2)\cdot r_{12}^{-1}\cdot \chi_k(x_1)\chi_l(x_2) = \langle ij|kl\rangle$$

In physcist's notation: i,k refer to S.O. of electron one & j,l refer to S.O. of electron two

$$\langle ij\|kl\rangle = \langle ij|kl\rangle - \langle ij|lk\rangle$$

$$\langle \Psi_i|\upsilon^{HF}|\Psi_j\rangle = \sum_b \langle ib|jb\rangle - \langle ib|bj\rangle = \sum_b \langle ib\|jb\rangle$$

Møller-Plesset PT

$$\lambda^0 : \hat{H}^{(0)}\left|\Psi_n^{(0)}\right\rangle = E_n^{(0)}\left|\Psi_n^{(0)}\right\rangle$$

$$\hat{H}^{(0)} = \sum_i^N \left[h(i) + \upsilon^{HF}(i)\right]$$

$$E_0^{(0)} = \sum_a \varepsilon_a$$

Note: This is **NOT** the HF energy

$$\sum_a \varepsilon_a = \sum_a \langle a|h|a\rangle + \sum_{ab} \langle ab\|ab\rangle$$

Møller-Plesset PT

$$E_0^{(1)} = \left\langle \Psi_0^{(0)} \middle| \hat{V} \middle| \Psi_0^{(0)} \right\rangle$$

$$E_0^{(1)} = \left\langle \Psi_0^{(0)} \middle| \sum_{i<j}^{N} r_{ij}^{-1} \middle| \Psi_0^{(0)} \right\rangle - \left\langle \Psi_0^{(0)} \middle| \sum_{i<j}^{N} \upsilon^{HF}(i) \middle| \Psi_0^{(0)} \right\rangle$$

$$E_0^{(1)} = \frac{1}{2} \sum_{ab} \langle ab \| ab \rangle - \sum_{a} \langle a | \upsilon^{HF} | a \rangle$$

$$E_0^{(1)} = \frac{1}{2} \sum_{ab} \langle ab \| ab \rangle - \sum_{a} \sum_{b} \langle ab \| ab \rangle$$

$$E_0^{(0)} + E_0^{(1)} = \sum_{a} \varepsilon_a - \frac{1}{2} \sum_{a} \sum_{b} \langle ab \| ab \rangle$$

This **IS** the HF energy!

Møller-Plesset PT

$$E_n^{(2)} = \left\langle \Psi_n^{(0)} \middle| \hat{V} \middle| \Psi_n^{(1)} \right\rangle$$

$$\left| \Psi_n^{(1)} \right\rangle = \sum_{\mu \neq n} \frac{\left\langle \Psi_\mu^{(0)} \middle| \hat{V} \middle| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_\mu^{(0)} \right)} \left| \Psi_\mu^{(0)} \right\rangle$$

$$E_n^{(2)} = \sum_{\mu \neq n} \frac{\left\langle \Psi_n^{(0)} \middle| \hat{V} \middle| \Psi_\mu^{(0)} \right\rangle \left\langle \Psi_\mu^{(0)} \middle| \hat{V} \middle| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_\mu^{(0)} \right)} = \sum_{\mu \neq n} \frac{\left| \left\langle \Psi_n^{(0)} \middle| \hat{V} \middle| \Psi_\mu^{(0)} \right\rangle \right|^2}{\left(E_n^{(0)} - E_\mu^{(0)} \right)}$$

Ground State:
Sum over everything but the ground state

$$E_0^{(2)} = \sum_{\mu \neq 0} \frac{\left| \left\langle \Psi_0^{(0)} \middle| \hat{V} \middle| \Psi_\mu^{(0)} \right\rangle \right|^2}{\left(E_0^{(0)} - E_\mu^{(0)} \right)}$$

Møller-Plesset PT

$$E_0^{(2)} = \sum_{\mu \neq 0} \frac{\left| \left\langle \Psi_0^{(0)} \middle| \hat{V} \middle| \Psi_\mu^{(0)} \right\rangle \right|^2}{\left(E_0^{(0)} - E_\mu^{(0)} \right)}$$

Which terms survive?

<u>Excitation level</u>

Singles $\left| \Psi_a^r \right\rangle$

Brillouin's Theorem:
Singly excited determinants
will not interact directly with the reference

$$\left\langle \Psi_0 \middle| \hat{V} \middle| \Psi_a^r \right\rangle = 0$$

Doubles $\left| \Psi_{ab}^{rs} \right\rangle$

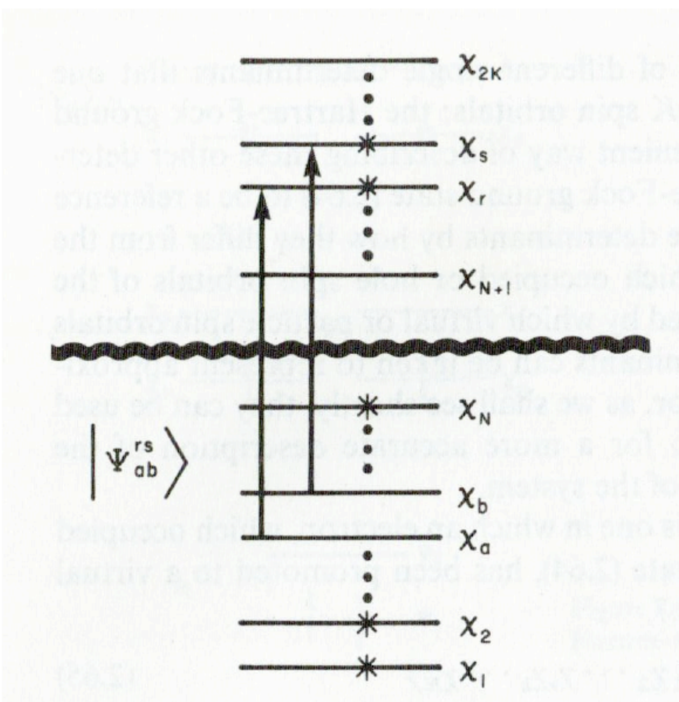
Survive! (will evaluate on next slide)

>= Triples $\left| \Psi_{abcd\ldots}^{rstu\ldots} \right\rangle$

Higher excitations:
Zero because the perturbation is
a two-particle operator.

$$\left\langle \Psi_0 \middle| \hat{V} \middle| \Psi_{abcd\ldots}^{rstu\ldots} \right\rangle = 0$$

Møller-Plesset PT



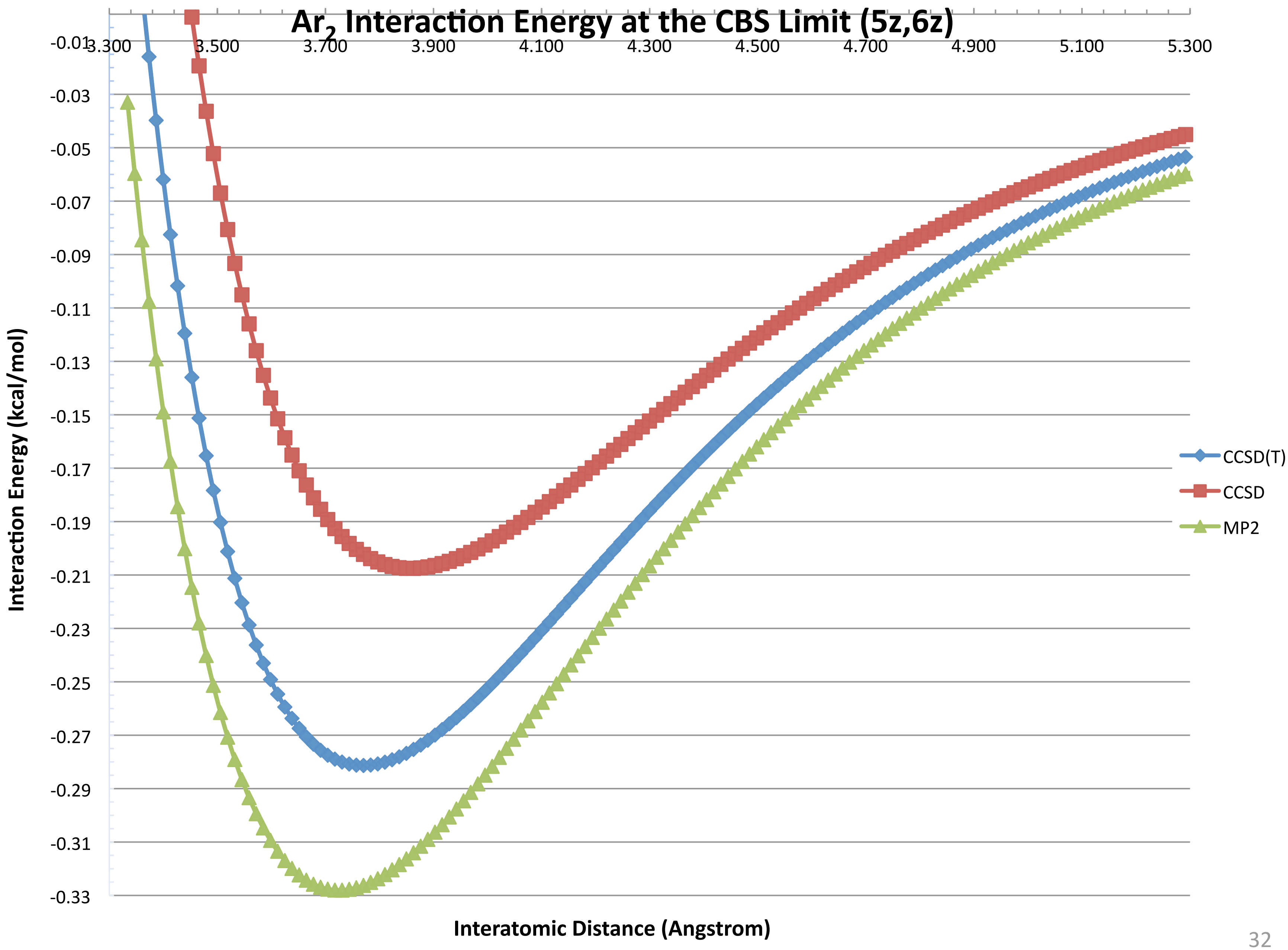
$$E_0^{(2)} = \sum_{\mu \neq 0} \frac{\left| \left\langle \Psi_0^{(0)} \middle| \hat{V} \middle| \Psi_\mu^{(0)} \right\rangle \right|^2}{\left(E_0^{(0)} - E_\mu^{(0)} \right)}$$

$$H_0 \left| \Psi_{ab}^{rs} \right\rangle = E_0^{(0)} - (\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s) \left| \Psi_{ab}^{rs} \right\rangle$$

$$\left\langle \Psi_0^{(0)} \middle| r_{12}^{-1} \middle| \Psi_{rs}^{ab} \right\rangle = \langle ab \| rs \rangle$$

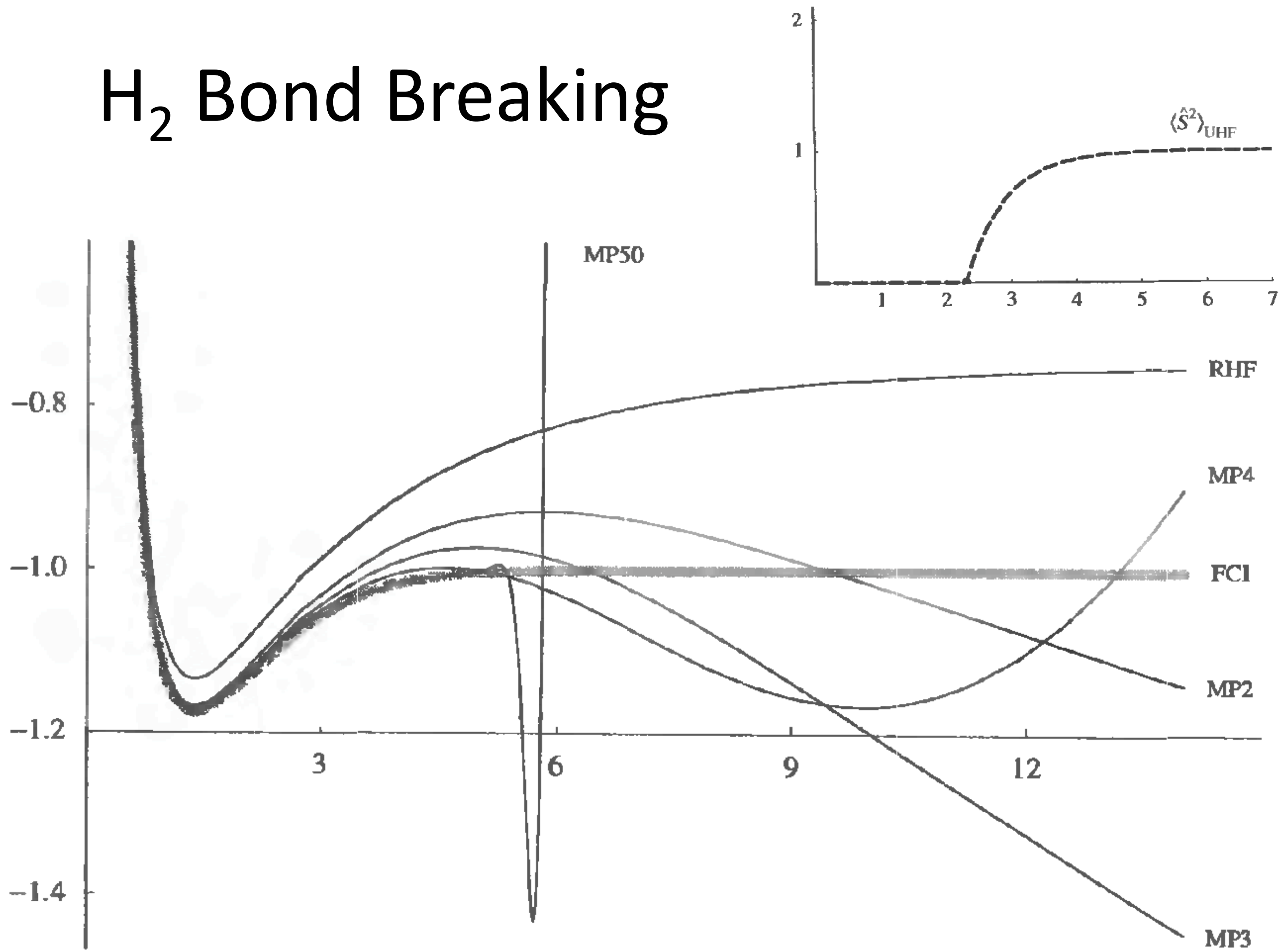
From CI we saw we could get all doubly excited determinants from summing all a **and** all b greater than a **and** all r **and** all s greater than r

$$E_0^{(2)} = \sum_{\substack{a<b \\ r<s}} \frac{\left| \langle ab \| rs \rangle \right|^2}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)}$$

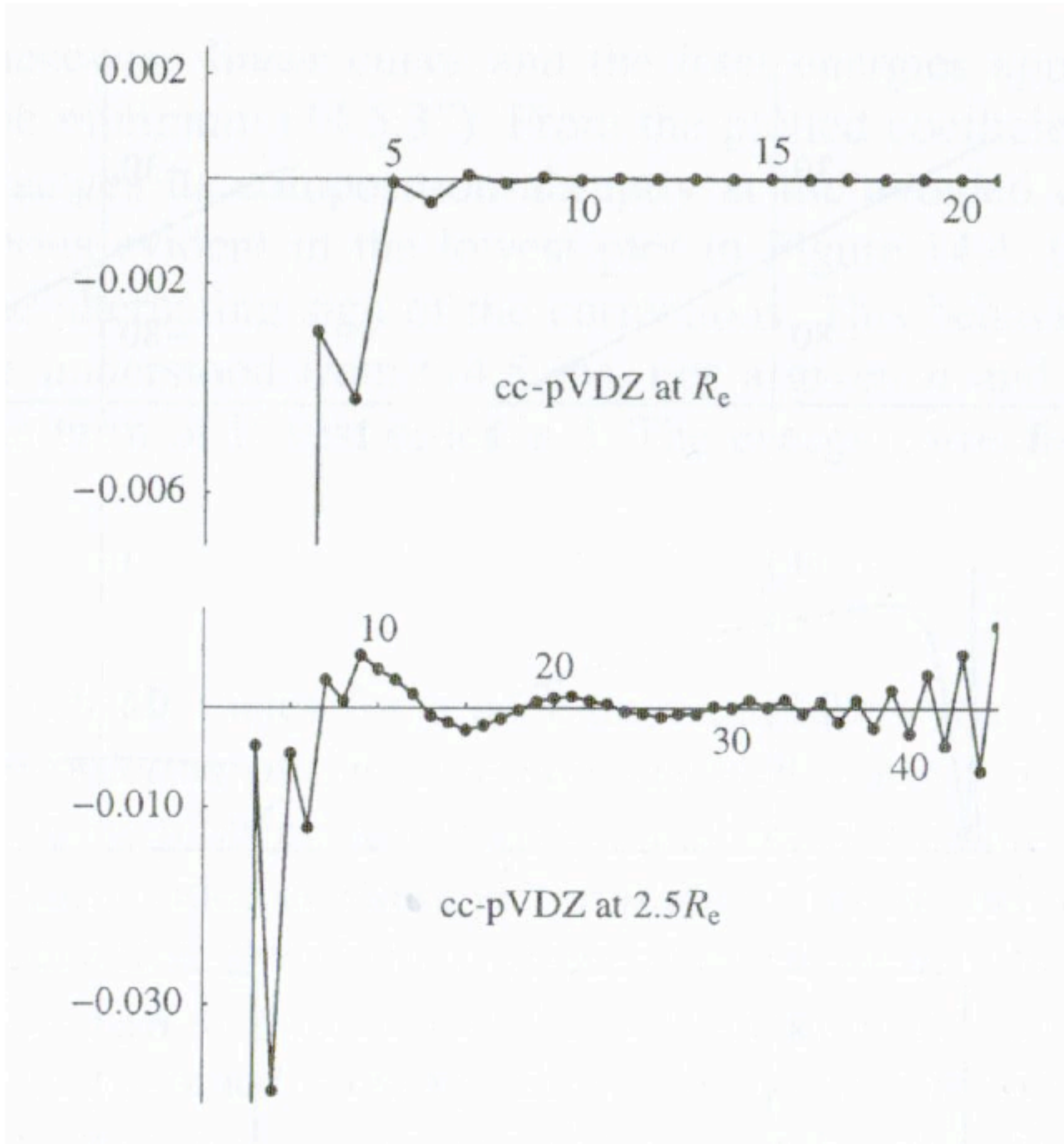


Ar$_2$ Interaction Energy at the CBS Limit (5z,6z)
3.300
3.500
3.700
3.900
4.100
4.300
4.500
4.700
4.900
5.100
5.300
-0.01
-0.03
-0.05
-0.07
-0.09
-0.11
-0.13
-0.15
-0.17
-0.19
-0.21
-0.23
-0.25
-0.27
-0.29
-0.31
-0.33
Interaction Energy (kcal/mol)
Interatomic Distance (Angstrom)
CCSD(T)
CCSD
MP2

H_2 Bond Breaking



MPn Series


0.002
5
15
10
20
−0.002
cc-pVDZ at R_e
−0.006
10
20
30
40
−0.010
cc-pVDZ at $2.5R_e$
−0.030

Questions?

Thanks for Listening