

STRATEGIES FOR THE MANY-BODY PROBLEM

- Start with **Independent Particle model**, e.g. Hartree-Fock (“the best” Independent Particle model)
- Define a zeroth order configuration (a “vacuum level”)
- Expand beyond this stepwise

SIMPLE PERTURBATION APPROACH FOR 2 PARTICLES

- Basic idea
- H_0 is simple
- and solved

$$H = H_0 + V \qquad H_0 = \sum_i h_i \qquad H_0 \Psi_0 = E_0 \Psi_0 = \left(\sum_i \epsilon_i \right) \Psi_0$$

Simple Example he-like system

$$H = \sum_{i=1,2} \left(\frac{\hbar^2}{2m} \left(-\frac{\partial^2}{\partial r_i^2} + \frac{\ell_i(\ell_i + 1)}{r_i^2} \right) - \frac{e^2}{4\pi\epsilon_0} \frac{Z}{r_i} \right) + \frac{1}{r_{12}} = \sum_{i=1,2} h_i + \frac{1}{r_{12}}$$

$$\begin{aligned} \Psi &= \Psi_0 + \delta\Psi \\ \Psi_0 &= \frac{1}{\sqrt{2}} \left(|ab\rangle - |ba\rangle \right) \end{aligned}$$

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$$\begin{aligned} H\Psi &= E\Psi \\ (H_0 + V)(\Psi_0 + \delta\Psi) &= (E_0 + \delta E)(\Psi_0 + \delta\Psi) \\ (E_0 - H_0)\delta\Psi &= V(\Psi_0 + \delta\Psi) - \delta E(\Psi_0 + \delta\Psi) \end{aligned}$$

- intermediate normalization
- integrate with Ψ_0 from the left

$$\langle \Psi_0 | \Psi_0 \rangle = 1, \quad \langle \Psi_0 | \delta\Psi \rangle = 0$$

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$$\begin{aligned}
 (E_0 - H_0)\delta\Psi &= V(\{ab\} + \delta\Psi) - \langle \{ab\} | V | \{ab\} + \delta\Psi \rangle - \\
 &\quad \delta E \delta\Psi
 \end{aligned}$$

SIMPLE PERTURBATION APPROACH FOR 2 PARTICLES

$$\sum_{rs} |\{rs\}\rangle \langle \{rs\}| = 1$$

$$(\epsilon_a + \epsilon_b - h_1 - h_2) \delta \Psi^i = \sum_{\{rs\} \neq \{ab\}} |\{rs\}\rangle \langle \{rs\}| \frac{1}{r_{12}} |\{ab\} + \delta \Psi^{i-1}\rangle - \delta E \delta \Psi^{i-1}$$

$$\delta E = \langle ab | \frac{1}{r_{12}} | ab \rangle - \langle ba | \frac{1}{r_{12}} | ab \rangle + \dots$$

$$\delta \Psi^{(1)} = \sum_{\{rs\} \neq \{ab\}} \frac{|\{rs\}\rangle \langle \{rs\}| \frac{1}{r_{12}} |\{ab\}\rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

- possible to solve iteratively
- slightly more to consider with $N > 2$ (but the idea is the same)
- Economical since only one (or a few) states are solved for

PERTURBATION THEORY: HF STARTING-POINT

- with Hartree-Fock starting point $V = \frac{1}{r_{12}} - u_{hf}$
- small enough V required! Convergence not guaranteed.

$$\Psi_0 = |\alpha\rangle$$
$$|\alpha\rangle = |\{abc \dots\}\rangle, \quad E_0 = \epsilon_a + \epsilon_b + \epsilon_c + \dots$$

$$\delta\Psi^{(1)} = \sum_{\beta \neq \alpha} \frac{|\beta\rangle \langle \beta| V |\alpha\rangle}{E_0 - E_0^\beta}$$
$$V = \sum_{i < j}^N \frac{1}{r_{12}} - \sum_i u_{hf}(r_i)$$

- One one-particle perturbation and one two-particle perturbation!

LOWEST ORDER CORRECTION TO THE WF

- the contribution from u_{hf}

$$\delta\psi_u^{(1)} = - \sum_{\beta \neq \alpha} \frac{|\beta\rangle \langle \beta | \sum_i u_{hf}(r_i) | \alpha \rangle}{E_0 - E_0^\beta}$$

- β must be a single excitation from α : $\beta = \alpha_a^r$

$$\begin{aligned} \delta\psi_u^{(1)} &= - \sum_{ar} \frac{|\alpha_a^r\rangle \langle \alpha_a^r | \sum_i u_{hf}(r_i) | \alpha \rangle}{\epsilon_a - \epsilon_r} \\ &= - \sum_{ar} \frac{|\alpha_a^r\rangle \langle r | u_{hf} | a \rangle}{\epsilon_a - \epsilon_r} \\ &= - \sum_{ar} \sum_b \frac{|\alpha_a^r\rangle \langle \{rb\} | \frac{1}{r_{12}} | \{ab\} \rangle}{\epsilon_a - \epsilon_r} \end{aligned}$$

LOWEST ORDER CORRECTION TO THE WF

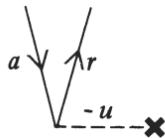
- the contribution from $1/r_{ij}$

$$\delta\psi_C^{(1)} = \sum_{\beta \neq \alpha} \frac{|\beta\rangle \langle \beta | \sum_{i < j} \frac{1}{r_{ij}} | \alpha \rangle}{E_0 - E_0^\beta}$$

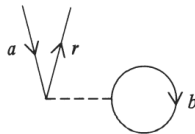
- β can be single OR a double excitations from α

$$\begin{aligned} \delta\psi_C^{(1)} &= \frac{|\alpha_a^r\rangle \langle \alpha_a^r | \sum_{i < j} \frac{1}{r_{ij}} | \alpha \rangle}{\epsilon_a - \epsilon_r} + \sum_{abrs} \frac{|\alpha_{ab}^{rs}\rangle \langle \alpha_{ab}^{rs} | \sum_{i < j} \frac{1}{r_{ij}} | \alpha \rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \\ &= \sum_{ar,b} \frac{|\alpha_a^r\rangle \langle \{rb\} | \frac{1}{r_{12}} | \{ab\} \rangle}{\epsilon_a - \epsilon_r} + \frac{1}{2} \sum_{abrs} \frac{|\alpha_{ab}^{rs}\rangle \langle \{rs\} | \frac{1}{r_{12}} | \{ab\} \rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \end{aligned}$$

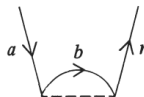
THE DIAGRAMS



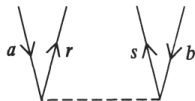
$$= \frac{|\alpha_a^r\rangle \langle r | -u | a \rangle}{\varepsilon_a - \varepsilon_r}$$



$$= \frac{|\alpha_a^r\rangle \langle rb | r_{12}^{-1} | ab \rangle}{\varepsilon_a - \varepsilon_r}$$



$$= - \frac{|\alpha_a^r\rangle \langle br | r_{12}^{-1} | ab \rangle}{\varepsilon_a - \varepsilon_r}$$



$$= \frac{1}{2} \frac{|\alpha_{ab}^{rs}\rangle \langle rs | r_{12}^{-1} | ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}.$$

- Goldstone diagrams

LOWEST ORDER CORRECTION TO THE WF

- when starting from Hartree-Fock there are no single excitation corrections in first order!

$$\delta\Psi_C^{(1)} + \delta\Psi_{u_{hf}}^{(1)} = \frac{1}{2} \sum_{abrs} \frac{|\alpha_{ab}^{rs}\rangle \langle\{rs\} | \frac{1}{r_{12}} | \{ab\}\rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

$$\delta E^{(2)} = \frac{1}{2} \sum_{abrs} \frac{\langle\{ab\} | \frac{1}{r_{12}} | \{rs\}\rangle \langle\{rs\} | \frac{1}{r_{12}} | \{ab\}\rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

- (second order) correlation energy or
- Møller-Plesset perturbation theory in Quantum Chemistry
- will always lower the energy
- how does it scale?

REMEMBER FROM LAST TIME:

$$\begin{aligned}\langle \alpha | H | \alpha \rangle &= E_0 + \delta E^{(1)} \\ &= \langle \alpha | \sum_i^N h_{HF}(i) + \sum_{i < j}^N \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{ij}} - \sum_i^N u_{HF}(i) | \alpha \rangle \\ &= \sum_a^{occ} \epsilon_a - \frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0} \sum_{ab}^{occ} \langle ab | \frac{1}{r_{12}} | ab \rangle - \langle ba | \frac{1}{r_{12}} | ab \rangle \right)\end{aligned}$$

Example Beryllium $1s^2 2s^2$ a.u.

$$E_{HF} \quad -14.573\,023$$

$$\delta E^{(2)} \quad -0.076\,358$$

$$\text{h.o.} \quad -0.017\,309$$

THE PERTURBED WAVE FUNCTION CONCEPT

- whenever there is a perturbation we can construct the perturbed wave functions caused by it
- also when the perturbation is time-dependent

$$i\hbar \frac{\partial}{\partial t} \Psi = H\Psi$$

if H is time-independent

$$\Psi(t, \mathbf{r}) = \Psi(0, \mathbf{r}) e^{-iEt/\hbar}, \text{ if } H\Psi(0, \mathbf{r}) = E\Psi(0, \mathbf{r})$$

- with a time-dependent perturbation (for example $\mathbf{r} \cdot \mathbf{E}$, with $\mathbf{E} = 2E_z \cos(\omega t) \hat{z}$)

$$V(\mathbf{r}, t) = 2z \cos(\omega t) E_z = z (e^{i\omega t} + e^{-i\omega t}) E_z$$

THE PERTURBED WAVE FUNCTION CONCEPT

- the solution $|a\rangle$ to h_{hf}

$$\psi_a(t) = |a\rangle e^{-i\epsilon_a t/\hbar}$$

- With the time dependent perturbation added

$$h = h_{hf} + z(e^{i\omega t} + e^{-i\omega t}) E_z$$

- There is a new time-dependent equation

$$\begin{aligned} & \left(i\hbar \frac{\partial}{\partial t} - h_{hf} \right) (\psi_a(t) + \delta\psi_a(t)) \\ &= zE_z (e^{i\omega t} + e^{-i\omega t}) (\psi_a(t) + \delta\psi_a(t)) \end{aligned}$$

- keep just the lowest order
- divide up in $\pm$

$$\left(i\hbar \frac{\partial}{\partial t} - h_{hf} \right) \delta\psi_a^\pm(t) = zE_z (e^{\mp i\omega t}) \psi_a(t) = zE_z |a\rangle e^{-i(\epsilon_a \pm \hbar\omega)t/\hbar}$$

- starting from $\alpha = \{abc \dots\}$ we can couple to $\alpha_a^r = \{rbc \dots\}$

THE PERTURBED WAVE FUNCTION CONCEPT

- what about the time dependence of $\delta\psi_a^\pm$?
- we expect it to oscillate with $\exp(-i(\epsilon_a \pm \hbar\omega)t/\hbar)$

$$\delta\psi_a^\pm = \rho_a^\pm(r) e^{-i(\epsilon_a \pm \hbar\omega)t/\hbar}$$

$$\begin{aligned} \left(i\hbar \frac{\partial}{\partial t} - h_{hf} \right) \rho_a^\pm e^{-i(\epsilon_a \pm \hbar\omega)t/\hbar} &= |r\rangle \langle r| z E_z |a\rangle e^{-i(\epsilon_a \pm \hbar\omega)t/\hbar} \\ (\epsilon_a \pm \hbar\omega - h_{hf}) \rho_a^\pm &= |r\rangle \langle r| z |a\rangle E_z \end{aligned}$$

- time-independent equation with solution

$$\rho_a^\pm = \sum_r \frac{|r\rangle \langle r| z |a\rangle}{\epsilon_a \pm \hbar\omega - \epsilon_r} E_z$$

- if the denominator strictly $\neq 0$ localized correction

- The photon field interacts with all the electrons
- they all get a slight perturbation
- then the interaction between them changes!
- how can we account for that?

$$\begin{aligned}\langle r | u_{HF} | a \rangle &= \sum_b^{occupied} = \langle \{rb\} | \frac{1}{r_{12}} | \{ab\} \rangle \\ &\rightarrow \langle r | u_{HF} | a \rangle + \langle r | \delta u_{HF}^{\pm} | a \rangle\end{aligned}$$

$$\langle r | \delta u_{HF}^{\pm} | a \rangle = \sum_b^{occupied} \langle \{rb\} | \frac{1}{r_{12}} | \{a\rho_b^{\pm}\} \rangle + \langle \{r\rho_b^{\mp}\} | \frac{1}{r_{12}} | \{ab\} \rangle$$

RPAE - TIME DEPENDENT HF

$$\begin{aligned}
 \langle r | \delta u_{HF}^{\pm} | a \rangle &= \sum_b^{\text{occupied}} \langle \{rb\} | \frac{1}{r_{12}} | \{a\rho_b^{\pm}\} \rangle + \langle \{r\rho_b^{\mp}\} | \frac{1}{r_{12}} | \{ab\} \rangle \\
 &= \sum_b^{\text{occ.}} \sum_{rs}^{\text{unocc.}} \frac{\langle \{rb\} | \frac{1}{r_{12}} | \{as\} \rangle}{\epsilon_a \pm \hbar\omega - \epsilon_r} \frac{\langle s | z | b \rangle}{\epsilon_b \pm \hbar\omega - \epsilon_s} \\
 &\quad + \sum_b^{\text{occ.}} \sum_{rs}^{\text{unocc.}} \frac{\langle b | z | s \rangle}{\epsilon_b \mp \hbar\omega - \epsilon_s} \frac{\langle \{rs\} | \frac{1}{r_{12}} | \{ab\} \rangle}{\epsilon_a \pm \hbar\omega - \epsilon_r}
 \end{aligned}$$

RPAE - TIME DEPENDENT HF

